RAMAN SPECTRA IN ORGANIC CHEMISTRY

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I. INTRODUCTION

Raman spectra in inorganic chemistry have been reviewed in a previous article (311). In addition to a summary of most of the data accumulated by 1934, this review included in some detail the theoretical background, such as the conditions which give rise to the Raman effect, selection rules, its relation to infra-red absorption, and the magnitude, intensity, and polarization of Raman shifts. It would serve no useful purpose, therefore, in this survey of Raman spectra in organic chemistry to repeat in detail all the theoretical aspects of the subject, as these are equally applicable to the inorganic and organic fields. Furthermore, while theoretical concepts have been perfected during the past two years, there has been no fundamental alteration in them. In order to reduce the wide scope of this review as much as possible, reference to the inorganic spectra will be avoided. It cannot be overemphasized, however, that the principles treated and the information obtained are nearly identical in both cases.

The Raman effect of considerably over a thousand organic compounds has been investigated. It is the purpose here to discuss the spectra of these compounds in somewhat general terms, rather than to record every

individual Raman shift for all compounds. The shifts attributed to the types of linkage in each class of compounds, however, will be discussed. In order that reference to original work may be made conveniently, the attempt has been made to include in the bibliography all publications giving original data on organic compounds since the discovery of the Raman effect by Sir. C. V. Raman in 1928. Each compound studied is listed alphabetically by name and according to its empirical formula, with the appropriate literature citations. An additional bibliography of articles on inorganic Raman spectra which have appeared since the earlier compilation (311) is included.

The particular efficacy of the Raman effect lies in the fact that it is a physical method causing no chemical change and is roughly independent of the state of aggregation of the material to be examined and its chemical composition. From it can be obtained considerable information regarding the internal and external characteristics of the molecule. The strength of the bonds between the atoms in their normal state and the frequency and amplitude of atomic vibration can be calculated. In some cases the spacial configuration and the anisotropy of the molecule may be determined. From this information the specific heats, relative heats of dissociation, and the possible heats of fusion of pure organic compounds may be estimated. In addition, it may serve as a method of identification of compounds in mixtures and in the determination of complex molecular structure. The activity in this field, then, is not surprising. Its progress has paralleled that of other scientific discoveries: first, the correlation of an experimental observation with theory and other phenomena—in this case spectroscopic; second, an accumulation of qualitative data; and finally, a development in a more quantitative fashion. Raman spectra have attained, at least partially, the final status.

II. DEFINITION OF TERMS

The Raman lines or Raman shifts are generally given in terms of wave numbers or the number of vibrations per centimeter. Any spectroscopic line may be defined by $\lambda\nu = 3 \times 10^{18}$, where λ is the wave length in Ångström units (A.U.), the digits represent the velocity of light in A.U., and ν the frequency, or $\lambda\bar{\nu} = 10^8$ where $\bar{\nu}$ is defined in wave numbers per centimeter. Since the Raman lines are the differences between spectroscopic lines it is more or less customary to employ $\Delta\bar{\nu}$ to express this. The Raman shifts will be given in wave numbers per centimeter, that is, $\Delta\bar{\nu} = 500$ cm.$^{-1}$, for example, or more simply, $\Delta\bar{\nu}$ 500. The relative intensities, when given, are in parentheses and follow the Raman shift numbers, for example, $\Delta\bar{\nu}$ 500 (7); they are on a basis of ten.

Other terms used are as follows: $\bar{\mu}$ represents the reduced mass, that is,

$$\frac{1}{\bar{\mu}} = \frac{1}{M} + \frac{1}{m}$$

where M and m represent the weights in a vibrating system. F is the elastic restoring force, or the force per unit displacement expressed in dynes per centimeter. d is the deformation force constant in dynes per centimeter. h is Planck's constant, 6.54×10^{-27} erg seconds. N is Avogadro's number, 6.06×10^{23}. ρ is the degree of depolarization. k is the Boltzmann constant, 1.37×10^{-16} ergs per degree.

III. ORIGIN OF RAMAN SPECTRA

Raman spectra owe their origin to the interaction of a light quantum ($h\nu$) and a molecule. This is not unlike an inelastic collision between
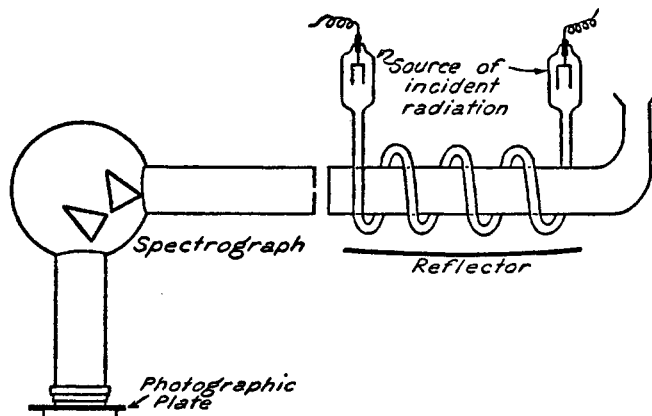
FIG. 1. Experimental arrangement for recording Raman spectra

two molecules. In this case it is conceivable that one molecule will be deflected with less energy after the impact and the other molecule will absorb some of the energy as kinetic or potential energy. In the Raman effect each mode of oscillation in the molecule which interacts with the light quantum results in an absorption of energy from this quantum and its consequent rescattering with less than its initial energy. This rescattered radiation may be recorded photographically by means of a spectrograph. The light quantum giving rise to this scattering is generally obtained from the emission spectrum of mercury or helium and is similarly recorded. This source of monochromatic light is generally termed the exciting radiation. The scattered radiations of less energy than the

exciting frequency are the Raman frequency shifts or Raman lines. If a molecule in a vibrational or rotational level above the ground level interacts with a quantum of light, Raman lines of higher frequency than the exciting radiation may be emitted. These are anti-Stokes lines and are identical with the lower frequency shifts, but have intensities proportional to the population of the molecules in the upper levels. Each exciting source will give rise to a complete series of Raman lines. A commonly used excitation line is the mercury violet line at 4047 A.U., the Raman shifts appearing in the spectrum from 4047 A.U. to the blue-green region near 4800, depending on the compound irradiated. A schematic diagram of the experimental arrangement for recording Raman spectra is given in figure 1. Since each type of vibration or rotation gives rise to a Raman line, in a diatomic molecule only one vibrational Raman line is probable. These vibrations are analogous to a simple mechanical
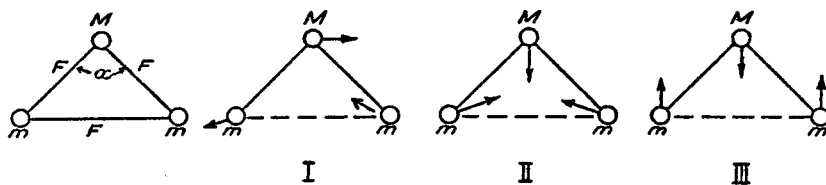
FIG. 2. The motions of a non-linear triatomic model

system consisting of two masses held together with a spring. The frequency at which they vibrate is represented by the simple equation

$$\nu = \frac{1}{2\pi} \sqrt{F/m} \tag{1}$$

where ν represents the mechanical frequency of vibration, m the mass of vibrating components, and F the force per unit displacement exerted between them. In an atomic system with ν expressed in wave numbers per centimeter and the masses by the relative atomic weights, this becomes

$$\Delta\bar{\nu} = 4.125 \sqrt{\frac{F}{m}} \tag{2}$$

from which either F or $\Delta\bar{\nu}$ may be calculated.

A system of three atoms of type AX_2 may exist in linear or non-linear forms. The motions of a non-linear model are illustrated in figure 2. Here the asymmetrical oscillation is indicated by I, the symmetrical by II, and the deformation motion by III.

For the linear model the Raman shift $\Delta\tilde{\nu}_1$ may be calculated if $\Delta\tilde{\nu}_2$ is known, by the relation,

$$\Delta\tilde{\nu}_1 = \Delta\tilde{\nu}_2 \sqrt{\frac{M + 2m}{M}} \tag{3}$$

and similarly for a model where spacial arrangement is in the form of an equilateral triangle of type X_3,

$$\frac{\Delta\tilde{\nu}_1}{\Delta\tilde{\nu}_2} = \sqrt{\frac{3F/m}{3F/2m}} = \sqrt{2} \tag{4}$$

The valence angle in non-linear simple diatomic models can be roughly approximated from the equation

$$\frac{\Delta\tilde{\nu}_1}{\Delta\tilde{\nu}_2} = \sqrt{\frac{M + 2m \sin^2 \alpha}{M + 2m \cos^2 \alpha}} \tag{5}$$

The greatest amplitude of vibration of the masses is given by

$$\bar{a} = \sqrt{\frac{2hN}{2\pi^2 c}} \cdot \sqrt{\frac{1}{\mu\Delta\tilde{\nu}}} \tag{6}$$

The frequencies calculated from these formulas are in many cases in reasonable accord with the experimental observations. Conversely, the molecular configuration necessary to give rise to the correct number and distribution of Raman lines can be determined. The mechanical models of Andrews and his coworkers (16, 331, 587) and of Trenkler (599, 600), which simulate the vibrations of atoms in molecules, give rise to frequencies of vibrations in fair agreement, in some cases, with observed Raman shifts. Any lack of agreement in either case is due primarily to oversimplification either mathematically or mechanically.

The usefulness of mechanical models is restricted largely to the study of certain relatively simple and stable types of vibration. Nevertheless, they indicate the realistic nature of the Raman effect and have a useful purpose. The valence force systems and central force systems of calculating the vibrational frequencies in more complicated molecules have been sufficiently fruitful (particularly the former) to indicate the general applicability of the more or less mechanical conception. Recently Wilson (648, 649, 650) has treated the problem analytically by means of the group theory, with calculable results compatible with the observed frequencies. A Raman spectrum is not, therefore, a matter of prestidigitation but has a sound statistical and theoretical basis. Furthermore, a reasonable extrapolation can be made in its application which carries its usefulness far beyond a spectroscopic phenomenon. Before proceeding further with

this phase of Raman spectra it should be emphasized that while these applications are treated more or less as a static manifestation they are in reality dynamic. All chemical linkages actually are not entirely fixed but may resonate between themselves. In discussing the shifts for particular organic compounds no attempt has been made to give a weighted value, but rather typical results. Reference should be made to the index of compounds for more detailed data. It is not possible to cite in the text all the contributions made by the large number of workers in this field. Those thus cited have been chosen for context or to illustrate different methods of approach.

IV. THE RAMAN SPECTRA OF ORGANIC COMPOUNDS

A. The Raman spectra of saturated aliphatic hydrocarbons

It has already been indicated that the magnitudes of Raman shifts are a function of the force exerted between the atoms in a molecule, the type

TABLE 1

Valence forces (F) for different types of linkage

LINKAGE	$F \times 10^{-5}$ DYNES CM.$^{-1}$	LINKAGE	$F \times 10^{-5}$ DYNES CM.$^{-1}$
H—H	5.38	N—H	6.39
C—H	5.02	O—H	6.72
C—C	4.40	C—N	4.53
C—O	5.05		
C=C	11.0	C≡C	14.82
C=O	11.7	C≡N	19.23
O=O	11.4	C≡O	18.83

of motion, and the relative masses of the atoms. Andrews (11) early noted that the force constant calculated from equation 2 was relatively constant for a single homopolar linkage, namely, approximately 5×10^5 dynes per centimeter, and nearly double and treble this value for double or triple bonds. This is indicated in table 1.

As the masses of the vibrating components decrease, the Raman shifts will increase. It is not surprising, therefore, that the shifts corresponding to the linear oscillation of the C—H are of large magnitude. These vary from 2800 to 3400 wave numbers per centimeter. This rather wide scale is due to some variation in the force constant as a function of constitution, as will be seen later. In table 2 are given some of the shifts for C—H observed by Bhagavantam (47) in the simpler hydrocarbons, and in figure 3 a reproduction of their Raman spectra as recorded on a photographic plate.

Methane is a molecule of the type AX₄ and has a tetrahedral structure, consequently there should exist several frequencies describing the atomic motions. Not all of these are present either as Raman lines or infra-red absorption. In order to have infra-red absorption by a molecule there must be a change in moment arising from an atomic oscillation. Infrared absorption bands may be absent when a given transition from one energy level to another is forbidden. Raman lines may be excited even if a transition between two characteristic levels is forbidden, if a common third discrete level exists to which a transition is possible from any two levels. In methane there appear $\Delta\bar{\nu}$ 1304 and $\Delta\bar{\nu}$ 3019 as infra-red absorption, and these are attributed to the unsymmetrical motion of the carbon atom. The latter frequency appears in Raman spectra as a weak line.

TABLE 2

The hydrogen to carbon oscillations of some simple hydrocarbons

HYDROCARBON	HYDROGEN OSCILLATIONS IN $\Delta\bar{\nu}$										
Methane......							2918 (10)			3018 (2b)	3066 (1)
Ethane........							2900 (9)	2955 (10)			
Propane.......	1453 (4)		2728 (3)	2767 (1)	2874 (10)	2903 (3)	2920 (5)	2948 (3)	2968 (3)		
Butane........	1453 (10b)	2665 (1)	2706 (1)	2736 (2)	2864 (4)	2879 (8)	2910 (3)	2938 (6)	2964 (3)		
Isobutane.....	1453 (10b)	2624 (1)	2720 (4)	2777 (2)	2870 (10)	2892 (2)	2910 (3)	2936 (3)	2962 (8)		

On the other hand $\Delta\bar{\nu}$ 2918 is the inactive oscillation forbidden in infra-red absorption but strong in Raman spectra and probably arising from the symmetrical motion of the hydrogen atoms in the expansion and contraction of the tetrahedron. In liquid methane Daure (194) and McLennan, Smith, and Wilhelm (424) have observed additional lines. It is not possible to obtain all the fundamental oscillations of methane as Raman lines.

While one strong line is characteristic of the linear C↔H oscillation in methane, in ethane there are two strong lines, $\Delta\bar{\nu}$ 2900 and 2955. This multiplicity of lines increases with the complexity of the molecules up to butane, after which there is no marked change. The appearance of these new lines is attributed to the perturbing influence of valence forces. The linear oscillation of the hydrogen attached to the central carbon atom in propane is obviously going to be affected by the adjacent methyl
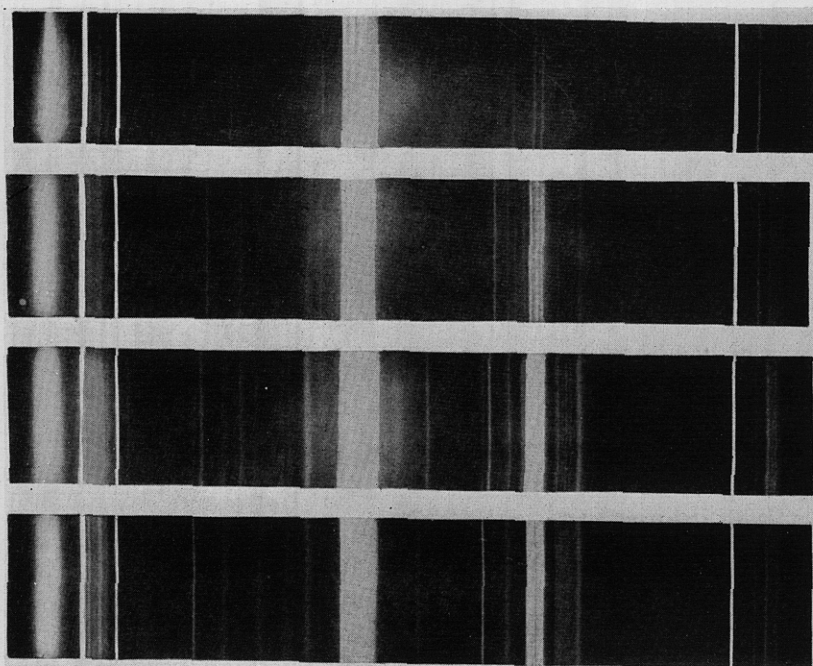
FIG. 3. The Raman spectra of some simple hydrocarbons as recorded on photographic plates (after Bhagavantam)

TABLE 3

Raman shifts for C—H vibrations

LINKAGE	$\Delta\tilde{\nu}$	LINKAGE	$\Delta\tilde{\nu}$
C—H (aliphatic)...............	2918	H │ C—C—C......................	2970
C—H (aromatic)...............	3054	│ H	
H │ C—C—H......................	2930 2862	H │ C (transverse)............ │ H	1450
│ H			

groups. Petrikaln (497), Andrews (11), Dadieu and Kohlrausch (175), and High (316) conclude that the approximate assignment of frequencies for C⟷H is as shown in table 3.   The shift at $\Delta\tilde{\nu}$ 1450 appearing in pro-

pane arises from the transverse oscillation of the hydrogen in respect to carbon and appears in all organic compounds having the

$$R—\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}—R$$
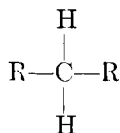
group.   The force constant for this type of vibration is approximately one-fifth that of the linear oscillation.   All these frequencies are absent in carbon tetrachloride and similar compounds containing no hydrogen.   It

TABLE 4

The carbon to carbon oscillations of some simple hydrocarbons

HYDROCARBON	CARBON OSCILLATIONS IN $\Delta\tilde{\nu}$									
Methane..............										
Ethane..............			993 (5)							
Propane..............		377 (2)	867 (10)				1055 (2b)		1155 (2)	
Butane..............	320 (0)	430 (6)	793 (4)	834 (10)	960 (3)	983 (3)	1060 (6)	1067 (0)	1146 (4)	1303 (3b)
Isobutane..........	372 (4b)	436 (2b)		796 (10)	967 (5b)				1177 (5b)	1355 (4b)

is to be noted that even in methane there may be combination frequencies which have not been mentioned.   For the higher members of the homologous series there are "inner vibrations" roughly independent of the rest of the molecule and "outer vibrations" which depend on the mass of the vibrating aggregates.

The carbon to carbon linkages in these compounds present a much more complex problem.   In ethane appears the shift $\Delta\tilde{\nu}$ 993, corresponding to the symmetrical C↔C vibration.   This decreases to $\Delta\tilde{\nu}$ 867 in propane, to $\Delta\tilde{\nu}$ 834 in butane, and thereafter becomes relatively constant. The transverse shifts due to the bending moment for the C—C linkage appear below $\Delta\tilde{\nu}$ 600, decreasing slightly with each added CH_2 increment. The total number of lines which occur will depend on the molecular configuration and the interaction of the valence forces.   Those which lie between $\Delta\tilde{\nu}$ 800 and $\Delta\tilde{\nu}$ 1100 are generally attributed to the carbon to carbon oscillations, although Simons (562) would extend this in some cases to as high as $\Delta\tilde{\nu}$ 1400.   Between $\Delta\tilde{\nu}$ 1100 and $\Delta\tilde{\nu}$ 1460 are the deformation oscil-
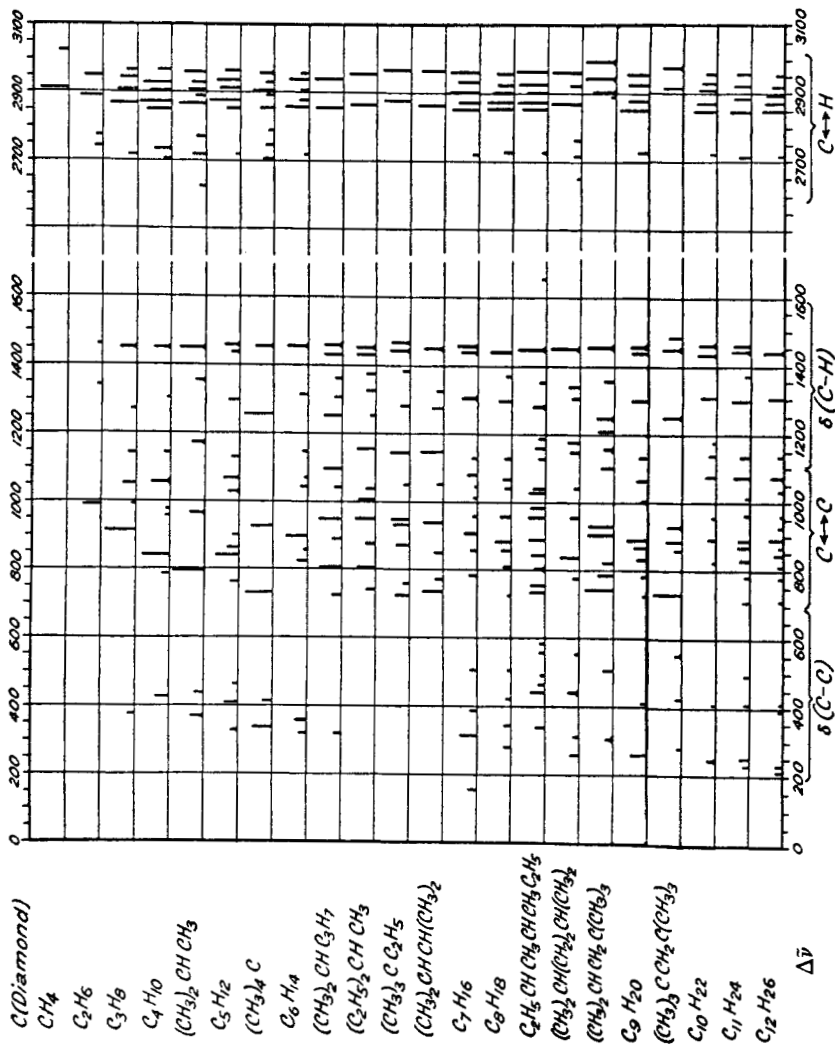
FIG. 4. Comparison spectra of saturated aliphatic hydrocarbons. (In order to have a uniform system of presentation in the figures, intensity estimates of other authors have been translated into the height of vertical lines.)

lations of C—H and finally, beginning at approximately $\Delta \bar{\nu}$ 2700, occur the symmetrical C—H oscillations. The C—C Raman shifts for the simpler hydrocarbons (49) are given in table 4. That the distribution of the lower carbon shifts is influenced by the centralization of the molecular groups is evidenced by the change in spectra proceeding from normal butane to tetramethylmethane or in the isomeric hexanes studied by Andant, Lambert, and Lecomte (9). Kohlrausch (341) suggests a constitutional influence in n-butane attributed to a zigzag or ⁀⌣⁀-shaped chain. In figure 4 are given the comparison spectra of most of the saturated aliphatic hydrocarbons which demonstrate the differentiating characteristic shifts.

The isomeric paraffins have been considered in detail by Tetetleni (588), Kohlrausch and Köppl (347, 349), and Dadieu, Pongratz, and Kohlrausch (191). According to Tetetleni the isomeric derivatives of the aliphatic compounds are richer in Raman lines and are more similar to each other than the cyclic compounds. Kohlrausch and his coworkers believe the chain frequency is slightly higher in the branched than in the normal chain compounds. The central force system fails to describe all the results, and the valence force system is only moderately accurate. As has been indicated, there is some decrease in the frequency shift which corresponds to the linear oscillation of the end vibrating group against the rest of the chain in the isomeric paraffins and possibly some differences in hydrogen frequencies depending on the type of branching. Individually there are considerable differences between the various isomers, as for example in the hexanes whose spectra are given in figure 4.

In interpreting these comparison spectra it must be borne in mind that differences in the spectra presented may not be real but may be due to the experimental conditions employed by several observers. A short exposure, designed to record only the strong lines in one compound, would make its spectrum apparently more simple than a much less complex compound exposed a longer time. There are undoubtedly other hydrogen lines in the $\Delta \bar{\nu}$ 3000 region for the hexanes, for example, which were not recorded. By comparing intensities of low wave number shifts and common shifts, both strong and weak, it is usually possible to distinguish actual spectral differences from fictitious ones. There is, of course, no difficulty when the spectra of the compounds are taken under reasonably comparable circumstances.

B. The Raman spectra of halogen derivatives of saturated aliphatic hydrocarbons

In a diatomic molecule of the type HCl, HBr, or HI one would expect a progressive diminution of the Raman shift with increased mass of the
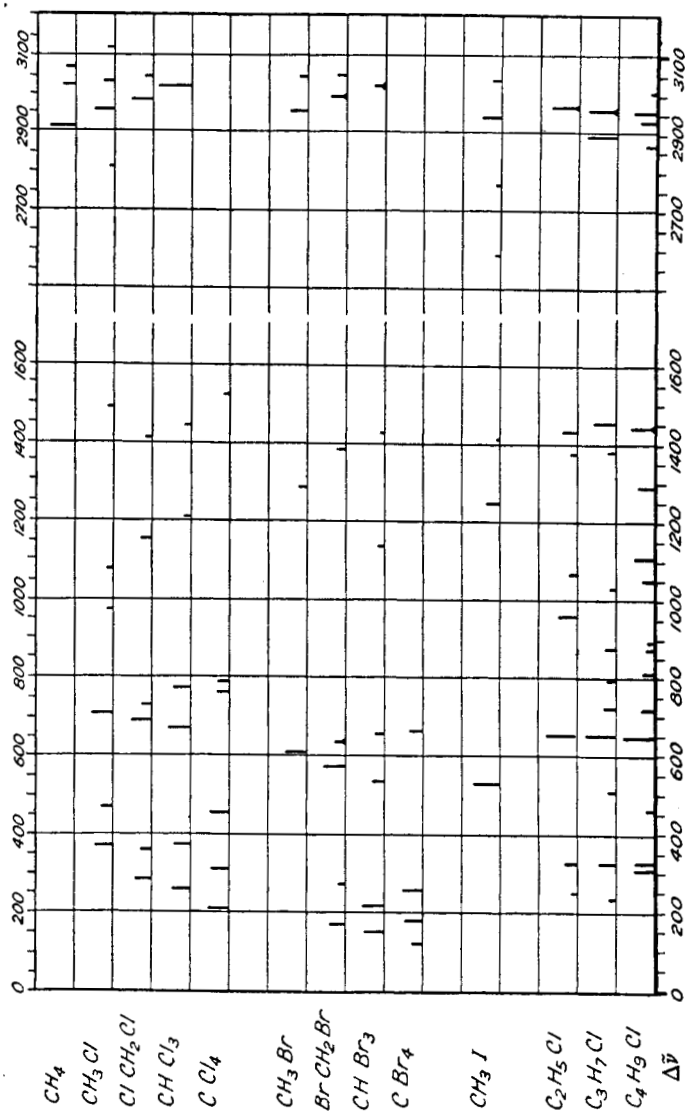
FIG. 5. Comparison spectra of some halogenated aliphatic hydrocarbons

anion. This is realized experimentally, the observed shifts being $\Delta\tilde{\nu}$ 2880, 2558, and 2233, respectively. Similarly in halogen-substituted methanes there is a corresponding progressive decrease in the values for the symmetrical oscillation $X \leftrightarrow CH_3$, concomitant with a change in the vibrational quantum number of ± 1. For methyl chloride, bromide, and iodide the decreases are $\Delta\tilde{\nu}$ 710, 600, and 530, and in ethyl chloride, bromide, and iodide, $\Delta\tilde{\nu}$ 654, 566, and 497. The change in masses alone is insufficient to explain this decrease. Harkins and Bowers (295) calculate the force constants which will balance the equation for the halogen derivatives of methane as being respectively 3.02, 2.6, and 2.17 $\times$ 10^5 dynes cm.$^{-1}$ and hence much lower than the average value of 5 $\times$ 10^5 dynes cm.$^{-1}$ found for ethane. Furthermore, the decrease in value from bromine to iodine is only slightly greater than 50 per cent of the decrease between chlorine and bromine. The results are further substantiated by West and Farnsworth (642), who observe that increasing the length of the chain beyond three carbon atoms causes no further decrease in the longitudinal Raman shift in a homologous series of monohalogen derivatives. Apparently the effective vibrating mass of carbon and hydrogen is 17, or slightly greater than one CH_2 group, regardless of the length of the chain. If, however, branching occurs near to the halogen atom the shift is reduced by approximately 30 wave numbers.

In addition to the wave numbers cited there occurs another series of shifts of lower value, possibly attributable to the transverse motion of the C—X linkage. These are for R—Cl $\Delta\tilde{\nu}$ 333, R—Br $\Delta\tilde{\nu}$ 280, and R—I $\Delta\tilde{\nu}$ 260, although the last item is confined to a few observations (175). The changes are depicted graphically in figure 5. The absence of shifts in methyl bromide below $\Delta\tilde{\nu}$ 600 is without significance. Practically all those occurring below $\Delta\tilde{\nu}$ 800 are attributed to the halogen substitution. By comparing figures 4 and 5 it will be seen that the presence of a halogen derivative could be detected in a hydrocarbon mixture by means of these characteristic shifts. The effect of increasing halogen substitution in a hydrocarbon on the C—H oscillations is to augment progressively the frequency of oscillation indicative, in this case, of greater bond strength, as the increased mass would diminish rather than enlarge this frequency. On the other hand, when substitution takes place on the β-carbon atom relative to the methyl group, there is little or no effect on the linear hydrogen vibration.

Cleetin and Dufford (129) have advanced the hypothesis that the shifts observed are fundamental and combination frequencies. Assuming an unobserved fundamental of $\Delta\tilde{\nu}$ 90, then the spectrum of methyl iodide is accounted for as follows:

	observed		*calculated*
$\Delta\tilde{\nu}$	534		ν_3
	2859		$\nu_4 - 4\nu_1$
	2771		$\nu_4 - 2\nu_1$
	2946		ν_4
	3036		$\nu_4 + \nu_1$

where $\nu_1\,\nu_2\,\ldots$ is somewhat inconsistently but universally used with reference to fundamentals and is equivalent to $\Delta\tilde{\nu}$. It will be used here in this manner. The results are in fair agreement in this and other cases. As these authors themselves point out, however, calculated results obtained with the *ad hoc* assumption of one or more fundamental frequencies are to be accepted with caution. Nevertheless, there is no doubt that combination frequencies may exist in Raman spectra.

Adel and Barker (1) have reviewed Bennet and Meyers' and Dennison's analyses of the vibrations of the methyl monohalides based on infra-red absorption.

By applying the wave function

$$\Psi_0 = \Psi_{(\sigma)}^{\nu'_1}\Psi_{(\rho)}^{\nu_4^l}e^{\pm il\varphi}$$

where ν_1, ν_4 and l are the quantum numbers of vibration and $\Psi_{(\sigma)}^{\nu'_1}$ and $\Psi_{(\rho)}^{\nu_4^l}$ are respectively the Hermitian orthogonal function with argument σ and the associated Laguerre orthogonal function with argument ρ^2 to determine the zero[th] order solution of the zero[th] order system of vibration, they conclude that there is an interaction between vibrational levels at $\Delta\tilde{\nu}$ 1460 and $\Delta\tilde{\nu}$ 2955 representing the fundamentals ν_4, ν_1, the former combining to $2\nu_4$ which interacts with ν_1, producing a resonance splitting of energy levels which will account for the C—H lines.

C. The Raman spectra of aliphatic alcohols

From the point of view of Raman spectra the delineation of the structures of the alcohols is one of its less fruitful applications. This is primarily because the force constant for C—OH is very much the same as that of C—C, and the relative mass of the OH group differs from that of a CH_3 group by only two units. There have been numerous attempts to assign specific Raman frequencies to types of vibrations in the alcohols. In the simpler cases this is undoubtedly a correct procedure. In the more complicated molecules, however, it is exceedingly difficult to distinguish between the vibrations of a hydrocarbon and those of a corresponding alcohol. It is of course obvious that the frequency at $\Delta\tilde{\nu}$ 1030 which appears in methyl alcohol is analogous to $\Delta\tilde{\nu}$ 993 in ethane and is attribut-
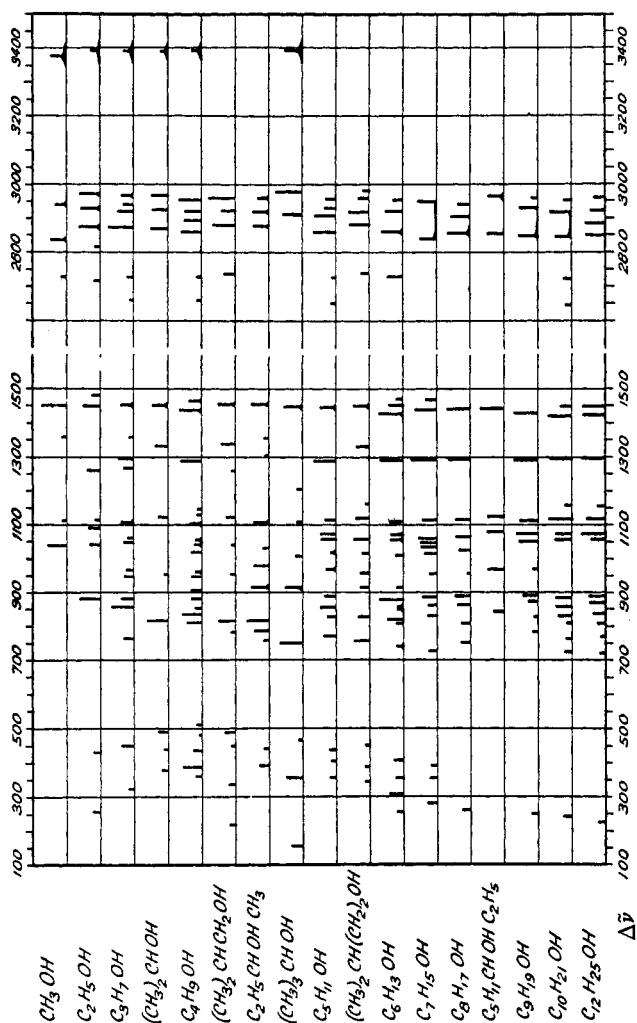
FIG. 6. Comparison spectra of aliphatic alcohols

able to the linear oscillation of the HO against the CH_3 group. Furthermore, as with the first members of the hydrocarbon series, there is a decrease in the magnitude of this oscillation with increased chain length. From ethyl to butyl alcohol inclusive this displacement has the values $\Delta\tilde{\nu}$ 885, 856, and 825, which is in reasonable accord with the change in vibration arising from the increased mass of one of the vibrating components as calculated by Trumpy (602).

With some alcohols there appears a very broad band of a width from 80 to 500 wave numbers, which can be resolved into several components; this is undoubtedly caused by the $H\leftrightarrow O$ oscillation. This generally occurs with a maximum near $\Delta\tilde{\nu}$ 3400. Unfortunately, however, this can only be detected in less than half of the alcohols studied. The infra-red counterpart of this shift, according to Wulf, is a sharp band. In figure 6 are given the spectra obtained from a series of aliphatic alcohols, mainly based on the work of Collins (133), Wood and Collins (661), Nevgi and Jatkar (471), and Kohlrausch (336). The shifts near $\Delta\tilde{\nu}$ 3400 are those observed by Médard (427).

Venkateswaran and Bhagavantam (626) attribute the shifts occurring near $\Delta\tilde{\nu}$ 1050, 1240, and 1360 to the C—OH group. The shifts between $\Delta\tilde{\nu}$ 1000 and 1250 are so numerous, and they are so close to those appearing in the normal hydrocarbons that is is impossible to say for a certainty that they owe their origins to the OH group. The shifts near $\Delta\tilde{\nu}$ 1450 occur likewise in the hydrocarbons, and are probably exclusively due to the transverse hydrogen vibration. The shifts near $\Delta\tilde{\nu}$ 1360 are present in only a few alcohols and those near $\Delta\tilde{\nu}$ 1300 in most hydrocarbons. It is noteworthy, however, that this latter shift is undoubtedly displaced toward a higher frequency in the isomeric alcohols. Furthermore, the spectra from the isomers are apparently more simple than those from the straight chain compounds. After the molecule reaches a length corresponding to nine carbon atoms there is very little change in the spectra (31).

Nevgi and Jatkar (471) attribute the frequencies from $\Delta\tilde{\nu}$ 2880 to $\Delta\tilde{\nu}$ 2960 to the longitudinal hydrogen vibration, $\Delta\tilde{\nu}$ 2880 arising from the α-CH, $\Delta\tilde{\nu}$ 2930 from the β-CH, and $\Delta\tilde{\nu}$ 2970 from the end CH which is the most free to vibrate. The assignment of $\Delta\tilde{\nu}$ 2880 to the α-CH is supported by its absence in tertiary butyl alcohol, but this conclusion is annulled by its presence in tertiary amyl alcohol. The $\Delta\tilde{\nu}$ 2747 occurring in isobutyl and isoamyl alcohols was attributed by them to the linear oscillation of a hydrogen atom in juxtaposition to two methyl groups. This view seems to be untenable, as this frequency shift occurs in several of the other alcohols which contain no substituted methyl groups.

Collins (133) has systematically investigated the lower frequency shifts

in a series of octanols whose structures differ only in the relative position of a methyl and hydroxyl group. When the compound has methyl groups only at the end of the molecule $\Delta\bar{\nu}$ 1300 is sharp, but if the molecule is branched this shift becomes either a doublet or broad. The inference is that the branched methyl groups have a slightly different frequency which accounts for this change. However, when the side-chain methyl group is attached to the same carbon atom as the hydroxyl group, as in 2-methyl-
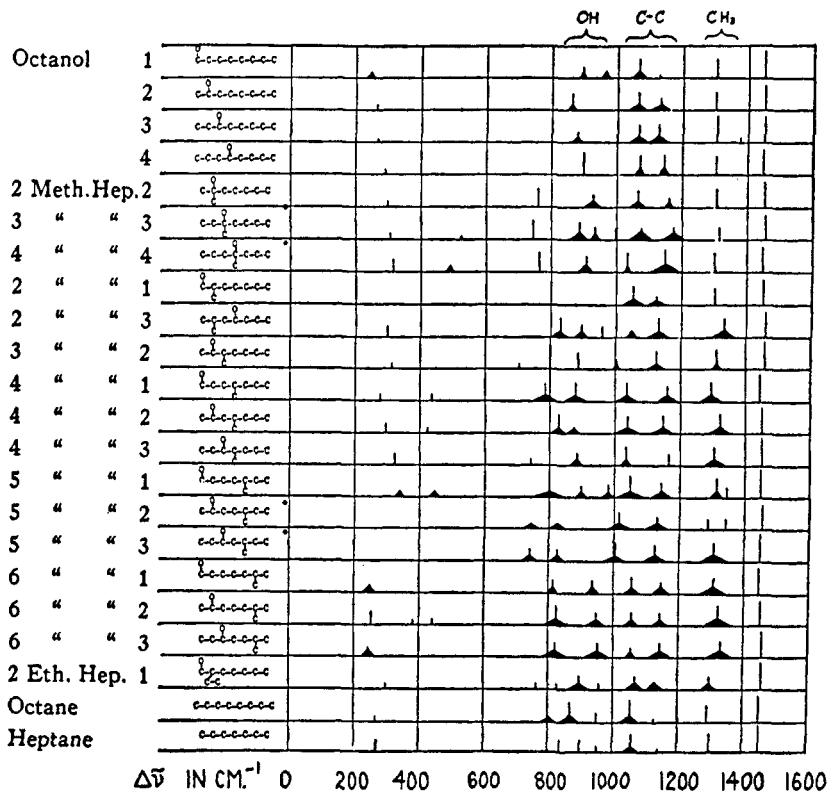
FIG. 7. Comparison spectra of nineteen octanols (after Collins)

2-heptanol, 3-methyl-3-heptanol, and 4-methyl-4-heptanol, the line at $\Delta\bar{\nu}$ 1300 remains sharp and a new line appears at $\Delta\bar{\nu}$ 755. The origin of the Raman line between $\Delta\bar{\nu}$ 800 and $\Delta\bar{\nu}$ 1000 is ascribed to the vibration of the hydroxyl group against the chains and the apparent doubling of the lines between $\Delta\bar{\nu}$ 1000 and $\Delta\bar{\nu}$ 1200 to the influence of the hydroxyl or methyl group in the side chain. Neither of these conclusions is completely tenable, as a comparison of figure 4 with figure 7 will demonstrate.

Assuming a valence angle of $\theta = 108°$ obtained from x-ray measurements and a force constant of 4.3×10^5 dynes per centimeter between the carbon atoms in a long chain, the $\Delta\bar{\nu}$ calculated from the equation

$$\Delta\bar{\nu} = \frac{1}{2}\left(\frac{2F\cos\theta/2}{\bar{\mu}}\right)^{1/2}$$

is 1075 for the inner C—C vibration.

The most comprehensive investigation of an alcohol has been undertaken by Bolla (63, 64), who observed approximately fifty-six frequencies in ethyl alcohol. He was able to account for forty-two of these as combination frequencies with an accuracy of less than 5 wave numbers. This leaves fourteen fundamental frequencies which are as given in table 5. Of these, $\Delta\bar{\nu}$ 3632, 3359, 3240, 1618, 814, and 256 are somewhat analogous

TABLE 5

Fundamental frequencies for ethyl alcohol

FREQUENCY	$\Delta\bar{\nu}$	INTENSITIES (BASIS 100)	FREQUENCY	$\Delta\bar{\nu}$	INTENSITIES (BASIS 100)
1	257	2	8	1455	46
2	433	6	9	1618	4
3	814	3	10	2879	59
4	883	60	11	2929	100
5	1051	32	12	2972	61
6	1096	27	13	3240	3
7	1274	17	14	3359	10

to the Raman spectrum of water. Titéica (597) considers $\Delta\bar{\nu}$ 426, 883, and 1046 as the fundamentals for the C—C oscillations, and $\Delta\bar{\nu}$ 1456, 2823, 2928, and 2974 as the fundamental C—H oscillations, $\Delta\bar{\nu}$ 1273, 2637, and 2876 being combinations. It is felt, however, that the assignments of Bolla (63, 64) are probably more compatible with the observations.

The polybasic alcohols have not been so widely investigated, with the exception of glycerol. Glycol, taking the average values of the observations of Whiting and Martin (645), Howlett (321), Morris (456), and Hibben (309), yields $\Delta\bar{\nu}$ 510, 660, 865 (7), 960, 1035 (5), 1070, 1090, 1260, 1465 (5), 2873 (7), 3400, where $\Delta\bar{\nu}$ 865, and possibly the 1035 to 1090 lines, are connected with the R—OH oscillation and the remainder have the significance already indicated. The $\Delta\bar{\nu}$ 3400 corresponding to the H↔O vibration is much sharper than in water or methyl alcohol, owing apparently to a more specific quantization of the vibrational energy.

Propylene glycol (456) yields $\Delta\bar{\nu}$ 830 (7), 919, 1050, 2918 (7). Glycerol has been investigated by several observers (645, 616, 516, 309, 552) and the values $\Delta\bar{\nu}$ 485, 690, 845 (7), 925, 1080, 1455 (7), and 2910 (6) obtained. There is a strong continuous scattering from glycerol attributed by Venkateswaran to its viscosity, but by Bär (26) to fluorescence on the basis of its depolarization, and by others to impurities (559). The continuous spectra decreased with increased dilution and temperature. A similar behavior in phosphoric acid solutions was noted by Hibben (309). It is certain that either fluorescent impurities or a slightly fluorescent material will be the source of a somewhat continuous spectrum. In some cases, however, the effect of temperature and dilution is so marked as to make this less probable as a universal explanation. Hibben (310) has observed that the fluorescence arising from concentrated alcoholic zinc chloride solutions can be quenched by the addition of traces of potassium iodide or nitrobenzene, which is indicative of deactivation by collisions of the second kind (Perrin).

Sugars, which may be considered in part as polybasic alcohols, have been little investigated. In view of the intense interest in the constitution of sugars from an organic or biochemical point of view, this seems rather remarkable. Kutzner (386) observed a shift at $\Delta\bar{\nu}$ 1140 in glucose and 1179 in fructose, the remaining sugars having the shift at approximately 1150. Other lines were lost behind a strong continuous spectrum. Whiting and Martin (645) obtained $\Delta\bar{\nu}$ 1090, 1480, 2870, and 3420 as the stronger lines from sucrose. Polara (516) investigated dilute solutions of a sugar, presumably glucose, and obtained the following shifts: $\Delta\nu$ 625, *668, 689, 858, 945, 1037*, 1134, 1224, 1339, *1425*, 1488, 1683, 2016, 2025, 2113, 2164, 2404, 2718, *2873*, where the italicized digits are shifts not far removed from those observed in glycol, glycerol, and propylene glycol. While low-frequency hydrogen shifts between $\Delta\bar{\nu}$ 2000 and 2600 have been observed rarely, this never has occurred at exposures which failed to bring out also the chain deformation oscillations ($<\Delta\bar{\nu}$ 650) in a molecule of this size. It seems probable, therefore, that these are either spurious or wrong assignments. The significance of $\Delta\bar{\nu}$ 1683 will be discussed later.

The investigation of characteristic frequency shifts for the alcohols is far from clear. This is primarily due to the equivalence of the hydroxyl and methyl groups. Neither the higher frequencies corresponding to the hydrogen oscillations, nor the lower frequencies corresponding to the C—OH oscillations are precisely equivalent to those observed in the hydrocarbons. Most of the intermediate frequencies, however, appear in both types of compounds. It is possible that shifts near $\Delta\bar{\nu}$ 1050 and 1300 may be connected with a carbon to oxygen vibration. Unless, however, compounds are investigated under identical conditions and with sufficient

dispersion, a precise assignment of frequencies in this region is precarious. By ignoring contemporaneous data obtainable from other types of compounds one can justify the specific assignment of these shifts with some accuracy. By taking everything into consideration it is certainly possible to identify some of the alcohols in a mixture—particularly the isomeric alcohols—when it is not possible to identify the alcohols in the presence of some hydrocarbons. A further study of the O↔H vibrations in the alcohols would be of value.

D. The Raman spectra of saturated aliphatic ethers

The ethers present many of the same problems as the alcohols. An ether is an alcohol which has had its alcoholic hydrogen replaced by an organic radical. The ethers have been investigated by Lespieau (409, 410), Dadieu and Kohlrausch (173), Gopala Pai (266), Sirkar (569), Ganesan and Venkateswaran (242), Bär (25), Daure (193, 194), High (316), and others. For the most part attention has been directed primarily to diethyl ether, the observed shifts for which are $\Delta\tilde{\nu}$ 375 (0), 440 (5), 500 (0), 840 (3), 928 (2), 1025 (1), 1077 (0), 1150 (2), 1270 (1), 1453 (5), 2693 (1), 2804 (2), 2870 (8), 2930 (6), 2978 (4). For dimethyl ether the values $\Delta\tilde{\nu}$ 333 (0), 416 (0), 930 (2), 1102 (0), 1160 (1), 1455 (1), 2814 (7), 2869 (3), 2920 (3), 2955 (2), 2990 (4) were observed. Dipropyl, diisopropyl, diamyl, and diisoamyl ethers have been investigated by High (316). The hydrogen spectrum of these ethers consists primarily of three lines located near $\Delta\tilde{\nu}$ 2865, 2920, and 2960, the lower frequency shifts beginning with $\Delta\tilde{\nu}$ 930 in dimethyl ether become $\Delta\tilde{\nu}$ 840 in diethyl, 790 in isopropyl, and 765 in amyl and isoamyl ethers in the same fashion as has been observed previously for the outer vibration of a unit on the end of a chain. Either dipropyl ether is an exception or else the expected shift at approximately $\Delta\tilde{\nu}$ 820 was not recorded. With the exception of dimethyl ether and the iso ethers all the remainder have shifts at approximately $\Delta\tilde{\nu}$ 1280. There are no shifts recorded between 1150 and 1450 for diisopropyl or diisoamyl ethers. This makes it quite easy to distinguish the presence of the iso forms. There is a fairly strong similarity between the spectra of the alcohols and the equivalent ethers, although the intensities of the lines obtained from the ethers in the region below $\Delta\tilde{\nu}$ 1450 are relatively much weaker than for the equivalent lines in the alcohols. Gopala Pai (266) has attempted to calculate the valence angle of the oxygen in dimethyl ether on the assumption that it is a symmetrical triatomic molecule. Its valence angle is calculated to be 102° (which is near the tetrahedral angle of 109.5°), from the observed fundamental Raman frequencies of $\Delta\tilde{\nu}$ 1102, 921, and 416. On the other hand, similar calculations for ethylene oxide, assuming $\Delta\tilde{\nu}$ 1115, 865, and 810 as the fundamentals,

yield a value of only 61° as the angle calculated. This large decrease in the oxygen valence angle is because of the bond between the two carbons in ethylene oxide. This view is supported by the relatively permanent dipole moments of these compounds.

Titéica (597) considers the fundamental frequencies for diethyl ether (corresponding to $\nu_1 \nu_2 \ldots$) as $\Delta \tilde{\nu}$ 927, 1148, 494, 540, 438, 840, 375 for the C—C and $\Delta \tilde{\nu}$ 1455, 2930, 2866, 2978 as the fundamentals for the C—H. The combination frequencies are $\Delta \tilde{\nu}$ 1038, representing $\nu_3 + \nu_4$, and $\Delta \tilde{\nu}$ 1077, a higher harmonic of ν_4, and finally $\Delta \tilde{\nu}$ 1270, a combination of ν_5 and ν_6.

A series of the ethylene oxides has been investigated by Lespieau and Grédy (409). The ethylene oxides will be considered here even though they are cyclic compounds which have been reserved for later treatment. It is believed that they more properly may be considered ethers. Frequencies observed for ethylene oxide are $\Delta \tilde{\nu}$ 808 (8), 869 (8), 1119 (5), 1269 (7), 2917 (7), 2959 (7), and 3009 (7). On comparing this with dimethyl ether it is observed that the spectra are remarkably different. There are only three lines which even approximately have any similarity. These are $\Delta \tilde{\nu}$ 869—which is $\Delta \tilde{\nu}$ 830 in dimethyl ether—and the two hydrogen vibrations, $\Delta \tilde{\nu}$ 2917 and 2959, which are approximately the same in dimethyl ether. It is particularly noteworthy that $\Delta \tilde{\nu}$ 1450, observed in all the alcohols, ethers, and hydrocarbons, with the exception of methane, is entirely absent. One would expect on substituting ethylene oxide with a side chain that the resulting spectra would have some shifts in common with the hydrocarbon radical and the increased mass would have a tendency to decrease the outer vibrations. This apparently is the case. For ethylethylene oxide the following shifts are obtained: $\Delta \tilde{\nu}$ 405 (2), 455 (1), 475 (1), 732 (5), 762 (2), 802 (2), 835 (8), 905 (8), 957 (1), 1021 (1), 1051 (1), 1110 (2), 1264 (9), 1415 (2), 1456 (6), 1487 (2), 2887 (2), 2925 (10), 2945 (10), 2976 (5), 3002 (5), 3055 (2). The comparison spectra of the ethylene oxides investigated are given in figure 8.

It can be seen from the numerical values given, that the effect of the introduction of the ethyl group is to produce a number of frequencies in the region between $\Delta \tilde{\nu}$ 900 and 1100, $\Delta \tilde{\nu}$ 1456 and 1487 as a doublet, and $\Delta \tilde{\nu}$ 2887 as well as some additional lower frequencies. The $\Delta \tilde{\nu}$ 1456, as has been pointed out previously, owes its origin to the transverse motion of the hydrogen. The frequency of this transverse motion is considerably reduced when the hydrogen is attached to a ring carbon, but immediately reappears in its usual position following the substitution of a side chain containing a hydrogen attached to a carbon outside the ring structure. The $\Delta \tilde{\nu}$ 2887 would seem to owe its presence to the linear oscillation of a hydrogen atom attached to a chain CH_2 group, since it is absent in 1,2-dimethylethylene oxide. On the other hand, it is present in 1,1-dimethyl-
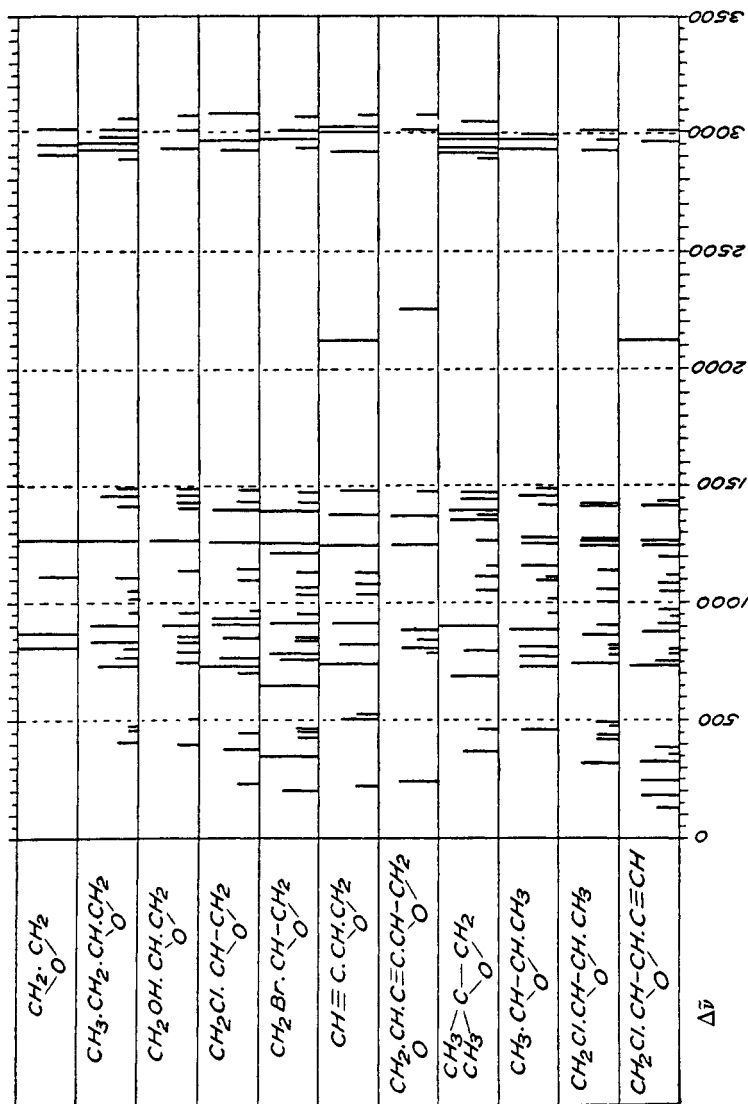
FIG. 8. Comparison spectra of ethylene oxides (after Lespieau and Grédy)

ethylene oxide. The most consistent shift is the one at $\Delta\bar{\nu}$ 1265, which remains unchanged practically throughout the series except for a doubling effect, and must be considered, therefore, the most characteristic vibration of this inner ring structure. It is strong and easily identified. The other outstanding characteristic is the first appearance of the hydrogen lines above $\Delta\bar{\nu}$ 3000, as will be discussed later. This is a characteristic of hydrogens attached to a ring or to an ethylenic linkage and is consequently present in cyclopropane and benzene. Apparently the introduction of an acetylene radical in a side chain produces a number of very low frequency oscillations all out of proportion to the masses involved. The number of frequency shifts in the region below $\Delta\bar{\nu}$ 600 is fewer when the molecule is symmetrically balanced. For the disubstituted ethylene oxides the $\Delta\bar{\nu}$ 1269 becomes double (1256–1277). Lespieau and Grédy attribute this doubling to the presence of two stereoisomers which give a spectrum consisting of two distinct lines. These isomeric forms are:

$$
\begin{array}{ccc}
\text{R} & \text{R}' & \qquad \text{H} \qquad \text{R}' \\
| & | & \qquad | \qquad\quad | \\
\text{C} \!\!-\!\!-\!\! \text{C} & \qquad \text{C} \!\!-\!\!-\!\! \text{C} \\
| \;\diagdown\!\text{O}\!\diagup\; | & \qquad | \;\diagdown\!\text{O}\!\diagup\; | \\
\text{H} \qquad \text{H} & \qquad \text{R} \qquad \text{H}
\end{array}
$$

The spectra of the ethers are very close in general to the spectra obtained from the alcohols and the hydrocarbons. The addition of an oxygen is in some respects quite similar to the addition of a carbon. Nevertheless, there are considerable differences in particular lines between the ethers and the other compounds so far described. The iso ethers, like the iso alcohols, have marked differences in their spectra from the spectra of the normal compounds. The cyclic ethers have spectra more nearly like those of the cyclic hydrocarbons.

So far the Raman spectra of alcohols, ethers, and hydrocarbons have been considered as a function of constitution. It has been shown that they vary not only in a particular homologous series but also among themselves. From the evidence so far presented it is possible to calculate the force exerted between the atomic constituents of the molecules under normal conditions and in simple cases their relative configuration. Furthermore, the type of vibrations which give rise to certain frequencies is quite clear. The effect of substitution on these frequencies is notable and can be calculated if the molecules are not too complex. If the substituent group is markedly different in mass, or if the force constant between the carbon and a substituent atom or group is markedly different, it has a pronounced effect on Raman spectra obtainable from the molecules. This is clear in the case of the halogen substitutions. When the
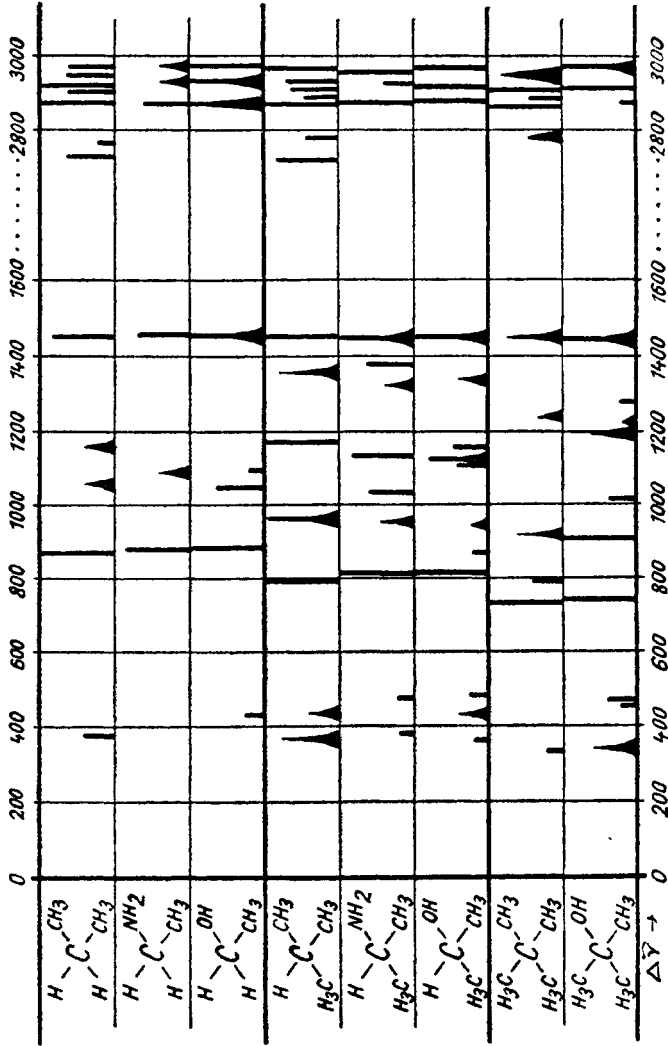
Fig. 9. The effect of substitution on some simpler hydrocarbons (after Kohlrausch, Pongratz, and Seka)

mass and the force constants remain very much the same it is more diffi-
cult, but not impossible, to distinguish the effect of the substitution in a
not too complicated mixture.   In figure 9 are shown the effects of different
substituent groups on similarly constituted hydrocarbons, as taken from
the summary of Kohlrausch, Pongratz, and Seka (369).

It is to be emphasized most strongly that the discussion thus far rests
primarily upon the magnitude of the Raman shift.   There are two other
parameters, however, which may be invoked to describe the type or char-
acter of oscillations besides the actual displacements.   These are the
intensities, which have been given only roughly, and the degree of depolari-
zation.   As has been pointed out, in Raman spectra the symmetrical oscil-
lations are the most intense and most strongly polarized; this is reflected
in the smallest depolarization constant.   In comparing, for example, the
types of oscillations which will give rise to Raman lines in bromoform or
chloroform, even though the magnitude of displacement may be radically
different, it is possible to distinguish from their degree of depolarization
what lines are attributable to a symmetrical oscillation.

As the hydrocarbon radical will present a more or less constant rôle,
for future considerations the remainder of the treatment of Raman spectra
from hydrocarbons and their derivatives will be based mainly on the
effects of types of linkage rather than on complete spectra.   This is for
a twofold purpose: first, because the effects of substitution on the linkage are
made more clear if the summary is confined to the linkage involved, and
second, because of space and time considerations.   Recourse may be had
to the indices for complete details on every compound.   In most cases it
is sufficient to illustrate the correlation between Raman spectra and the
types of linkage without discussing in complete detail the entire Raman
shifts for every compound studied.

E. Raman spectra and the ethylenic linkage

It has already been shown that a pronounced effect upon a single bond
takes place on the substitution of atoms of a quite different nature from
the organic radicals.   In the case of the ethylenic linkage this effect is
equally pronounced and much more easily measurable.   The Raman
spectrum for $C{=}C$ falls in the region of $\Delta\bar{\nu}$ 1600 to 1650 more or less
completely separated from any lines due to any other type of oscillation.
The lines are sharp and can be measured with accuracy.   Therefore, the
effects of mass and of the binding force of the atoms in the molecule can
be determined with considerable exactness.   The reason for this unique
displacement is that the force constant is roughly twice that involved in
a single bond and hence carries the emission to a region free from other
Raman lines.   This opens up a more or less endless avenue in the investi-

gation of constitutional problems where ethylenic linkages are involved. An example of this is in the terpenes, which will be discussed later, and in the identification of various isomers. It may be stated categorically that any straight chain compound and most cyclic compounds having the structure —C=C— will show a Raman shift in the 1600 region. If the structure is —C=C=C—, however, this is not true and the characteristic shift will fall elsewhere, for reasons which will be explained later. Most of this evidence is empirical, although in the simpler ethylenic hydrocarbons one can calculate quite easily the relative forces and spacial configurations. The empirical approach nevertheless is the same approach by which the chemist knows that barium sulfate is precipitated on the addition of barium salts to a solution containing soluble sulfates. The physicist might rest more tranquilly if the cloak of respectability could be given these procedures by clothing them with eigenfunctions and Greek letters. Nevertheless the probabilities are, under these conditions, that barium sulfate is the precipitate. Likewise the appearance of a Raman shift in the region between $\Delta\bar{\nu}$ 1600 and 1650 is equally indicative of a double linkage in this type of compound.

In table 6 are given the Raman shifts of many of the ethylenic hydrocarbons. In some cases the studies have not been complete, and in other cases the relative intensities have not been recorded. In table 7 are given the Raman shifts for some of the ethylenic hydrocarbons as a function of substitution. It has been observed that substitution affects the saturated hydrocarbons, particularly in the lower frequencies and occasionally in the higher frequencies. This is easily discernible with the ethylenic hydrocarbons by the reaction on the double-bond linkage. The ethylenic hydrocarbons have five shifts more or less characteristic. Those shifts in the $\Delta\bar{\nu}$ 1600 to 1650 region are correctly attributable to the C=C linkage and those between $\Delta\bar{\nu}$ 3000 and 3100 to the C—H. In the saturated hydrocarbons any frequency beyond $\Delta\bar{\nu}$ 3000 is exceptional, save those attributable to cyclic compounds. The intensity relations make it very easy to distinguish between a hydrogen attached to a double bond and the shift arising from a hydrogen in a ring structure without a double bond. Bourguel (97, 99) has indicated the effect of substitution. If one replaces the hydrogen in ethylene with a hydrocarbon radical or substituted radical the ethylenic shift $\Delta\bar{\nu}$ 1620 is increased. For example, in propylene it becomes $\Delta\bar{\nu}$ 1647. This decreases gradually, so that with benzylethylene it has become $\Delta\bar{\nu}$ 1640. If, however, a hydrogen atom in ethylene is replaced by an aldehyde group or a halogen atom the frequency is markedly reduced, becoming $\Delta\bar{\nu}$ 1608 in monochloroethylene and

TABLE 6
Raman shifts for some ethylenic hydrocarbons

COMPOUNDS	$\Delta\bar{\nu}$ 0 to 700	$\Delta\bar{\nu}$ 700 to 1000	$\Delta\bar{\nu}$ 1000 to 1500	$\Delta\bar{\nu}$ 1500 to 1700	$\Delta\bar{\nu}$ 1700 to 3000	$\Delta\bar{\nu}$ 3000 to 3200
Ethylene			1340(3)	1620(3)		3000(5) 3082(3)
Propylene (incomplete)			1295(8) 1414(6)	1647(8)		3007(7) 3086(7)
Trimethylethylene	253(1)* 388(5) 444(5) 528(5)	767(7) 803(2)	1338(7) 1383(7) 1446(7)	1653(1) 1679(8)	2732(1) 2861(8) 2885(2) 2922(10) 2973(8)	3055(2)
1-Pentene	386(5) 427(2) 628(1)	851(5) 881(5) 913(5) 993(1)	1047(2) 1095(2) 1232(2) 1296(8) 1416(8) 1447(7)	1642(8)	2847(3) 2866(3) 2877(8) 2910(8) 2938(8) 2966(5)	3000(8) 3080(8)
2-Pentene	211(3) 412(5) 488(7) 578(3) 698(2)	752(3) 800(5) 860(5) 880(2) 943(3) 966(2)	1027(5) 1066(5) 1248(7) 1268(7) 1290(7) 1310(7) 1379(7) 1450(8)	1658(7) 1674(8)	2857(7) 2887(8) 2920(10) 2941(10) 2966(8)	
1-Hexene	358(2)	818(2) 873(1) 912(2)	1056(2) 1296(7) 1417(8) 1448(7)	1642(8)	2859(5) 2876(8) 2909(8) 2963(5)	3002(8) 3076(5)
2-Hexene (mixture)	389(2)	857(2) 892(2)	1042(2) 1095(5) 1216(1) 1258(5) 1290(5) 1308(7) 1378(5) 1445(7)	1658(5) 1674(7)	2875(8) 2920(8) 2939(7)	
4-Methyl-2-pentene	333(2) 345(2) 484(5)	820(5) 905(2) 956(2)	1043(2) 1103(5) 1256(2) 1300(7) 1380(5) 1456(7)	1659(5) 1673(7)	2870(8)	

* The values for the intensities are those given in parentheses.

TABLE 6—*Continued*

COMPOUNDS	$\Delta\tilde{\nu}$ 0 to 700	$\Delta\tilde{\nu}$ 700 to 1000	$\Delta\tilde{\nu}$ 1000 to 1500	$\Delta\tilde{\nu}$ 1500 to 1700	$\Delta\tilde{\nu}$ 1700 to 3000	$\Delta\tilde{\nu}$ 3000 to 3200
3-Methyl-2-pentene (mixture)	320(2) 395(2) 490(5) 551(1)	749(7) 825(1) 125(1)	1071(5) 1117(2) 1255(5) 1317(2) 1350(5) 1383(7) 1451(7)	1673(8)	2852(8) 2879(8) 2920(8) 2966(7)	
2-Methyl-2-pentene	356(5) 473(2) 513(5)	745(5) 816(7) 833(7) 908(7)	1007(5) 1063(7) 1120(2) 1262(5) 1306(7) 1351(5) 1381(7) 1452(7)	1676(8)	2879(8) 2912(8) 2932(8) 2964(7)	
2,5-Dimethyl-2-hexene (incomplete)		702 769 805 848 949	1107 1264 1328 1376 1445	1669		
3,5-Dimethyl-3-hexene (incomplete)		775 844 956	1032 1120 1282 1327 1380 1450	1667		
3,6-Dimethyl-2-heptene (incomplete)		803 840 953	1025 1108 1330 1381 1449	1668		
4,6-Dimethyl-3-heptene (incomplete)		804 954	1038 1103 1295 1327 1380 1452	1667		
2,3,5-Trimethyl-2-hexene (incomplete)		850 958	1105 1330 1382 1454	1667		

TABLE 6—*Concluded*

COMPOUNDS	$\Delta\bar{\nu}$ 0 to 700	$\Delta\bar{\nu}$ 700 to 1000	$\Delta\bar{\nu}$ 1000 to 1500	$\Delta\bar{\nu}$ 1500 to 1700	$\Delta\bar{\nu}$ 1700 to 3000	$\Delta\bar{\nu}$ 3000 to 3200
2,4-Dimethyl-2-octene (incomplete)		786 862 955	1103 1163 1295 1328 1377 1450 1465			
2-Methyl-2-octene	187(5) 403(7) 445(3)	761(2) 795(2) 852(3) 893(5) 968(3)	1017(1) 1110(5) 1302(7) 1320(5) 1383(10) 1442(10)	1677(8)	2800(10) 2975(10)	
3-Methyl-2-octene (incomplete)	166(1)		1072(5) 1117(5) 1170(5) 1258(1) 1299(5) 1360(1) 1380(5) 1445(10)	1671(9)	2855(10) 2876(5) 2899(5) 2920(7) 2940(7) 2966(10)	
2,4,6-Trimethyl-3-heptene (incomplete)		702 797 860 956	1102 1165 1300 1329 1377 1449	1665		
2,4,7-Trimethyl-4-octene (incomplete)		952	1098 1283 1329 1375 1448	1663		

$\Delta\bar{\nu}$ 1595 in monobromoethylene. If the effects of different substituents be compared, it is evident that a hydrocarbon substituent on the one hand and an alcohol or a halogen on the other reacts on the C=C linkage in the opposite sense. Furthermore, if the substitution takes place in the β-position in reference to the double bond, the effect is much less marked than in the α-position. This is in accord with the classical organic theory, in regard to the continuing effect of substitution in the hydrocarbon chain.

1. Cis-trans isomerism

The compounds given in table 7 are essentially those of the type R—CH=CH$_2$. The question now is what effect on the C=C shift have substitutions of the type R—CH=CH—R'. This brings immediately to the fore the problem of *cis-trans* isomerism. The isomers of this type examined earliest were the 1,2-dichloroethylenes, studied by Bonino and Brüll (77), and the geometrical isomers ethyl fumarate and ethyl maleate which were investigated by Ffolliott (231). Pestemer (496), and Dadieu,

TABLE 7

Raman shifts characteristic of C=C and other shifts common to olefins

SUBSTANCE	Δν̃					
CH$_2$=CH·H		1340		1620	3000	3080
CH$_2$=CH·CH$_3$	1295	1414		1647	3007	3086
CH$_2$=CH·C$_2$H$_5$	1294	1416		1642	3003	3083
CH$_2$=CH·C$_3$H$_7$	1296	1416		1642	3001	3079
CH$_2$=CH·C$_4$H$_9$	1295	1416		1642	3002	3076
CH$_2$=CH·C$_5$H$_{11}$	1299	1416		1642	3000	3081
CH$_2$=CH·C$_6$H$_{13}$	1296	1416		1642	3001	3081
CH$_2$=CH·CH$_2$·C$_6$H$_5$	1296	1413		1642	3006	3067
CH$_2$=CH·C$_7$H$_{15}$	1300	1416		1642	3003	3081
CH$_2$=CH·CH$_2$·C≡C·C$_6$H$_5$		1416		1642		
CH$_2$=CH·CH$_2$OH	1290	1416		1646	3014	3089
CH$_2$=CH·CHOH·CH$_3$	1287	1416		1646	3013	3089
CH$_2$=CH·CHO	1277	1363		1618		
CH$_2$=CH·COOH	1288	1397		1638		3111
CH$_2$=CH·Cl	1271	1355		1608	3036	3134
CH$_2$=CH·CH$_2$Cl	1291	1411		1640	3022	3090
CH$_2$=CH·CH$_2$Br	1295	1409		1635	3016	3089
H$_2$C=CH·CH=CH$_2$	1277	1436		1634	3000	3090
H$_3$C·CH=CH·CH=CH$_2$	1288	1443	1597	1646	2998	3089
H$_2$C=C(CH$_3$)·CH=CH$_2$	1291	1420		1640	3012	3090
H$_2$C=CHCH$_2$CH=CH$_2$	1295	1413		1644	3010	3084
H$_2$C=CHCH$_2$CH$_2$CH=CH$_2$	1298	1416		1641	3004	3081

Pongratz, and Kohlrausch (180, 181, 182, 183) have also considered the *cis-trans* isomerism in halogen and oxygen derivatives of ethylene. Apparently the effect on the ethylenic linkage is rather small in these types of compounds. There is, however, a pronounced change in the spectra, particularly in reference to the middle and lower frequency shifts. In table 8 are given recent results of Trumpy (608) with dichloroethylene. It is observable that there is considerable difference between the spectra of the two compounds.

In the hydrocarbons, however, on account of the multiplicity of lines in the lower frequency regions, it is much more important to ascertain if there is an effect on the C=C linkage which can be clearly observed. Bourguel, Grédy, and Piaux (104) examined some of the substituted unsaturated hydrocarbons, with the results presented in table 9. The *cis*-ethylenic compounds of the type R—CH=CH—R′, where R′ is an ethyl group, give $\Delta\bar{\nu}$ 1658. In the corresponding *trans*-forms, however, the shift becomes $\Delta\bar{\nu}$ 1674. If R′ is a phenyl group in lieu of an ethyl group the external C=C shift is decreased and becomes $\Delta\bar{\nu}$ 1642 for the *cis*-form and $\Delta\bar{\nu}$ 1664 for the *trans*. In all cases the *trans*-compound has a shift greater by 15 wave numbers than the *cis*-compound. The band between $\Delta\bar{\nu}$ 1255 and 1260 in the *cis*-compound is slightly elevated and $\Delta\bar{\nu}$ 1376

TABLE 8

The Raman effect in two isomeric derivaties of ethylene

cis-DICHLOROETHYLENE			trans-DICHLOROETHYLENE		
$\Delta\bar{\nu}$ cm.$^{-1}$	i	p	$\Delta\bar{\nu}$ cm.$^{-1}$	i	p
171	18	0.50	350	20	0.29
407	10	0.82	752	5	0.7
561	5	0.88	840	6	0.08
711	15	0.05	1271	15	0.2
806	0.5		1575	10	0.07
880	1	D	1625	0.5	P
1180	10	0.7	1690	1	P
1586	15	0.08	3072	10	0.2
1688	2		3140	1	
3078	20	0.31			
3158	1				

appreciably stronger in the *trans*-compound. This work has been repeated by Grédy (281) with similar results. Grédy and Piaux (283) have examined the *cis*- and *trans*-forms of crotonyl acetate, methylvinylcarbinol acetate, crotonyl alcohol, methylvinylcarbinol, crotonaldehyde, 1-methylallyl bromide, and 2-butenyl bromide. For the aldehyde $\Delta\bar{\nu}$ 1647 is attributed to the *trans*-form and $\Delta\bar{\nu}$ 1625 to the presence of 1 per cent of the *cis*-form. Similarly with the crotonyl alcohol, $\Delta\bar{\nu}$ 1677 and a very feeble $\Delta\bar{\nu}$ 1657 shift are attributed to the *trans*- and *cis*-forms. Methylvinylcarbinol yields $\Delta\bar{\nu}$ 1647, and crotonyl acetate $\Delta\bar{\nu}$ 1664 *cis* and $\Delta\bar{\nu}$ 1679 *trans*, and methylvinylcarbinol acetate $\Delta\bar{\nu}$ 1648. The bromine derivative, 1-methylallyl bromide, yields $\Delta\bar{\nu}$ 1638; 2-butenyl bromide yields $\Delta\bar{\nu}$ 1651 *cis*, and $\Delta\bar{\nu}$ 1665 *trans*. This is in contrast to $\Delta\bar{\nu}$ 1646 observed for allyl alcohol, and $\Delta\bar{\nu}$ 1635 for allyl bromide. Bourguel (97) notes that the

ethylenic linkage shift is increased by disubstitution, but this augmentation is less if the two substituent groups are on the same carbon than if they are on different atoms. For the external double bond in limonene

TABLE 9

Some Raman shifts in cis-trans isomers of unsaturated hydrocarbons

COMPOUNDS	$\Delta\bar{\nu}$		
cis-2-Pentene...............................	1248–1266(7)	1375(2)	1658(10)
trans-2-Pentene............................	1298–1313(7)	1378(7)	1674(10)
cis-2-Octene...............................	1256(7)	1376(2)	1658(10)
trans-2-Octene............................	1305(7)	1379(7)	1673(10)
cis-2-Nonene...............................			1658(10)
cis-2-Cyclohexyl-6-hexene...................	1260(7)		1657(10)
cis-1-Phenyl-1-propene.....................	1192(7)	1373(2)	1642(10)
trans-1-Phenyl-1-propene...................	1210(7)	1378(7)	1664(10)

TABLE 10

The effect of disubstitution on the C=C shifts

RADICAL R	$CH_2=CH-R$	$CH_2-CH=CH-R$		RADICAL R	$CH_2=CH-R$	$CH_2-CH=CH-R$	
		cis	trans			cis	trans
CH_3	1647			$CH_2C\equiv CC_6H_5$	1642		
$CH_2O(COCH_3)$	1649	1665	1679	$CHClCH_3$	1640		
CH_2OH	1646	1658	1677	$CH_2C_6H_5$	1640		
$CHOHCH_3$	1646			CH_2Cl	1640		1671
$CHOHC\equiv CH$	1646		1676	$CHCl_2$			1666 (Kirrmann)
$CHOHCH=CH_2$	1646		1674	$CHBrCH_3$	1635	1651	1666
C_2H_5	1642	1658	1674	COOH	1638	1645	1652⎫ (Kohlrausch)
C_3H_7	1642	1658	1674	COOR		1644	1655⎭
C_4H_9	1642	1658	1674	C_6H_5	1631	1642	1665
C_5H_{11}	1642	1658	1674	H	1620	1647	
C_6H_{13}	1642	1658	1674	CN		1628	1645 (Kohlrausch)
C_7H_{15}	1642			CHO	1618	1625	1642
CH⟨$^{CH_3}_{CH_3}$		1659	1673	Cl	1608		
				Br	1598		
$CH_2C_5H_9$	1642	1658	1674				
$(CH_2)_3C_6H_{11}$		1657					

is observed $\Delta\bar{\nu}$ 1647, in 2-methyl-1-butene $\Delta\bar{\nu}$ 1652, in 2-pentene $\Delta\bar{\nu}$ 1657, and in cyclohexene $\Delta\bar{\nu}$ 1654. In trisubstituted products such as trimethylethylene, $\Delta\bar{\nu}$ 1679 results, and in the intranuclear double bond in limonene it is likewise $\Delta\bar{\nu}$ 1679. Comparison of the effect of halogen substitution

in 2-bromohexene with 1-hexene shows that this results in a retardation of the frequency from $\Delta\bar{\nu}$ 1642 to 1632.

Grédy (281) has summarized some of these conclusions on the effect of disubstitution as given in table 10. Risseghem, Grédy, and Piaux (544), and Grédy (282) obtained the results with trisubstituted ethylenes as given in table 11.

The precise shifts attributed to ethylenic double bonds have been considered in some detail, because of their utility in determining the structure of the terpenes, styrenes, furans, and similar compounds. It is quite possible to determine the composition of mixtures containing *cis-* and *trans-*isomers and to follow their transitions from one form to the other. It is likewise possible to follow the change in composition on the distilla-

TABLE 11

The Raman shifts in some trisubstituted ethylenes

COMPOUND	$\Delta\bar{\nu}$	COMPOUND	$\Delta\bar{\nu}$
$(CH_3)_2C{=}CHCH_3$	1679	CH_2Br $\quad\diagdown$ $\qquad C{=}CHCH_3$ $\quad\diagup$ Br	1648
CH_3 $\quad\diagdown$ $\qquad C{=}CHCH_3$ $\quad\diagup$ C_2H_5	1773		
C_6H_{13} $\quad\diagdown$ $\qquad C{=}CHCH_3$ $\quad\diagup$ CH_3	1671	CH_3 $\quad\diagdown$ $\qquad C{=}CHCH_3$ $\quad\diagup$ CHO	1648
$(CH_3)_2C{=}CHC_2H_5$	1676	C_2H_5 $\quad\diagdown$ $\qquad C{=}CHCH_3$ $\quad\diagup$ CHO	1647
$(CH_3)_2C{=}CHC_5H_{11}$	1677		
$(CH_3)_2C{=}C(CH_3)_2$	1676	CH_3 $\quad\diagdown$ $\qquad C{=}CHC_2H_5$ $\quad\diagup$ CHO	1645
CH_3 $\quad\diagdown$ $\qquad C{=}CHCH_3$ $\quad\diagup$ Br	1658		

tion of various olefins and terpenes, all of which has not only a bearing upon the constitution of the molecule involved but also a practical importance in relation to the effect of chemical treatment and fractionation of these compounds. An example of the delineation of structure in a mixture is in the observations of Grédy (273) and of Naves, Brus, and Allard (470) on the isomerism of rhodinol and citronellol. The two forms known are:

$$\alpha\text{-}CH_2OH\text{---}CH_2\text{---}\underset{\underset{CH_3}{|}}{CH}\text{---}CH_2\text{---}CH_2\text{---}CH_2\text{---}\underset{\underset{CH_3}{|}}{C}{=}CH_2$$

Type $R_1R_2C{=}CH_2$ ($\Delta\bar{\nu}$ 1650)

$$\beta\text{-}CH_2OH\text{---}CH_2\text{---}\underset{\underset{CH_3}{|}}{CH}\text{---}CH_2\text{---}CH_2\text{---}CH{=}\underset{\underset{CH_3}{|}}{C}\text{---}CH_3$$

Type $RCH{=}CR_1R_2$ ($\Delta\bar{\nu}$ 1678)
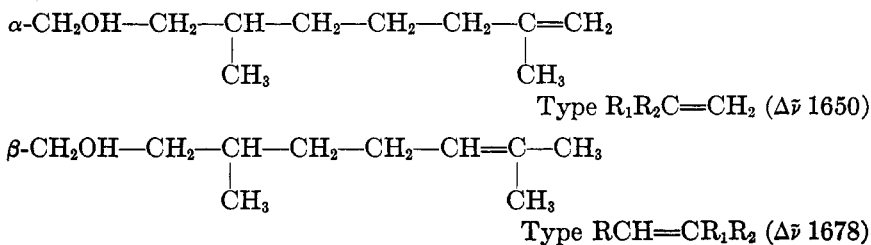
It was found that compounds of the type of 2-methyl-1-octene yield $\Delta\tilde{\nu}$ 1647 and compounds of the type of 3-methyl-2-nonene yield $\Delta\tilde{\nu}$ 1672. These are analogous to the α- and β-forms. Citronellol gives $\Delta\tilde{\nu}$ 1677 with a very faint line at 1645, and from this it is probably correctly concluded that in this compound the β-form is predominant.

F. The Raman spectra of the diolefins

In table 7 were given some of the characteristic shifts of the diolefins as compared with the monoölefins. It is to be expected that the substitution of a hydrocarbon group for a hydrogen next to one of the double bonds would cause an increase in the characteristic C=C linkage. In butadiene the shift is $\Delta\tilde{\nu}$ 1634 and in 1,3-pentadiene $\Delta\tilde{\nu}$ 1646 as compared with ethylene ($\Delta\tilde{\nu}$ 1620). In 3-methyl-1,3-butadiene the increase is less marked, the resulting shift being $\Delta\tilde{\nu}$ 1640. In general the effect of conjugation on the normal ethylenic linkage is to produce a fairly constant frequency shift in the region of $\Delta\tilde{\nu}$ 1644. Bourguel (100) and Piaux (508) postulate that the effect of conjugation is to reduce the ethylenic frequency over what would be expected theoretically. Multiple conjugation such as found in benzene and styrene can best be discussed under cyclic compounds, because one must consider here not only the influence of multiple conjugation but also the effect of the ring. Until the contribution of the ring has been dealt with, consideration of this aspect of the ethylenic double-bond frequency is postponed. There is, however, one other phase of conjugation which properly belongs in the discussion of olefinic derivatives of hydrocarbons. This is the interesting problem of the allenes.

The allenes have a general structure RC=C=CR'. On first inspection it would seem that the thesis so far presented regarding the relative constancy of the shift in the region of $\Delta\tilde{\nu}$ 1640 for a doubly bound carbon was not tenable, as this shift is entirely absent in the allenes. Indeed, in a strict interpretation this is apparently true. There do appear, however, other shifts in the region of $\Delta\tilde{\nu}$ 1080 to 1130 which are quite characteristic of these compounds. The explanation of the displacement of $\Delta\tilde{\nu}$ 1640 to the $\Delta\tilde{\nu}$ 1100 region as characteristic of the double-bond carbon in this type of compound is both reasonable and consistent. The ethylenic shift $\Delta\tilde{\nu}$ 1640 is considered an inner vibration, that is, only depending secondarily upon the mass relationship in the rest of the molecule. In calculating the force constant from the observed frequency displacement and the reduced masses or vice versa for the C=C linkage only the relative masses of the two carbons are taken into consideration. In the case where the double bond is attached to the same carbon atom as in the allenic compounds this is no longer true. If it is assumed that the relative vibrat-

ing masses in this case are not simply two carbon atoms but three carbon atoms, then from equation 2 the ratio of the expected frequencies is

$$\frac{\Delta\bar{\nu}_1}{\Delta\bar{\nu}_2} = \frac{1}{\sqrt{2}}$$

If $\Delta\bar{\nu}_2$ is $\Delta\bar{\nu}$ 1625, then $\Delta\bar{\nu}_1$ will be $\Delta\bar{\nu}$ 1145. This is not greatly removed from the observed frequencies. When substitution in the allenes takes place there appear two frequencies, one near $\Delta\bar{\nu}$ 1130 and one in the region of $\Delta\bar{\nu}$ 1090 to 1070. It is to be admitted that in allene the shift $\Delta\bar{\nu}$ 1073 is not in entire agreement with this hypothesis, but no allowance has been made for a possible change in value of the force constant which could account for this discrepancy. The appearance of two frequencies in the unsymmetrical substituted derivatives is reasonable in view of the possible perturbations as a result of the disymmetry.

In any case the allenic compounds have a well-defined shift or shifts quite characteristic of their structures, and it is believed that this explanation of the displacement of the usual shift is not far removed from the correct one. These compounds have been investigated by Bourguel and Piaux (105, 106), by Piaux (508), and by Kopper and Pongratz (371). In figure 10 are given the Raman spectra of some of the allenes.

G. Raman spectra and the carbonyl linkage

From the point of view of Raman spectra it is more logical to proceed with the discussion of similar types of linkage and their effect on the Raman shifts than to consider the compounds in the same sequence as employed in organic chemistry. There is, however, a much greater demarcation between the triple-bond and the double-bond spectra than there is between the carbonyl and the ethylenic spectra. For this reason the carbonyl spectra are considered here, and the acetylenic and cyclic compounds are considered later.

The carbonyl linkage is found in the aldehydes, ketones, acyl halides, acids, esters, and anhydrides. The magnitude of this shift varies from approximately $\Delta\bar{\nu}$ 1645 to 1800, depending on the influence of adjacent groups. While it is possible in specific instances that the lowest frequency carbonyl shifts might be confused with the higher frequency ethylenic shifts, as a rule this causes no difficulty. Since the mass of oxygen is greater than that of carbon, the increase in the frequency displacement is caused by the somewhat greater force exerted between the carbon and oxygen atoms than exists between the carbon atoms in $C{=}C$.

1. Acids. The lowest displacement for the carbonyl oscillation is in the acids. The average shift for aliphatic acids is approximately $\Delta\bar{\nu}$ 1654.
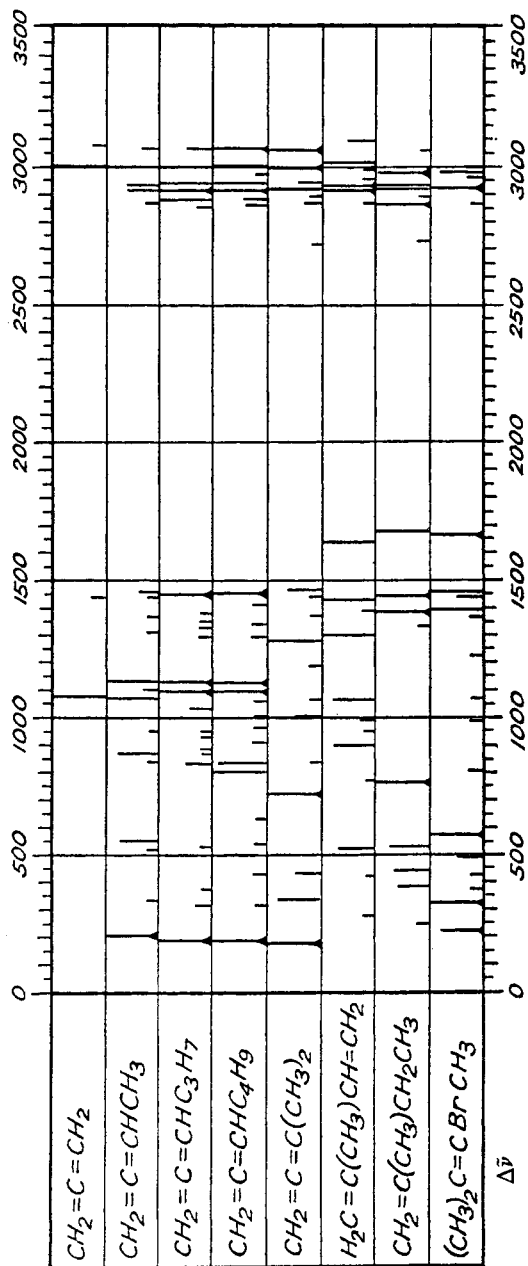
FIG. 10. The Raman spectra of some allenes and some olefins (after Lespieau and Grédy)

This frequency may be influenced, however, by side-chain substitution. A decrease in the magnitude of this shift is illustrated in the following acids: propionic $\Delta\tilde{\nu}$ 1652, butyric $\Delta\tilde{\nu}$ 1654, isobutyric $\Delta\tilde{\nu}$ 1649, trimethyl-
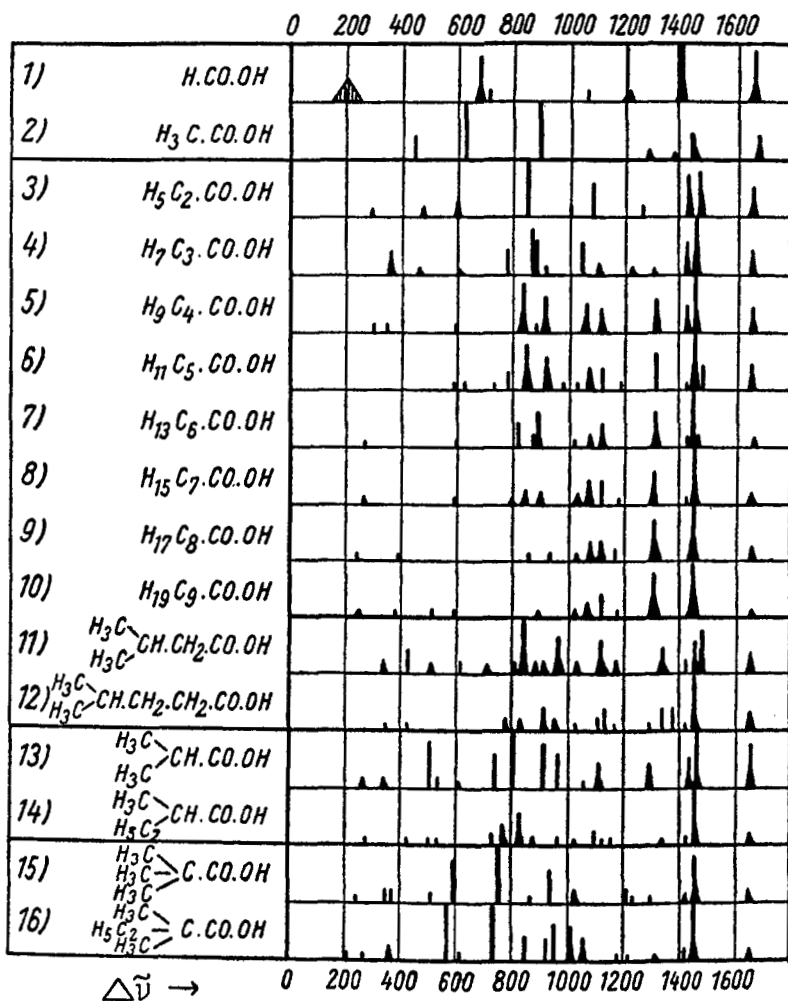
FIG. 11. The lower frequency shifts of the aliphatic acids (after Kohlrausch, Köppl and Pongratz)

acetic $\Delta\tilde{\nu}$ 1645. Formic acid is omitted, as the first member in each series of carbonyl compounds has a slightly different Raman shift for the carbonyl group in every case. The characteristic frequency shifts for the lower oscillations in the acids are given in figure 11 from the data compiled

by Kohlrausch, Köppl, and Pongratz (352), and Dadieu and Kohlrausch (152, 158). The shift in the region of $\Delta\tilde{v}$ 1440 appears even in formic acid (489) at $\Delta\tilde{v}$ 1400. This shift, corresponding to the usual bending moment of the hydrocarbon, appears as a doublet and in some cases as a triplet practically throughout the series. In the isomeric acids there appear strong frequency shifts between $\Delta\tilde{v}$ 500 and 800. In pivalic acid there are two, $\Delta\tilde{v}$ 589 (4) and 753 (10), and in α,α-dimethylbutyric acid $\Delta\tilde{v}$ 575 (5) and $\Delta\tilde{v}$ 736 (8). The very broad band appearing in formic acid at $\Delta\tilde{v}$ 200 is unique for a molecule of this size. There are a large number of fairly strong hydrogen lines. For acetic acid the values are $\Delta\tilde{v}$ 2937 (10), 2986 (1), and 3033 (1), but for propionic acid and the remainder of the series there appear at least four or five fairly strong hydrogen lines (352, 618). The first of these, $\Delta\tilde{v}$ 2756 (2), is the weakest. The $\Delta\tilde{v}$ 2756 in propionic acid is 2739 in butyric, absent in isobutyric, $\Delta\tilde{v}$ 2730 in valeric,

TABLE 12

Influence of substitution on the carbonyl frequencies

SUBSTANCE	$\Delta\tilde{v}$				
	H_2CCOX	RH_2CCOX	R_2HCCOX	R_3CCOX	C_6H_5COX
Acid, X = OH	1666	1652	1648	1644	1647
Methyl ester, X = OCH$_3$	1736	1735	1732	1728	1720
Ethyl ester, X = OC$_2$H$_5$	1736	1732	1728	1724	1721
Ketone, X = CH$_3$	1710	1709	1709	1702	1677
Acid chloride, X = Cl	1798	1793	1788	1790	
Aldehyde, X = H	1715	1719	1719	1723	1689

and 2729 in caproic acid. The $\Delta\tilde{v}$ 2888 (4) in propionic acid becomes 2875 (9) in butyric acid and remains fairly constant at this frequency throughout the series. The shift $\Delta\tilde{v}$ 2921 (6) in propionic acid decreases to $\Delta\tilde{v}$ 2912 in butyric acid, and thereafter is practically unaltered. The $\Delta\tilde{v}$ 2944 (12) in propionic acid decreases slightly until it becomes $\Delta\tilde{v}$ 2935 in caproic and 2930 in pelargonic acid; $\Delta\tilde{v}$ 2986 (8) decreases with increased chain length until in caprylic acid it is reduced to $\Delta\tilde{v}$ 2963.

The effect of substituting halogens in the molecule to form the chloro-acetic acids has been studied by Cheng (124), Ghosh and Kar (248), Thatte and Ganesan (592), Woodward (664), and Parthasarathy (490). The carbonyl frequency is considerably augmented and decreased somewhat in intensity. It becomes a broad band from $\Delta\tilde{v}$ 1675 to 1740 in the mono-substituted acid and splits into two lines corresponding to $\Delta\tilde{v}$ 1678 and 1740 in the disubstituted acid and $\Delta\tilde{v}$ 1682 and 1740 in the trisubstituted acid. The intensity in all cases is not relatively greater than two.
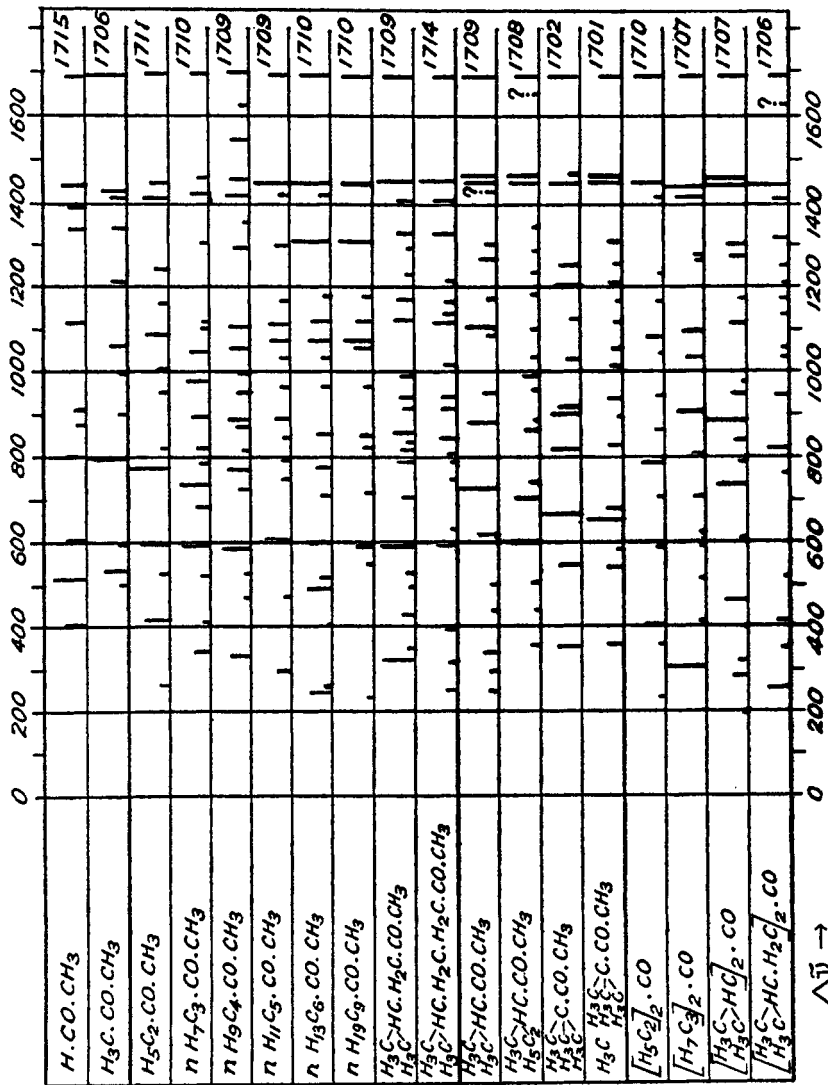
Fig. 12. The lower frequency Raman spectra of aliphatic ketones (after Kohlrausch and Köppl)

2. Ketones. The aliphatic ketones have a slightly greater displacement than the acids and slightly less than the aldehydes. On the average the frequency shift is approximately $\Delta\bar{\nu}$ 1710 for the aliphatic ketones. Substituting aliphatic radicals on the carbon atom in the α-position to the carbonyl group slightly diminishes the carbonyl frequency. In general this is true for all the carbonyl compounds and is illustrated in table 12. In compounds of the type X—CO—R the relative influences of different radicals are respectively in the following order (342, 366): C_6H_5, CH_3, C_2H_5, H, OR', and Cl. If X represents any of these groups and Y is replaced by these groups in the order given, the frequency will increase. The converse is true, of course, if Y is held constant and X is replaced. If both are replaced the frequency will also increase if the replacement is in the order given.

The diminution of frequency influence in the ketones by the substitution of aliphatic radicals is given in figure 12. Nevertheless, the effect of isomerism is not negligible in methyl *tert*-butyl ketone. The carbonyl frequency is 8 wave numbers less than that of the corresponding straight chain aliphatic compounds. Cheng and Lecomte (127) have investigated the halogen derivatives of the ketones.

3. Aldehydes. The next in the series of the carbonyl frequencies are the aldehydes. The carbonyl frequencies corresponding to the aldehydes are in the immediate neighborhood of $\Delta\bar{\nu}$ 1720 and remain constant within a few wave numbers of this value in the entire homologous series. There is apparently a slight increase amounting to not more than 10 wave numbers brought about by the substitution of methyl groups in place of the hydrogen on the α-carbon atom. This is shown in table 12. The aldehydes have been investigated in detail by Kohlrausch and Köppl (348).

Formaldehyde in solutions containing a large excess of the formaldehyde, or in the gaseous state, apparently has a shift corresponding to $\Delta\bar{\nu}$ 1768. An interesting phenomenon was observed, however, by Hibben (309). If formaldehyde is dissolved in water so that the concentration is not in excess there is no carbonyl frequency obtainable. The spectrum has a relatively close similarity to that of glycol, pointing to the formation in solution of methylene glycol ($CH_2O + H_2O \rightleftharpoons CH_2(OH)_2$). These results have been confirmed by Krishnamurti (376). In paraformaldehyde Hibben (309) has also noted that there is no carbonyl shift similar to the result obtained with paraldehyde by Venkateswaran and Bhagavantam (627). It was also supposed that the paraldehyde, and possibly in this case the paraformaldehyde, formed a ring structure consisting of three molecules, bound together through the oxygen atoms, in consequence of which no normal carbonyl shift would be present. Such a frequency is also missing in chloral hydrate (500), but is present in chloral (173, 500).

4. Esters. The esters have been investigated in considerable detail (124, 353, 444, 445, 488, 605). There is a nearly negligible change in the ester carbonyl shift caused by increasing the chain length of the ester radical. It is to be pointed out that substitutions in the ester radical are in the β-position so far as the carbon atom of the carbonyl group is concerned. Changes in substituent groups have a much more pronounced effect on the carbonyl frequency in the α-position. The effect of substitution in the α-position to the ester carbon atom may be quite marked, however, and may extend over 50 wave numbers, as shown in table 13, taken from the data of Cheng (124). This author has attempted to evaluate the characteristic frequency shifts of the substituted esters.

TABLE 13

Carbonyl frequency in esters of the type XCOOR

ESTER (XCOOR)	Δν̃						
	X = H	X = Cl	X = CH₃	X = CH₂Br	X = CH₂Cl	X = CHCl₂	X = CCl₃
1. R = CH₃	1717	1780	1738	1740	1748	1755	1768
2. R = C₂H₅	1715	1772	1736	1738	1747	1750	1763
3. R = C₃H₇	1719	1775	1739	1736	1742	1749	1764
4. R = C₄H₉	1718	1773	1737	1732	1739	1751	1765
5. R = C₅H₁₁	1718	1774	1738		1744	1756	1769

With compounds having the radical $BrCH_2C\!\!\overset{\nearrow O}{\underset{\searrow O}{}}$, these are Δν̃ 370, 550,

670, 710, 1740, 2960; with $ClCH_2C\!\!\overset{\nearrow O}{\underset{\searrow O}{}}$, Δν̃ 410, 590, 700, 790, 1740, 2960;

with $Cl_2CHC\!\!\overset{\nearrow O}{\underset{\searrow O}{}}$, 230, 420, 770, 1750, 3010, and with $Cl_3CC\!\!\overset{\nearrow O}{\underset{\searrow O}{}}$, 200, 290,

430, 680, 830, 1765. In figure 13 are given the Raman spectra of some esters and salts of acetic acid, taken from the data of Cheng (111). The most unique point illustrated in this figure is the lack of lines corresponding to the carbonyl frequency in the acid salts. This has been noted by Krishnamurti (376), Ghosh and Kar (248), and Hibben (313). This is not explicable on the same basis as the disappearance of the double-bond

frequency, as in the allenes. Generally this has been accounted for by a type of hydration, that is, the formation of an OH group in place of a double bond, such as in the case of formaldehyde and in urea (376, 485). It has been reported (162, 163) that this frequency may be present but
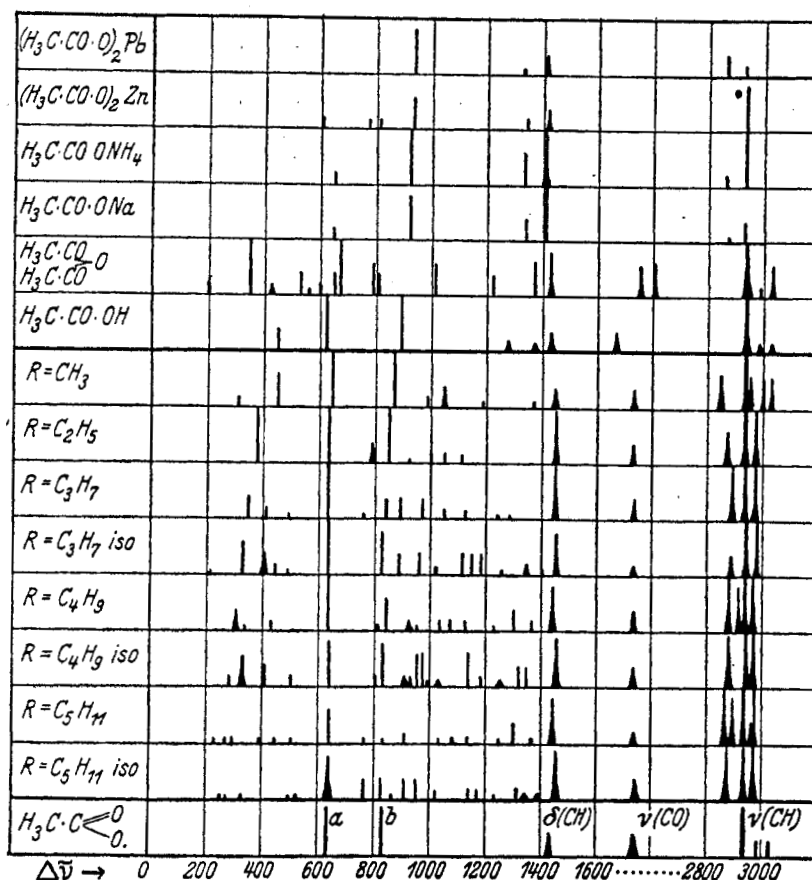
FIG. 13. The Raman spectra of acetic acid and of some of its salts and esters (after Cheng)

exceedingly weak in the acid salts. The dibasic acids present a definite problem which will be discussed shortly.

5. Anhydrides. While some of these compounds could be considered heterocyclic, it is believed that they may be more properly treated in connection with the carbonyl frequencies. The anhydrides have been sparingly investigated (369, 490, 592). Nevertheless, they present the unique

property of having two carbonyl frequencies. The shifts observed for the aliphatic anhydrides are $\Delta\bar{\nu}$ 1754 (2) to 1745 (2) for one of the shifts, depending upon the length of the chain, and $\Delta\bar{\nu}$ 1804 (3), which remains constant, for the other shift. Both of these values are higher than observed with any other carbonyl compound with the exception of the halogen substituted ketones which may have shifts near $\Delta\bar{\nu}$ 1800. Succinic, methylsuccinic, maleic, and phthalic anhydrides yield $\Delta\bar{\nu}$ 1775 and 1845. This augmentation of the frequencies of the latter group may possibly be ascribed to the ring structure for these compounds. It may be noted, however, that both phthalid and furfural, while containing a ring oxygen adjacent to the carbonyl group, possess only one carbonyl frequency shift.

6. *Polybasic acids and derivatives.* The saturated polybasic acids which have been investigated are oxalic (313, 376, 536), malonic (248), tartaric (502), and citric (476). The dibasic acids have frequency shifts which may be strongly affected by their ionization and other factors. In oxalic acid there are two frequency shifts in the aqueous solution and in the anhydrous material near $\Delta\bar{\nu}$ 1650 and 1750; one of these corresponds to the normal acid shift and one is nearer the ester or anhydride frequency that that of the normal acid. Hibben (313) has observed that there is apparently some suppression of the carbonyl frequencies in oxalic acid dihydrate. This is explained on the assumption that it has a chelate structure extending throughout long chains in the crystals, but that on solution this structure breaks down, permitting at least one of the carboxyl groups to function normally. The other less ionized group functions more as an ester. In alcoholic solution there is only one carbonyl shift $\Delta\bar{\nu}$ 1755, so that both carboxyl groups must function identically in alcoholic solution. The increase in the force constant resulting from the increased carbonyl frequency is indicative of a stronger bond between the carbon and the oxygen in oxalic acid than in the other organic acids. It has been noted that a similar phenomenon results on the substitution of chlorine adjacent to the carboxyl group in the aliphatic acids with the consequent increase in strength of these acids. Apparently the proximity of one carbonyl group to another increases the Raman frequency. This is notable in the case of pyruvic acid (168, 354), which has a shift $\Delta\bar{\nu}$ 1735 (3) and a doubtful one at $\Delta\bar{\nu}$ 1769, and in malonic acid (278), which yields $\Delta\bar{\nu}$ 1737, and citric acid, which gives $\Delta\bar{\nu}$ 1730. Rao (536) attributes $\Delta\bar{\nu}$ 1430 observed in oxalic acid as due to the hydroxyl group oscillation. A shift $\Delta\bar{\nu}$ 1450 is present in all the alcohols, but is more properly ascribed to the bending moment of the hydrogen. With oxalic acid this is not a possible allocation of this frequency, since no C—H group is present. Nevertheless, there is no other evidence in support of $\Delta\bar{\nu}$ 1430 as a hydroxyl vibration. The $\Delta\bar{\nu}$ 850 and 480 observed are due to the linear chain and bending oscillations, respectively.

The salts of tartaric acid give, according to Peychès (502) but not according to Nisi (476), a frequency shift $\Delta\bar{\nu}$ 1620 or 1660 depending on the mass of the anion. The presence of this carbonyl frequency in these salts is in contradistinction to the lack of this frequency in salts of the dibasic acids, oxalic acid (313) and malonic acid (248), already mentioned.

7. *Unsaturated carbonyl compounds.* The unsaturated carbonyl compounds such as crotonyl chloride have two strong shifts $\Delta\bar{\nu}$ 1744 and 1761, —a considerable reduction over the saturated acyl halide carbonyl shifts. The same diminution is also present in ethylideneacetone (366), which has $\Delta\bar{\nu}$ 1668 for the carbonyl frequency; phorone has $\Delta\bar{\nu}$ 1668. Apparently the conjugation of the double-bond carbonyl with the double-bond ethylenic group in unsaturated compounds causes a reduction in the carbonyl frequencies of roughly 40 wave numbers. The effect on the ethylenic linkage shift, on the contrary, is rather slight, and is to increase it by a small amount.

With the unsaturated acids the usual or modified carbonyl shift is weakened to the point of extinction. There have been so few compounds, however, of this type investigated, that it is dangerous to extrapolate too far in the direction of accounting for this phenomenon. Furthermore, most of these compounds have been studied from the point of view of the ethylenic rather than the carbonyl shifts. Nevertheless, the salts of dibasic unsaturated acids like fumaric acid may possibly show a frequency shift corresponding to the carbonyl group, which is in the region $\Delta\bar{\nu}$ 1650 (603). The esters of saturated dibasic acids (171, 485) give frequency shifts at $\Delta\bar{\nu}$ 1742, which is a slightly higher value than for monobasic acids. The unsaturated esters (180, 231, 283, 366) yield $\Delta\bar{\nu}$ 1725, on the average, which is slightly less than for the saturated compounds.

There have been a few unsaturated aldehydes investigated. Here likewise there is a very marked lowering of the carbonyl frequency. This has been noted in 2-methyl-2-penten-1-al by Grédy (282) and in crotonaldehyde by Hibben (310). In both cases the shift was $\Delta\bar{\nu}$ 1689. However, if the ethylenic double bond is sufficiently removed from the carbonyl group there is no longer any interaction between them, and the carbonyl frequency becomes normal, as in the case of citronellal (86), where the shift is $\Delta\bar{\nu}$ 1719, and in undecylenaldehyde, where it is $\Delta\bar{\nu}$ 1721, as observed by Bonino and Manzoni-Ansidei (90).

H. Keto–enol isomerism

The demonstration of keto–enol isomerism by means of the Raman effect was one of its earliest applications. A number of the acetoacetates have been investigated by Milone (444), Dadieu and Kohlrausch (165), Kohl-

rausch and Pongratz (354, 358, 359), and Pal and Sen Gupta (485). The last-named authors early pointed out the presence of two frequencies, $\Delta\tilde{\nu}$ 1656 and 1750, in the ethyl acetoacetates. On reëvaluation these are more nearly $\Delta\tilde{\nu}$ 1632 and 1725. The methyl acetoacetate yields $\Delta\tilde{\nu}$ 1626 and 1737; methyl methylacetoacetate yields $\Delta\tilde{\nu}$ 1618, 1714, and 1734. Methyl dimethylacetoacetate shows no ethylenic shift, but yields $\Delta\tilde{\nu}$ 1709 and 1738 as a doublet carbonyl frequency (358). Methyl and ethyl pyruvate have the shift $\Delta\tilde{\nu}$ 1735. These shifts are in all cases relatively strong. It may be seen immediately that only those compounds which can exist in enolic form show evidence of the ethylenic linkage. Since the possibility of a migrating hydrogen ceases to exist on their substitution by methyl groups, there is no longer any evidence of C=C in the disubstituted compounds. These shifts are illustrated in figure 14 (12). The possible tautomerism of β-aminocrotonic esters has been discussed by Kohlrausch and Pongratz (358). The possibility of another type of keto-
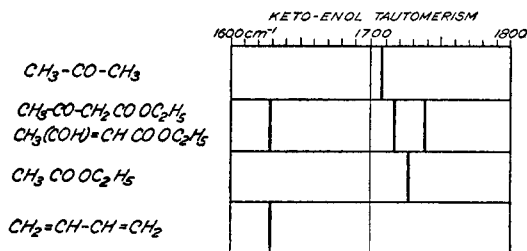
FIG. 14. The Raman shifts of the keto and enol forms of ethyl acetoacetate as compared with similar compounds (after Andrews)

enol isomerism exists in aldol, which Hibben (310) showed has both a reduced carbonyl frequency and an ethylenic shift similar to crotonaldehyde. Crotonaldehyde, however, was not present as an impurity.

Hayashi (298) has investigated the Raman spectra from diacetyl, acetylacetone, and acetonylacetone. He observed two shifts for diacetyl, $\Delta\tilde{\nu}$ 1677 and 2056, in the double-bond region. The $\Delta\tilde{\nu}$ 2056 has a frequency much higher than for any ketone so far observed. It is suggested that there is a type of tautomerism not involving the migration of a hydrogen atom. The $\Delta\tilde{\nu}$ 1677 is attributed to the C=C in the tautomer. These two forms are indicated as follows:

$$\begin{array}{ccc} \text{CH}_3\text{—C—C—CH}_3 & \rightleftarrows & \text{CH}_3\text{C=C—CH}_3 \\ \quad\;\|\;\;\| & & \quad\;|\;\;| \\ \quad\;\text{O}\;\;\text{O} & & \quad\;\text{O—O} \end{array}$$
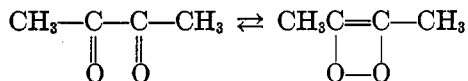
These results are not compatible with those of Kohlrausch and Pongratz (358), who obtain $\Delta\tilde{\nu}$ 1725 (2) for diacetyl. Hayashi pointed out

that acetylacetone may be tautomeric in nature, as a stable salt is isolable from its enolic form.   With this compound were observed $\Delta\bar\nu$ 1600 attributed to C=C, $\Delta\bar\nu$ 1859 for the C=O, and two frequencies $\Delta\bar\nu$ 3467 and 3563.   These frequencies could be explained by the equilibrium between two tautomers:

$$\text{H}_3\text{C}-\underset{\underset{\text{O}}{\|}}{\text{C}}-\text{CH}_2-\underset{\underset{\text{O}}{\|}}{\text{C}}-\text{CH}_3 \rightleftarrows \text{CH}_3-\underset{\underset{\text{OH}}{|}}{\text{C}}=\overset{\overset{\text{H}}{|}}{\text{C}}-\underset{\underset{\text{O}}{\|}}{\text{C}}-\text{CH}_3$$
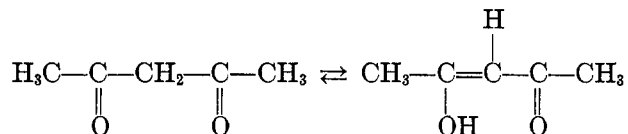
The frequency shift in the region of $\Delta\bar\nu$ 3500 is ascribed to the OH shift. The frequency shift $\Delta\bar\nu$ 1600 (8) is confirmed by Kohlrausch and Pongratz (359), who found also $\Delta\bar\nu$ 1655 (2) and 1723 (2) for this compound.   Dimethylacetylacetone yields simply $\Delta\bar\nu$ 1710.   The observations of Kohlrausch cannot be reconciled with those of Hayashi.   Acetonylacetone yields, according to Hayashi, $\Delta\bar\nu$ 3670, 3613, 3272, 1710, and 1625.   In these acetone derivatives only the significant shifts have been mentioned. Here the presence of two frequencies in the double-bond region is again ascribed to a tautomeric arrangement such as:

$$\begin{array}{ccc} \text{CH}_2-\text{CO}-\text{CH}_3 & \rightarrow & \text{CH}=\text{C} \diagup^{\text{CH}_3}_{\diagdown\text{OH}} \\[2ex] | & & | \\[2ex] \text{CH}_2-\text{CO}-\text{CH}_3 & \leftarrow & \text{CH}=\text{C} \diagup^{\text{OH}}_{\diagdown\text{CH}_3} \end{array}$$
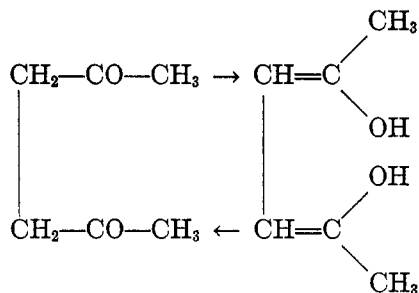
It might be mentioned that resorcinol has the double-bond frequencies $\Delta\bar\nu$ 1874, 1816, 1746, and 1697, despite the fact that it behaves more as a hydroxyphenol.   It is suggested that there, too, tautomerism may play a rôle, leaving a ketonic group in the ring.   This evidence would be more convincing if the observers had employed filtered radiation rather than an unfiltered mercury spectrum.   Hayashi's results are at least interesting and by no means entirely inconsistent.

I. The Raman effect and the acetylenic linkage

The calculation of the force exerted between two carbon atoms bound by a triple bond, such as in acetylene, gives a value which is approximately three times the force between singly bound atoms.   This means then that

the frequency for the acetylenic grouping should occur between $\Delta\tilde{\nu}$ 2100 and 2250, depending upon slight variations in the force constant. This is indeed the case, as all acetylenic compounds show a frequency shift in this region, with the exception of acetylene itself whose characteristic frequency is approximately $\Delta\tilde{\nu}$ 1975. Consequently in acetylene it is probable that the force is slightly less between the carbon atoms than in its substituted products.

Numerous workers have investigated acetylene. Among these are Bhagavantam (45, 46), Daure (194, 195, 196, 197), Glockler and Davis (251), Glockler and Morrell (255), Lewis and Houston (411), Morino (455), Nisi (478), Segré (555), and Venkateswaran and Sibaiya (615). Not only is the carbon to carbon frequency exalted in acetylene but also the carbon to hydrogen frequency is increased to $\Delta\tilde{\nu}$ 3320, which is one of the highest values observed for hydrogen and is exceeded only by the hydrogen in H↔O and N↔H. The acetylenic shift is quite sensitive to substitution, but in a somewhat different sense from the ethylenic frequency. In methylacetylene, for example, there is an increase in the frequency, as compared with acetylene, of 163 wave numbers, the observed value being $\Delta\tilde{\nu}$ 2123 for the symmetrical oscillations in methylacetylene. In dimethylacetylene there is an additional increase of approximately 100 wave numbers or more and the appearance of a new line, the resultant shifts being $\Delta\tilde{\nu}$ 2234 and 2312. The $\Delta\tilde{\nu}$ 2312 shift corresponds to a completely symmetrical linear vibration and $\Delta\tilde{\nu}$ 2234 to the linear asymmetrical one.

The maximum number of vibration frequencies to be expected from a molecule depends upon the number of its degrees of freedom, there being three for each atom, less six translational and rotational degrees for the molecule as a whole. Consequently the maximum number of vibrational frequencies which may be expected is 3 × the number of atoms − 6 or (3n − 6). Placzek (511) has indicated that this expected maximum number of frequencies is reduced if the molecule has symmetry. Glockler and Davis (251) have analyzed the vibrations in methylacetylene and conclude that there are eleven Raman frequencies of a possible fifteen, one of which can be interpreted as an overtone. The frequency shifts for methylacetylene and the modes of oscillation which may give rise to these frequencies are indicated in table 14 (251).

As has been observed, with any of the hydrocarbons the lower frequencies are deformation oscillations. The shift $\Delta\tilde{\nu}$ 929 is probably a linear vibration of a methyl group against the rest of the molecule. $\Delta\tilde{\nu}$ 1382 appears in most of the acetylenes. It is doubted, however, that this can be ascribed to a hydrogen attached to a CH_2 or CH_3 group adjacent to an unsaturated carbon atom. The other lines have the significance which has been described already. Dimethylacetylene has in addition to the

two strong lines already mentioned three other lines $\Delta\bar{\nu}$ 2180, 2201, and 2280, which are weak and are interpreted as rotational changes occurring with the C≡C vibration. In vinylacetylene there is one acetylenic shift $\Delta\bar{\nu}$ 2098 and one ethylenic shift $\Delta\bar{\nu}$ 1595. The acetylenic shift is slightly lower than that for methylacetylene. The ethylenic shift is also depressed by a considerable amount from its average value.

Bourguel and Daure (102, 103) and Grédy (275, 279, 280) investigated the effect of substitution on the acetylenic linkage. Blanche Grédy has prepared and examined a large number of acetylenes and has ably discussed them in some detail (280). The effect of substitution on the acetylenes is given in table 15. This includes cyclic compounds as well as straight chain radicals, inasmuch as the acetylenic linkage never appears in a ring, as does the ethylenic linkage. In the index of compounds, how-

TABLE 14

The frequency shifts for methylacetylene and the modes of vibration which give rise to these frequencies

MODES OF VIBRATION	$\Delta\bar{\nu}$	INTENSITY
(H_3C) ↓ —C ↑ :C ↑ —H ↓	336	9(b)
(H_3C) ↓ —C ↑ :(CH) ↓	643	5(b)
(H_3C)→ — ←(C:CH)	929.5	8(s)
H ↑ —H_2 ↓ —(C—C:C) ↑ —H ↓	1382.5	6(b)
H ↑ —H ↓ —(HC—C:CH)	1448	2(b)
(H_3C)—C→:←C(H)	2123.5	11(s)
(H_3)→ — ←(C—C:C)—H→	2867	6(s)
(H_3)→ — ←(C—C:CH)	2926.2	10(s)
H→ — ←(H_2C—C:CH)	2971	4(b)
(H_3C—C:C)→ — ←H	3305	2(s)

ever, the acetylenes are divided into the respective class compounds, that is, the aromatic derivatives of the acetylenes are under the aromatic compounds.

It has been mentioned that the first members of the series of "true" acetylenes (RC≡CH) have only one linear C≡C Raman shift. This is the case for all the monosubstitution derivatives. Furthermore, this shift will fall approximately at $\Delta\bar{\nu}$ 2119, practically regardless of the length or constitution of the chain attached to the other triply bound carbon atom. The principal exceptions are acetylene itself and vinylacetylene. In the disubstituted acetylenes there is an immediate appearance of two strong lines which are, in general, constant throughout a given series. This is indicated in table 15 under section II of the hydrocarbons. For each homologous series, as in the methylacetylenes, the character of the

TABLE 15

The effect of substitution on acetylenic frequencies

$\Delta\bar{\nu}$

Hydrocarbons

I		II				III		
CH≡CH	1960(5)							
CH₃C≡CH	2123(7)							
CH₂=CHC≡CH	2098(7)							
C₄H₉C≡CH	2121(7)							
(CH₃)₂CHCH₂C≡CH	2118(7)							
C₅H₁₁C≡CH	2118(7)							
C₆H₁₃C≡CH	2119(7)							
HC≡C(CH₂)₅C≡CH	2118(7)							
C₆H₉C≡CH	2116(10)							
C₅H₉CH₂C≡CH	2119(10)							
C₆H₅C≡CH	2111(10)							
C₆H₅CH₂C≡CH	2120(8)							
C₆H₁₁C≡CH	2118(7)							
C₆H₁₁CH₂C≡CH	2118(7)							
		CH₃C≡CCH₃	2234(10)		2312(5)	C₅H₁₁C≡CCH₃	2233(10)	2301(5)
		C₂H₅C≡CCH₃	2238(10)		2304(5)	C₅H₁₁C≡CC₂H₅	2232(8)	2293(5)
		C₃H₇C≡CCH₃	2238(10)		2304(5)	C₆H₁₁C≡CC₃H₇	2234(7)	2293(5)
		C₄H₉C≡CCH₃	2235(10)		2303(5)	C₆H₁₁C≡CC₄H₉	2231(7)	2293(5)
		C₅H₁₁C≡CCH₃	2233(10)		2301(5)	C₆H₅C≡CCH₃	2214(10)	2253(10)
		C₆H₁₃C≡CCH₃	2233(10)		2303(5)	C₆H₅C≡CC₂H₅	2210(5)	2238(7)
		C₆H₉C≡CCH₃	2239(10)	2280(1)	2320(1)	C₆H₅C≡CC₃H₇	2210(2)	2238(7)
		C₆H₉CH₂C≡CCH₃	2234(10)		2302(5)	C₆H₁₃C≡CCH₃	2233(10)	2305(5)
		C₆H₅C≡CCH₃	2214(10)	2253(10)		C₆H₁₃C≡CC₂H₅	2232(70)	2294(5)
		C₆H₁₁C≡CCH₃	2239(10)	2259(2)	2316(2)	C₆H₁₃C≡CC₃H₇	2233(7)	2294(2)
		C₆H₁₁CH₂C≡CCH₃	2235(7)		2303(5)	C₆H₁₃C≡CC₄H₉	2233(7)	2294(2)

Ethers

I			
HC≡CCH₂OCH₃	2118(10)		

II			
C₅H₁₁C≡CCH₂OCH₃	2216(5)	2237(5)	2282(8)
C₆H₁₃C≡CCH₂OCH₃	2115(5)	2237(5)	2282(8)
C₅H₅CH₂C≡CCH₂OCH₃	2216(5)	2235(5)	2282(8)
C₆H₁₁CH₂C≡CCH₂OCH₃	2217(5)	2234(5)	2281(8)
C₆H₅C≡CCH₂OCH₃	2200(5)	2240(10)	

Alcohols

I			
HC≡CCH₂OH	2118(10)		
HC≡CC(CH₃)₂OH	2120(8)		
C₅H₁₁C≡CCH₂OH		2226(7)	2290(8)
C₆H₁₃C≡CCH₂OH		2227(7)	2289(8)
C₅H₉CH₂C≡CCH₂OH		2227(10)	2289(8)
C₆H₁₁CH₂C≡CCH₂OH		2228(7)	2290(8)
C₆H₅C≡CCH₂OH	2198(2)	2239(10)	2290(8)

III

C₅H₁₁C≡CCH(OCH₃)CH₃	2240(10)	2308(1)
C₅H₉CH₂C≡CCH(OCH₃)CH₃	2239(7)	2304(1)
C₆H₁₁CH₂C≡CCH(OCH₃)CH₃	2241(10)	2307(1)
C₆H₅C≡CCH(OCH₃)CH₃	2221(10)	2241(10)

IV

C₅H₁₁C≡CC(CH₃)₂OCH₃	2236(10)	
C₅H₁₁C≡CC(CH₃)(C₂H₅)OCH₃	2236(10)	
C₆H₁₁CH₂C≡CC(CH₃)₂OCH₃	2234(10)	
C₆H₅C≡CC(CH₃)₂OCH₃	2215(7)	2238(10)

V

HC≡CCH—CH₂ \O/	2126(7)
HC≡CH—CHCH₂Cl \O/	2138(7)
CH₂—CHC≡CCH CH₂ \O/	2253(5)

Esters

C₅H₁₁C≡CCOOCH₃	2238(10)
C₆H₁₃C≡CCOOCH₃	2238(10)

II

C₅H₁₁C≡CCHOHCH₃	2250(8)	2312(1)
C₆H₁₃C≡CCHOHCH₃	2250(10)	2310(1)
C₅H₉CH₂C≡CCHOHCH₃	2249(10)	2303(1)
C₅H₁₁C≡CCHOHCH₃	2237(8)	incomplete
C₆H₁₁CH₂C≡CCHOHCH₃	2250(10)	2314(1)
C₆H₅C≡CCHOHCH₃	2233(10)	

III

C₅H₁₁C≡CC(CH₃)₂OH	2239(10)	
C₅H₁₁C≡CCOH(CH₃)C₂H₅	2238(10)	
C₆H₁₁CH₂C≡CC(CH₃)₂OH	2237(10)	
C₆H₅C≡CC(CH₃)₂OH	2230(10)	
(C₅H₁₁C≡C)₂CHOH	2250(7)	2304(1)
(C₅H₁₁C≡C)₃COH	2236(7)	

Halogen derivatives

ClC≡CCl	2109(8)
C₆H₅C≡CCl	2225(10)

substitution on the other acetylenic carbon does not change in general the
magnitudes of the shifts. There is, however, one exception, and that is
the substitution of a phenyl group. In the true acetylenes this substitu-
tion has a slight effect. In the methylacetylenes the shift whose average
frequency is $\Delta\bar{\nu}$ 2236 is reduced to $\Delta\bar{\nu}$ 2214 by phenyl substitution, and
the shift whose average is $\Delta\bar{\nu}$ 2304 is reduced to $\Delta\bar{\nu}$ 2253 with a concomitant
marked increase in its intensity. Substitution with cyclohexane causes
the appearance of a weak line at $\Delta\bar{\nu}$ 2259. Under section III of the hydro-
carbons is shown the effect of increasing the mass of one substituent group
while holding constant the mass of the other substituent group. This
demonstrates that as both substituent groups are increased in mass there
is relatively little change in the frequency shifts beyond the initial marked
effect caused by substituting a more complex group for a single hydrogen.
Following the initial effect of substituting a phenyl group on one of the
acetylenic carbons, it is evident that increasing the mass of the second
substituent beyond that of a methyl group does not seriously alter the
frequency shifts.

On considering next the changes which may take place when a carbinol
group is substituted for a hydrocarbon group it is apparent that in the
true acetylenes there is little effect, the average shift being $\Delta\bar{\nu}$ 2119. This
is shown under section I of the alcohols. Furthermore, on disubstitution
there is a similar appearance of two strong frequencies corresponding
fairly closely to those observed in the methylacetylenes. There is an
apparent decrease, however, of approximately 10 wave numbers in the
larger of the two frequency shifts. If the phenyl group is one of the sub-
stituents, in place of $\Delta\bar{\nu}$ 2253 present in methylphenylacetylene there ap-
pears a weak frequency at $\Delta\bar{\nu}$ 2198.

However, if the substituent carbinol group represents a secondary alco-
hol of the general form $R—C\equiv C—CHOHCH_3$, as shown under section
II of the alcohols, then there is approximately an increase of 20 wave
numbers in both observed acetylenic frequencies. Here again the phenyl
group causes a different effect from the other radicals represented by R.
It gives rise to only one Raman frequency, $\Delta\bar{\nu}$ 2233. If the alcohol sub-
stitution is represented by $R—C\equiv CC(CH_3)_2OH$, then in place of two
characteristic frequency shifts there is only one, $\Delta\bar{\nu}$ 2238, which appears
very strong. This behavior is quite remarkable in contrast to the effect
of substitution so far presented.

The monosubstituted ethers are practically identical with the other
monosubstituted derivatives. In the compounds of the form $RC\equiv C-$
CH_2OCH_3 there are three $C\equiv C$ frequency shifts, $\Delta\bar{\nu}$ 2216, 2237, and 2282.
These shifts remain constant throughout the normal series except for
the usual influence of the phenyl radical, which eliminates the highest
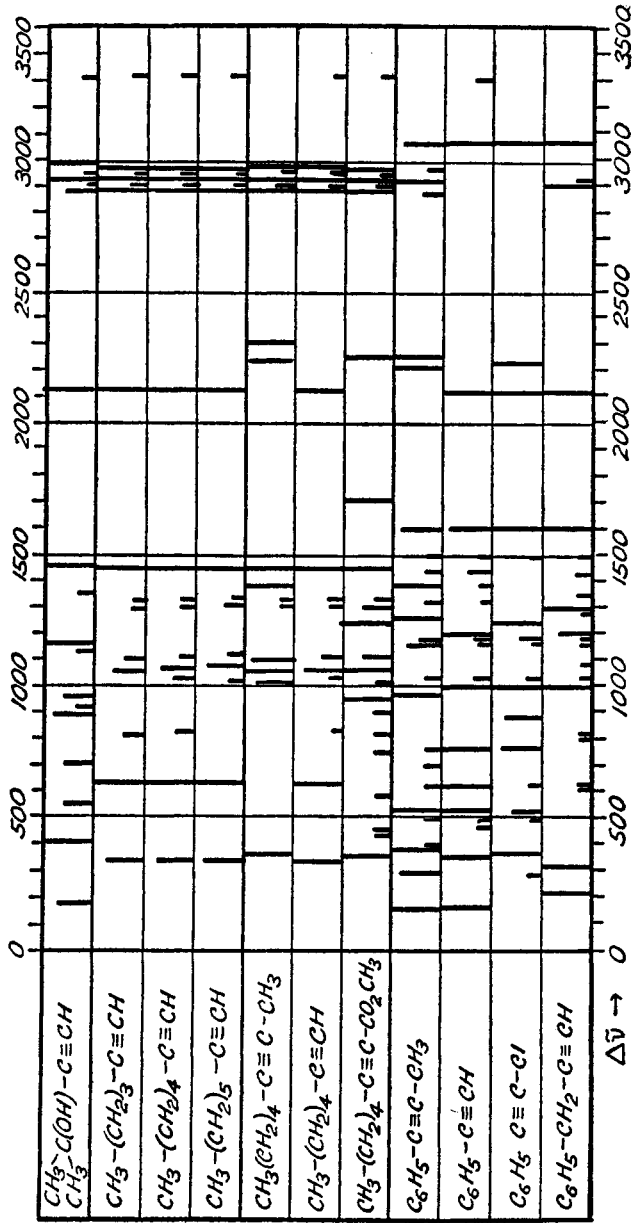
Fig. 15. The Raman spectra of some acetylenic compounds (after Bourguel and Daure)

frequency and slightly diminishes the lowest frequency shift. The secondary ethers as indicated under section III of the ethers have only two shifts, one of which is of approximately the same magnitude as the medium frequency shift in the normal ether, and the other considerably larger than the highest frequency shift of the normal ethers. The tertiary ethers have one strong shift at $\Delta\bar{\nu}$ 2235 with the exception of the phenyl derivative, which in this case has two shifts instead of one, namely, $\Delta\bar{\nu}$ 2215 and 2238. The decrease in the number of characteristic frequencies in going from the normal to the tertiary derivatives somewhat parallels the behavior with the alcohols. The epoxy derivatives of normal acetylene give a frequency close to that observed with other similar acetylenes.

These figures demonstrate in a clear-cut fashion the very definite influence of the substitution on characteristic frequency shifts. Nevertheless, in the acetylenic compounds the displacement attributed to this linkage is not the only criterion of identification. Bourguel and Daure (102) and Grédy (280) have pointed out that other frequencies are also quite characteristic in the normal acetylenes. The $\Delta\bar{\nu}$ 340 is generally present in the normal, and $\Delta\bar{\nu}$ 375 and 1380 in the disubstituted compounds. They are almost equally characteristic frequencies. In figure 15 are given the complete Raman spectra for a typical group of these compounds.

J. The Raman spectra of cyclic compounds

The simplest of the cyclic compounds are the cyclopropanes. The Raman spectra of cyclopropane and some of its derivatives have been determined by Lespieau, Bourguel, and Wakeman (407, 408). Cyclopropane can be considered a system of three masses substituted on the corners of a triangle. By assuming equal force and an equilateral triangle Yates (668) calculated the probable frequencies as being $\Delta\bar{\nu}$ 400 and 1350. The observed frequencies, however, follow more closely the calculations of Bhagavantam (36), where the ratios of the principal C—C frequencies are as $\sqrt{2}$. This follows from the fact that the normal frequencies of a system of type X_3 are given by

$$\Delta\bar{\nu}_1 = k\sqrt{\frac{3F}{2M}} \qquad \text{and} \qquad \Delta\bar{\nu}_2 = k\sqrt{\frac{3F}{M}}$$

Since it may be assumed, as a first approximation, that F and M remain constant, then

$$\Delta\bar{\nu}_2 = \Delta\bar{\nu}_1 \sqrt{2}$$

This gives a calculated value for the two frequencies of $\Delta\bar{\nu}$ 1212 and 858 on the assumption that the C—C frequency in ethane $\Delta\bar{\nu}$ 990 may be applied in this connection. The observed values are $\Delta\bar{\nu}$ 1188 and 867, respectively, which are in moderate agreement.

In table 16 are given the principal Raman shifts of the cyclopropanes. Some of the very weak lines are omitted. Lespieau, Bourguel, and Wakeman postulated that there is a frequency varying from $\Delta\bar{\nu}$ 1188 to 1214, which remains fairly constant throughout the series. On the other hand another characteristic frequency varies progressively with the number of carbon atoms in the molecule. This changes from $\Delta\bar{\nu}$ 1188 in cyclopro-

TABLE 16

The Raman spectra of some cyclopropanes

			$\Delta\bar{\nu}$		
CH₂—CH₂ \/ CH₂	CH₃—CH—CH₂ \/ CH₂	CH₃—CH—CH—CH₃ \/ CH₂	CH₃—CH—CH—C₂H₅ \/ CH₂	CH₃—CH—CH—C₃H₇ \/ CH₂
---	---	---	---	---
			737(5)	
		746(5)	746(8)	
	759(5)	765(8)	756(5)	760(8)
		783(5)	783(1)	786(5)
			813(8)	825(1)
867(5)	851(5)	866(1)	869(5)	861(1)
			889(5)	
		915(7)		
	892(7)			
			967(1)	967(5)
		1035(1)	1043(1)	1035(8)
1188(10)		1173(1)	1172(5)	1172(1)
	1207(7)	1214(7)	1209(8)	1207(7)
			1221(5)	1221(5)
1439(1)	1462(1)	1455(7)	1305(1)	1455(7)
				2850(5)
	2874(5)	2875(7)	2870(7)	2876(7)
				2906(7)
			2912(7)	
	2931(5)	2933(7)	2937(7)	2937(7)
	2957(5)	2954(7)		2963(7)
			2966(7)	
		2983(5)		
3011(7)	2998(7)	2999(10)	2999(10)	3000(10)
3029(7)				
3076(1)	3074(1)	3064(5)	3066(7)	3065(7)

pane to $\Delta\bar{\nu}$ 982 in methylcyclopropane, $\Delta\nu$ 915 in dimethylcyclopropane, $\Delta\bar{\nu}$ 813 in methylethylcyclopropane, and $\Delta\bar{\nu}$ 760 in methylpropylcyclopropane. These changes follow the equation

$$\Delta\bar{\nu} = 1188 \sqrt{\frac{3}{n}}$$

where n is the number of carbon atoms in the molecule. This is shown in figure 16 where the calculated values are indicated by dotted lines. The intent of the authors is somewhat obscured by errors in printing. Nevertheless, it is clear that a frequency appears near $\Delta\bar{\nu}$ 3065 to 3074 which does not occur in the aliphatic hydrocarbons. This occurs in other cyclic compounds such as cyclopentene, benzene, and cyclohexadiene. It apparently is not present, however, in cyclopentane, cycloheptane, cyclooctane and derivatives, but may occur in cyclohexene. It is a disputed point that this frequency is characteristic of the ring linkage in the larger rings or primarily characteristic of unsaturation. In any case the $\Delta\bar{\nu}$ 3000 and approximately 3070 are quite characteristic of the cyclopropane C—H vibration. There is no accounting for the absence of a shift near $\Delta\bar{\nu}$ 1450 in the methylethylcyclopropane. Apparently the band at $\Delta\bar{\nu}$ 3070, which
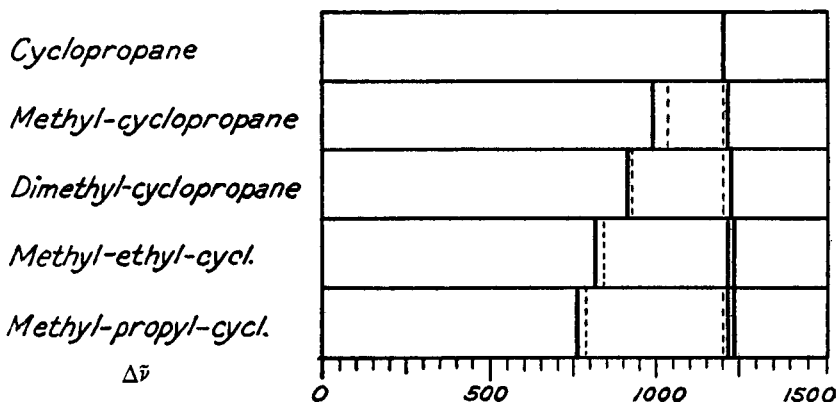
FIG. 16. The alteration of one of the principal lines in the Raman spectrum of cyclopropane as a function of substitution (after Lespieau, Bourquel, and Wakeman)

is feeble in cyclopropane, readily increases in intensity with substitution until it becomes nearly as strong as the band at $\Delta\bar{\nu}$ 3000. The relatively strong shift at $\Delta\bar{\nu}$ 3029 in cyclopropane disappears on further substitution. Canals, Godchot, and Cauquil (118) and Weiler (634, 635, 636) have investigated cyclopropane. The first-named authors have also studied other cyclic compounds. These results are given in table 17. It is presumed (118) that $\Delta\bar{\nu}$ 1188, 1290, 1268, and 1293 are frequency shifts characteristic of a five-carbon nucleus. This is partially confirmed by Grédy (289) in her extensive studies. The shifts she gives, however, are $\Delta\bar{\nu}$ 890, 1020, 1224, 1305 on the average. The shifts characteristic of the cyclohexane nucleus (259) are $\Delta\bar{\nu}$ 440, 801, 1029, 1165, 1268. This is also confirmed by Grédy (280) with, however, $\Delta\bar{\nu}$ 788 considered as the first identifying shift. In the ethylenic derivatives of cyclopentane observed

by Piaux (508) it is presumed that $\Delta\tilde{\nu}$ 890 is characteristic of the saturated cyclopentyl group. In these unsaturated derivatives, shifts appear near $\Delta\tilde{\nu}$ 3000 and 3070, which substantiate the general observation that shifts in this region are attributable to the unsaturated C—H linkage. With the cyclohexanes there exists a possibility of *cis-trans* isomerism. This has been carefully studied by Miller and Piaux (440, 441) and by Miller and Lecomte (439) and the results are indicated in table 18 for the dimethylcyclohexanes. While these show extraordinary similarity there are, nevertheless, notable differences which would enable their being distinguished from each other. The presumption that $\Delta\tilde{\nu}$ 1164 and 1355 are characteristic shifts of the *trans*-form and $\Delta\tilde{\nu}$ 1260 and 1053 of the *cis-*

TABLE 17

The Raman spectra of some saturated cyclic compounds

			$\Delta\tilde{\nu}$			
Cyclopentane	Methylcyclopentane	Cyclohexane	Cycloheptane	Methylcycloheptane	Cyclooctane	Methylcyclooctane
		379	335	320	243	
301						
	523	425	397	381	371	
889	845	801	729	722	700	703
	890					
1032		1029	1005	1000	988	996
1205	1205	1165	1165	1177	1171	1159
1290	1299	1268	1282	1278	1293	1286
1370	1374	1346	1345	1351	1367	1347
1450	1458	1440	1439	1444	1439	1452
2873	2873	2854	2858	2855	2857	2864
2942	2942	2926	2903	2922	2914	2904
2973	2974	2933	2933	2945	2939	2927–2954

form (472) is not particularly tenable. Hayashi (302) and Nevgi and Jatkar (472) have also investigated the cyclohexanes and cyclohexenes. The C—H bond appears in the cyclohexanes in much the same position as the aliphatic C—H. In general $\Delta\tilde{\nu}$ 600 to 1300 are identified with C—C bonds and $\Delta\tilde{\nu}$ 200 to 600 with C—C—C bonds.

The oxygenated derivatives such as the cyclohexanols have been studied by Piaux (504) and by Nevgi and Jatkar (472). The latter authors postulate $\Delta\tilde{\nu}$ 798 to 779 as characteristic of the alcoholic grouping. The change in position of the substituent as in *o-*, *m-*, and *p*-methylcyclohexanol results in a progressive increase in the frequencies $\Delta\tilde{\nu}$ 443, 457, 482, and $\Delta\tilde{\nu}$ 522, 551, and 649, respectively. In *o-*, *m-*, and *p*-methylcyclohexanones these

TABLE 18

Raman spectra of some isomeric cyclohexanes

1,2-Dimethylcyclohexane		1,3-Dimethylcyclohexane		1,4-Dimethylcyclohexane	
trans	*cis*	*trans*	*cis*	*trans*	*cis*
		253(1)			
	333(2)				
			353(1)		
			373(2)	374(5)	372(5)
		407(5)			
415(5)	414(5)	420(8)			
440(5)		446(2)	453(2)	452(5)	463(2)
498(7)			487(1)	473(2)	474(5)
	537(5)	545(8)			
	593(2)				
			625(2)		637(5)
				701(1)	702(1)
749(7)	730(7)	771(7)	752(7)	760(7)	760(7)
				784(1)	787(5)
819(5)			802(1)		
857(5)	842(8)	847(5)	861(2)		
	920(2)	935(1)	937(2)	927(1)	
950(5)	944(5)	956(1)		951(2)	954(5)
	977(8)	991(2)	980(2)		976(2)
1005(8)	1005(8)		1009(2)	1005(1)	1000(5)
	1053(5)	1058(7)	1055(8)	1061(7)	1055(8)
1078(5)			1074(1)		
	1095(8)		1100(2)		1099(5)
		1113(2)			
1164(8)	1159(5)	1165(5)	1163(8)	1163(5)	1163(5)
		1181(5)		1183(5)	
1218(8)	1221(5)	1219(5)	1212(5)		1206(5)
1252(5)	1256(8)			1247(8)	1244(2)
		1269(5)	1266(8)		1263(8)
1292(5)	1302(8)	1303(2)	1305(2)	1307(5)	1301(2)
					1318(1)
1343(8)	1320(8)	1339(5)	1327(1)	1346(8)	1343(8)
1355(8)		1355(2)	1364(1)	1361(2)	
1446(7)	1441(7)	1441(5)	1440(8)	1432(8)	1439(8)
1460(7)	1455(5)	1460(5)	1460(8)	1456(7)	1462(7)
2660(5)					
2844(7)		2845(7)	2846(7)	2848(7)	2853(10)
2854(7)	2854(10)				
	2873(8)	2870(1)	2870(7)	2868(7)	2873(8)
	2894(8)		2883(8)		2898(7)
2915(7)		2912(5)	2912(8)	2907(5)	2913(8)
2931(10)	2927(10)	2929(7)	2928(7)	2926(7)	2930(7)
2950(5)	2959(5)	2955(7)	2960(7)	2952(8)	2960(7)
2975(5)	2973(5)				

are respectively $\Delta\bar{\nu}$ 312, 410, 500, and $\Delta\bar{\nu}$ 577, 641, 692. The C=O shift in the cyclohexanones is $\Delta\bar{\nu}$ 1712 and does not vary with the position of the alkyl radical in the substituted cyclohexanones (504). In the esters, cyclohexyl acetate and cyclohexyl propionate, the C=O frequency is $\Delta\bar{\nu}$ 1742 and 1733, respectively, and is nearly identical in all cases with the aliphatic carbonyl shift (472).

In the cyclopentyl oxygenated compounds, according to Piaux (504), the C=O shift is for cyclopentanone $\Delta\bar{\nu}$ 1726 (8), 1746 (8); for 2-methyl-cyclopentanone $\Delta\bar{\nu}$ 1735; and for 3-methylcyclopentanone $\Delta\bar{\nu}$ 1744. These values are slightly higher than in the corresponding cyclohexane derivatives. There is no evidence of keto–enol isomerism. The presence of two carbonyl shifts in cyclopentanone is anomalous.

K. The Raman spectra of cycloölefins

The simplest cycloölefin so far investigated is cyclopentadiene. This is not only a cyclic compound but it also contains a conjugate double-bond system. Truchet and Chapron (601) obtained $\Delta\bar{\nu}$ 945 (4), 993 (3), 1109 (5), 1364 (4), 1441 (3), 1500 (5), 2870 (3), 3095 (3) as the principal lines. For the polymeric dicyclopentadienes were observed $\Delta\bar{\nu}$ 675 (3), 774 (3), 946 (3), 954 (3), 1124 (3), 1137 (3), 1439 (3), 1574 (4), 1614 (4), 2069 (2), 3058 (2). The particular feature in connection with cyclopentadiene is the shift $\Delta\bar{\nu}$ 1500 attributable to the ethylenic linkage. While this extraordinary decrease is not analogous to that observed with the allenes, it is much lower than observed in other unsaturated cyclic hydrocarbons. Godchot, Canals, and Cauquil (259, 260, 261) have investigated a series of cycloölefins, and Piaux (505, 506, 507, 508) and Weiler (636) have investigated cyclopentene and its derivatives in particular. In table 19 are given the principal Raman lines of cyclopentene and four of its hydrocarbon derivatives based on the data of Piaux, Godchot, Canals, and Cauquil. It is noticeable that the C=C shift in cyclopentene, namely $\Delta\bar{\nu}$ 1615, is approximately 27 wave numbers lower than the average ethylenic shift in the aliphatic hydrocarbons of the type R—CH=CH₂ as given in table 10. With substitution on the carbon atom adjacent to the double bond in cyclopentene the frequency is increased to $\Delta\bar{\nu}$ 1658, a value more comparable with the ethylenic shift obtained in compounds of the type R—CH=CH—R'. If the substituent is a phenyl radical the augmentation in the double bond shift as compared with cyclopentene is less marked, becoming $\Delta\bar{\nu}$ 1627, but if the phenyl radical is one carbon atom removed from the ethylenic group, as in benzyl-Δ^1-cyclopentene, the shift is $\Delta\bar{\nu}$ 1652. In other words, the effect of the phenyl radical does not persist through an intermediate carbon atom. The hydrogen to carbon shift in unsaturated aliphatic compounds, it will be remembered, was
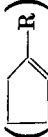
$\Delta\bar{\nu}$ 3005 and 3080, as given in table 7.   This type of hydrogen frequency appears strongly in all the cyclopentenes at about $\Delta\bar{\nu}$ 3055.

The principal shifts of the oxygenated derivatives of the cyclopentenes are as follows: for Δ^1-cyclopentenylcarbinol (505, 508), $\Delta\bar{\nu}$ 420 (5), 870 (5),

TABLE 19

The Raman spectra of cyclopentene and some of its derivatives

		$\Delta\bar{\nu}$		
Cyclopentene	1-Methylcyclo-pentene	1-Ethylcyclo-pentene	1-Phenylcyclo-pentene	Benzylcyclo-pentene
				210(8)
				231(5)
	325(5)	336(5)	339(5)	
385		404		
	578(8)		619(5)	622(5)
	851(5)			
	881(8)	867		
900(8)	903(5)	906	958(5)	968(5)
964(8)		949	982(5)	
	1008(8)	993	1004(7)	1003(10)
1025(5)	1026(5)	1031(7)	1033(5)	1030(8)
1108(7)		1131		
			1157(5)	1155(5)
			1184(5)	1181(5)
1207(5)	1207(8)	1200(5)	1208(7)	1205(5)
	1259(5)			
1296(5)	1295(5)		1296(8)	
	1333(8)		1342(5)	
	1383(8)	1385		
1441(7)	1439(10)		1442(8)	1441(7)
		1445(8)		
1467(5)	1465(8)		1495(8)	1466(5)
1615(7)		1660(10)	1600(10)	1603(10)
	1658(10)		1627(10)	1652(10)
2857(7)	2848(10)	2844(8)	2845(7)	2846(7)
2878(5)		2858(5)		
2913(7)	2910(10)		2897(8)	2902(7)
			2926(8)	
2953(7)	2959(8)	2966(7)	2955(8)	2960(7)
				3037(8)
3060(7)	3045(8)	Incomplete	3061(10)	3060(8)

888 (8), 983 (5), 1022 (5), 1202 (8), 1296 (5), 1443 (7), 1466 (5), 1656 (7), 2848 (10), 2902 (10), 2952 (10), 3048 (5); for Δ^1-cyclopentenylethanol (505, 508), $\Delta\bar{\nu}$ 329 (5), 506 (5), 853 (7), 893 (7), 948 (8), 1006 (5), 1026 (5), 1079 (5), 1160 (5), 1207 (8), 1294 (5), 1444 (10), 1468 (8), 1651 (10),

TABLE 20

Characteristic frequencies of substituted Δ^1-cyclopentene (⬠—R)

R				$\Delta\tilde{\nu}$				
H	899(4)	1025(3)	1207(2)	1296(1)	1441(7)	1467(2)	1615(6)	3060(3)
CH₃	881–903(4)	1026(3)	1207(5)	1295(1)	1439(8)	1465(5)	1658(6)	3045(2)
C₂H₅	890–908(2)	(1033)(10)	1208(6)	1296(4)	1442(6)	1462(1)	1627(8)	(3061)(4)
CH₂C₂H₅	887–902(1)	(1030)(10)	1205(2)	1297(3)	1441(7)	1466(2)	1652(8)	3037(3)
CH₂OH	888(8)	1022(2)	1202(6)	1296(3)	1443(8)	1466(3)	1656(8)	3048(4)
CH₂OCOCH₃	889–907(4)	1025(3)	1206(3)	1296(1)	1443(8)	1466(6)	1658(8)	3058(3)
CHOHCH₃	893(10)	1026(1)	1207(4)	1294(2)	1444(8)	1468(5)	1651(8)	3051(3)
CHOHC₂H₅	895(7)	1029(2)	1206(2)	1294(2)	1441(8)	1464(5)	1650(7)	3052(2)
CH₂Br			1205(2)		1440(7)		1640(7)	
CHO	882(3)		1205(1)	1289(2)	1434(7)		1616(9)	Broad
COOCH₃	903(3)	1023(2)	1206(2)	1297(3)	1437(9)	1469(4)	1631(8)	3072(7)
CN	896(7)	1020(2)	1210(3)	1299(3)	1437(9)	1468(4)	1615(8)	3076(8)

2848 (10), 2901 (10), 2956 (8), 2978 (10), 3051 (8); for Δ^1-cyclopentenyl-propanol (505, 508), $\Delta\bar{\nu}$ 854 (5), 895 (8), 950 (8), 1029 (5), 1206 (5) 1229 (5), 1441 (7), 1464 (8), 1650 (7), 2848 (7), 2876 (5), 2908 (7), 2937 (7), 2965 (8), 3052 (5); for Δ^1-cyclopentenealdehyde (508), $\Delta\bar{\nu}$ 381 (5), 480 (8), 882 (5), 954 (8), 1158 (5), 1289 (5), 1383 (8), 1434 (8), 1616 (10), 1676 (10); for methyl-Δ^1-cyclopentenylcarboxylate (508), $\Delta\bar{\nu}$ 378 (5), 870 (5), 903 (5), 946 (5), 967 (5), 1206 (5), 1297 (5), 1437 (7), 1469 (5), 1631 (7), 1715 (7), 2844 (7), 2894 (8), 2915 (8), 2954 (10), 3072 (8); and for 1-cyano-Δ^1-cyclopentene (505, 508), $\Delta\bar{\nu}$ 175 (7), 505 (5), 866 (8), 896 (8), 953 (7), 1020 (5), 1139 (5), 1210 (5), 1257 (5), 1299 (5), 1325 (5), 1437 (7), 1468 (5), 1615 (10), 2218 (10), 2848 (5), 2868 (5), 2950 (10), 3076 (8). Shifts weaker than (5) have not been included in this tabulation. The effects of different substituent groups on the characteristic frequency shifts for cyclopentene are given in table 20 from the data of Piaux (508). The modifications in the ethylenic shift for cyclopentene show approximately the same relative order as those observed by Bourguel for the modifications of this shift in the aliphatic ethylenes, which were indicated in tables 7 and 10. In the cyclic compounds, however, these modifications are more pronounced. This is particularly noticeable toward the extremes of the two respective series. The radicals generally considered negative, such as the acid, ester, and aldehyde groups, have a tendency to decrease the frequency. On the other hand, the radicals considered positive, such as alkyl groups, increase the frequency. This is only a rough approximation, however.

Like most first members of a homologous series, cyclohexene has received considerable attention. It and its derivatives have been examined by Andant (6, 7, 8), Godchot, Canals, and Cauquil (260, 261), Hayashi (302), Lespieau and Bourguel (404, 405), Morris (456), Nevgi and Jatkar (472), Weiler (634, 635, 636), and Wood and Collins (661). Unlike the ethylenic shift in cyclopentene, this shift in cyclohexene is in its average position and is found at $\Delta\bar{\nu}$ 1650. The C—H shift of the cyclic hydrocarbons, which appears near $\Delta\bar{\nu}$ 3060 in cyclopentene and benzene, is reduced to $\Delta\bar{\nu}$ 3024 (6) in cyclohexene. This shift was not recorded by Godchot, Canals, and Cauquil for this compound or with the other members of the homologous series, although it is possible that it is present. This weakening may be for reasons of symmetry. The shifts observed for a series of cyclohexenes are indicated in table 21. No notation is given as to the relative intensities. It is noted that the position of the double bond in the ring influences the ethylenic shift, as indicated in 1-methyl-Δ^3-cyclohexene. This is compatible with the already established principles indicating that the greater the distance the double bond is from a substituent group, the less effect this group has. While the other cyclo-

hexenes have a frequency displacement between $\Delta\bar{\nu}$ 1650 and 1680, cyclo-octene shows an unusual anomaly in having this frequency at $\Delta\bar{\nu}$ 1604, which is not far removed from that of cyclopentene. This may indicate

TABLE 21

Raman spectra of some cycloölefins

				$\Delta\bar{\nu}$				
Cyclohexene	1-Methyl-cyclohexene	1-Methyl-cyclohexene	1-Ethyl-cyclohexene	1,4-Di-methyl-Δ¹-cyclohexene	Cyclo-heptene	1-Methyl-cyclo-heptene	Cyclo-octene
176	132	145			144		158
273					212		243
					315	305	294
396	437	392		398		386	
451	495	447	439	417			
494	588	495		447			424
	618		625	525		603	
	695			658			
703	758	732	752	757	738	722	695
825	821	791	835	786		796	
		894	852	801			
	859	957	894	894			
997	990	995	993	996	996	996	996
1069	1069		1055		1043	1082	1096
	1087			1095		1120	
1139	1152	1229		1171		1196	1171
1220							
1272	1266	1258	1213	1256	1273	1258	1271
	1309		1381	1295		1323	
	1367				1348	1379	
1431	1445	{1443, 1450}	1432	{1443, 1449}	1445	1445	1439
1650	1675	1650	1675	1680	1651	1672	1604
2821							
2868	2876	2803	2817	2807	2867	2861	2864
2914	2914	2914					
2940	2940	2944	2926	2872	2912		2912
	2964	2967	2942	2944	2944	2940	2950
						2966	
3024							

a weakening of the bond in rings of five or eight carbon atoms as compared with the six- or seven-membered rings.

There have been two cyclohexadienes investigated. These are 1,3-cyclohexadiene, examined by Andant (8), Bonino and Manzoni-Ansidei (90, 92), Kohlrausch and Seka (370), and Murray (461), and 1,4-cyclo-

hexadiene, which has been studied by Andant (8) and Kohlrausch and Seka (370). The spectrum for the 1,3-compound, according to Murray, is: $\Delta\tilde{\nu}$ 298 (4), 394 (2), 458 (1), 505 (0), 559 (1), 618 (1), 823 (10), 848 (8), 945 (4b), 992 (15), 1060 (2), 1174 (4), 1220 (3), 1240 (2), 1266 (1), 1324 (1), 1411 (1), 1432 (5), 1576 (20), 1615 (3), 2823 (8b), 2864 (8b), 2908 (4), 2936 (8), 3018 (5), 3041 (10), 3056 (7). There are obviously two bonds distinctly ethylenic in character, corresponding to $\Delta\tilde{\nu}$ 1576 and 1615. The first of these is exceedingly low for this type of frequency displacement, but it is not so low as that observed for cyclopentadiene, namely $\Delta\tilde{\nu}$ 1500. The larger displacement is more comparable to that observed in benzene than that yielded by cyclohexene. Most of the strong lines in benzene have a counterpart in 1,3-cyclohexadiene. In 1,4-cyclohexadiene the strongest shift is practically identical with that of the 1,3-compound. The other ethylenic shift is $\Delta\tilde{\nu}$ 1635, and like $\Delta\tilde{\nu}$ 1615 is relatively very weak. Both compounds show a strong displacement corresponding to the linear hydrogen to carbon oscillation at $\Delta\tilde{\nu}$ 3040.

The oxygenated derivatives of cyclohexene have been investigated by Piaux (508) and Guillemont (288). The principal shifts observed for these compounds are as follows: 1-methyl-Δ^1-cyclohexen-6-ol (508), $\Delta\tilde{\nu}$ 343 (5), 432 (5), 474 (5), 584 (5), 637 (5), 747 (5), 790 (5), 855 (5), 875 (5), 1005 (5), 1015 (5), 1035 (5), 1062 (5), 1186 (5), 1255 (5), 1312 (5), 1379 (5), 1436 (7), 1457 (8), 1670 (7), 2837 (7), 2872 (7), 2914 (7), 2943 (7); 1-ethyl-Δ^1-cyclohexen-6-ol (288), $\Delta\tilde{\nu}$ 707 (5), 793 (5), 849 (5), 918 (5), 1051 (7), 1080 (5), 1102 (5), 1183 (5), 1253 (7), 1271 (7), 1300 (5), 1347 (5), 1433 (10), 1451 (7), 1667 (10); 1-methyl-Δ^1-cyclohexen-6-one (508), $\Delta\tilde{\nu}$ 472 (5), 710 (5), 1023 (5), 1083 (5), 1175 (5), 1360 (8), 1434 (7), 1456 (5), 1640 (7), 1670 (7), 2878 (8), 2924 (8), 2950 (8); 1-ethyl-Δ^1-cyclohexen-6-one (288), $\Delta\tilde{\nu}$ 879 (5), 1057 (5), 1093 (5), 1175 (5), 2448 (5), 1380 (5), 1434 (7), 1460 (5), 1636 (10), 1670 (10); 1-methyl-6-ethoxy-Δ^1-cyclohexene (508), $\Delta\tilde{\nu}$ 1254 (5), 1306 (5), 1372 (8), 1437 (7), 1450 (8), 1673 (7), 2837 (8), 2872 (7), 2912 (7), 2936 (7); and 1-ethyl-Δ^1-cyclohexen-6-ol acetate (288), $\Delta\tilde{\nu}$ 851 (7), 921 (7), 1065 (5), 1188 (5), 1254 (5), 1302 (5), 1332 (5), 1381 (5), 1434 (10), 1448 (10), 1672 (10), 1737 (5). The figures tabulated are only for the stronger shifts. In many cases, however, the C—H displacements were not determined.

The ethylenic bond in the Δ^1-substituted cyclohexenes gives $\Delta\tilde{\nu}$ 1670 for the hydrocarbons, $\Delta\tilde{\nu}$ 1668 for the alcohol, $\Delta\tilde{\nu}$ 1638 for the ketone, $\Delta\tilde{\nu}$ 1673 for the ether, and $\Delta\tilde{\nu}$ 1672 for the ester derivatives, all of which are larger than the corresponding shifts in cyclopentene derivatives. In some of these oxygenated derivatives may be noted the effect of the conjugation of the C=C on the C=O vibration. It will be recalled that the aliphatic aldehydes, ketones, and esters gave $\Delta\tilde{\nu}$ 1720, 1705, and 1735

respectively for the average C=O shift as shown in table 12. But in Δ^1-cyclopentenealdehyde the shift has become $\Delta\bar{\nu}$ 1676 instead of $\Delta\bar{\nu}$ 1720 and in methyl-Δ^1-cyclopentenecarboxylate $\Delta\bar{\nu}$ 1715 in lieu of $\Delta\bar{\nu}$ 1735, while the ketonic derivatives of cyclohexene and benzene yield $\Delta\bar{\nu}$ 1673 for the C=O as compared with $\Delta\bar{\nu}$ 1705 for the normal ketones. Thus conjugate C=C with C=O and this will reduce the characteristic carbonyl shift from 10 to 35 wave numbers and, as has been pointed out previously, the C=O will reduce the C=C shift by as much as 40 wave numbers.

One of the most peculiar cycloölefins investigated is cedrene, which presumably has the formula

$$\underset{H_{20}C_{12}}{}\diagup\overset{\displaystyle CH}{\underset{\displaystyle C\!\!-\!\!CH_3}{\parallel}}\diagdown$$
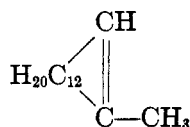
This compound was investigated by Matsuno and Han (423). These authors found one hundred and nineteen Raman lines, of which $\Delta\bar{\nu}$ 1666 is attributed to the ethylenic linkage. A very careful analysis was made of the Raman lines observed and an attempt was made to correlate them with a possible structure. A frequency at $\Delta\bar{\nu}$ 1375 is associated with the structure —C=C—. While the results are not conclusive, this is an

$\qquad\qquad\overset{|}{CH_3}$

excellent example of the method employed in the application of Raman spectra to the delineation of molecular constitution. Other examples will be given after the discussion of benzene and its derivatives.

L. The Raman spectra of aromatic hydrocarbons

1. Benzene. Benzene has been more extensively investigated than any other compound. It is impossible to cite in the text all the contributions of the large number of workers who have examined this compound and its derivatives. The material presented has been chosen with the view of presenting typical effects of substitution and the Raman spectra of some of these compounds, rather than a detailed summary of each compound.

The Raman spectrum of benzene has been determined carefully by Grassmann and Weiler (272). They observed forty-one lines whose frequency shifts and intensities are as follows: $\Delta\bar{\nu}$ 404 (1), 607 (8), 692 (1), 781 (0), 802 (0), 824 ($\frac{1}{2}$), 849 (4), 971 (1), 984 (2), 993 (15), 1005 (1), 1034 (1), 1176 (4), 1285 (0), 1326 ($\frac{1}{2}$), 1402 (2), 1449 (0), 1480 (0), 1584 (12), 1606 (8), 1697 (0), 1827 ($\frac{1}{2}$), 1936 (1), 1988 ($\frac{1}{2}$), 2030 ($\frac{1}{2}$), 2128 ($\frac{1}{2}$), 2296 (1), 2358 ($\frac{1}{2}$), 2455 (1), 2545 (1), 2618 (2), 2688 ($\frac{1}{2}$), 2927 (1),

2949 (4), 3049 (8), 3063 (12), 3166 (3), 3187 (4), 3463 (0), 3680 (0), 3916 (0). It is believed that these may be explained as a result of ten ground frequencies and their combinations. These fundamental frequencies are given in table 22. Two of these, indicated by *, are members of doublets. The frequencies most important are $\Delta \bar{\nu}$ 992, 1585, 1606, 3049, and 3063. The first of these is attributable to the carbon to carbon vibration, the second two to the C=C, and the last two to the linear carbon–hydrogen oscillation. The frequency at $\Delta \bar{\nu}$ 984 is attributed by Grassmann and Weiler and by Bhagavantam (54) to the influence of the carbon isotope of mass 13. Langseth (397) has previously explained the fine structure of $\Delta \bar{\nu}$ 455 in carbon tetrachloride as due to the isotopes of chlorine. Bhagavantam, who has investigated the fine structure of $\Delta \bar{\nu}$ 992 in benzene, 1188 in cyclopropane and 993 in ethane, comes to the conclusion that all these lines have satellites whose intensities and frequency displacements can be accounted for on the assumption that one of

TABLE 22

Fundamental frequencies of benzene

	$\Delta \bar{\nu}$	i		$\Delta \bar{\nu}$	i
ν_1	400	1	ν_7	1176	4
ν_2	606.8	8	ν_8	1480	0
ν_3	692	1	ν_9	1585.4	12
ν_4	849	4	ν_9*	1606.4	8
ν_5	992.5	15	ν_{10}	3049	8
ν_6	1034	1	ν_{10}*	3063.6	12

the carbon atoms has a mass 13. The shift $\Delta \bar{\nu}$ 992 is almost perfectly polarized, its depolarization constant being 0.05, and consequently represents an inactive oscillation which appears only weakly in infra-red absorption in view of its symmetrical vibration. This frequency appears in practically all the derivatives of benzene in a slightly shifted position and with variations in intensity, depending on the complexity of the substitution. Under high dispersion Howlett (319) has broken this line into five components. Bhagavantam (42) attributes $\Delta \bar{\nu}$ 607, 851, 992, 1181 to the hexagonal carbon ring in benzene, among which $\Delta \bar{\nu}$ 607 is attributed to the alternate expansion and contraction of the hexagon, and $\Delta \bar{\nu}$ 851, 1181 to the unsymmetrical modes of oscillation of the extension type. He has ascribed the doublet frequency $\Delta \bar{\nu}$ 1584 and 1606 to oscillations especially involving the hydrogen atom. This raises the question as to the Kekulé or the centric or the Claus formula for benzene. It is one of the anomalies in the elucidation of the structure of organic compounds,

in general, that what would seem to be one of the simplest applications, namely, the differentiation of these two structures, has not met with conspicuous success. Neither has the application of the mechanical models of Andrews and his coworkers solved this problem. As pointed out in the beginning, it is possible that the rigid chemical method of depicting formulas is too static and not sufficiently dynamic. Heretofore, Raman spectra have preceded rather than followed the interpretation of bonds on the basis of resonating bonds as employed more recently by Pauling. The triple-bond structure of nitrous oxide and possibly that of carbon monoxide are pertinent examples. In the case of benzene it was originally presumed that shifts in the region of $\Delta\tilde{\nu}$ 1585 and 1608 were due to the same type of double bond as found in the ethylenic linkage. Subsequently this was questioned. Wilson (647, 648), in his very competent analysis of the spectrum from a mathematical view, attributes $\Delta\tilde{\nu}$ 1584 to an accidental degeneration. Originally Kettering, Shutts, and Andrews (331) assumed that the evidence was in favor of the double-bond structure from the vibration of the mechanical models. Murray, Deitz, and Andrews (465) conclude that there are no effective forces acting between the carbon atoms para to one another in the ring, and that this, therefore, is evidence against the centric formula, and that with the assumption that the average force constant of the carbon to carbon bond in the ring is roughly one and one-half times those of the normal homopolar single bonds, the results are in accord with the resonance formula of Pauling or the Kekulé formula. Bonino (69, 71) has discussed the entire situation in regard to benzene in considerable detail. He believes that the line at $\Delta\tilde{\nu}$ 1580 is somewhat analogous to the line for $C{=}C$, and it is because of other conditions that there is doubt whether this represents a true double bond. Bonino and Manzoni-Ansidei (92) doubt the existence of ethylenic linkage in benzene. Truchet and Chapron (601) express the view that the shift at $\Delta\tilde{\nu}$ 1584 or 1608 is well within the variation in the $C{=}C$ shift observed in other compounds whose structure is generally accepted as containing a $C{=}C$ group. Lespieau and Bourguel (405) and Bourguel (97) consider these shifts as arising from double bonded carbon. This shift may actually vary from $\Delta\tilde{\nu}$ 1409 in thiophene to $\Delta\tilde{\nu}$ 1679 in trimethylethylene, excluding $\Delta\tilde{\nu}$ 1074 observed in allene. In any case it does not seem to be tenable that this shift can owe its origin to any carbon and hydrogen vibration, since it is present in pentachlorobenzene and slightly shifted in hexachlorobenzene.

It is believed by this writer that while the Kekulé notation may represent too static a picture, for the purposes of representation of the modification in the changes of Raman spectra as a function of constitution $\Delta\tilde{\nu}$ 1580 or 1608 may be treated in the same fashion as any other $C{=}C$

TABLE 23

Fundamental frequencies of benzene and its monosubstitution derivatives

Derivatives	Δν̄						
C₆H₆	605(3)	992(10)			1178(3)	1605(1) / 1584(3)	3057(1) / 3060(5)
a. Hydrocarbon derivatives							
C₆H₅CH₃	622(2)	1002(8)	1029(1)	1154(1)	1209(3)	1604(2)	3054(5)
C₆H₅CH₂CH₃	620(2)	1003(8)	1029(1)	1157(3)	1203(2)	1604(5)	3052(5)
C₆H₅CH=CH₂	623(5)	999(7)	1029(1)	1154(1)	1205(8)	1601(10)	3057(8)
C₆H₅C≡CH	623(5)	1000(7)	1029(1)	1158(1)	1195(8)	1601(10)	3059(9)
C₆H₅CH₂CH=CH₂	623(5)	1000(7)	1029(1)	1158(1)	1205(5)	1599(10)	3057(8)
C₆H₅CH=CHCH₃	621(5)	999(8)	1031(1)	1149(5)	1210(8)	1599(10)	3055(8)
C₆H₅—CH—CH₂ (CH₂)	623(5)	999(7)	1026(1)	1156(1)	1220(8)	1604(8)	3061(8)
C₆H₅—CH₂—C≡CH	623(1)	1000(8)	1033(1)	1158(1)	1200(5)	1601(7)	3059(8)
C₆H₅C₆H₅	611(1)	994(5)	1022(2)	1146(1)	1191(1)	1589(3) / 1609(5)	3047(8)
C₆H₅CH₂C₆H₅	623(4)	1012(8)	1037(4)	1145(2)	1175(4)	1593(6)	3054(4)
C₆H₅CH₂CH₂C₆H₅	619(3)	1002(10)	1032(4)	1153(2)	1200(4)	1600(5)	3052(4)
C₆H₅CH=CHC₆H₅ (trans)	620(3)	1004(10)			1188(15)	1590(15)	
C₆H₅CH=CHC₆H₅ (cis)	615(2)	1000(10)	1027(2)	1150(4)	1190(4)	1596(10)	3059(4)
C₆H₅C≡CC₆H₅	621(2)	997(15)	1028(1)	1140(15) / 1155(2)	1174(2) / 1188(2)	1590(20)	
b. Benzyl compounds							
C₆H₅CH₂Cl	619(4)	1000(3)	1034(1)	1159(1)	1211(1)	1600(1)	3054(3)
C₆H₅CH₂NH₂	622(4)	1001(8)	1028(2)	1156(4)	1201(4)	1606(4)	3055(8)
C₆H₅CH₂OH	610(0)	1000(3)			1196(1)	1594(2)	3050(3)
C₆H₅CH₂NO₂	623(4)	1005(8)	1029(3)	1160(2)	1197(3)	1596(5)	3059(4)
C₆H₅CH₂CN	620(2)	1007(4)	1030(1)		1187(2)	1597(2)	3057(4)

c. Various derivatives

C_6H_5OH	614(2)	1002(5)	1024(3)	1170(3)		1598(3)	3059(5)
C_6H_5CHO	615(3)	1001(8)	1023(1)	1164(5)	1203(6)	1597(10)	3063(5)
C_6H_5COCl	615(3)	1003(6)	1028(2)	1168(2)	1206(3)	1592(6)	3067(4)
$C_6H_5COOCH_3$	613(3)	1000(7)	1023(1)	1160(1)		1602(10)	3070(5)
$C_6H_5COCH_3$	613(3)	999(5)	1025(3)	1155(1)		1597(6)	3063(4)
C_6H_5Cl	615(6)	1001(10)	1021(6)	1156(4)		1581(6)	3066(10)
C_6H_5Br	608(1)	1000(4)	1022(2)	1159(1)		1576(2)	3060(5)
C_6H_5I	610(3)	998(7)	1012(4)	1158(2)		1568(5)	3054(2)
$C_6H_5NH_2$	617(3)	996(10)	1029(5)	1147(3)		1601(10)	3046(4)
$C_6H_5NHC_6H_5$	620(2)	1000(12)	1030(5)		1181(4)	1603(12)	3064(3)
$C_6H_5NO_2$	604(1)	1000(3)		1175(2)		1587(4)	3052(1)
C_6H_5CN	619(1)	998(5)			1190(3)	1595(4)	3063(4)
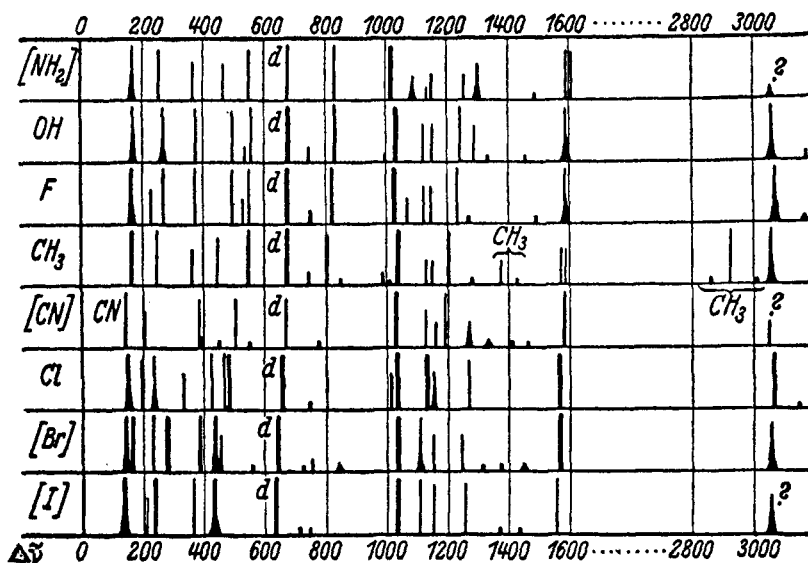
FIG. 17. The Raman spectra of ortho-substituted chlorobenzenes (after Kohlrausch and Pongratz)
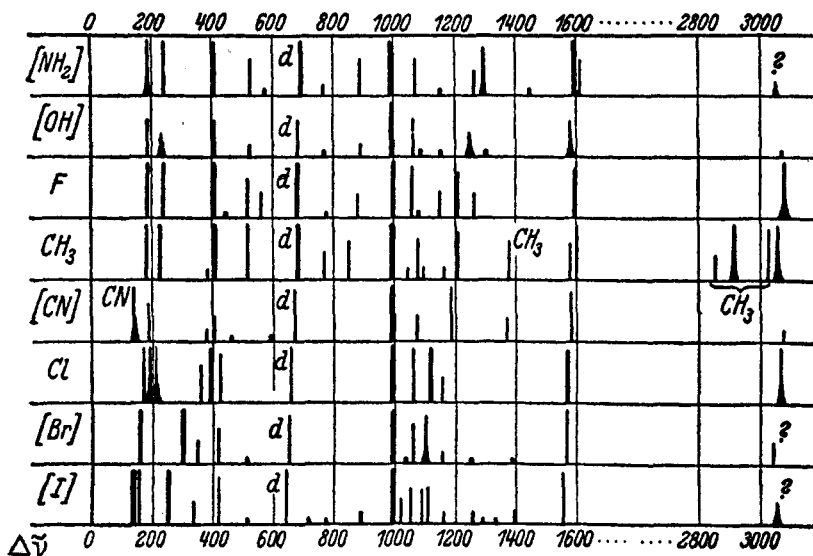
FIG. 18. The Raman spectra of meta-substituted chlorobenzenes (after Kohlrausch and Pongratz)

line. It is difficult to conceive that the method of treating cyclopentene, cyclohexene, or their respective dienes and the terpenes should be different from that for benzene and its derivatives. From the point of view of the analysis of their spectra, therefore, these compounds will be considered in the same fashion as any other hydrocarbons.

1. *Monosubstituted benzenes.* In an extensive series of publications Kohlrausch and Pongratz (355, 360, 361, 365, 366) and Dadieu, Pongratz, and Kohlrausch (191) have determined the effect of substitution on benzene. Murray and Andrews (462, 463) and many others (note bibliography) have also investigated monosubstituted and polysubstituted benzenes. In table 23 are given the principal lines from benzene and its
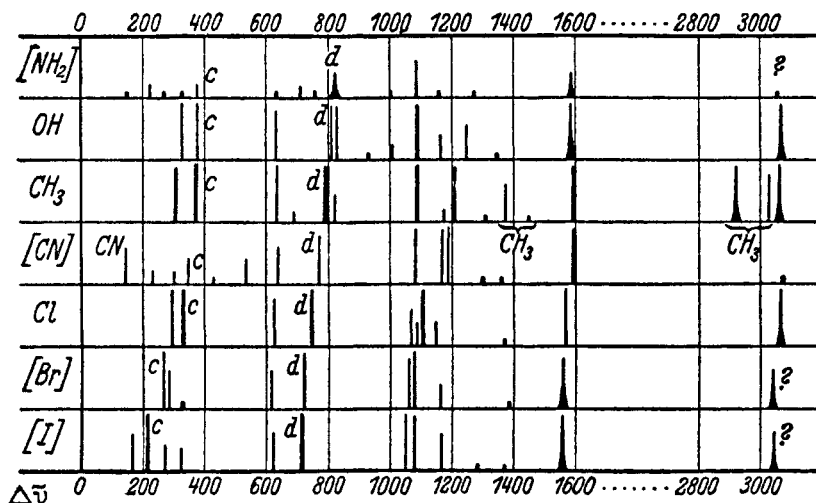
FIG. 19. The Raman spectra of para-substituted chlorobenzenes (after Kohlrausch and Pongratz)

monosubstitution derivatives. These data are taken from Bourguel (100) and are based partially upon observations of Dadieu, Pongratz, and Kohlrausch, and of Kohlrausch and Pongratz.

2. *Disubstituted benzenes.* The effect of disubstitution in benzene is illustrated in figures 17, 18, and 19, which illustrate the behavior of substituted chlorobenzenes containing different substituent groups (367). Figure 17 represents the effect of ortho substitution, figure 18 meta substitution, and figure 19 para substitution. On considering first figure 19, it is quite evident that there are at least seven frequencies which remain reasonably constant throughout all the compounds of benzene and its monosubstitution products. These are frequencies which are dependent upon the structural features of either the ring or the ring double bond. In

those cases where a double bond occurs external to the ring the shifts characteristic of the ring double bond alone are given. The C—H oscillation varies from approximately $\Delta\bar{\nu}$ 3047 to 3070 depending on the nature of the substituent group. It is noticeable that there is a reinforcement of the intensity of the C=C shift when there is a double bond external to the ring. This shift remains constant within 15 wave numbers, irrespective of the nature of the hydrocarbon substituent group. If, however, the substituent group is not a hydrocarbon radical but some other derivative, there is a greater alteration in the C=C frequency. This is particularly notable in the case of the halogens, where there is a progressive decrease in the frequency with the increase in molecular weight of the halogen. There is likewise an effect on the C—H oscillation which decreases progressively from the $\Delta\bar{\nu}$ 3066 to 3054 with the same halogen substitution. If, however, the halogen is removed from direct contact with the ring, as in benzyl chloride, the effect is much smaller. There is an appreciable reaction from conjugation with the carbonyl group. The net result, however, is that the effect of substitution on the ethylenic shift is less marked than in the case of the normal ethylenes, the cyclopentenes, or the cyclohexenes. In view of the conjugate nature of the ethylenic linkage in benzene it is of some importance that a substituent on one carbon atom in the aromatic nucleus must necessarily be attached to one ethylenic linkage and removed by one carbon from the next double bond. Nevertheless, this unsymmetrical arrangement results in only one strong Raman shift in this region. This would seem to give some weight to the dynamical conception of the nucleus in this case.

While it has been observed that the substitution of a methyl group in the aliphatic ethylenes and in cyclopentene and cyclohexene markedly increases the ethylenic shift, the passage from benzene to toluene causes only a very slight modification. Similarly in going from the methyl derivatives of unsaturateds, including cyclopentene, to the aldehyde derivative there is a marked decrease in the ethylenic shift. By progressing from toluene to benzaldehyde, however, the decrease is only about one-third of that observed in the other compounds. On the other hand, a similar progression of the carbonyl derivatives indicates that the esters of the aliphatic unsaturateds and of cyclopentene have the largest carbonyl shifts and the aldehydes the least. By comparing methyl benzoate with benzaldehyde one observes a change in $\Delta\bar{\nu}$ from 1647 to 1689. This, therefore, is in the opposite direction from the frequency changes observed with the other compounds and is compatible with the classical effect of phenyl groups as contrasted with the alkyl radicals.

3. Polysubstituted benzenes. In the disubstituted aromatics there are definite progressive changes in the Raman spectra depending on the sub-
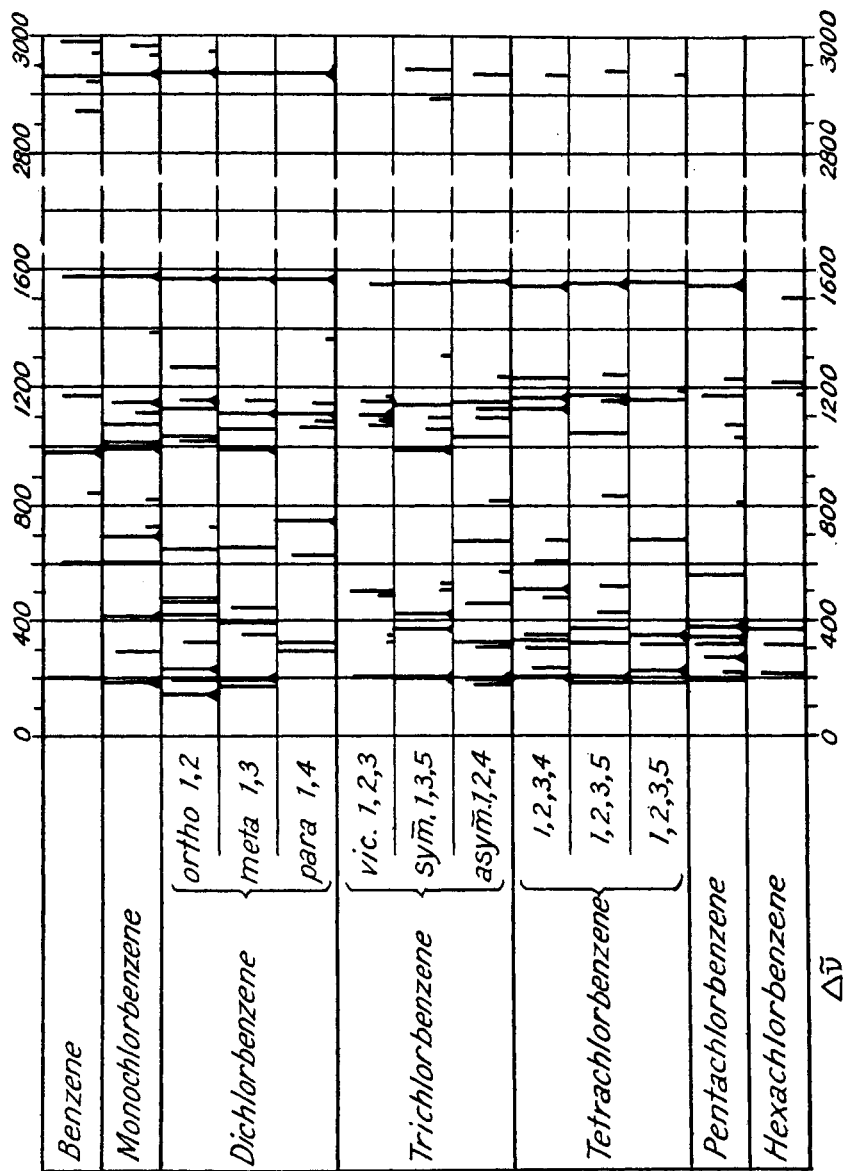
FIG. 20. The Raman spectra of polysubstituted chlorobenzenes (after Dadieu, Kohlrausch, and Pongratz)

stituent groups and the position of substitution. Kohlrausch and Pongratz have indicated some of these in the figures cited. It is particularly noticeable in the differences in para-substituted chlorobenzene as compared with the ortho and meta derivatives. In the substituted xylenes the frequency of the linear C—H shift increased from $\Delta\tilde{\nu}$ 3047 in *o*-xylene to $\Delta\tilde{\nu}$ 3070 in *o*-chlorotoluene. Kohlrausch and Pongratz (365) give the frequency of aliphatic C—H binding in the series from toluene to pentamethylbenzene as being $\Delta\tilde{\nu}$ 1378 (6), 1445 (3), 2728 (1), 2862 (4), 2916 (8), 3019 (4). The effect of multiple substitution on the double-bond linkage is shown in table 24, taken from data of Kohlrausch (340). The shifts

TABLE 24

The change in C=C shift as a function of substitution in polysubstituted benzene

SUBSTANCE	POSITION OF SUBSTITUENT GROUPS	$\Delta\tilde{\nu}$		
		X = Cl	X = CH₃	
C_6H_6			1584 (3)	1606 (1)
C_6H_5X	1	1580 (7)	1580 (1)	1603 (5)
	1, 2	1572 (8)	1584 (1)	1606 (5)
$C_6H_4X_2$	1, 3	1572 (8)	1590 (1)	1612 (4)
	1, 4	1572 (7)	1575 (1)	1616 (6)
	1, 2, 4	1564 (8)	1567 (4)	1617 (7)
$C_6H_3X_3$	1, 3, 5	1563 (6)		1604 (6)
	1, 2, 3	1554 (2)		
	1, 2, 4, 5	1563 (5)	1560 (4)	1620 (5)
$C_6H_2X_4$	1, 2, 3, 5	1558 (6)	1572 (3)	1614 (7)
	1, 2, 3, 4	1552 (8)		
C_6HX_5	1, 2, 3, 4, 5	1553 (5)	1572 (3)	1607 (4)
C_6X_6	1, 2, 3, 4, 5, 6	1503 (2)		1565 (1)

in the entire spectra as a result of multiple substitution are shown in figure 20, which gives the spectra of the polysubstituted chlorobenzenes (191).

The changes in the spectra of benzene with progressive halogen substitution have been painstakingly investigated by Murray and Andrews (463). These authors observed new lines not observed by Dadieu, Kohlrausch, and Pongratz and have confirmed most of their observations. In particular they have found multiple lines in the $\Delta\tilde{\nu}$ 1600 region, most of which were not previously observed and are rather weak. In all the halogen derivatives very strong frequencies are noted between $\Delta\tilde{\nu}$ 200 and 400. The Raman spectrum of fluorobenzene resembles the spectra of the heavier monohalogen derivatives of benzene, but shows a certain marked difference. It is very similar to the spectrum of toluene, whose side chain has approximately the same mass as fluorine. Between $\Delta\tilde{\nu}$ 1000 and 1200

the fluorobenzene spectrum is very different from the other halogen deriva-
tives.   This is indicated in figure 21, which shows the effect of different
halogen substitution.   The frequencies indicated between $\Delta\bar{\nu}$ 2200 and
2600 are stronger in the figure, in order to indicate them, than actually
observed.

4. Summary.   While the characteristic frequencies of the double and
triple bonds and the influence of substitution on them have been given in
detail in tables 7 to 13, 15, 19 to 21, 23, and 24, table 25 is included to give
a rough summary of these conclusions.

In this table the shifts for the unsubstituted hydrocarbon are given in
parentheses.   In column 1 is the type of linkage whose shifts as a function
of chemical constitution are given in columns 3 to 8 inclusive.   When
this linkage is conjugated with another of the same or different types
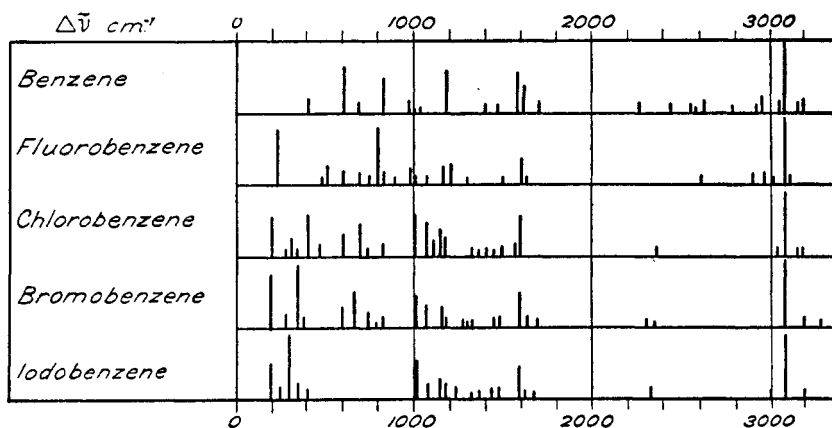
FIG. 21. The Raman spectra of halogen substituted benzenes (after Andrews)

this is indicated in column 2.   When the conjugate double bond is in the
phenyl radical this is indicated.   When two shifts are paired, it indicates
a possibility of a marked difference usually attributed to *cis-trans* isomer-
ism.   It is to be borne in mind that these shifts are not constant values,
but will vary in each homologous series depending on the position and
character of substituent groups.

It has been demonstrated in general that each type of chemical linkage
so far discussed has its characteristic frequencies, and each kind of mole-
cule gives rise to a series of Raman shifts whose frequencies and intensities
depend upon the molecular configuration.   It is thus often possible to
determine the constitution of some compounds and the composition of
certain mixtures.

Lespieau and Bourguel (404), for example, determined the Raman spec-
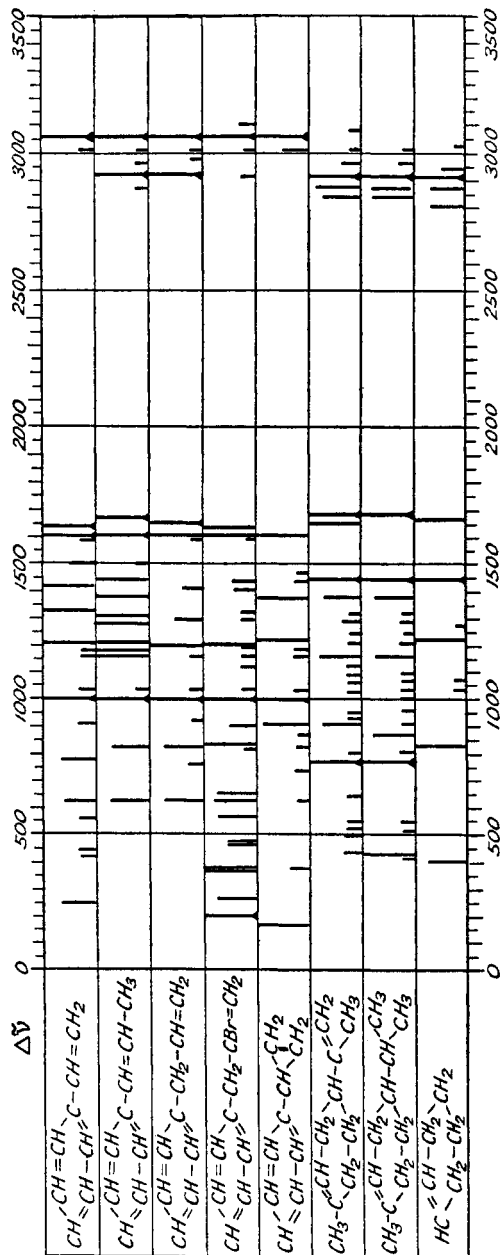
FIG. 22. The Raman spectra of some derivatives of benzene and cyclic compounds containing internal and external double bonds (after Lespieau and Bourguel)

TABLE 25

Influence of substitution on C=C, C=O, *and* C≡C *linkages*

	$\Delta\bar{\nu}$					
Linkage	Hydrocarbon	Aldehyde	Ke-tone	Acid	Ester	Anhydride
Aliphatic hydrocarbons						
1 2						
*C=C	(1620)1644–1678					
C=C, C=C	1634–1660					
C=C, C=O		1620–1647	1600	1638	1664–1679	
		1720	1705	1654	1735	
C=O, C=O			1725	1735	1735	1750, 1820
C=O, C=C		1689	1668		1740	
Cyclic compounds						
		C₅				
C=C	(1615)1658					
C=C, C=C	1500					
C=C, C=O		1616			1631	
C=O			1735			
C=O, C=C		1676			1715	
		C₆				
C=C	(1650)1675					
C=C, C=C	1576 1615–1635					
C=C, C=O			1638		1672	
C=O			1712		1740	
C=O, C=C			1670		1735	
C=C (cf. benzene)	(1584) (1605)1604	1597	1597	1601	1602	
C=O, C=C(phenyl)		1690	1677	1670	1724	
		C₇				
C=C	(1651)1672					
		C₈				
C=C	(1604)					
Acetylenes						
C≡C	(2119), 2236, 2293				2238	
C≡C, C=C(phenyl)	2221, 2241					
C=C(phenyl), C≡C	1600					
C≡C, C≡C	2250, 2304					
C=O, C≡C					1715	

* The $\Delta\bar{\nu}$ are given for the linkage indicated in column 1.

tra of three isomers, namely, isoallylbenzene, benzylethylene, and a bi-cyclic compound which was believed to be phenylcyclopropane. The ease with which the last compound will break down its bicyclic structure made

it difficult to determine by chemical means its molecular constitution. The following Raman spectra, however, were observed for isoallylbenzene: $\Delta\bar{\nu}$ 2599 (10), 1645 (1), 1663 (10). The highest of these shifts is fairly characteristic of a disubstituted ethylenic linkage, and the lowest is characteristic of the ethylenic linkage in the phenyl radical. For benzylethylene were observed $\Delta\bar{\nu}$ 1599 (8) and $\Delta\bar{\nu}$ 1645 (8), where $\Delta\bar{\nu}$ 1645 is the shift for a monosubstituted ethylene and the 1599 shift has the same significance that it has in isoallylbenzene. For the supposed bicyclic compounds was observed $\Delta\bar{\nu}$ 1604 (8), which demonstrates that no unsaturated side chain was present. Furthermore, the C—H shifts in isoallylbenzene were $\Delta\bar{\nu}$ 2864 (2), 2920 (8), 2968 (2), and 3055 (8). In benzylethylene were found $\Delta\bar{\nu}$ 2914 (8), 2978 (10), and 3057 (8). In the other compound, however, were observed only $\Delta\bar{\nu}$ 3007 (6) and 3062 (6). The lack of frequencies below $\Delta\bar{\nu}$ 3000 indicates conclusively the absence of side chains containing a methyl group. The shift $\Delta\bar{\nu}$ 3062 belongs to the hydrogen attached to the benzene ring and $\Delta\bar{\nu}$ 3007 is characteristic of the hydrogen attached to a cyclopropane nucleus which appears at $\Delta\bar{\nu}$ 3011 in cyclopropane and $\Delta\bar{\nu}$ 3015 in methylcyclopropane. The complete Raman spectra of these compounds and of limonene, carvomenthene, and cyclohexene are given in figure 22 to indicate the interrelations between external and internal double bonds.

M. The Raman spectra of the terpenes, terpene derivatives, and terpenoids

Perhaps one of the most fruitful applications of the Raman effect lies in the field of the terpenes. Many of their structures are as yet questioned, and the mixtures found in practice may be extraordinarily complex.

It may be noted in figure 22, in comparing the spectra of the last three compounds and their constitutional formulas, that there are very strong similarities. Limonene has an external double bond of the general formula $R_1R_2C\!\!=\!\!CH_2$, whose frequency shift is in the neighborhood of $\Delta\bar{\nu}$ 1650. Its internal double-bond shift $\Delta\bar{\nu}$ 1681 is similar to that of methylcyclohexene, $\Delta\bar{\nu}$ 1675. Carvomenthene likewise gives $\Delta\bar{\nu}$ 1681. Consequently the magnitudes of the frequency displacement in these compounds are compatible with their presumed structure.

Nevgi and Jatkar (473) have studied a series of terpenes to determine if there were any differences in the frequency shifts from terpenes identical except for optical activity. These results are indicated in figure 23.

The abbreviated formulas for these compounds are given in the figure. All these terpenes contain double bonds; some of these double bonds, however, are within the ring and some without, and their position is not always identical. The Δ^3-carene and Δ^4-carene are identical except for the position of the double bond in the cyclohexene ring and its relation to the
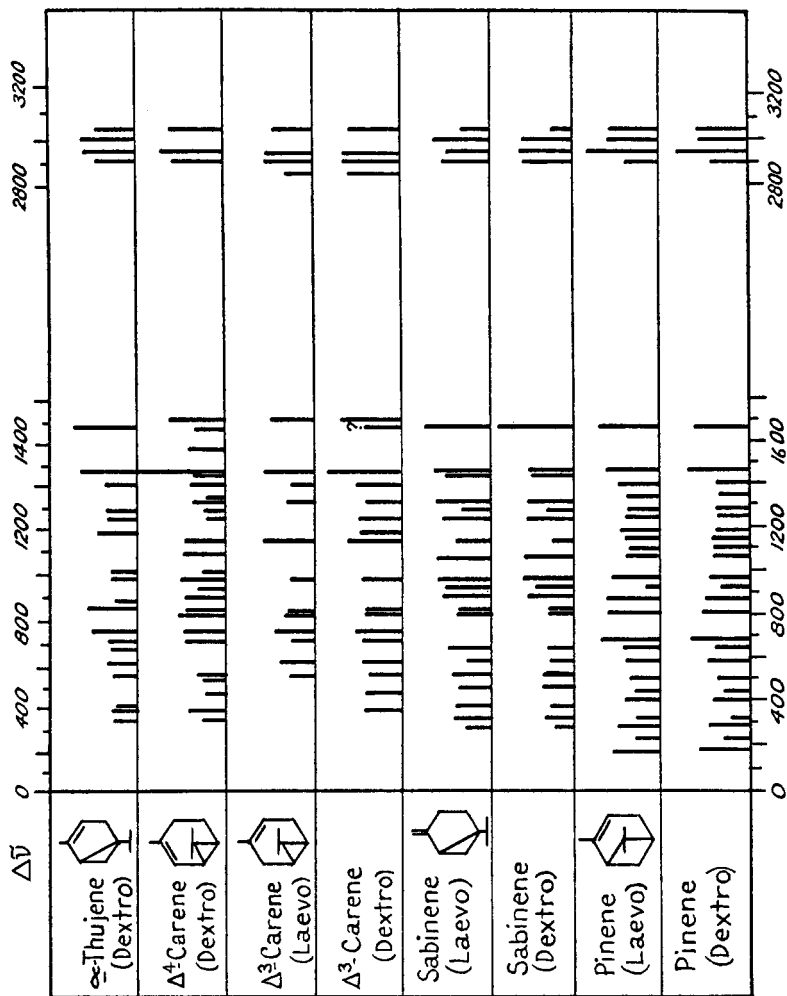
FIG. 23. The Raman spectra of some polycyclic terpenes (after Nevgi and Jatkar)

C_3 ring. The spectra so far as the $C=C$ shift is concerned are somewhat different, d-Δ^4-carene giving $\Delta\bar{\nu}$ 1554, 1639, and 1670, as compared with $\Delta\bar{\nu}$ 1641 and 1683 for d-Δ^3-carene. The l-Δ^3-carene has $\Delta\bar{\nu}$ 1685, the only observed frequency shift in the region which is comparable with that from substituted cyclohexene. The other isomers containing a ring double bond give, however, a lower frequency shift, such as $\Delta\bar{\nu}$ 1642 for d-α-thujene and $\Delta\bar{\nu}$ 1657 for the d- and l-α-pinenes. Apparently when the bridge in the cyclohexene nucleus is so situated that it is close to the ring double bond as in Δ^4-carene and the pinenes, the $C=C$ frequency is reduced. If, however, it is more distantly removed as in Δ^3-carene, the normal cyclohexene shift is present. The two sabinenes give identical $C=C$ shifts at $\Delta\bar{\nu}$ 1653, which is an approximately correct position for a compound of the type $R_1R_2C=CH_2$.

All these compounds show a shift near $\Delta\bar{\nu}$ 1440 characteristic of the CH_2 group. The pinenes, however, possibly show a rotational spectrum of the hydrogen around the carbon. The linear $C-H$ oscillation occurs at $\Delta\bar{\nu}$ 3008 in the carenes and in the thujenes, at $\Delta\bar{\nu}$ 3030 in the pinenes, and at $\Delta\bar{\nu}$ 3046 in the sabinenes. While these shifts are given an intensity of 1 to 3 in these terpenes, it is to be noted that they are apparently absent or very much weakened in ordinary cyclohexene derivatives. The conclusion is that while these isomers differ one from another, particularly in the lower frequency region, and they may thus be distinguished without too much difficulty, there is no apparent difference in the intensity or magnitude between the dextro and levo forms of the same compound.

Hayashi (302) has discussed the alkyl derivatives of cyclohexane and cyclohexene with particular reference to their Raman spectra in connection with the terpene derivatives. He observes that the methyl-, ethyl-, and isopropylidenecyclohexanes have $\Delta\bar{\nu}$ 1655, 1676, and 1674, respectively, and the substituted cyclohexenes have shifts close to that expected from multisubstituted ethylenes (299, 300).

Bonino and Cella (82, 86) have made a comprehensive investigation of the Raman effect of the terpenes and their derivatives. In figure 24 are given the Raman spectra of a number of compounds which are not terpenes but are isomeric with them. These are geranial, geraniol, citronellol, citronellal, and linalool. These give for the corresponding $C=C$ and $C=O$ shifts respectively: geranial $\Delta\bar{\nu}$ 1640, 1681; geraniol $\Delta\bar{\nu}$ 1675; citronellol $\Delta\bar{\nu}$ 1675; citronellal $\Delta\bar{\nu}$ 1675, 1719; linalool $\Delta\bar{\nu}$ 1672 with 1646 very weak. In every case the double-bond shift falls within the expected frequency region for a compound of that composition. The Raman spectra of a number of terpenes as determined by Bonino and Cella (86) are given in figure 25, which shows the influence of molecular constitution on the respective shifts.

Geranial (Citral)	$(CH_3)_2C=CH(CH_2)_2C(CH_3)=CHCHO$
Geraniol	$(CH_3)_2C=CH(CH_2)_2C(CH_3)=CHCH_2OH$
Citronellal	$CH_2=C(CH_3)(CH_2)_3CH(CH_3)CH_2CHO$
Citronellol	$CH_2=C(CH_3)(CH_2)_3CH(CH_3)CH_2CH_2OH$
Linalool	$(CH_3)_2C=CH(CH_2)_2C(CH_3)OH\,CH=CH_2$

$\Delta\bar{\nu}$ IN cm^{-1}
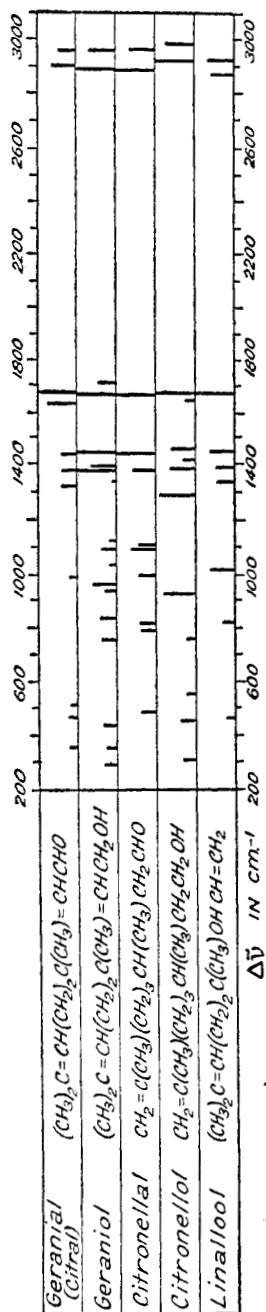
FIG. 24. The Raman spectra of some unsaturated aliphatic compounds isomeric with terpenes (after Bonino and Cella)

Menthone

Fenchone

β-Thujone

Pulegone

Carvenone

Carvone

α-Terpineol

Eucalyptol

$\Delta\bar{\nu}$ IN cm^{-1}
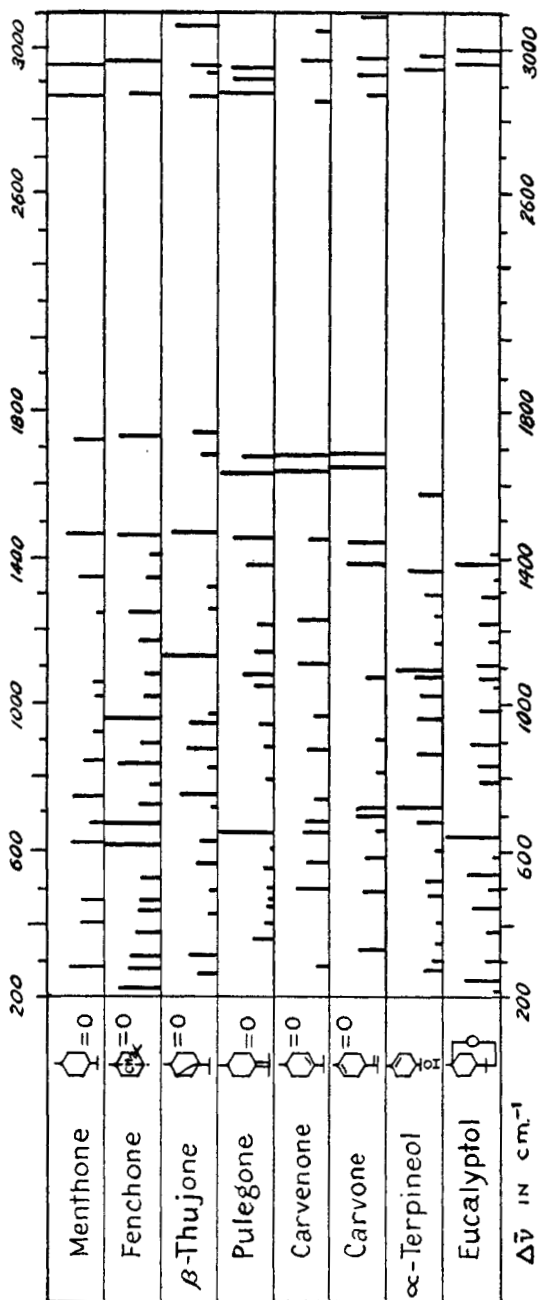
FIG. 25. The Raman spectra of some terpene derivatives (after Bonino and Cella)

On considering first the C—H shifts of these and other terpene compounds it is noticed that pulegone contains a $-C{=}C\Big\langle{\overset{CH_3}{\underset{CH_3}{}}}$ group but no $\Big\rangle C{=}CH_2$ group. The maximum frequency for the C—H line obtained is, therefore, $\Delta\bar\nu\ 2951$, which is in agreement with the precepts already enunciated. Carvenone possesses a ring —C=C— group which may give rise to $\Delta\bar\nu\ 3048$ (1) for C↔H (a type of shift which has not yet been observed in the substituted cycloölefins). This may also be present as $\Delta\bar\nu\ 3034$ (3) in d-pinene and as $\Delta\nu\ 3082$ (2) in limonene. Carvone having a $\Big\rangle C{=}CH_2$ group yields $\Delta\bar\nu\ 3085$ (3). From the behavior of pulegone, menthone, and fenchone it is clear the C=O cannot be responsible for any C—H frequency in excess of $\Delta\bar\nu\ 3000$, nor does a C_3 ring structure as in sabinane ($\Delta\bar\nu\ 2964$) or the C_4 ring in pinane ($\Delta\bar\nu\ 2924$) produce a frequency greater than $\Delta\bar\nu\ 3000$. Sabinene, however, having both C_3 rings and —C=CH₂, shows $\Delta\bar\nu\ 3043$ (3) and 3076 (3). β-Thujone, possessing no —C=C— and only a C_3 ring in addition to the C=O group, gives rise to $\Delta\bar\nu\ 3067$ (4), according to Bonino and Cella (86). By employing tables 10, 11, and 25 and the known shifts for the alkylcyclohexanones and cyclohexenes, it is now possible to analyze the spectra of these terpenes with particular reference to the C=C and C=O shifts, and consequently determine if the observations are in accord with their constitution. This is shown in table 26.

It is evident that there is a general agreement between the observed and expected frequencies. In determining the calculated frequencies the effects of conjugation or multiple double bonds and the type of substitution are included. In pulegone, for example, the C=C and C=O shifts were corrected for conjugation, and in carvone the two frequencies $\Delta\bar\nu\ 1638$ and 1670 were also corrected. However, the extranuclear double bond under the influence of multiple bonding should yield $\Delta\bar\nu\ 1600$ to 1610, which is not present. When it is remembered that this double bond is removed from the C=O by a distance of two carbon atoms, it is not unreasonable, in the light of the evidence so far presented, to assume that the effect of conjugation is negligible and consequently the external C=C should yield a normal shift corresponding to $R_1R_2C{=}CH_2$ ($\Delta\bar\nu\ 1650$). This is within the accuracy of these measurements and not distinguishable from the observed $\Delta\bar\nu\ 1646$. The same conditions were employed in calculating the shifts for the compounds given in figure 24. If one double bond were far removed from any other in the molecule, it was considered

to function as a separate unit and consequently yielded a shift the same as any other substituted ethylenic bond. If it were close to a $C=O$ group the conjugation was considered effective. In citronellal conjugation was ignored. Geranial should yield $\Delta\bar{\nu}$ 1640 (conjugate $C=C$) and $\Delta\bar{\nu}$ 1689 (conjugate $C=O$) and a shift of conjugate type $R_1R_2C=CHR_3$ ($\Delta\bar{\nu}$ 1678). The latter shift, however, falls so close to the observed frequency at $\Delta\bar{\nu}$ 1681 that its presence is indeterminate. In geraniol and linalool the conjugation is ignored for the reasons already given.

TABLE 26

The observed and calculated $C=C$ and $C=O$ shifts for some terpenes

COMPOUND	$\Delta\bar{\nu}$			
	Observed		Calculated	
	C=C	C=O	C=C	C=O
Pulegone......................	1617	1673	1600	1670
Carvenone....................	1632	1673	1638	1670
β-Thujone....................		1688(2)		1712
		1750(3)		
Menthone.....................		1714		1712
Fenchone.....................		1731		1712
Terpineol.....................	1675		1675	
Carvone......................	1646	1673	1638	1670
α-Pinene	1656		1675	
l-Limonene...................	1658		1650	
	1680		1675	
Sabinene......................	1650		1650	
Menthene.....................	1673		1675	
Geranial......................	1647	1681	1640	1689
			1678	
Citronellal...................	1675	1719	1650	1720
Citronellol...................	1675		1650	
Linalool......................	1672		1678	
	1646		1640	
Geraniol.....................	1675		1678	

The net result of this is that, with the exception of β-thujone, perhaps α-pinene, and the $C=C$ shift for citronellal and citronellol, the calculated results are in accord with the experimental observations. In view of the relative accuracy of measurements which are only accurate to within perhaps $\pm$ 5 wave numbers in comparison with other observers, this is a reasonably close agreement.

Citronellal and citronellol are generally considered as compounds of the type $R_1R_2C=CH_2$, so far as the first ethylenic shift is concerned. If,

however, this were of the type $RCH=CHR_1$ (*trans*), the observed and calculated results would be practically identical. In view of the indeterminate nature of the structure of this compound from an organic chemical point of view, there remains a possibility that this may be the explanation. On the other hand, α-pinene and fenchone have an internal bridge structure which joins close to the double bond, and this may have some effect on the characteristic ethylenic shifts and might account for the departure in this case. It has already been remarked that β-thujone, as reported by Bonino and Cella, has an anomalous C—H shift ($\Delta\bar{\nu}$ 3067 (4)) indicative of a C=C group which is presumably not present. The observed shifts $\Delta\bar{\nu}$ 1688 (2) and 1750 (3) cannot be reconciled with the calculated frequencies. If there were an impurity present containing an unsaturated ethylenic linkage, however, this might explain the $\Delta\bar{\nu}$ 1688 and 3067 shifts observed.

These conclusions are not in agreement with Bonino and Cella, who discuss a reversed C=C frequency for carvenone, carvone, pulegone, and geranial. The lower frequencies near $\Delta\bar{\nu}$ 1650 are ascribed to C=O instead of C=C, and the larger frequency shift ($\Delta\bar{\nu}$ 1675) to C=C instead of C=O. This does not seem as logical or as compatible with the observation on the terpenes and other compounds as the explanation which is given. These authors have calculated the H—H angle in the $-C=C\begin{smallmatrix}\;H\\\\\\\;H\end{smallmatrix}$ α groups in these compounds as ranging from 104° in sabinane to 141° in carvenone. The force and deformation constants for the C—H linkage and the characteristic low frequency shifts in the terpene derivatives were determined. Any of the frequencies between $\Delta\bar{\nu}$ 1045 and 1450 have been accounted for on the basis of combination or rotational frequencies.

The differences in the Raman spectra of simple monocyclic terpenes possessing internal and external double bonds, and terpenes without double bonds are indicated in figure 26, taken from the data of Dupont, Daure, Allard, and Levy (216). These and other terpenes have been investigated by Daure (198, 199), Dulou (208), Dupont, Daure, and Allard (212), Dupont, Daure, Allard, and Levy (213, 214, 215), Dupont, Daure and Levy (217), Dupont and Gachard (218), Dupont and Joffre (219), Dupont, Levy, and Marot (220), Dupont and Dulou (211), Tabuteau (585), and Venkateswaran and Bhagavantam (628). Terpene mixtures have been analyzed by Dupont, Daure, Allard, and Levy (216). Bonichon (66, 67), after investigating a large number of alcohol and ester derivatives of the terpenes, concluded that there are enough distinguishing lines to differentiate the esters of a given terpene from each other and to determine the
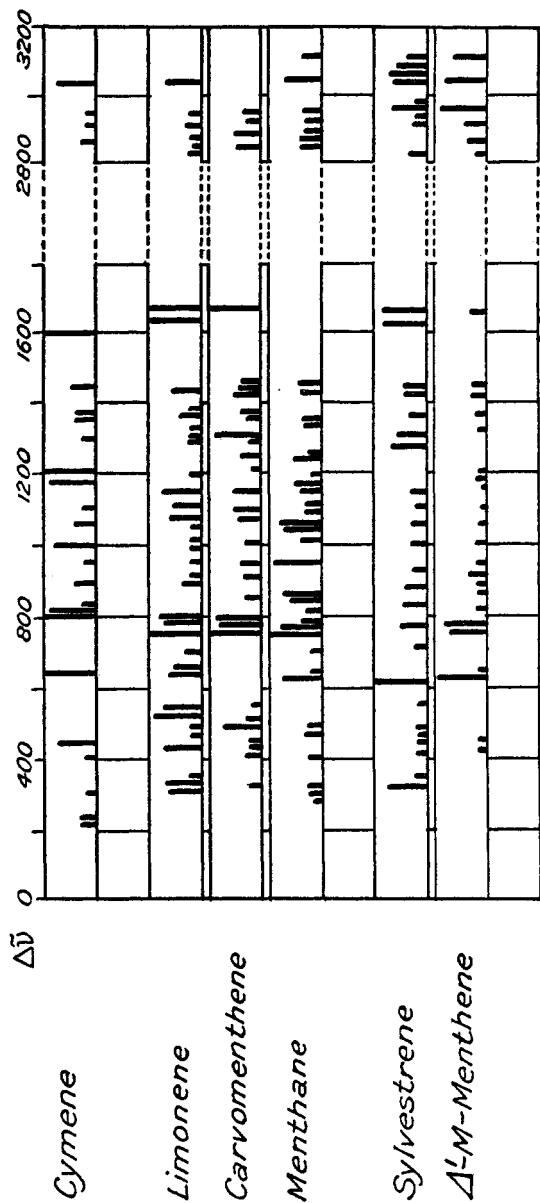
FIG. 26. The Raman spectra of some simple terpenes (after Dupont, Daure, Allard, and Levy)

composition of mixtures of such closely allied compounds as the spacial isomers borneol and isoborneol. Borneol shows the characteristic frequencies $\Delta\tilde{\nu}$ 600, 1230, 1300, and isoborneol $\Delta\tilde{\nu}$ 627, 857, and 1023. The structures of these two compounds are indicated as follows:

Borneol   Isoborneol
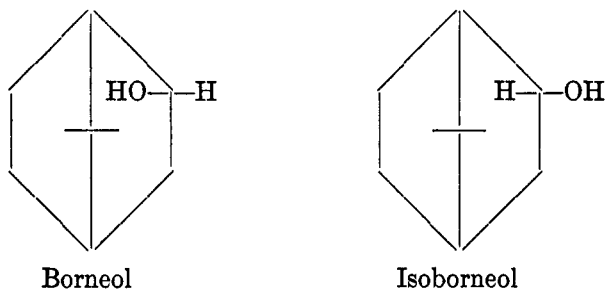
The analysis of the essence of terpenes, *Pinus longifolia*, by Raman spectra leads to the conclusion that there are present two forms of carene, namely, Δ^3-carene and β-carene (219). The distillation of oil of indienne likewise has been followed and shows the presence of pinene, β-pinene, and Δ^3-carene in successive distillates. Pinane and nopinane give identical Raman frequencies. Camphene yields $\Delta\tilde{\nu}$ 1672 for the double bond, which is practically identical with that observed from β-pinene. There are, however, other lines which enable this compound to be distinguished from the pinenes. Tabuteau (585) has fractionated the essence of citronel of Java, and has found pinene, β-pinene, and limonene and other terpenes in the distillate. Dupont and Gachard (218) have investigated a number of the camphenes and other terpenes and the composition of complex mixtures. In particular a change in constitution on hydrogenation has been shown. This combination chemical and Raman-spectra method has also been followed by Dupont, Levy, and Marot (220), who studied the dehydration products of the terpinenes and terpineol. The action of heat on some terpenes has been investigated by Dupont and Dulou (211). The pyrolysis produced a mixture of terpenes of a new type, given the name pyronenes. These show $\Delta\tilde{\nu}$ 1596 and 1657 for the double-bond linkage and to them are attributed the formulas:
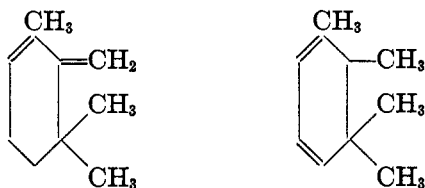
A detailed consideration of the terpenes could be continued indefinitely. This field of investigation is still somewhat in its infancy. It has been

given this much space since the problems presented are of the same type as would be met in any complicated investigation. It is believed that the Raman spectra method has already made a genuine contribution in the delineation of the structure of the terpenes and in the identification of their constituents.

Before leaving entirely the question of the determination of the constitutional arrangements by means of Raman spectra based on the internal and external ethylenic linkages in benzene and its derivatives, there may be cited some work of Hayashi (299, 301). He determined the spectra of the following compounds:

$$CH_3O\underset{}{\bigcirc}CH{=}CHCH_3$$
Anethole

$$CH_3O\underset{HO}{\bigcirc}CH{=}CHCH_3$$
Isoeugenol
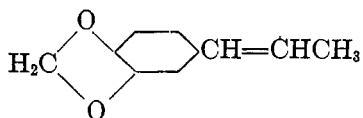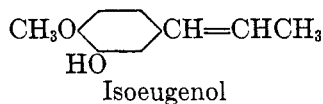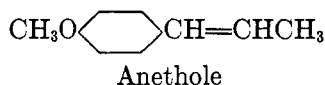
$$H_2C\overset{O}{\underset{O}{\diamond}}\bigcirc CH{=}CHCH_3$$
Isosafrole

The principal frequencies obtained for anethole are $\Delta\tilde{\nu}$ 1591 (9), 1644 (10); for isosafrole $\Delta\tilde{\nu}$ 1601 (6), 1641 (7); for isoeugenol $\Delta\tilde{\nu}$ 1604 (6), 1646 (7). The question here is whether there may exist geometric isomers of these compounds as found in nature. The frequency of the ethylenic linkage external to the ring is approximately 10 wave numbers lower than that observed for the cis-form of compounds of the type $R_1CH{=}CHR_2$ ($\Delta\tilde{\nu}$ 1658). Therefore, it was originally concluded that the cis-form of these compounds probably predominated, because the trans-form of the ordinary disubstituted ethylenic linkage yields $\Delta\tilde{\nu}$ 1673 (see table 9). On closer inspection, however, it was observed that the ether and hydroxy groups even in the para-position were not without their effect on the external ethylenic linkage. On comparing trans-isoallylbenzene $\Delta\tilde{\nu}$ 1663, styrene $\Delta\tilde{\nu}$ 1636, and p-methoxystyrene $\Delta\tilde{\nu}$ 1620, there is shown a progressive decrease in the external ethylenic linkage. The constitution of isosafrole, isoeugenol, and anethole, so far as the side chain is concerned, is more like isoallylbenzene. One would expect, therefore, a shift near $\Delta\tilde{\nu}$ 1663, but, as just shown, the influence of the methoxyl group is to lower the side chain frequency by approximately 15 wave numbers. This would diminish the expected $\Delta\tilde{\nu}$ 1663 to $\Delta\tilde{\nu}$ 1648, which is approximately the observed frequency. It is concluded, therefore, that these compounds exist ordinarily in the trans-form rather than the cis. It may be remarked that the influence of the methoxy group in the para-position is also notice-

able by contrasting $\Delta\bar{\nu}$ 1700 for the C=O frequency in benzaldehyde with $\Delta\bar{\nu}$ 1687 observed in anisaldehyde. The conclusions, therefore, are compatible with the evidence. While this seems a perfectly straightforward deduction, it is somewhat in conflict in principle with the tenets which have been given in regard to the lack of influence of one group upon another if it were removed by any distance in the molecule.

N. The Raman spectra of diphenyl and its derivatives

Diphenyl and its derivatives have been investigated principally by Bonino and Manzoni-Ansidei (89). These are considered more as an entity rather than with the benzene derivatives and the terpenes, because they are thus considered in organic chemistry. Diphenyl, of course, is simply a phenyl derivative of benzene from the standpoint of Raman spectra. The observed spectra are very close to the spectra of benzene and its derivatives and have not been discussed in detail. It can only be remarked that the C—H shift occurs at approximately $\Delta\bar{\nu}$ 3067 and the C=C shift at $\Delta\bar{\nu}$ 1597. It is to be expected that substitution of the methyl groups in the diphenyl ring produces increasing complexity of the Raman spectra as a function of the number of substitutions. Dadieu and Kohlrausch (163) and Wood (658, 659) have investigated diphenyl. The hydrocarbon and halogen derivatives are confined to the observations of Bonino and Manzoni-Ansidei (89). It is to be admitted that this is a somewhat cursory dismissal of the subject, but from the characteristic linkage point of view there is little to be added.

O. The Raman spectra of polycyclic compounds

The Raman spectra of the polycyclic compounds are very much an extrapolation of the observations on benzene and cyclohexane and their derivatives. While naphthalene has been investigated by a great many observers, its derivatives have been investigated primarily by Bonino (69), Bonino and Cella (81, 85), Gockel (258), Hayashi (299), Mukerji (457, 458), and Ziemecki (671). Mukerji has studied dekalin, which is the completely saturated naphthalene, and tetralin, which represents the saturation of one of the benzene rings but not the other. These spectra have been compared to those of naphthalene and cyclohexane. Bonino and Cella have likewise observed the spectra of these compounds. There is a marked similarity among the entire group with the exception of the $\Delta\bar{\nu}$ 3046, which exists in naphthalene and tetralin but not in dekalin. In tetralin there is also $\Delta\bar{\nu}$ 2940. $\Delta\bar{\nu}$ 1037 appears weakly in dekalin and naphthalene and strongly in cyclohexane. $\Delta\bar{\nu}$ 699 in these observations corresponds to $\Delta\bar{\nu}$ 695 in cyclohexane. Many of the other shifts have the same significance which has been previously mentioned. For example,

$\Delta\tilde{\nu}$ 1448 corresponds to the transverse oscillation of the hydrogen. $\Delta\tilde{\nu}$ 1602, according to Bonino and Cella (81), occurs primarily in the tetralin compound; $\Delta\tilde{\nu}$ 1583 in tetralin is absent in dekalin and is present as $\Delta\tilde{\nu}$ 1573 in naphthalene. There are other differences in these compounds in the very low frequency shifts. Naphthalene shows $\Delta\tilde{\nu}$ 3046 (1) and $\Delta\tilde{\nu}$ 1573
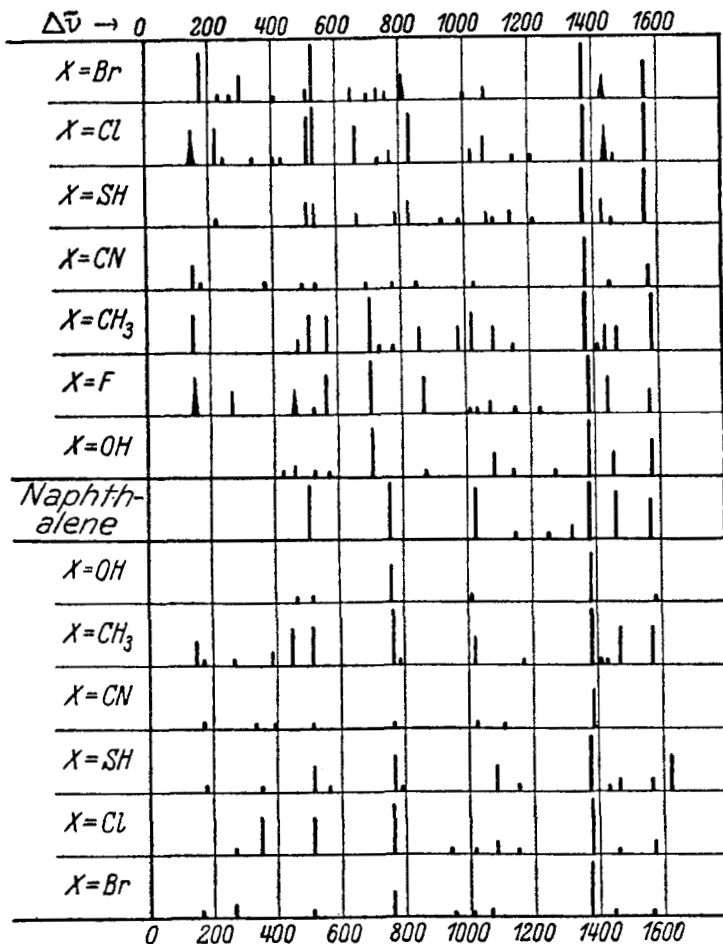
FIG. 27. The partial Raman spectra of naphthalene and its derivatives (after Gockel)

(3) for the C—H and C=C linkages. This is slightly lower than the C=C linkage in benzene. In α-bromonaphthalene this is reduced still further and becomes approximately $\Delta\tilde{\nu}$ 1550 (5). The most complete survey of the naphthalene derivatives has been made by Gockel (258). This author studied the derivatives in the α- and β- (or 1,2-) positions. There is some

modification in the spectra depending upon the ring position of the intro-
duced radical. There is a very profound modification in the spectra of
naphthalene on substitution. Many of the lines, however, such as
$\Delta \tilde{\nu}$ 515, 1012, 1146, 1385, and 1573, remain fairly constant. The influence
of substitution of different groups is shown in figure 27, which gives the
middle and low Raman spectra of the naphthalene derivatives as a func-
tion of substitution. The upper half of the figure represents the substitu-
tion in the α-position and the lower half in the β-position.

Kohlrausch (343) has discussed the formula of naphthalene as a con-
stitutional problem. Gross and Vuks (286, 287) have examined the very
low frequency shifts of naphthalene. Some of these occur as low as
$\Delta \tilde{\nu}$ 45, 73, and 109, and are accompanied by wings, which are not connected
with rotation as originally supposed, but with a slow oscillation character-
istic of the crystal lattice.

P. The Raman spectra of organic sulfur compounds

Quasi-organic sulfur compounds such as carbon disulfide and the in-
organic thiocyanates have been discussed by Hibben (311). The organic
thioethers and mercaptans have been investigated by Bonino, Manzoni-
Ansidei (90), Crigler (140), Dadieu, Pongratz, and Kohlrausch (186, 189),
Kohlrausch and Köppl (346), Kohlrausch and Pongratz (366), Matossi
and Aderhold (419), Meyer (437), Gopala Pai (268), Thatte and Ganesan
(591, 593), and Venkateswaran (620, 623, 625).

The experimental observations by different workers are not in as close
agreement as in other compounds. Nevertheless, it is quite apparent
that the chain and C—H vibrations of the organic molecule are not seri-
ously altered by the introduction of a sulfur atom. On the introduction
of sulfur, however, new lines appear which are generally strong. This is
the usual result when any heavy atom is introduced. There occur two
inner vibrations, one characteristic of the C↔S linkage and one of the
S↔H linkage. The latter appears near $\Delta \tilde{\nu}$ 2570, which is unique for a shift
in this region, and hence this linkage is easily identified. The increased
mass as represented by the sulfur would tend to reduce the S↔H frequency
in comparison to the C↔H one. The reduction would be greater as
calculated than is actually observed, consequently there must be a com-
parative increase in the force constant of the S—H binding. The strong-
est C↔S shift falls near $\Delta \tilde{\nu}$ 645, although this depends somewhat on the
amount of branching, where the force constant is slightly low after correct-
ing for the mass influence. In figure 28 are given the comparison spectra
of the mercaptans, taken from the summary of Kohlrausch (339) and based
on the work of various observers.

Venkateswaran (620) has indicated that the C—S shift in methyl mer-

captan [$\Delta\tilde{\nu}$ 704 (10)] decreases to $\Delta\tilde{\nu}$ 659 (10) in ethyl mercaptan and to approximately $\Delta\tilde{\nu}$ 652 in the higher homologs. In the branched chain compounds this shift becomes first a doublet, and subsequently the lower frequency component of the doublet decreases in the magnitude of its shift with increased branching. The shift at $\Delta\tilde{\nu}$ 700 to 770, which persists in weakened form, is also characteristic of this linkage.

The thioethers contribute to the knowledge of the C—S shift. The stronger and more significant shifts of some of the thioethers are given in table 27, based on the results of Venkateswaran (620, 623) and of Thatte and Ganesan (593). The intensities recorded are difficult to correlate, as they are apparently given by authors on a somewhat different scale.
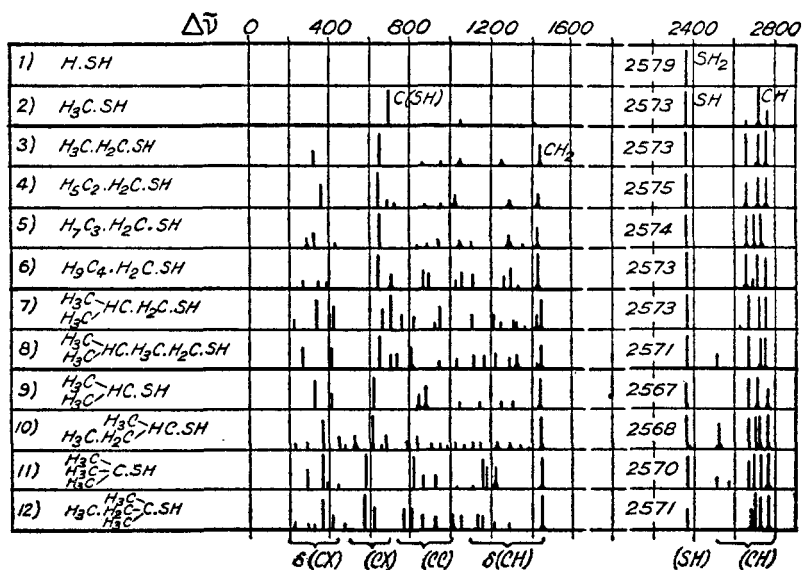
FIG. 28. Comparison spectra of some mercaptans (after Kohlrausch)

The shifts pertaining more definitely to the oscillations involving the sulfur atom are underlined. In dimethyl sulfide there is a tendency for the shifts to pair. A comparison of the scattered spectra obtained with that of diethyl ether shows that $\Delta\tilde{\nu}$ 441 and 845 in the ether corresponding to $\Delta\tilde{\nu}$ 648 and 696 in the thioether and $\Delta\tilde{\nu}$ 928 and 1027 occurring in the ethyl ether correspond to $\Delta\tilde{\nu}$ 972 and 1052 in the sulfur compound.

In dipropyl sulfide most of the lower frequency shifts are attributable to the influence of the sulfur and occur in pairs. This tendency is continued in most of the higher sulfides. The strongest characteristic shifts of allyl sulfide are $\Delta\tilde{\nu}$ 416, 590, and 748. $\Delta\tilde{\nu}$ 1206 and 1300, which are relatively weak in the other sulfides, are intensified in allyl sulfide. It

is not entirely clear in the thio acids just what shifts may be ascribed to the contribution of the sulfur. Presumably they are $\Delta\tilde{\nu}$ 638 and 818 in the two acids. From another point of view, however, these acids are very interesting. The carbonyl shift in thioglycolic acid is very weak and possibly a doublet $\Delta\tilde{\nu}$ 1553 and 1707. In thioacetic acid $\Delta\tilde{\nu}$ 1695 corre-

TABLE 27

The partial Raman spectra of the thioethers and thioacids

$\Delta\tilde{\nu}$

CH₃SCH₃	C₂H₅SC₂H₅	C₃H₇SC₃H₇	[(CH₃)₂CHCH₂]₂S	C₄H₉SC₄H₉	[CH₂=CHCH₂]₂S	CH₃COSH	CH₂◻COSH
		290(2)					
	318(1)	*378*(1)			*416*(3)		
					590(5)	459(3)	438(1)
691(6)	*648*(4)	*652*(2)		*655*(3)		*638*(5)	
	696(3)				*688*(1)		
743(2)		*730*(2)	731(2)	*753*(1)	*748*(8)		
			814(2)	794(1)	753(8)	841(2)	818(4)
				867(3)			
		895(1)		892(3)			
	972(2)		950(2)		918(2)		
	1052(1)	1033(2)		*1054*(3)		1007(2)	914(2)
				1102(3)	1206(4)		
	1245(1)			1298(3)	1300(6)		
1424(1)	1453(3)	1445(2)	1458(2)	1417(4)	1405(6)	1426(1)	*1409*(2)
				1454(6)	1430(4)		
							1563(10)
					1634(10)	1695(4)	
							1707(1)
	2870(3)	2858(2)	2875(5)	2873(5)	2914(8)		
2912(8)	2918(2)	2900(4)		2914(8)	2943(3)	2920(3)	
	2932(10)	2920(6)		2934(5)	2978(5)		
2984(4)	2977(4)	2965(6)	2962(3)	2960(5)			2950(1)
					3009(6)		
					3084(4)		

sponds to the carbonyl shift. There is, however, in neither case a shift which would correspond to a S—H linkage. In view of the prominence of this shift its omission is indicative of the absence of this bond. In general it may be assumed in agreement with Venkateswaran (623) that $\Delta\tilde{\nu}$ 691 and 746 are more or less characteristic of the sulfur to carbon link-

age. Other shifts such as $\Delta \tilde{\nu}$ 284, 1033, 1252, and 1335 which are variously ascribed to the linkage must be accepted with caution. While it is true that these make their appearance with increased complexity of the molecule, the appearance of any line with increased complexity is not a phenomenon solely confined to the thioethers. Most of these last-named shifts may be found as a first approximation in the hydrocarbons.

There is another type of organic sulfur compound which has been somewhat investigated and is of considerable interest. This is the class of the polysulfides. They have been investigated by Venkateswaran (623), Bonino and Manzoni-Ansidei (90), Gopala Pai (268), and Meyer (437). Results with some of the compounds investigated are in table 28. The polysulfides as well as the monosulfides show a strong frequency near $\Delta \tilde{\nu}$ 700. As noted in the case of sulfides with an increased complexity in the molecule there results an increased multiplicity of these sulfur frequencies. For example, in dimethyl disulfide appears $\Delta \tilde{\nu}$ 509; in diethyl disulfide this becomes $\Delta \tilde{\nu}$ 508 and 526. This appears as $\Delta \tilde{\nu}$ 513 in dimethyl trisulfide, but is completely absent in the ethyl derivatives. This is an anomalous behavior. There are frequencies in the polysulfides which are not far removed from those in sulfur. The $\Delta \tilde{\nu}$ 433 and 470 in sulfur appear as $\Delta \tilde{\nu}$ 446 and 489 in the trisulfide, and as $\Delta \tilde{\nu}$ 450 and 486 in the tetrasulfide. What significance may be attached to this is doubtful because the spectrum of sulfur is not determined in the form of S_2 or S_4. Presumably the shift for the S—S bond is near $\Delta \tilde{\nu}$ 500. This would give a calculated value of approximately $\Delta \tilde{\nu}$ 725 for a S=S linkage. This apparently is absent. Consequently it is presumed that the sulfur in the polysulfides is bound together by a single homopolar linkage.

The cyclic organic sulfur compounds which have been investigated are chiefly thiophene and its derivatives, 2-methylthiophene, 2,5-dibromothiophene, and 2,3,5-trichlorothiophene. Bonino and Manzoni-Ansidei (91) obtain $\Delta \tilde{\nu}$ 446 (1), 602 (3), 691 (1), 743 (2), 830 (7), 1030 (5), 1076 (5), 1356 (4), 1404 (6), 3081 (2), 3113 (4) for thiophene. Especially characteristic are $\Delta \tilde{\nu}$ 3113 and 3083 for the C↔H and $\Delta \tilde{\nu}$ 1404 to 1439. The frequencies occurring at $\Delta \nu$ 602 (3) and 743 (2) in thiophene become $\Delta \tilde{\nu}$ 661 (4) and 739 (3) in 2-methylthiophene and $\Delta \tilde{\nu}$ 654 (4) and 704 (1) in 2,5-dibromothiophene; they are reduced to a single frequency, $\Delta \tilde{\nu}$ 683, in the trichloro compound. The absence of a line corresponding to a classical C=C oscillation will be discussed later.

Q. The Raman spectra of nitrates, nitrites, and nitro compounds

The organic nitrates yield as principal frequencies of the NO_3 group $\Delta \tilde{\nu}$ 730, 1074, 1391, and 1659. The spectrum of concentrated nitric acid yields $\Delta \tilde{\nu}$ 607, 667, 916, 1292, 1665, and 1685, which spectrum radically alters with dilution.

The organic nitrogen oxide derivatives have been investigated by Dadieu, Jele, and Kohlrausch (151), Dadieu and Kohlrausch (170, 173), Ganesan and Venkateswaran (242), Milone (442), Médard (429, 430), Médard and Alquier (431), Petrikaln and Hochberg (498), Ganesan and Thatte (240, 241), and Thatte and Ganesan (592). These compounds are

TABLE 28

Raman spectra of the polysulfides

$\Delta\bar{\nu}$			
C₂H₅S | C₂H₅S	CH₃S\ >S CH₃S/	C₂H₅S\ >S C₂H₅S/	C₂H₅—S—S | C₂H₅—S—S
		157(3)	154(1)
	184(1)		
197(3)		203(3)	202(1)
	240(1)		
	282(1)		
332(2)			
372(2)		371(1)	
	446(2)	439(2)	450(0)
	489(3)	487(4)	486(6)
508	513(3)		491(1)
526			
644(5)		644(4)	644(3)
672(5)	700(5)	670(3)	665(1)
759(1)			
974(4)	958(1)	970(2)	965(½)
1026(1)			
1055(3)		1050(2)	
	1152(1)		
	1225(0)	1199(1)	
1255(1)		1266(1)	1254(½)
1353(2)	1312(0)		
1421(2)	1435(3)	1418(2)	1417(2)
1456(3)		1456(2)	1448(2)
2870(2)		1578(1)	2876(1)
2924(4)			2913(3)
			2931(4)
2971(4)	2985(2)	2970(0)	2969(2)
	3044(2)		

characterized by the relative intensity of their identifying shifts. The frequencies characteristic of the NO_3, or more correctly the $O—NO_2$ group, on the average are $\Delta\bar{\nu}$ 575, 868, 1290, and 1640. These may vary somewhat from compound to compound but are easily recognizable from their intensities. In table 29 are given all except the weakest lines for

ten organic nitrates, taken from the work of Médard (429) and of Médard and Alquier (431). It is presumed by Médard that the frequencies at $\Delta\tilde{\nu}$ 1307 and 1455 pertain to the CH_2 and CH_3 groups, respectively, and those between $\Delta\tilde{\nu}$ 2700 and 3047 to the C—H oscillation. Many of the frequencies observed are common to those obtained from the aliphatic alcohols and hydrocarbons. On the other hand, there are some peculiarities. The shift near $\Delta\tilde{\nu}$ 1450 appears as a doublet beginning with amyl

TABLE 29

Raman spectra of some alkyl nitrates

$\Delta\tilde{\nu}$									
CH_3NO_3	$C_2H_5NO_3$	$C_3H_7NO_3$	$C_4H_9NO_3$	$C_5H_{11}NO_3$	$C_6H_{13}NO_3$	$C_7H_{15}NO_3$	$C_9H_{19}NO_3$	$C_{10}H_{21}NO_3$	$C_{12}H_{25}NO_3$
365(5)	385(5)	352(5)							
582(7)	570(5)	571(5)	569(5)	574(5)	573(5)	570(5)	570(5)	570(5)	568(5)
		611(1)		616(5)	615(5)				
669(5)	657(1)		702(5)	706(5)					
864(7)	864(5)	866(5)	848(5)	869(7)	869(7)	864(7)	864(8)	862(8)	861(8)
			880(5)						
							1080(5)	1080(5)	1078(5)
1290(10)	1285(7)	1282(7)	1281(7)	1285(7)	1283(1)	1284(5)	1280(5)	1279(5)	1279(5)
				1315(5)	1313(5)		1307(5)	1308(5)	1307(5)
				1392(5)		1388(5)			
1437(5)					1439(8)		1440(5)	1441(5)	1440(5)
1460(5)	1455(5)	1454(5)		1450(5)		1455(5)	1463(5)	1464(1)	1464(1)
				1473(5)	1476(8)				
				1531(1)		1568(5)			
1644(8)	1633(5)	1635(5)	1632(5)	1640(8)	1640(8)	1632(5)	1635(5)	1635(5)	1633(5)
	2725(1)	2739(1)	2744(1)	2741(1)	2744(1)	2730(1)			
2839(1)	2890(1)	2888(1)	2881(1)	2881(1)	2878(1)	2852(1)	2885(5)	2885(5)	2857(5)
						2899(5)	2899(8)	2897(8)	2895(5)
2910(5)			2917(5)	2920(7)	2916(5)				
2968(7)	2948(7)	2945(7)	2941(7)	2949(7)	2943(7)	2936(7)	2936(5)	2933(5)	2936(5)
	2991(7)	2985(5)	2976(5)	2980(5)	2973(5)	2968(5)	2967(5)	2963(5)	2963(5)
3047(5)									

nitrate, becomes a single line in heptyl nitrate, and appears again as a doublet in the remainder of the series. The shift at $\Delta\tilde{\nu}$ 1080 (5) appears only in nonyl, decyl, and dodecyl nitrates with any intensity. It is present but faint in lower homologs. The shift at $\Delta\tilde{\nu}$ 1640 may be indicative of the N=O binding as the ethylenic shift is indicative of the C=C binding. Although the two lower frequencies in concentrated nitric acid are somewhat displaced, there is a general correspondence between the frequencies

observed in this compound and those obtained from the organic $O-NO_2$ group. This is in contradistinction to the complete lack of agreement between the $R-NO_3$ frequencies and those observed in the alkali nitrates. Consequently there is a reasonable presumption that concentrated nitric acid has the ester structure $HO-NO_2$ in lieu of the structure HNO_3. On dilution, however, the HNO_3 frequencies are so modified that there is

TABLE 30

Partial Raman spectra of some aliphatic nitrites and nitro compounds

			$\Delta\tilde{\nu}$			
CH_3NO_2	$CH(NO_2)_3$	$C(NO_2)_4$	$C_2H_5NO_2$	$C_5H_{11}NO_2$	CH_3ONO	C_4H_9ONO
		193 (5)				
	200 (5)	227 (5)	295 (3)	255 (2)		
	374 (7)	355 (10)	389 (2)	349 (1)	364 (2)	
483 (5)	410 (8)	410 (5)	492 (5)			
					580 (4)	
657 (8)			614 (4)	603 (2)	610 (2)	605 (3)
				769 (3)		796 (2)
	837 (5)	857 (7)	875 (8)		833 (3)	833 (3)
918 (10)	942 (8)	998 (5)	995 (3)	904 (5)		
			1101 (4)	1128 (3)		1123 (2)
	1249⎱ 1307⎰ (8)	1270 (7)				
	1309⎱ 1366⎰ (10)	1342 (5)	1367 (7)	1342 (2)		
1376 (7)	1371 (7)		1394 (5)	1379 (5)		
1402 (7)			1447 (4)	1455 (4)	1431 (2)	1438 (6)
1560 (5)			1556 (4)	1551 (3)		
	1613 (7)	1610 (8)			1603 (3)	
		1646 (8)			1648 (8)	1640 (5)
				2873 (3)		
						2915 (5)
2968 (7)			2950 (7)	2965 (4)		2937 (3)
			2998 (3)			
3057 (1)						

unquestionably a conversion to the nitrate ion identical with the alkali nitrates.

There are two other nitrogen oxide derivatives of organic compounds. These are the nitro compounds with a group $R-NO_2$ and the nitrites with the group $O-NO$. Nitromethane, CH_3NO_2 (430), yields $\Delta\tilde{\nu}$ 483 (5), 610 (1), 657 (8), 918 (10), 1109 (1), 1376 (7), 1402 (7), 1560 (5), 2968 (7), 3057 (1), and methyl nitrite, CH_3ONO (151), $\Delta\tilde{\nu}$ 364 (2), 580 (4), 610 (2), 833 (3), 977 (0), 1431 (2), 1603 (3), 1648 (3), and 2944 (4).

In table 30 are given the Raman spectra of some of the substituted nitromethanes and nitrites. Apparently the characteristic frequencies of the nitro group are approximately $\Delta\bar\nu$ 420, 1340, and 1607. In the higher homologs of the nitrites the doublet appearing between $\Delta\bar\nu$ 1600 to 1650 in the methyl nitrite reduces to a single frequency at $\Delta\nu$ 1640. Consequently the nitrates and nitrites have the common frequency $\Delta\bar\nu$ 1640, which is displaced to $\Delta\bar\nu$ 1590 in the nitro compounds. The nitro group possesses $\Delta\bar\nu$ 1376, which is 1290 in the nitrates and non-existent in the nitrites. By these strong lines alone these compounds can be easily identified. The inorganic nitrites possess $\Delta\bar\nu$ 696, 785, 1303 to 1330. No $\Delta\bar\nu$ 1600 was observed. It is to be remarked that the inorganic nitrites have been little investigated, and there is little correlation between these organic and inorganic observations. This would possibly indicate a true NO_2 group in this case rather than an $O—N{=}O$ group. Médard considers the C—N linkage as varying from $\Delta\bar\nu$ 910 to 850 in the nitro compounds. It is believed by Médard that the structures of the nitromethanes are
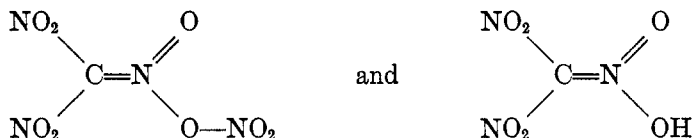
rather than
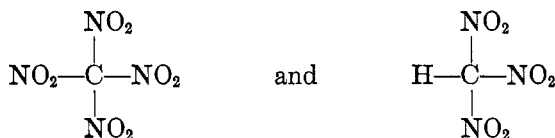
Chloropicrin and bromopicrin, observed by Milone (442), yield among other lines $\Delta\bar\nu$ 420, 1333, and 1578 as constant frequencies. It is possible that the $\Delta\bar\nu$ 1575 to 1650 frequency is attributable to the C=N linkage rather than to the N=O. This will be discussed under the oximes. In N_2O the shifts are $\Delta\bar\nu$ 1284 and 2224, indicating a triple bond (N≡N) group and possibly an N=O group, although the N=O shift in NO is $\Delta\bar\nu$ 1877.

The cyclic nitro derivatives yield a strong line at $\Delta\bar\nu$ 1340 and $\Delta\bar\nu$ 1520 to 1590.

R. The Raman spectra of the oximes

It is quite apparent from the preceding discussion that the linkage between nitrogen and carbon in the form of N—C or the linkage between

nitrogen and oxygen as N=O is of the same order of magnitude, at least, as the equivalent linkages between carbon and carbon, and carbon and oxygen. The problem of the N=C linkage becomes a necessity in the discussion of the oximes. Bonino and Manzoni-Ansidei (87, 88) have studied the oximes, and according to these authorities the following formulas have been proposed to represent their structure:

$$
\begin{array}{ccccc}
\text{R—C—R'} & \text{R—C—R'} & \text{R—C—R'} & \text{R—CH—R'} & \text{R—C—R'} \\
\| & \| & \diagdown \text{O} & | & \| \\
\text{N—OH} & \text{H—N=O} & \text{H—N} \diagup & \text{N=O} & \text{Na—N}\rightarrow\text{O} \\
1 & 2 & 3 & 4 & 5
\end{array}
$$
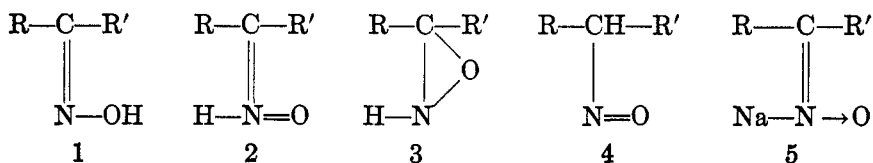
While not entirely clarifying the problem of this structure, the Raman spectra throw some light on the subject and eliminate beyond question as possibilities some of the formulas given above.

The frequencies observed for some of the oximes studied are given in table 31. First of all, there are no frequency shifts near $\Delta\bar{\nu}$ 1300 or 1370 observed in the nitrates and nitro compounds. There is, however, the strong and constant frequency in the aliphatic ketoximes at $\Delta\bar{\nu}$ 1655 to 1665. This is appreciably higher than the corresponding frequency in the nitrates, which occurs at $\Delta\bar{\nu}$ 1635. It is natural to suppose that the C=N frequency would occur somewhere within this region. From an analogy with the ethylenic double bond one would expect that it would be a frequency less than that observed for N=O. In spite of this it would seem from the total evidence that the double-bond frequency occurring in the ketoximes corresponds to the C=N linkage. This is further substantiated by the non-concordance of the double-bond shift with any of the nitrogen oxides. On the other hand, the N=O shift as determined from the nitrogen oxides is never with a single oxygen but always with at least two oxygen atoms. Consequently the —N=O determined in this way may be somewhat lower than its ordinary position. Other evidence in favor of attributing the linkage in the oximes to a C=N rather than to a C=O is obtained from the Raman spectrum of benzalaniline, which yields $\Delta\bar{\nu}$ 1630, a shift practically identical with that observed in α-benzaldoxime. This would eliminate as possible formulas 2, 3, and 4 given above. Formula 2 is also discarded on the ground that the effect of a linkage of the type =N= presumably would result in a strong modification of the double-bond shift as observed in the allenes, which have been discussed, and in the isocyanates, which will be treated later. A summary of the frequencies observed for C=N is given in table 32.

In the phenyl derivatives of the oximes the C=C shift remains practically constant and the C=N shift is relatively constant for each class of

compound. The aliphatic ones yield the shift near $\Delta\tilde{\nu}$ 1655 and the aromatic near $\Delta\tilde{\nu}$ 1625. However, the sodium salts of the aromatic oximes have a frequency shift which is nearly 70 wave numbers less than for the corresponding normal oximes, occurring at approximately $\Delta\tilde{\nu}$ 1545. This reduction is of the same order of magnitude as that occurring in the $N=O$ shift of the nitro compounds, as compared with the same shift in the nitrites and nitrates. Bonino and Manzoni-Ansidei consider this attrib-

TABLE 31

Raman spectra of some oximes

$\Delta\tilde{\nu}$				
Methyl ethyl ketoxime	Methyl propyl ketoxime	Methyl heptyl ketoxime	α-Benzaldoxime	Na benzaldoxime
			308(2)	
351(3)				
	377(2)	368(2)	371(2)	
411(3)				
			452(1)	473(3)
525(3)	531(3)	578(2)	511(1)	518(3)
			618(3)	
606(5)	600(3)	648(2)		
			746(1)	
			788(1)	
802(5)	814(4)	818(4)		
928(3)	901(1)	880(3)	858(2)	
993(4)	953(1)	947(4)	996(5)	996(4)
1082(4)	1078(2)	1003(4)	1020(2)	
		1188(4)	1180(3)	1176(3)
			1207(5)	1205(4)
1261(3)		1295(5)	1285(2)	
1426(5)	1441(5)	1430(5)	1433(2)	1440(2)
			1603(5)	1547(5)
1663(5)	1658(5)	1655(5)	1628(5)	1589(5)
	2858(3)	2862(3)		
2913(3)				
2948(3)	2931(3)	2928(4)		
			3052(3)	3046(3)

utable to the perturbation caused by the establishment of a semi-polar bond in both of these compounds as postulated by Sugden (581) and Sidgwick (558) and as represented by formula 5. The general problem of shared electrons and semi-polar valencies has been discussed by Noyes (477, 478). There are other lines which occur in these compounds besides the double-bond shift. The one at $\Delta\tilde{\nu}$ 1440 was originally supposed to be connected with the nitrogen double bond (83). Regardless of the

fact that this occurs in the aromatic compounds it is more likely that this is connected with the CH_2 group. It is probable that the generally accepted formula to depict the structure of the oximes is the correct one.

S. The Raman spectra of cyano compounds and their derivatives

This class of compounds is of particular interest because it illustrates the triple linkage between carbon and nitrogen. It will be recalled that the monosubstituted acetylenes gave $\Delta\bar{\nu}$ 2120 and the disubstituted acetylenes $\Delta\bar{\nu}$ 2235 and 2305 for the $C\equiv C$ linkage. The simplest cyanide is HCN. According to Bhagavantam (44) the shifts obtained are $\Delta\bar{\nu}$ 2076, 2097, and 2122, of which the middle shift is the strongest. Dadieu (145, 148) obtained $\Delta\bar{\nu}$ 2094 and 2062. The 2062 shift was attributed to the isomer HNC. Other organic and inorganic nitriles have been investigated

TABLE 32

Characteristic C=N shifts

COMPOUND	$\Delta\bar{\nu}$	
	C=N	C=C
Methyl ethyl ketoxime	1663	
Methyl propyl ketoxime	1658	
Methyl butyl ketoxime	1655	
Camphor O-methyloxime	1651	
α-Benzaldoxime	1628	1603
Sodium α-benzaldoxime	1547	1589
Acetophenone oxime	1623	1595
Sodium acetophenone oxime	1548	1586
Sodium o-chlorobenzaldoxime	1541	1583

by Dadieu (145, 148), Dadieu and Kohlrausch (163, 165, 166, 167, 169, 172), Cheng (125), Kastler (330), Lechner (400), Venkateswaran (625), Kopper and Pongratz (371), Hemptinne and Wouters (306), Pal and Sen Gupta (485), Petrikaln and Hochberg (500, 501), and Howlett (320). Beginning with acetonitrile and ending with isocapronitrile there is complete agreement between observers that the characteristic shift of these compounds for this linkage is $\Delta\bar{\nu}$ 2245 (6) as an average. This is not far removed from the frequency observed in the acetylenes for the triple-bond linkage. This is further evidence of a rough correspondence of the strength of the normal bond between carbon and carbon, and carbon and nitrogen. One of the earliest demonstrations of the utility of the Raman spectra method in determining the structure of organic compounds was its application to the isonitriles. The derivatives investigated were the methyl and ethyl isonitriles. For these compounds Dadieu obtained

$\Delta\bar{\nu}$ 2161 (5) and 2146 (7), respectively. This shows clearly that there exists a triple bond between the carbon and nitrogen in the nitriles and isonitriles. In the case of the latter, however, the frequency is reduced by roughly 100 wave numbers. This is approximately the magnitude of shift alteration in going from dimethylacetylene to methylacetylene. Consequently this behavior is by no means anomalous. The only wide departures from these two characteristic shifts are in cyanogen (501), which yields $\Delta\bar{\nu}$ 2335, and the inorganic cyanides, which yield $\Delta\bar{\nu}$ 2080 comparable with the shift observed in hydrogen cyanide. As Dadieu and Kohlrausch (175) have pointed out, however, this lower shift is confined to those compounds which are dissociated readily. In the complex cyanides, such as potassium ferrocyanide, and in mercury cyanide, the shift appears near $\Delta\bar{\nu}$ 2150. The inorganic cyanides have been treated in detail by Hibben (311).

Cheng (125) has studied the chlorine derivatives of acetonitrile. In going from chloroacetonitrile to trichloroacetonitrile the frequency remains unchanged. The substitution of a phenyl group, however, will reduce the average $\Delta\bar{\nu}$ 2250 shift by 25 wave numbers, so that in benzonitrile and tolunitrile or dimethylbenzonitrile the shift remains $\Delta\bar{\nu}$ 2225. Cheng believes there is a shift characteristic of the C—CN group which occurs between $\Delta\bar{\nu}$ 150 and 187 in all these compounds.

Hemptinne and Wouters (306) have investigated the nitrile derivatives of the unsaturateds and obtained $\Delta\bar{\nu}$ 2235 to 2255. The ethylenic shift in vinylnitrile is $\Delta\bar{\nu}$ 1629, in crotononitrile $\Delta\bar{\nu}$ 1645, and in isocrotononitrile $\Delta\bar{\nu}$ 1627.

1. Thiocyanates and isothiocyanates. Aside from a differentiation in the structure of nitriles and isonitriles it has also been possible to investigate the thiocyanates and isothiocyanates. Dadieu, for example, observed $\Delta\bar{\nu}$ 2145 (6) in methyl thiocyanate, and $\Delta\bar{\nu}$ 2152 (7) in ethyl thiocyanate. In the ethyl isothiocyanate was observed $\Delta\bar{\nu}$ 2106 (3) and 2182 (2), in isobutyl isothiocyanate $\Delta\bar{\nu}$ 2100 (3) and $\Delta\bar{\nu}$ 2172 (3), and in phenyl isothiocyanate, $\Delta\bar{\nu}$ 2100 (3) and 2172 (3). The constitution of the isothiocyanates was formerly indicated by —N=C=S. It has been suggested

$$(175) \text{ that this constitution should be } -\text{N}\underset{\diagdown}{\overset{\diagup}{\underset{\text{S}}{\overset{\text{C}}{\big|}}}}\text{, or } (87) \text{ R}-\overset{+}{\text{N}}\!\equiv\!\text{C}\!-\!\text{S}. \text{ In}$$

comparing the two isomers, C_2H_5SCN and C_2H_5NCS, both show strong shifts near $\Delta\bar{\nu}$ 630 and $\Delta\bar{\nu}$ 942. There is no shift in the region corresponding to the linear vibration of the ethyl group against the SCN or NCS radical which is markedly different in the two isomers. The isothiocyanate compound shows $\Delta\bar{\nu}$ 1069 (6) and 1340 (3) not present in the ethyl

thiocyanate. On comparing acetonitrile with methyl isonitrile, little difference appears in the spectra other than that attributable to the $C\!\!=\!\!N$ linkage.

It will be recalled that the C—S shifts in the mercaptans and thioethers occurred near $\Delta\tilde{\nu}\,650$ and 733. All inorganic thiocyanates exhibit a frequency at approximately $\Delta\tilde{\nu}\,745$. This is reflected in both the RNCS and RSCN compounds by a strong shift varying from $\Delta\tilde{\nu}\,626$ to 690.

2. Isocyanates. The isocyanates have been considered to have the structure $R\!\!-\!\!N\!\!=\!\!C\!\!=\!\!O$. This structure has an air of familiarity and is more than reminiscent of the allenes $(R\!\!-\!\!C\!\!=\!\!C\!\!=\!\!R)$. The allenes show no $C\!\!=\!\!C$ shift at $\Delta\tilde{\nu}\,1640$ but show a strong displacement at $\Delta\tilde{\nu}\,1100$. The isocyanates (145, 371) exhibit no shift at $\Delta\tilde{\nu}\,1650$ for $C\!\!=\!\!N$ or $C\!\!=\!\!O$, but have a medium strong shift at $\Delta\tilde{\nu}\,1409$ (5) and 1434 (5) in the methyl and ethyl cyanates respectively; $\Delta\tilde{\nu}\,1421$ (4) in isopropyl isocyanate, $\Delta\tilde{\nu}\,1440$ (5) and 1510 (4) for phenyl isocyanate, and $\Delta\tilde{\nu}\,1438$ (5) and 1513 (4) for α-naphthyl isocyanate. This is excluding the $\Delta\tilde{\nu}\,1450$ shifts attributable to C—H, which also occur in the aliphatic compounds, and the $C\!\!=\!\!C$ shift at $\Delta\tilde{\nu}\,1590$, which is present in the aromatic compound. The perturbating effect of adjacent double bonds seems to reduce seriously the frequency of the $C\!\!=\!\!N$ and $C\!\!=\!\!O$ linkages. As the mass factor is not greatly different from that in the allenes this reduction must be concomitant with the change in force.

3. Summary. Thus far it has been observed that all the carbon–nitrogen and nitrogen–oxygen compounds have distinct shifts. The $N\!\!=\!\!O$ inner vibration appears at $\Delta\tilde{\nu}\,1565$ in the $R\!\!-\!\!NO_2$ compounds, $\Delta\tilde{\nu}\,1640$ in the $R\!\!-\!\!O\!\!-\!\!NO_2$ compounds, and $\Delta\tilde{\nu}\,1640$ in the $R\!\!-\!\!O\!\!-\!\!NO$ compounds. From the oximes it is deduced that the $C\!\!=\!\!N$ inner vibration is $\Delta\tilde{\nu}\,1650$ and from the nitriles the $C\!\!=\!\!N$ vibration is $\Delta\tilde{\nu}\,2150$. This is subject to some variation dependent on the adjacent groups. There is no possibility of a quadruple bond in the isonitriles. The $C\!\!=\!\!N\!\!=\!\!O$ type of linkage yields $\Delta\tilde{\nu}\,1440$ (5) as a modified frequency. The C—S linkage in the thiocyanogens occurs near $\Delta\tilde{\nu}\,626$ to 690. The $N\!\!\equiv\!\!CS$ and $SC\!\!\equiv\!\!N$ inner vibrations for the carbon–nitrogen groups are $\Delta\tilde{\nu}\,2100$ and 2175 for the first of these last two types of linkage, and $\Delta\tilde{\nu}\,2150$ for the second. Up to this point the C—N linkage can only be estimated from the isonitriles, isothiocyanates, or nitro compounds. Although this is a somewhat precarious approach in the case of the C—N linkage, $\Delta\tilde{\nu}\,910$ to 930 would seem a possible estimate. This is only slightly higher than the C—C inner vibration. Bonino and Cella (83) consider the C—N vibration to be $\Delta\tilde{\nu}\,1042$. An examination of the amines may shed some light on this question.

Just as the C≡C oscillation may occur at $\Delta\tilde{\nu}$ 1500 under special circumstances (cyclopentadiene), so may the C≡N shift appear at a frequency much lower than its normal amount. This will be discussed later under heterocyclic compounds.

T. The Raman spectra of amines, amides, and imido compounds

1. Amines. The amines have the general formula RNH_2, the amides $RCONH_2$, and the imido compounds

$$R-C\overset{\displaystyle O}{\underset{\displaystyle |}{\diagdown}}$$
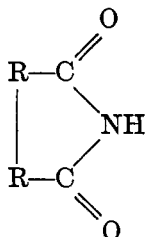
and are all represented in Raman spectra.

There are two inorganic compounds which will help to define the N—H linkage. These are NH_3 and NH_2—NH_2. Ammonia yields $\Delta\tilde{\nu}$ 3210 (3), 3310 (5), 3380 (3), hydrazine yields $\Delta\tilde{\nu}$ 904 (1), 1112 (1), 3212 (2), 3272 (2), 3340 (2), and phenylhydrazine yields $\Delta\tilde{\nu}$ 3366 (2) for its characteristic linkage, from the observations of Pal and Sen Gupta (485), Sutherland (582), and Imanishi (326).

As to methylamine there is some discrepancy between observers. Venkateswaran and Bhagavantam (626) observe $\Delta\tilde{\nu}$ 1033 (2), 2870 (2), 2955 (2), 3301 (2) in the liquid, and Dadieu and Kohlrausch (168) $\Delta\tilde{\nu}$ 1038 (4), 1470 (3), 2901 (4), 2965 (5), 3319 (5), and 3378 (3) in solution. In the higher homologs the N—H shift remains near $\Delta\tilde{\nu}$ 3320 and 3375. Both shifts are reduced somewhat in ethylenediamine. The disubstituted amines (173) R_2NH yield only one frequency near $\Delta\tilde{\nu}$ 3320.

So far as a C—N frequency is concerned this occurs at $\Delta\tilde{\nu}$ 1038 in methylamine. But, as has been shown in the alcohols and hydrocarbons, the group oscillation in the first member of a series gradually diminishes. In ethylamine this becomes $\Delta\tilde{\nu}$ 880 and in propylamine $\Delta\tilde{\nu}$ 868. The cyclic hydrocarbons may have an increased C—H frequency, namely, $\Delta\tilde{\nu}$ 3360 (3) and 3420 (2) in aniline (176). This augmentation is because of the adjacent phenyl group. This is shown by the fact that in benzylamine the frequency has returned to normal. Benzalaniline gives $\Delta\tilde{\nu}$ 1637 for the C≡N but no recorded shift for N—H. Practically all the substituted benzenes exhibit a frequency near $\Delta\tilde{\nu}$ 1030, so that the presence of this shift is not to be correlated necessarily with the nitrogen influence even

though it is present in the aniline derivatives. Ganesan and Thatte (239) observe that all the benzene lines appear in aniline. In xylidine no line appears near $\Delta\tilde{\nu}$ 3432.

2. Amides. Formamide according to Thatte and Joglekar (594) yields $\Delta\tilde{\nu}$ 394 (1), 605 (1), 726 (2), 1109 (1), 1306 (1), 1382 (2), 1675 (1), 3340 (1), and acetamide $\Delta\tilde{\nu}$ 377 (1), 571 (1), 870 (3), 1400 (1), 1608 (1), 2940 (2), and 3375 (1). These observations were made on the liquid compounds. They are not in too great agreement with Dadieu and Kohlrausch (162, 176) and Kohlrausch and Pongratz (366), taken, however, under different conditions. In the higher homologs of formamide have been observed (366) two carbonyl frequencies, $\Delta\tilde{\nu}$ 1606 (2) and 1664 (3). The frequency corresponding to the aliphatic carbonyl shift ($\Delta\tilde{\nu}$ 1710) is appreciably lowered by the NH group. From the benzamide (594) appear $\Delta\tilde{\nu}$ 1702 (1) for C=O, and $\Delta\tilde{\nu}$ 3360 for the N—H. Comparing this to benzophenone ($\Delta\tilde{\nu}$ 1651 (4)) shows a notable increase in frequency in the amide and a decrease in intensity. Acetanilide yields only $\Delta\tilde{\nu}$ 1600 (10). The reason for the diminution in the frequency is not entirely clear.

3. Imides. Succinimide has been found (369) to give $\Delta\tilde{\nu}$ 1760 (4), 3332 (1) for the C=O and N—H frequencies, while potassium phthalimide yields $\Delta\tilde{\nu}$ 1575 (2), 1599 (3), and $\Delta\tilde{\nu}$ 1602 ($\frac{1}{2}$). Their allocation is indeterminate.

4. Other compounds. The compound dicyanodiamide (176)

$$H_2N-\underset{\underset{NH}{\|}}{C}-\underset{\underset{H}{\diagdown}}{N}-C\equiv N$$
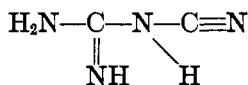
gives $\Delta\tilde{\nu}$ 655 (1), 927 (2), 1648 (1), 2156 (3), 2195 (3), which aids in establishing the C=N frequency.

Methyl nitramine, $C_2H_5-\underset{\underset{CH_3}{|}}{N}-NO_2$, yields among other shifts $\Delta\tilde{\nu}$ 1563 (2) and $\Delta\tilde{\nu}$ 1388 (1) of possible significance.

Urea, H_2NCONH_2, according to Pal and Sen Gupta (485), shows $\Delta\tilde{\nu}$ 830, 1002, 1162, 3226, and 3374; Kohlrausch and Pongratz (366) obtained $\Delta\tilde{\nu}$ 525 (2), 585 (1), 1000 (8), 1157 (1), 1593 (2), 1655 (0), 3218 (1), 3383 (3), and 3462 (2). Liquid urea was observed by Thatte and Joglekar (594) to have $\Delta\tilde{\nu}$ 1008 (2), 1180 (1), 3230 (1), and $\Delta\tilde{\nu}$ 3374 (1).

There is doubt concerning any frequencies assignable to C=O in this compound, but the C—N frequency would seem to be in the neighborhood of $\Delta\tilde{\nu}$ 1000. Its structure as written above seems inconsistent with the observations.

U. The Raman spectra of some heterocyclic compounds

1. Furans. The first of the heterocyclic compounds to be considered will be the five-membered rings with oxygen as the odd atom. In this series furan has been the most investigated. This has been studied by Bonino (69, 70), Bonino and Manzoni-Ansidei (91), Glockler and Wiener (257), Médard (426), and Prévost, Donzelot, and Balla (517). It will be remembered that cyclopentadiene gave $\Delta\bar{\nu}$ 1500 (5) in contrast to $\Delta\bar{\nu}$ 1615 (7) for cyclopentene. Since furan is structurally somewhat similar to cyclopentadiene, it is to be expected that any ethylenic shift in this compound would be especially low, which is indeed the case. The observed ethylenic shift is of the order of $\Delta\bar{\nu}$ 1486, as obtained by Glockler and Wiener (257). This was attributed by them to the furan ring. The C—H shift in furan and its derivatives occurs at approximately $\Delta\bar{\nu}$ 3155, so far as the ring hydrogen is concerned. This is considerably in excess of the same type of shift observed in other cyclic compounds containing only carbon in the ring, although there are instances where an occasional very weak shift may equal or exceed this amount. This shift also appears in other heterocyclic five-atom rings including thiophene, although it may be somewhat displaced. The derivatives of furan have been studied by Bonino and Manzoni-Ansidei (91), Glockler and Wiener (257), and Matsuno and Han (422). The results are indicated in table 33 for furan and three typical derivatives. The data given in this table are taken from the work of two of the above-named authors (257, 422). The work of Matsuno and Han is the more complete, so that the absence of lines in the first two compounds as compared with the rest is not always significant. There is one point which stands out strikingly, namely, on the introduction of a side chain to the ring the ethylenic shift is augmented at times by as much as 150 wave numbers, although it is not too certain to what mode of oscillation this shift may be assigned. In 2-methylfuran, for example, instead of $\Delta\bar{\nu}$ 1486 observed in furan, the double-bond frequency becomes either $\Delta\bar{\nu}$ 1510 or 1605. The augmentation is independent of the constitution of the side chain, which may contain an alcohol, aldehyde, or ester group. In practically all cases there appear doublet shifts connected with the ethylenic linkage. In addition to the ring double-bond shift there may appear ethylenic or carbonyl shifts if side chains containing these bonds are added to the furan nucleus. In the case of the aldehyde derivatives there appear two, $\Delta\bar{\nu}$ 1668 and 1688. Both of these frequencies were observed by Kohlrausch, Pongratz, and Seka (369) and by Matsuno and Han, but not by Glockler. In the esters appear $\Delta\bar{\nu}$ 1721 to 1745 of the carbonyl frequencies, depending on the ester group. Consequently it is to be noted that the carbonyl frequency is increased by the presence of

the furan group. There is also present a shift which remains fairly constant near $\Delta\tilde{\nu}$ 1000, which might possibly be attributable to the C—O linkage. Matsuno and Han have discussed the attribution of the frequencies to the various derivatives. The lines corresponding to $\Delta\tilde{\nu}$ 888,

TABLE 33

Raman spectra of some furans and derivatives

$\Delta\tilde{\nu}$			
Furan	2-Methylfuran	2-Furaldehyde	Methyl α-furoate
		172	170(2)
	253(5)		233(5)
	343(3)		395(4)
483		497	443(3)
		581	
604	626(3)	624	602(1)
	654(6)		618(2)
735	718(1)	758	770(3)
	796(1)		798(6)
857	883(3)	878	888(6)
990	917(4)	929	911(5)
			922(8)
	1018(3)	1021	1019(6)
1058(3)	1084(8)	1078	1081(6)
1139	1147(3)	1156	1122(5)
	1215(4)	1212	1172(4)
	1233(3)		1236(5)
	1376(3)	1378	1307(4)
1381(5)	1386(9)		1390(8)
1486(7)	1453(4)	1467(10)	1478(10)
	1510(10)		
	1605(6)	1567(8)	1572(5)
		1677(10)	1583(6)
		1688(8)	
			1726(8)
		2181	
	2745(2)		
	2883(3)		2845(1)
	2928(7)		
	2955(2)		2956(5)
	3119(6)	3129	3122(4)
3165(3)	3153(4)		3155(2)

1088, and 1390 are found in most five-atom rings. They believe that $\Delta\tilde{\nu}$ 1507 and 1605 are characteristic of a furan derivative containing CH_2 in the side chain. The α-derivatives of furan give $\Delta\tilde{\nu}$ 1460 and 1507, which are not assigned to the transverse vibration of the hydrogen. These

frequencies are associated with the furan ring. It is believed that the double-bond formula for these compounds is more probable than the centric formula.

2. Other oxygen rings. There are other types of heterocyclic compounds involving oxygen which are somewhat analogous to an anhydride. It has been pointed out that the anhydrides yield shifts between $\Delta\bar{\nu}$ 1775 and 1845. The anhydrides are generally ring compounds bound together through an oxygen. The shift referred to is the carbonyl shift of the oxygen, which does not enter into the ring structure. Ôeda (479) has investigated acetone lactic acid and acetone leucic acid having the formulas:

CH₃CH——CO (CH₃)₂CHCH₂CH——CO

O   O   O   O

C(CH₃)₂   C(CH₃)₂

Acetone lactic acid   Acetone leucic acid
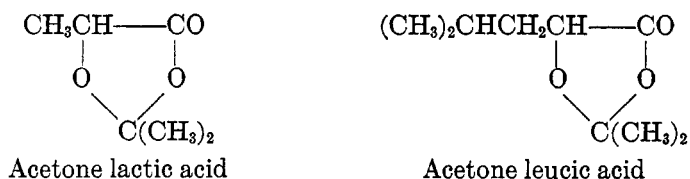
These yield $\Delta\bar{\nu}$ 1790 (5) and 1787 (5) for the lactic and leucic acid derivatives, respectively. These two compounds, therefore, behave like any other anhydride, but were included among the polycyclic compounds because of their peculiar cyclic structure. Although these are five-membered rings they show no shift in excess of $\Delta\bar{\nu}$ 1450 which can be attributed to the transverse hydrogen vibration. The maximum C—H line is $\Delta\bar{\nu}$ 2994, so that the ring hydrogen does not differ materially from that observed in cyclopentane.

Dioxane, investigated by Villars (630) and Wolkenstein and Syrkin (652), exhibits no peculiarities, the principal frequencies being the usual C—H ones and a relatively strong shift in $\Delta\bar{\nu}$ 837 (4).

3. Pyrroles. The pyrroles have been studied extensively by Bonino and Manzoni-Ansidei (89, 93) and Bonino, Manzoni-Ansidei, and Pratesi (95, 96). The pyrroles, like the furans, are five-atom rings containing an odd atom. The spectra which they exhibit have many similarities. As in the case of furan, pyrrole exhibits an exceedingly low ethylenic shift if any. The only frequency displacement between $\Delta\bar{\nu}$ 1140 and 3073 occurs at $\Delta\bar{\nu}$ 1377, a shift which occurs in slightly modified form in every derivative of the pyrroles and the furans. While this may be connected indirectly with the C—N linkage as shown by $\Delta\bar{\nu}$ 1367 in the nitro compounds, it is doubtful. The strongest shift occurring in pyrrole is at $\Delta\bar{\nu}$ 1140. This does not appear in its derivatives, with the possible exception of acetylpyrrole. This would apparently indicate a structure reminiscent of the allenes, where the double bonds are attached to the same

TABLE 34

Raman spectra of some pyrroles

				$\Delta\tilde{\nu}$				
Pyrrole	2-Methyl-pyrrole	2,5-Di-methyl-pyrrole	1-Methyl-pyrrole	1-Phenyl-pyrrole	1-Acetyl-pyrrole	2-Acetyl-pyrrole	2-Pyrrole-aldehyde	Tetra-chloro-pyrrole
								151(3)
								166(1)
	257(4)	266(4)		283(3)				
		297(3)		286(2)				
	338(2)	393(1)	354(1)	409(1)	405(1)			393(2)
		485(1)		442(1)				
					544(1)		502(2)	
	596(½)	603(2)	607(1)	619(2)				
		623(1)						
641(2)	648(6)	649(1)	660(4)		644(1)			
		690(3)	688(2)	690(3)				691(1)
706(1½)	710(1)							
	782(2)	765(1)		758(2)				
828(1)			813(2)					
852(1)	881(4)		868(2)		859(2)		869(2)	
	953(3)			916(2)	914(2)	929(4)		
	973(2)	991(5)	962(2)	962(2)	967(0)		954(3)	
				1001(5)				
				1022(1)	1027(0)	1045(3)		
1035(½)		1034(5)	1054(4)	1047(3)				
1078(½)	1089(6)		1084(4)		1082(0)		1087(4)	
				1122(2)				
1140(8)				1141(1)	1132(4)			
				1158(3)				
				1175(3)				
		1187(1)		1197(0)				
	1230(5)	1258(5)		1254(3)				
			1283(6)	1297(1)				
				1333(8)				
1377(3½)	1381(1½)	1367(3)	1380(7)	1395(4)	1382(3)	1367(3)	1350(5)	1383(3)
	1435(4)		1415(2)	1421(3)		1406(4)	1400(3)	
	1469(5)	1458(3)			1468(3)			1472(4)
		1514(8)	1504(3)	1501(2)				
				1522(4)				
	1571(1½)	1605(1)		1602(8)				
				1620(0)		1636(5)	1645(5)	
					1711(4)			
			2819(1)					
	2865(3)							
		2902(3)			2915(2)			
	2918(4)	2927(3)	2942(2)					
		2977(1)						
						2967(2)		
3073(1)				3073(3)				
		3107(2)	3103(2)	3117(2)				
3123(3)	3120(4)		3130(3)	3147(2)	3135(3)		3126(1)	
3380(2)	3378(3)	3379(1)						

carbon atom. On substitution, however, the double-bond linkage appears at $\Delta\tilde{\nu}$ 1571 and 1605 or $\Delta\tilde{\nu}$ 1469 and 1514. This doubling of the double-bond linkage, if this indeed can be attributed to that, depends upon whether the substitution is in the ring or on the nitrogen atom. When the substitution takes place on the nitrogen atom the spectrum is simpler. These results, summarized in table 34, are based on the observations of Bonino, Manzoni-Ansidei, and Pratesi (96). The carbonyl shifts observed in the carbonyl derivatives of pyrrole are slightly elevated from the normal position. The shift at $\Delta\tilde{\nu}$ 3380 is consistent with the H—N linkage. Its absence in 2-acetylpyrrole and 2-pyrrolealdehyde is not entirely clear, although there may be some coupling with the carbonyl group. Bonino and his coworkers assume that $\Delta\tilde{\nu}$ 1550 is associated with a central vibration somewhat analogous to that connected with the centric formula.

In many cases the determination of characteristic Raman lines in organic compounds is difficult, particularly those pertaining to the compound as a whole. With these five-membered heterocyclic rings, however, the difficulty seems to be not one of determining characteristic Raman lines, which are strong and moderately easy to secure, but of interpreting them after they are obtained. It is quite evident that these compounds are very different in their constitutional structure from the six-membered rings.

4. Furazans, oxdiazoles, and azoximes. These compounds are heterocyclic five-membered rings, and are somewhat related to the furans and pyrroles. They have been investigated by Milone (443) and Milone and Müller (446). All these compounds contain C=N linkages, and exhibit the same peculiarities as observed with the other cyclic compounds of this type.

The C=N shift in 3,4-dimethylfurazan occurs presumably at $\Delta\tilde{\nu}$ 1461 (3). This does not entirely eliminate $\Delta\tilde{\nu}$ 1396 (3). It may be argued that the former of these shifts is attributable to the methyl group. However, in 3,4-diphenylfurazan $\Delta\tilde{\nu}$ 1448 and 1489 also appear. Furazan itself unfortunately has not been studied. The compound 3-methyl-4-phenylfurazan exhibits a number of frequencies in the region which could be assigned to double-bond frequencies. Of these $\Delta\tilde{\nu}$ 1598 is attributable to the C=C in the benzene ring. In all the compounds involving a link between the nitrogen and oxygen atoms there is a shift near $\Delta\tilde{\nu}$ 1300 to 1320, which occurs strongly in the ester form of the nitrates but not in the nitrites. A shift near $\Delta\tilde{\nu}$ 2930 appears in all the compounds.

Most remarkable is the hydrogen shift occurring at $\Delta\tilde{\nu}$ 3217 or higher. This is nearly in the region of the N—H characteristic linkage and may indicate some kind of tautomerism. This is further indicated by the presence of $\Delta\tilde{\nu}$ 3075, which is characteristic of a hydrogen attached to C=C

and is present even in the furazan and oxdiazole derivatives which do not contain a phenyl group.

The aliphatic oxdiazoles are particularly characterized by the shift of $\Delta\bar{\nu}$ 1579, in contrast to the much lower frequency observed with the aliphatic furazans. The aromatic substituted oxdiazoles, furazans, and azoximes exhibit a very similar group of lines falling between $\Delta\bar{\nu}$ 1440 and 1600. The oxdiazoles are noted by the absence of a line near $\Delta\bar{\nu}$ 1300, as has been mentioned.

TABLE 35

The Raman spectra of some furazans, oxdiazoles, and azoximes

$\Delta\bar{\nu}$

3,4-Dimethyl-furazan	2,5-Dimethyl-oxdiazole	3-Methyl-4-phenylfurazan	2-Methyl-5-phenyloxdiazole	5-Methyl-3-phenylazoxime	3-Methyl-5-phenylazoxime
289(1)		283(1)			
649(1)	613(1)	621(1)	629(1)	635(1)	632(2)
709(2)					958(1)
964(1)	923(1)	998(2)	991(1)	989(2)	982(1)
	1043(1)		1030(2)	1020(1)	1036(2)
				1055(1)	1069(1)
	1108(2)		1102(2)		
		1168(2)	1175(2)		1183(2)
1308(2)		1278(1)		1305(2)	1320(1)
1396(3)					
1461(3)	1438(3)	1451(3)	1442(2)	1439(2)	1463(2)
		1502(2)	1482(3)	1483(2)	1499(2)
		1546(3)	1546(3)	1541(3)	1559(3)
	1579(3)	1598(3)	1591(2)	1576(2)	1601(2)
2938(2)	2957(2)	2936(2)	2919(2)	2928(2)	2940(1)
3070(1)	3082(1)	3083(2)	3071(2)	3065(2)	3091(2)
		3190(1)	3182(1)	3178(1)	
3217(1)					3204(1)
	3349(1)				

All these results are indicated in table 35. It is particularly interesting to note the quite different spectra of the two isomeric azoximes.

5. Pyridines, quinolines, and allied compounds. Piperidine is a saturated heterocyclic compound of the type C_6, and consequently its Raman spectrum bears a close resemblance to that of cyclohexane (568). The shifts $\Delta\bar{\nu}$ 3307 and 3339 are attributed to the well-established N—H frequency. Pyridine has received considerable attention (75, 129, 359, 379, 480, 498, 621, 625, 645). Its spectrum is similar to benzene. The =C—H shift occurs at $\Delta\bar{\nu}$ 3054 and the C=C (or C=N) at $\Delta\bar{\nu}$ 1571, which is lower than the equivalent shift in benzene by about 15 wave numbers. The

strongest frequency arising from a symmetrical ring oscillation occurs at $\Delta\tilde{\nu}$ 992 identical with that observed in benzene. A weak shift at $\Delta\tilde{\nu}$ 1379 (1) appears. Pyridine hydrochloride (379) yields $\Delta\tilde{\nu}$ 3103 in place of 3054 and two new lines at 1253 (1) and 1563 (0). Substituted pyridines have been examined by Bonino and Manzoni-Ansidei (89). The compound 2-methylpyridine (α-picoline) differs from β-picoline in the lower frequency brackets. Both yield $\Delta\tilde{\nu}$ 1373 (2), 1570 (2), 1599 (2), and 3052. Quinoline yields among other shifts $\Delta\tilde{\nu}$ 1369 (6), 1388 (2), 1428 (3), 1568 (4), 1589 (1), 3011 (1), 3062 (3); isoquinoline yields $\Delta\tilde{\nu}$ 1379 (7), 1427 (2), 1458 (2), 1496 (1), 1554 (2), 1582 (2), 1622 (1), 3020 (3), 3058 (3).

The methylindoles, peculiarly enough, exhibit no N—H shift. This is probably because of a lack of recording rather than a real absence. The double-bond shifts vary considerably with the position of the substituent groups. For 2-methylindole these shifts are $\Delta\tilde{\nu}$ 1554 (3), 1588 (2), 1615 (1); for 3-methylindole $\Delta\tilde{\nu}$ 1560 (2), 1577 (1), 1610 (1); for 7-methylindole $\Delta\tilde{\nu}$ 1507 (2), 1600 (1). Notwithstanding the careful work of Bonino and Manzoni-Ansidei on these compounds and their derivatives, no general conclusion can be drawn at this time in regard to the complete significance of these Raman frequencies. It does not seem reasonable, however, that the C=N shift can be assigned to $\Delta\tilde{\nu}$ 1433 to 1480 in the pyridine type of compounds, as noted by Bonino and Cella (83), except under such conditions that no other assignment is possible.

6. Summary. It may be generally concluded that the C=N characteristic frequency in the non-cyclic compounds is near $\Delta\tilde{\nu}$ 1640 to 1655, but in the multiple bond system of the allenic type this may be reduced by more than 150 wave numbers. In the cyclic compounds the C=N frequency is considerably less than in the non-cyclic compounds. If the rings are six-membered and have a multiple bond system this shift may occur near $\Delta\tilde{\nu}$ 1575. The five-membered rings exhibit a very reduced C=N shift just as the C=C shift is reduced in the C_5 cyclic or heterocyclic compounds. The double bonds in these heterocyclic compounds are very sensitive to substitution. This is not unusual as it is to be remembered that even the transition from cyclopentene to methylcyclopentene causes an augmentation in the C=C shift of 45 wave numbers; from cyclohexene to methylcyclohexene an increase of 25 wave numbers; from cyclopentadiene to cyclopentene 115 wave numbers, and finally in the substituted pyrroles the C=C shift appears at approximately $\Delta\tilde{\nu}$ 1515 for the strongest component of a doublet but varies considerably with substitution. The oxidiazoles, furazans, and azoximes have a C=N shift, which is probably near $\Delta\tilde{\nu}$ 1540 but also varies over a considerable range. The doubling of the double-bond shifts in this region for these last few compounds probably owes its origin to the lack of symmetry.

The C↔N vibration is more difficult to determine. It may apparently vary from $\Delta\bar{\nu}$ 930 to 1000 in the amines and isonitriles to near $\Delta\bar{\nu}$ 970 in the pyrroles, although this is also somewhat approximate. So far as the N—O is concerned the furazans, azoximes, and oximes would indicate a shift between $\Delta\bar{\nu}$ 1000 and 1078 as characteristic. Nevertheless the shift near $\Delta\bar{\nu}$ 1300 is also constant in these compounds. In hydroxylamine hydrochloride the N—OH shift has been noted by Hibben (315) to be about $\Delta\bar{\nu}$ 1050, consequently the $\Delta\bar{\nu}$ 1000 region is favored for this shift.

V. Metallo compounds

Metallo derivatives of the hydrocarbons have a useful significance. If the mass of the metallic component is sufficiently great, then it is not difficult to delineate the contributions of the radical.

Some of the earliest metallo derivatives determined were the alkyl magnesium halides, studied by Cleetin and Dufford (129). The ether solution of these compounds shows $\Delta\bar{\nu}$ 1076 for methylmagnesium iodide and 1131 for methylmagnesium bromide. These do not of course represent the complete spectra. Nickel carbonyl, according to Duncan and Murray (210), yields (on a scale of 100 for intensity) $\Delta\bar{\nu}$ 82 (100), 382 (20), 463 (8), 601 (4), 718 (0), 833 (2), 872 (2), 913 (2), 1609 (2), 2043 (30), 2132 (5), and 2223 (1). It is possible that this molecule has a structure in which all the atoms lie in a plane. The carbonyl frequencies are more in accord with those observed for C≡O than the ordinary carbonyl structure. Calculations of the Ni—CO bond yield 2.4×10^5 dynes cm.$^{-1}$ for the force constant. The phenyl metallo derivatives have been studied by Donzelot and Chaix (207). Mercury diphenyl yields $\Delta\bar{\nu}$ 158, 210, 651, 704, 998 (8), 1024, 1574 (8), 3049, and selenium diphenyl $\Delta\bar{\nu}$ 175 (5), 201 (5), 249 (1), 318 (8), 612 (5), 668 (5), 999 (10), 1021 (8), 1067 (1), 1087 (8), 1157 (5), 1180 (1), 1325 (1), 1577 (7), 3054 (7), 3155 (1), 3207 (1). The low frequency shifts are, as to be expected, notably reinforced.

Several alkyl metallo derivatives have been investigated by Gopala Pai (269). These results, together with the data on lead tetramethyl of Duncan and Murray (210), are given in table 36. In this table, as occasionally in others, it has been necessary to correct different coworkers' estimates of intensities to a common denominator. A few weak lines estimated by Duncan and Murray as 1/100 of the intensities of the strongest lines in lead tetramethyl have been omitted or indicated by an intensity of zero. The results obtained by Gopala Pai confirmed those of Venkateswaran (619) in so far as the work is duplicated. The usual C—H lines from $\Delta\bar{\nu}$ 2890 to 3000 are present, as well as lines near 1100. However, lines near $\Delta\bar{\nu}$ 1450 are absent in several of the compounds including the ethyl derivatives. For zinc dimethyl if $\Delta\bar{\nu}$ 488 and 505 are considered a

doublet then the fundamental frequencies are $\Delta\bar{\nu}$ 144, 488 to 505, and 620. This yields a value of 1.6×10^5 dynes cm.$^{-1}$ for the Zn—C force constant.

If the fundamentals for mercury dimethyl are considered to be $\Delta\bar{\nu}$ 156, 515, and 700 the force constant is found to be 2.1×10^5 dynes cm.$^{-1}$. The spectrum of bismuth trimethyl is somewhat similar to that of arsenic trichloride, antimony trichloride, bismuth trichloride, and trimethylamine. Its fundamental frequencies are $\Delta\bar{\nu}$ 171, 460, and 1147; presumably

TABLE 36

The Raman spectra of some metallo derivatives

$\Delta\bar{\nu}$					
Pb(CH₃)₄	Bi(CH₃)₃	Zn(CH₃)₂	Hg(CH₃)₂	Hg(C₂H₅)₂	Sn(CH₃)₄
		144(2)	156(2)	140(1)	152(7)
	171(4)			212(2)	
		248(1)	255(0)	259(3)	262(4)
				329(0)	
460(5)	480(8)	488(2)		486(8)	
473(2)		505(8)	515(8)		506(8)
			565(1)	562(0)	526(5)
		620(4)		633(0)	
			700(3)		
	784(0)				
				958(1)	952(0)
				1008(3)	
				1055(2)	1046(0)
1155(2)	1147(2)	1159(6)			
1170(1)	1165(3)		1182(6)	1178(6)	1200(5)
	1230(1)		1258(1)		1262(0)
	1347(0)	1346(0)		1370(1)	
				1421(3)	
				1455(3)	
2291(0)			2879(1)	2857(1)	
2918(5)	2915(1)	2897(3)	2910(2)	2896(3)	2915(3)
2999(3)			2965(1)	2942(1)	2979(2)
3679(0)					
3755(0)					

it has a pyramid structure. The spectrum of the tetraalkyls resembles that of the tetrachlorides. The fundamental frequencies for tin tetramethyl are $\Delta\bar{\nu}$ 152, 262, 506, and 526, and for lead tetramethyl $\Delta\bar{\nu}$ 96, 165, 444, 462.

It is concluded that the dialkyl metallo compounds may be treated as non-linear triatomic models of the type XY_2, that the trialkyls have a pyramidal structure, and that the tetraalkyls are represented by a regular tetrahedron.

W. The Raman spectra of deuterium compounds

Although hydrogen for the purpose of this discussion is considered with the inorganic compounds, it is of some interest to indicate the spectrum D_2 in comparison with it. For the transition in the zero vibrational level corresponding to Δj 0→2 according to Anderson and Yost, the Raman shift observed is $\Delta \tilde{\nu}$ 179.6. For Δj 1→3 the Raman shift is $\Delta \tilde{\nu}$ 298. In the first vibrational level where Δj corresponds to 2→2, the shift obtained is $\Delta \tilde{\nu}$ 2989. The shifts for the corresponding changes in the rotational and vibrational quantum numbers for ordinary hydrogen are respectively $\Delta \tilde{\nu}$ 354, 587, and 4144. In applying the simplest harmonic oscillator equation it is observed that

$$\frac{\Delta \tilde{\nu}_{D_2}}{\Delta \tilde{\nu}_{H_2}} = \frac{\sqrt{\bar{\mu}_{H_2}}}{\sqrt{\bar{\mu}_{D_2}}} = \frac{1}{\sqrt{2}}$$

or $\Delta \tilde{\nu}_{D_2} = 2935$ for the calculated D_2 shift.

For water the strong O↔D oscillation according to Wood is $\Delta \tilde{\nu}$ 2517. Rank, Larsen, and Bordner observed $\Delta \tilde{\nu}$ 2666 and Ananthakrishnan $\Delta \tilde{\nu}$ 2646, all of which indicate a mass effect without much change in force constant on comparing this shift with the $\Delta \tilde{\nu}$ 3660 band in water.

Dadieu and Engler (149) have studied CD_4 and obtained $\Delta \tilde{\nu}$ 2108 (8), 2141 (1), which are to be compared with $\Delta \tilde{\nu}$ 2915 and $\Delta \tilde{\nu}$ 3020 observed in CH_4. MacWood and Urey (416) found four vibrational lines in methane-d corresponding to $\Delta \tilde{\nu}$ 1330, 2183, 2302, and 2920. Redlick and Pordes (539) and Wood and Rank (662) investigated chloroform-d. It is observed that the two lower shifts $\Delta \tilde{\nu}$ 262 (10) and 366 (8) are identical with the equivalent shifts in chloroform. $\Delta \tilde{\nu}$ 668 (8) and 761 (8) in chloroform appear as $\Delta \tilde{\nu}$ 650 (8) and 738 (8) in $CDCl_3$. However, $\Delta \tilde{\nu}$ 1215 (4) and 3019 (8) in chloroform are much more strongly altered by the isotope effect and yield $\Delta \tilde{\nu}$ 908 and 2256. It is to be expected that where the chlorine is involved as an oscillator with respect to the carbon atom, a small increase in hydrogen mass will affect the spectra little, but where hydrogen is the origin of oscillation, whether of the bending or the linear type, the effect will be large, consequently the deuterium compounds will be of considerable value in correlating doubtful vibrations with the spectra. This is shown also in acetic acid-d_4. The shifts observed by Angus, Leckie, and Wilson are $\Delta \tilde{\nu}$ 411, 580, 800, 1025, 1093, 1657, 2150, and 2218 as compared with $\Delta \tilde{\nu}$ 447, 621, 895, 1360, 1430, 1666, 2942, and 3022 for CH_3COOH, which shows clearly what shifts are connected with the C—C, C=O, and C—H oscillations. The substitution of deuterium in oxdiazoles, furazans, and furans would aid considerably in the interpretation of their spectra.

The $O \leftrightarrow D$ vibration in CH_3OD appears at $\Delta \tilde{\nu}$ 2440, close to the expected value (539).

According to Trumpy (609) the strength of the C—D binding in the cis- and trans-dichloroethylene-d_2 and in tetrachloroethane-d_2 is slightly greater than in the corresponding hydrogen compounds. In tetrachloroethane the C—H ($\Delta \tilde{\nu}$ 2984) becomes $\Delta \tilde{\nu}$ 2240 for C—D and in dichloroethylene the C—H ($\Delta \tilde{\nu}$ 3080) becomes $\Delta \tilde{\nu}$ 2325 for C—D. Glockler and Davis (252) and Glockler and Morrell (256) have obtained $\Delta \tilde{\nu}$ 1762 and 2700 for $DC{\equiv}CD$ as compared with $\Delta \tilde{\nu}$ 1975 and 3374 in $HC{\equiv}CH$. In this case, the equation

$$\Delta \tilde{\nu} = 4.125 \sqrt{\frac{F}{\bar{\mu}}}$$

assuming a value for F of 15.05×10^5 dynes cm.$^{-1}$, calculated from ordinary acetylene linkage, leads to $\Delta \tilde{\nu}$ 1901 as the expected $C{\equiv}C$ frequency, taking into consideration mass changes only. This does not agree with the observed result. Sutherland (583), Morino (455), and Glockler and Morrell (256) have made other calculations, based on somewhat different equations, that result in reasonable agreement.

Of the aromatic deuterium compounds C_6H_5D (18, 334), C_6HD_5 (334), and C_6D_6 (18, 334, 660) have alone been investigated. From C_6D_6 (660) are obtained $\Delta \tilde{\nu}$ 581, 662, 873, 945, 1000, 1548, 2031, 2266, 2293, 2575, 3052 and 3108. $\Delta \tilde{\nu}$ 1000 and 2031 are faint. A comparison of these shifts obtained with C_6H_6 (605, 849, 991, 1178, 1584, 1606, 2947, 3042, 3062, 3157, 3176, 3573, and 3627) shows that the shifts most affected are those greater than 2900 attributed to C—H, and $\Delta \tilde{\nu}$ 1178 and 849. This would seem to settle beyond doubt that the last two frequencies involve hydrogen motions.

The possible types of motion giving rise to various frequencies are discussed by Angus and others (18).

While the deuterium compounds are of special interest in particular cases, their spectra are of no more importance, in general, than those of any other compounds.

V. VARIOUS APPLICATIONS OF THE RAMAN EFFECT

Up to this point the discussion of the Raman effect has been based primarily upon the intensity and magnitude of the Raman shifts and the fact that the Raman spectra are largely independent of the state of aggregation. It has been assumed that any variation from the normally expected Raman frequency was because of constitutional modification. In most cases these variations have been severely circumscribed. In this section will be dis-

cussed other causes of modified Raman spectra, such as the influence of solvents, hydrate formation, temperature, and electric fields.

A. Mixtures

Examples have already been given of polymerization and constitutional changes as depicted by Raman spectra. These were the cases of paraldehyde and formaldehyde. Before proceeding further in the discussion of other examples, it would be appropriate to point out the results of certain investigations with mixtures. Dadieu and Kohlrausch (170) investigated mixtures of benzene and chloroform, benzene and acetic acid, ethyl ether and hexachloroethane, methyl nitrite and methyl alcohol, and other mixtures of alcohols, esters, and acids in varying proportions. In all cases the final spectra obtained were the sum of the spectra of the individual com-
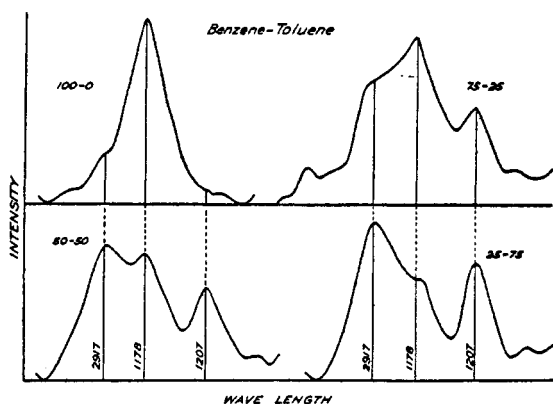
FIG. 29. The Raman spectra of benzene–toluene mixtures (after Crigler)

ponents for those lines which were observed. In a few cases where one of the components is known to be associated into double molecules (such as the case of acetic acid), there is a slight but noticeable change in the spectrum of the mixture as compared with the spectra of the individual components.

Krishnamurti (380) noted that a new faint line appears in 95 per cent acetic acid at $\Delta\bar{\nu}$ 1712 which is not present in the pure acid. The carbonyl shift in the pure acid is $\Delta\bar{\nu}$ 1667. The relative intensity of the $\Delta\bar{\nu}$ 1712 shift increases with dilution, until at 75 per cent concentration there remains only a broad line corresponding to this value. Mixtures of various acids, anhydrides, and alcohols have been studied by Parthasarathy (490). Whiting and Martin (645) examined mixtures of pyridine and acetic acid and of acetone and carbon disulfide. In every case the spectra of the pure substances appeared in solution. The abnormalities apparent in the

vapor pressure and other physical properties of non-ideal solutions are not necessarily visibly reflected in the Raman spectra. Krishnamurti (379), on the other hand, so far as pyridine is concerned, observed appreciable changes in the position and intensity of some of the lines of pyridine on dilution with water. The principal lines affected were $\Delta\tilde{\nu}$ 1029 and 1571. In methyl alcohol the line at $\Delta\tilde{\nu}$ 1030 broadens in solution but becomes sharper at 50 per cent and has shifted to $\Delta\tilde{\nu}$ 1018. It is suggested that these alterations indicate hydrate formations, particularly in view of the fact that the maximum change occurs at the proper hydrate concentration. Crigler (139, 141) has studied quantitatively mixtures of benzene and toluene in varying proportions. Twenty-five per cent changes in concentrations were easily perceptible, and 5 per cent changes possibly estimated. These results are shown in figure 29.

Lespieau, Bourguel, and Wakeman (406) have in a somewhat similar fashion determined the presence of unsaturateds in mixtures of cyclopropanes.

B. Solutions

The effect of water on the Raman spectra of nitric acid and sulfuric acid, and, conversely, the effect of inorganic compounds on the spectrum of water have been summarized by Hibben (311). Organic acids as well as inorganic acids also modify the water spectrum (535).

Hibben (310) has investigated compound formation between inorganic salts and organic alcohols. Zinc chloride in concentrated solution reduces the $\Delta\tilde{\nu}$ 1034 shift in methyl alcohol by 22 wave numbers and increases $\Delta\tilde{\nu}$ 2835 and 2944 by about the same amount; at the same time it diminishes the intensity at $\Delta\tilde{\nu}$ 1450. Simultaneously there is a marked intensity change in the spectrum of zinc chloride. There is considerably less effect in ethyl alcohol than in methyl alcohol. Goubeau (270) has noted a similar effect in alcoholic solutions of lithium perchlorate. Brodskiĭ and Sack (108) and Sack and Brodskiĭ (549) observe no change in the spectra of benzene, methyl alcohol, ethyl alcohol, and carbon tetrachloride on dissolving arsenic trichloride in them, but there is a reduction of about 25 wave numbers in the lower frequency shifts of the arsenic trichloride. Voge (631) observes that lithium bromide will modify the shifts $\Delta\tilde{\nu}$ 1034, 2835, and 2944 in methyl alcohol, first in the direction of slightly increased shifts with a 7 molal solution and subsequently in the direction of decreasing $\Delta\tilde{\nu}$ 1034 and increasing further the last two shifts in a 24 molal solution.

The hydrolysis and dissociation of weak organic bases such as urea and hexamine have been shown by Krishnamurti (377) from the alteration in the Raman spectra of these compounds.

C. Association and polymerization

The supposed association of ethyl alcohol has been noted by an alteration in the shift $\Delta\tilde{\nu}$ 623, according to Leitman and Ukhodin (403). Other evidence of association has been indicated by Meyer (436). Trumpy (606) has suggested a possible polymerization of formaldehyde in solution. More definite evidence of polymerization has been found by Signer and Weiler (559, 560). The spectrum of polystyrene is compared with that of ethylbenzene and styrene. The silica esters show modified spectra with increased polymerization. As has been previously mentioned, Venkateswaran and Bhagavantam (627) demonstrated the polymerization of acetaldehyde. Evidence of polymerization and depolymerization of inorganic compounds is plentiful.

D. Temperature

The effect of temperature on Raman spectra introduces no anomaly but some modification. As the number of molecules in the upper vibrational levels increases with increased temperature, there is a natural augmentation in the intensity of the anti-Stokes lines and other lines become more diffuse (236, 237). Bär (25) found a slight increase in intensity in some lines in diethyl ether at low temperature, but no discontinuity at $-105.4°C.$, where there is an anomalous specific heat and density. Similarly Hertlein (308) observed no change in the spectrum of nitrobenzene just above the melting point, where there is a sharp change in dielectric constant. Epstein and Steiner (227) found a decrease of 1.7 wave numbers in benzene at $-20°C.$ Sirkar (572) has noted modifications in some of the benzene lines at temperatures between 35° and 160°C. Experiments near the critical temperature by Placzek (510) indicate no alteration in the Raman spectra of the strong isobutyric acid lines, although this result is doubtful (672).

E. Electric and magnetic fields

Cotton (135) has noted that a strong magnetic field increases the intensities of $\Delta\tilde{\nu}$ 1112, 1342, and 1587 in nitrobenzene. An electric field of 15,000 to 25,000 volts cm.$^{-1}$ causes an alteration in the depolarization factor of some lines in cyclohexane, benzene, and chlorobenzene (573).

F. Liquid rotational scattering

Bhagavantam (51, 53) and Bhagavantam and Rao (55) have discussed the question of "wings" accompanying Rayleigh scattering. In gases these have been attributed to unresolved lines of Raman scattering, the intensity distribution first increasing to a maximum and then decreasing with the distance from the Rayleigh line. These wings also exist in certain liquids, but it is only in liquid hydrogen that they have been completely

resolved. In benzene the wings extend about 60 to 100 wave numbers. Bhagavantam (51) and Gross and Vuks (287) believe that the wings are attributable to internal oscillations in the liquid similar to those existing in solids, rather than to true rotational scattering. Mizushima and Morino (449, 450) and Mizushima, Morino, and Higasi (451, 452) have discussed the Raman effect and dipole moment in relation to free rotation. Meyer (438), Gross and Vuks (323), Rao (534), Sirkar (575, 576), Sirkar and Maiti (577), and Trumpy (607) have examined rotational scattering. There is still apparently some disagreement as to the explanation of the wings.

G. Specific heat and latent heat of fusion

If it is possible to identify Raman lines with definite modes of vibration in a molecule and to assign the correct number of degrees of freedom to each frequency, then, on the assumption that the vibrator in the molecule acts as an independent Einstein oscillator, it is possible to calculate the specific heat. In other words, since the Einstein expression gives the specific heat of a harmonic oscillator in terms of its frequency and temperature, the amount of heat a particular type of motion would absorb can be calculated by knowing its frequency and the number of degrees of freedom. The summation of these gives the specific heat of the molecule as a whole. This is the procedure Andrews (15) and Andrews and Southard (17) have used in calculating the specific heats of methyl alcohol, ethyl alcohol, benzene, bromobenzene, and other compounds with an average deviation of 5 per cent between 15° and 260°K.

With inorganic compounds Paramasivan has calculated the specific heats of compounds up to pentatomic molecules, using the Einstein specific heat functions and the Lindemann equation (311).

Phillips (503) has calculated the latent heat of fusion of some thirty-eight organic and inorganic substances from observed Raman shifts with reasonable agreement for the non-associated substances. The equation employed by him is

$$\lambda_\mu = \frac{mNhc}{JML_f} = \frac{m(2.845 \times 10^4)}{ML_f}$$

where m is an integer 1, 2. . . . , N is Avogadro's number, h is Planck's constant, c is the velocity of light, J is Joule's equivalent, ML_f is the molecular latent heat of fusion, and λ is the wave length, expressed in microns, in the infra-red corresponding to the Raman shift.

This may be expressed as:

$$\Delta\bar{\nu}(\text{cm.}^{-1}) = \frac{ML_f}{m} \times 0.351$$

This goes back to the fundamental assumption that $E = h\nu$ where E is the energy per molecule in the process involved. The extrapolation of this to the calculation of frequencies in chemical processes has been unsuccessfully attempted by Perrin. Phillips, on the other hand, proposes that since a change in vibrational states in the liquid or solid is possible, consequently the resultant energy change is equal to an integral part of the latent heat of fusion per molecule. There is no obvious explanation of these results, although the calculated latent heats agree with the observed values generally within ±4.5 per cent.

It is to be pointed out that

$$\frac{JML_f}{N} = H\bar{\nu}c = 1/2\ \bar{a}^2 F$$

where $\frac{1}{2}\bar{a}F$ is the mean restoring force and $\bar{a}$ is the displacement during oscillation.

H. Intensities

The relative intensities of the Raman lines have been given in most cases. These are generally visual estimates of unknown accuracy. Several references will be cited here of more accurate determinations or cases where the determination was made with reference to the primary intensity of the Rayleigh scattering. These references are as follows: Dhar (204), Ellenberger (221), Haberl (290), Ray-Chaudhuri (537, 538), Rekveld (541), Sirkar (563), Werth (640, 641), and Weiler (634, 636). The most comprehensive theoretical treatment of intensities and polarization is that of Placzek (511).

VI. DEPOLARIZATION AND RAMAN SPECTRA

It is well known that general Rayleigh scattering is polarized, or in other words the ratio of the intensity of the horizontal light vibration in the scattered light i to the vertical vibration I (which is usually preponderant) approaches zero. In Raman spectra, if the type of vibration giving rise to the Raman line is unsymmetrical, the scattered radiation will not be completely polarized but will be depolarized to a greater or less degree depending on the character of the oscillation. Consequently the ratio of i/I augments and approaches approximately 6/7 as a limit, because complete depolarization can never be realized. The ratio i/I is expressed by rho (ρ), the depolarization factor, and it is in terms of this factor that depolarization measurements are generally reported.

In actual practice depolarization measurements are exceedingly difficult, since the experimental arrangement requires the complete elimination of parasitic light. The various methods employed and results obtained with

inorganic substances have been summarized by Hibben (311). Placzek (510, 511) has discussed the theoretical aspects in complete detail.

The intrinsic importance of depolarization measurements can not be overemphasized. By them the types of motion giving rise to a Raman line in some cases can be determined irrespective of the magnitude of the Raman shift or its intensity. For example, the transverse oscillations of the C—H are strong but are not symmetrical. In consequence the depolarization factor is large. These shifts can thus be distinguished by this means from any —C=C— linkage of the furans which occur in the same neighborhood. Then again, in phosphorus trichloride and phosphorus tribromide the magnitudes of the Raman shifts are entirely different, but the relative depolarizations are nearly identical. Cabannes and Rousset (117) have determined the depolarization of a number of organic substances as well as inorganic ones. Simons (561) has likewise investigated and discussed the depolarization of organic compounds. His observations are given in table 37. Particular attention is called to the low depolarization in the neighborhood of 17 per cent ($\rho = 0.17$) for the symmetrical oscillations. Venkateswaran (625) has recently investigated the polarization of a variety of compounds. He observes in methyl mercaptan that the lowest depolarization factor is 0.3 (30 per cent) for $\Delta\bar{\nu}$ 2573 corresponding to the S—H linkage, $\Delta\bar{\nu}$ 2932 for the C—H linkage, $\Delta\bar{\nu}$ 704 for the C—S linkage, respectively. Other than $\Delta\bar{\nu}$ 1059 the remainder of the lines have depolarization values varying from 0.4 to 0.9. In carbon tetrachloride $\Delta\bar{\nu}$ 459 has a value of 0.04, as compared with 0.3 for $\Delta\bar{\nu}$ 1535 and 0.8 for the remainder of the lines. In pentane the two lowest values of ρ are found for $\Delta\bar{\nu}$ 839 and 2876, clearly indicating the most symmetrical vibrations. It is quite evident that $\Delta\bar{\nu}$ 1385 in pyrrole is a transverse oscillation, as its depolarization is 0.5. Generally the lines of the aliphatic compounds are more polarized than those of the aromatic. When a frequency becomes a doublet, the resulting pair of lines will usually have the same degree of polarization as the original. When a Raman line is excessively broad, as in the O—H shift, the depolarization will be marked, even though the oscillation corresponds to a supposedly symmetrical vibration.

Some other workers who have contributed to this field of Raman spectra are as follows: Bhagavantam (35, 41, 48, 49), Bhagavantam and Venkateswaran (58), Cabannes (112, 113, 114), Cabannes and Rousset (116), Daure (199), Hanle (291, 292, 293, 294), Kastler (329), Lindemann, Keeley, and Hall (412), Menzies (434), Mesnage (435), Ornstein and Stoutenbeek (482), Paulsen (494), Placzek (510, 511), Rousset (546, 547), Saha and Bhargava (550), Sirkar (573, 574), Trumpy (606, 607, 608, 610), Venkateswaran (624, 625), and Weiler (636).

It is with a feeling of regret—not unmixed with relief—that practically

TABLE 37

The degree of depolarization of some organic compounds

SUBSTANCE	Δν̄	i	ρ	Δν̄	i	ρ	Δν̄	i	ρ	Δν̄	i	ρ	Δν̄	i	ρ	Δν̄	i	ρ	Δν̄	i	ρ	Δν̄	i	ρ
C_6H_6																602	3	0.86	844	1		991	10	0.7
C_6H_5Cl	195	3	0.87	293	1	0.86	415	2	0.32							607	1	0.89	689	2	0.13	999	4	0.6
$C_6H_5CH_3$	211	4	0.91	258	2	0.85				484	½		517	2		619	2	0.85	781	4	0.10	1002	4	0.7
$C_6H_5OCH_3$	(194)	2	0.88							436	3 br.	(0.37)				607	2	0.87	778	4	0.7	991	5	0.7
C_6H_5CHO	214–280	2	(0.87)							438	3	0.33	529	½	0.34	612	3	0.89	824	3	0.7	1000	5	0.7
																(642)	1							
C_6H_5CN	170	4 br.	0.85				379	0		(460)	(½)		545	1		619	1	0.84	754	2 br.	0.15	998	5	0.4
$C_6H_5COCH_3$	161	4	0.87				388	1								613	3	0.82	731	3	0.22	999	5	0.4
																			946	1				
C_6H_5COCl	161	3 br.	0.84	(307)	½	(0.90)	314	3	0.24	412	1	0.39	505	3	0.19	615	3	0.92	670	3	0.15	1003	6	0.7
																			771	½				
$C_6H_4(CH_3)_2$	218	3	0.89							528	3 br.	0.25							724	4 br.	0.8	819	1 br.	0.15
$C_6H_4(CH_3)_2$ mixture	228	3	0.88	(312)	1	(0.87)				535	3 doub.	0.32	580	2	0.33				729	5 br.	0.7	825	3 br.	0.8
CH_3COOH	381	4	0.37				440	3	0.59				614	5	0.89				889	6	0.16			
$CH_3COOC_2H_5$	(367)	2	0.34	(385)	0											637	4	0.23	852	3	0.17	938	0 br.	
$C_2H_5COOC_2H_5$	323	1	0.42										(611)	0		778	00	0.43	855	2	0.15			
$C_3H_7COOC_2H_5$													604	0 br.	0.57				871	1 v. br.	0.23			
CH_3OH																			880	5	0.31			
C_2H_5OH							431	1	0.55										784	10	0.20			
CH_3COCH_3				391	2	0.87	491	1		526	3	0.70							757	2	0.19	902	00	
$CH_3COC_2H_5$				396	½	0.87				579	½	0.73							840	5	0.29	812	½	
$C_2H_5OC_2H_5$							436	5	0.48	510	1								782	2	0.16	(845)	2	
C_3H_7Cl	359	3	0.55										644	4	0.15	721	2 br.	0.30				(890)	2	

SUBSTANCE	Δṽ (C—C)	i	ρ	Δṽ (C—O)	i	ρ	Δṽ	i	ρ	Δṽ	i	ρ	Δṽ	i	ρ	Δṽ	i	ρ	Δṽ (C—H)	i	ρ
C₆H₆	1019	1					1178	3	0.89										1362	½ br.	
C₆H₅Cl	1027	1	0.19	1070	1 br.	0.10	1152	1 br.	0.88							(1294)	1 br.	0.31	(1381)	½ br.	
C₆H₅CH₃	1023	2 br.	0.27				1154	1	0.88										1376	1 br.	0.42
C₆H₅OCH₃			0.9	(1060)	2	0.11	1150	1	(0.94)	1174	3 br.	0.34	1207	3	0.25				1388	½	0.36
C₆H₅CHO							1159	3	(0.63)				1240	3 br.	0.25						
C₆H₅CN							1175	2					1200	4	0.35	1263	3	0.17			
C₆H₅COCH₃	1025	3	0.24	1074	4	0.16	1155	1	(0.72)				1190	3	0.24						
C₆H₅COCl				1028	2	0.13	1168	3 br.	(0.65)							(1342)	2	(0.35)			
C₆H₄(CH₃)₂	1004	4	0.5										1206	3 br.	0.30				1374	2	0.37
C₆H₄(CH₃)₂ mixture	1007	4	0.3	1044	2	0.30							1251	3	0.43				1373	4	0.38
CH₃COOH	1005	0 br.	0.62	1044	0 br.	0.60							1280	1 br.		1368	4 br.	0.21	1432	4 br.	0.85
CH₃COOC₂H₅	989	0 br.	0.54	(1092)	0	0.56	1100	2	0.60										1442	3 br.	0.88
C₂H₅COOC₂H₅				1034	1 br.	0.66	(1106)	½	(0.71)				(1277)	½ v. br.					1450	2 br.	0.86
C₃H₇COOC₂H₅				1035	4	0.64	1098	1											1447	3	0.89
CH₃OH				1050	3	0.59							1276	1	0.88				1454	3 v. br.	0.91
C₂H₅OH				1069	3	0.64													1457	4 br.	0.90
CH₃COCH₃	923	1 br.		(1069)	0	0.59				1192	3	0.88				(1340)	½	0.23	1430	5 br.	0.90
CH₃COC₂H₅													1227	5		1337	2 br.	0.16	1414	2 br.	0.89
C₂H₅OC₂H₅	928	3	0.61	1037	3	0.56				1147	3	0.90	1276	4 br.	0.90				1445 / 1454	2 br. / 4 br.	0.87 / 0.89
C₃H₇Cl	1026	3	0.53																1442	4 v. br.	0.85
	C—C			C—O															C—H		

TABLE 37—*Concluded*

SUBSTANCE	Δṽ	i	ρ	Δṽ	i	ρ	Δṽ	i	ρ	Δṽ	i	ρ	Δṽ	i	ρ	Δṽ	i	ρ	Δṽ	i	ρ	Δṽ	i	ρ
C₆H₆				1586	3 br.	0.89													2945	4 br.	0.89	3056	8 br.	0.34
				1603	1	0.87																		
C₆H₅Cl				1576	2 br.	0.87																3059	5 br.	0.32
				1599	2 br.	0.92																		
C₆H₅CH₃	1454	1 br.	0.87													2917	0 br.	0.29	2984	0	0.74	3048	5 br.	0.34
C₆H₅OCH₃	(1452)	0	0.91	1594	4	0.92													2949	3 br.	0.80	3062	5 br.	0.33
C₆H₅CHO				1594	7	0.88	1696	7	0.42										(2922)	3 br.		3057	3 br.	0.35
C₆H₅CN				1595	4	0.88				2227	5	0.23										3063	4 br.	0.30
C₆H₅COCH₃	1483	½	0.87	1597	6	0.86	1679	5	0.32							2923	4 br.	0.21				3063	4 br.	0.35
C₆H₅COCl				1592	6	0.84	1744	4	0.34							2917	4	0.27				3067	4 br.	0.33
C₆H₄(CH₃)₂	1443	1 br.	0.91	(1597)	2	0.85							2849	1	0.6							3042	4 br.	0.34
C₆H₄(CH₃)₂ mixture	1447	4	0.88	(1597)	4	0.85							(2863)	3	0.8	2917	5 br.	0.26				3048	4 br.	0.35
CH₃COOH	(1669)	4 br.	0.37				2940	10 br.	0.4	2960	3	0.87												
CH₃COOC₂H₅	(1724)	2	0.42	2868	3	0.4	2921	5	0.19	2977	3	0.86												
C₂H₅COOC₂H₅	(1719)	1	0.36				2936	3 br.	0.20															
C₃H₇COOC₂H₅	(1728)	1	0.38				2932	3 v. br.	0.19															
CH₃OH				2832	8	0.7	2941	7	0.22	2974	5	0.87												
C₂H₅OH				2873	5 br.	0.14	2926	8 br.	0.23				3388±85	2 br.	0.89									
CH₃COCH₃	1714	5	0.38				2922	10	0.22															
CH₃COC₂H₅	(1710)	2	0.38				2913	4 br.	0.15															
C₂H₅OC₂H₅				2866	10 br.	(0.30)	2932	10	0.20	2973	3 br.	0.89												
C₃H₇Cl				2870	5	0.8	2938	6 v. br.	0.25	2980	8 br.	0.89												
(band assignment)	C—H / C=O			C—H			C=O / C—H			C≡N / C—H			C—H / O—H			C—H			C—H			C—H		

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all reference in this discussion to infra-red absorption has been omitted. It might be considered a fourth parameter necessary in the complete treatment of Raman spectra, but is a separate field of investigation. The contributions of Wulf and Liddel and many others to the elucidation of organic structure by this means lead to conclusions reasonably compatible with the results obtainable from Raman spectra investigations. On the other hand, there are occasions involving the asymmetrical oscillations of light atoms when the infra-red is the more valuable approach. This has been omitted from consideration for reasons which have already been given.

VII. CONCLUSION

It has been the purpose of this review to discuss, at least in principle, all the developments in the Raman effect as applied to organic chemistry since its discovery in 1928. The spectra obtained from every type of organic compound and type of linkage have been given in some detail. The application of the Raman effect in the delineation of the structure of organic compounds has been indicated. It can not be too strongly emphasized that these same principles apply not only to organic chemistry but to inorganic chemistry as well. The utility of this method in providing information regarding other physical properties of compounds has been considered. An index and bibliography have been included in which are recorded most of the citations with reference to organic compounds so far published, in the hope that these will be of value to those who wish to investigate in more detail the spectrum of any type of compound.

The Raman effect has reached a stage of more quantitative investigation. Its development may be somewhat slower in the future than in the past. Its contributions, nevertheless, to a greater understanding of the constitution of matter regardless of the stage of aggregation have been by no means negligible.

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FORMULA INDEX

PART I. ALIPHATIC COMPOUNDS

PART I. ALIPHATIC COMPOUNDS[1]

A. SATURATED COMPOUNDS

I. Hydrocarbons

(1) CD_4	CD_4	methane-d_4 (149)
(2) $C_5H_{11}D$	$(CH_3)_3CCH_2D$	tetramethylmethane-d (533)
(3) C	C	diamond (34, 37, 40, 43, 54, 468, 527, 528, 545)
(4) CH_4	CH_4	methane (47, 49, 50, 59, 194, 195, 196, 197, 205, 344, 411, 416, 424, 425, 467, 613, 650)
(5) C_2H_6	C_2H_6	ethane (47, 54, 69, 194, 196, 197, 345, 349)
(6) C_3H_8	C_3H_8	propane (47, 69, 194, 197, 345, 349)
(7) C_4H_{10}	C_4H_{10}	butane (47, 345, 349, 462)
(8) C_4H_{10}	$(CH_3)_3CH$	isobutane (47, 345, 349)
(9) C_5H_{12}	C_5H_{12}	pentane (41, 73, 158, 242, 349, 523, 635)
(10) C_5H_{12}	$(CH_3)_2CHCH_2CH_3$	isopentane (349, 373)
(11) C_5H_{12}	$C(CH_3)_4$	tetramethylmethane (2,2-dimethylpropane) (344, 345, 349, 532, 533)
(12) C_6H_{14}	C_6H_{14}	hexane (6, 7, 9, 28, 259, 349, 359, 452, 480, 498, 510, 513)
(13) C_6H_{14}	$(CH_3)_2CH(CH_2)_2CH_3$	isohexane (9)
(14) C_6H_{14}	$(C_2H_5)_2CHCH_3$	methyldiethylmethane (3-methylpentane) (9)
(15) C_6H_{14}	$(CH_3)_3CC_2H_5$	trimethylethylmethane (2,2-dimethylbutane) (9)
(16) C_6H_{14}	$(CH_3)_2CHCH(CH_3)_2$	diisopropyl (2,3-dimethylbutane) (7, 9)
(17) C_7H_{16}	C_7H_{16}	heptane (73, 133, 242, 349, 569)
(18) C_8H_{18}	C_8H_{18}	octane (73, 133, 242, 349, 381)
(19) C_8H_{18}	$(CH_3)_2CH(CH_2)_2CH(CH_3)_2$	2,5-dimethylhexane (460)
(20) C_8H_{18}	$C_2H_5CH(CH_3)CH(CH_3)C_2H_5$	3,4-dimethylhexane (460)
(21) C_8H_{18}	$CH_3C(CH_3)_2CH_2CH(CH_3)_2$	2,2,4-trimethylpentane (533)
(22) C_9H_{20}	C_9H_{20}	nonane (6, 349)
(23) C_9H_{20}	$(CH_3)_3CCH_2C(CH_3)_3$	2,2,4,4-tetramethylpentane (533)

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[1] In this index are listed the empirical formula, the structural formula, the name, and the reference numbers for most of the organic compounds so far investigated. The order of arrangement in each group of compounds is approximately the same as used in *Chemical Abstracts* with the exception of the deuterium compounds, which are listed separately. Each compound is preceded by a number, which is its "formula number."

Such compounds as the nitro and cyano derivatives and the oximes are considered as saturated compounds unless they possess an ethylenic linkage. When an author publishes the same article in more than one journal (note, for example, many of the publications of Kohlrausch and his associates) both references are given in the bibliography, but both are not always cited in the formula index.

(24) $C_{10}H_{22}$ $C_{10}H_{22}$ decane (6, 73, 349)
(25) $C_{11}H_{24}$ $C_{11}H_{24}$ undecane (6, 349)
(26) $C_{12}H_{26}$ $C_{12}H_{26}$ dodecane (6, 349)
(27)   gasoline (8, 312)
(28)   oil (312)

II. Halogen derivatives of hydrocarbons

a. Fluorine derivatives

(29) CH_3F CH_3F methyl fluoride (1)

b. Chlorine derivatives

(30) $CDCl_3$ $CDCl_3$ chloroform-d (539, 662)
(31) $C_2D_2Cl_4$ $C_2D_2Cl_4$ tetrachloroethane-d_2 (609)

(32) CCl_4 CCl_4 carbon tetrachloride (24, 27, 34, 35, 36, 48, 57, 58, 108, 109, 112, 113, 117, 119, 120, 121, 122, 143, 157, 158, 170, 192, 193, 201, 221, 229, 236, 242, 291, 292, 293, 317, 344, 382, 390, 391, 392, 393, 394, 397, 412, 418, 433, 434, 435, 467, 482, 483, 512, 519, 525, 526, 534, 541, 543, 546, 552, 561, 563, 566, 567, 604, 625, 653, 654, 655)

(33) $CHCl_3$ $CHCl_3$ chloroform (27, 34, 35, 57, 113, 117, 129, 143, 162, 166, 170, 201, 242, 291, 292, 293, 304, 305, 394, 432, 433, 519, 561, 612, 625, 633, 654, 664)

(34) CH_2Cl_2 CH_2Cl_2 methylene chloride (57, 117, 162, 166, 169, 172, 400, 482, 519, 607, 608, 666)

(35) CH_3Cl CH_3Cl methyl chloride (1, 21, 117, 168, 169, 171, 172, 625, 642)

(36) C_2Cl_6 CCl_3CCl_3 hexachloroethane (57, 162, 166, 170, 376)
(37) C_2HCl_5 $CHCl_2CCl_3$ pentachloroethane (72, 495, 496, 595)
(38) $C_2H_2Cl_4$ $CHCl_2CHCl_2$ 1,1,2,2-tetrachloroethane (68, 129, 162, 166, 221, 294, 435, 518, 519, 561, 595, 609, 610)

(39) $C_2H_3Cl_3$ $C_2H_3Cl_3$ trichloroethane (294, 561)
(40) $C_2H_3Cl_3$ CH_3CCl_3 1,1,1-trichloroethane (324, 350, 351)
(41) $C_2H_3Cl_3$ $CH_2ClCHCl_2$ 1,1,2-trichloroethane (324, 350, 351)
(42) $C_2H_4Cl_2$ CH_3CHCl_2 1,1-dichloroethane (129, 337, 350, 351, 449, 450, 495, 496)

(43) $C_2H_4Cl_2$ CH_2ClCH_2Cl 1,2-dichloroethane (57, 72, 126, 129, 162, 166, 320, 337, 449, 450, 451, 452, 495, 496, 606, 610)

(44) C_2H_5Cl C_2H_5Cl ethyl chloride (129, 162, 166, 174, 177, 297, 578, 642)

(45) $C_3H_6Cl_2$ $CH_3CH_2CHCl_2$ 1,1-dichloropropane (350, 351, 495, 496)

(46) $C_3H_6Cl_2$ $CH_3CHClCH_2Cl$ 1,2-dichloropropane (495, 496)
(47) $C_3H_6Cl_2$ $CH_2ClCH_2CH_2Cl$ 1,3-dichloropropane (495, 496)
(48) $C_3H_6Cl_2$ $CH_3CCl_2CH_3$ 2,2-dichloropropane (350, 351, 495, 496)
(49) C_3H_7Cl C_3H_7Cl propyl chloride (57, 162, 166, 297, 495, 496, 561, 578, 642)

(50) C_3H_7Cl $(CH_3)_2CHCl$ isopropyl chloride (2-chloropropane) (57, 185, 189, 297, 495, 496, 642)

(51) $C_4H_8Cl_2$ $CH_3CH_2CH_2CHCl_2$ 1,1-dichlorobutane (350, 351)

(52) $C_4H_8Cl_2$ $(CH_3)_2CHCHCl_2$ dichloroisobutane (1,1-dichloro-2-methylbutane) (350, 351)

(53) C_4H_9Cl C_4H_9Cl butyl chloride (174, 177, 297)

(54) C_4H_9Cl $(CH_3)_2CHCH_2Cl$ isobutyl chloride (1-chloro-2-methylpropane) (57, 297, 373)

(55) C_4H_9Cl $C_2H_5CHClCH_3$ sec-butyl chloride (2-chlorobutane) (186, 190, 297)

(56) C_4H_9Cl $(CH_3)_3CCl$ tert-butyl chloride (2-chloro-2-methylpropane) (162, 166, 185, 189, 297)

(57) $C_5H_{10}Cl_2$ $CH_3(CH_2)_3CHCl_2$ 1,1-dichloropentane (350, 351)

(58) $C_5H_{10}Cl_2$ $(CH_3)_2CHCH_2CHCl_2$ dichloroisopentane (1,1-dichloro-3-methylbutane) (350, 351)

(59) $C_5H_{11}Cl$ $C_5H_{11}Cl$ amyl chloride (186, 190, 297, 532)

(60) $C_5H_{11}Cl$ $(CH_3)_2CH(CH_2)_2Cl$ isoamyl chloride (1-chloro-3-methylbutane) (186, 190, 297)

(61) $C_5H_{11}Cl$ $C_2H_5CH(CH_3)CH_2Cl$ 1-chloro-2-methylbutane (350, 351)

(62) $C_5H_{11}Cl$ $(CH_3)_2C(Cl)C_2H_5$ 2-chloro-2-methylbutane (185, 189, 297, 456)

(63) $C_5H_{11}Cl$ $CH_3(CH_2)_2CHClCH_3$ 2-chloropentane (350, 351)

(64) $C_5H_{11}Cl$ $C_2H_5CHClC_2H_5$ 3-chloropentane (350, 351)

(65) $C_5H_{11}Cl$ $(CH_3)_3CCH_2Cl$ 1-chloro-2,2-dimethylpropane (533)

(66) $C_6H_{13}Cl$ $C_6H_{13}Cl$ hexyl chloride (346, 347)

(67) $C_7H_{15}Cl$ $C_7H_{15}Cl$ heptyl chloride (346, 347, 349)

(68) $C_8H_{17}Cl$ $C_8H_{17}Cl$ octyl chloride (346, 347)

(69) $C_9H_{19}Cl$ $C_9H_{19}Cl$ nonyl chloride (346, 347)

(70) $C_{10}H_{21}Cl$ $C_{10}H_{21}Cl$ decyl chloride (346, 347)

c. Bromine derivatives

(71) CBr_4 CBr_4 carbon tetrabromide (174, 177, 344, 397, 586)

(72) $CHBr_3$ $CHBr_3$ bromoform (34, 35, 57, 117, 162, 166, 172, 201, 242, 625)

(73) CH_2Br_2 CH_2Br_2 methylene bromide (117, 169, 172, 174, 177, 258, 400, 608)

(74) CH_3Br CH_3Br methyl bromide (1, 21, 117, 129, 168, 169, 171, 172, 625)

(75) C_2Br_6 CBr_3CBr_3 hexabromoethane (258)

(76) $C_2H_2Br_4$ $C_2H_2Br_4$ tetrabromoethane (129, 162, 166)

(77) $C_2H_2Br_4$ $CHBr_2CHBr_2$ 1,1,2,2-tetrabromoethane (258)

(78) $C_2H_4Br_2$ CH_3CHBr_2 1,1-dibromoethane (129, 258, 450, 451)

(79) $C_2H_4Br_2$ CH_2BrCH_2Br 1,2-dibromoethane (57, 126, 129, 162, 166, 449, 450, 452, 610)

(80) C_2H_5Br C_2H_5Br ethyl bromide (57, 129, 162, 166, 578)

(81) $C_3H_5Br_3$ $CH_2BrCHBrCH_2Br$ tribromohydrin (1,2,3-tribromopropane) (371)

(82) C_3H_7Br C_3H_7Br propyl bromide (57, 162, 166, 295, 578)

(83) C_3H_7Br $(CH_3)_2CHBr$ isopropyl bromide (2-bromopropane) (185, 189, 295)

(84) $C_3H_6Br_2$ $CH_2BrCHBrCH_3$ 1,2-dibromopropane (258)

(85) $C_3H_6Br_2$ $CH_2BrCH_2CH_2Br$ 1,3-dibromopropane (174, 177)

(86) C_4H_9Br C_4H_9Br butyl bromide (140, 163, 167, 295, 661)

(87) C_4H_9Br $(CH_3)_2CHCH_2Br$ isobutyl bromide (1-bromo-2-methyl-propane) (57, 295, 373)

(88) C_4H_9Br $CH_3CH_2CHBrCH_3$ sec-butyl bromide (2-bromobutane) (186, 190, 295)

(89) C_4H_9Br $(CH_3)_3CBr$ tert-butyl bromide (2-bromo-2-methylpropane) (185, 189, 295)

(90) $C_5H_{11}Br$ $C_5H_{11}Br$ amyl bromide (186, 190, 295)

(91) $C_5H_{11}Br$ $(CH_3)_2CHCH_2CH_2Br$ isoamyl bromide (1-bromo-3-methylbutane) (186, 190, 295)

(92) $C_5H_{11}Br$ $(CH_3)_2C(Br)C_2H_5$ 2-bromo-2-methylbutane (185, 189)

(93) $C_6H_{13}Br$ $C_6H_{13}Br$ hexyl bromide (140)

(94) $C_7H_{15}Br$ $C_7H_{15}Br$ heptyl bromide (349)

d. Iodine derivatives

(95) CH_2I_2 CH_2I_2 methylene iodide (169, 172, 400)

(96) CH_3I CH_3I methyl iodide (1, 21, 117, 129, 168, 171, 174, 177, 263, 625)

(97) $C_2H_4I_2$ CH_2ICH_2I 1,2-diiodoethane (126)

(98) C_2H_5I C_2H_5I ethyl iodide (129, 168, 171, 174, 177, 264)

(99) C_3H_7I C_3H_7I propyl iodide (174, 177, 264)

(100) C_3H_7I $(CH_3)_2CHI$ isopropyl iodide (2-iodopropane) (185, 189)

(101) C_4H_9I C_4H_9I butyl iodide (174, 177)

(102) C_4H_9I $(CH_3)_2CHCH_2I$ isobutyl iodide (1-iodo-2-methylpropane) (264, 373)

(103) C_4H_9I $C_2H_5CHICH_3$ sec-butyl iodide (2-iodobutane) (186, 190)

(104) C_4H_9I $(CH_3)_3CI$ tert-butyl iodide (2-iodo-2-methylpropane) (185, 189)

(105) $C_5H_{11}I$ $C_5H_{11}I$ amyl iodide (186, 190)

(106) $C_5H_{11}I$ $(CH_3)_2CHCH_2CH_2I$ isoamyl iodide (1-iodo-3-methylbutane) (186, 190)

(107) $C_5H_{11}I$ $C_2H_5C(CH_3)_2I$ tert-amyl iodide (2-iodo-2-methylbutane) (373)

(108) $C_6H_{13}I$ $C_6H_{13}I$ hexyl iodide (350, 351)

e. Mixed halogen derivatives

(109) CCl_2F_2 CCl_2F_2 dichlorodifluoromethane (107)

(110) CCl_3Br $CBrCl_3$ trichlorobromomethane (655)

(111) $CHBrCl_2$ $CHBrCl_2$ dichlorobromomethane (79, 350, 351)

(112) $CHCl_2F$ $CHCl_2F$ dichlorofluoromethane (107)

III. Alcohols

a. Monohydric alcohols

(113) CDH_3O CH_3OD methyl alcohol-d (539)

(114) CH_4O CH_3OH methyl alcohol (28, 108, 168, 170, 171, 194, 242, 248, 270, 291, 310, 330, 379, 427, 436, 452, 510, 513, 523, 539, 541, 542, 549, 561, 606, 625, 626, 629, 631, 645, 654, 661)

(115) C_2H_5ClO CH_2ClCH_2OH β-chloroethyl alcohol (320, 428)

(116) C_2H_6O C_2H_5OH ethyl alcohol (31, 63, 64, 108, 129, 162, 166, 168, 171, 192, 194, 242, 270, 291, 310, 323, 427, 475, 490, 546, 549, 561, 568, 597, 606, 626, 629, 654, 661, 666)

(117) C_3H_8O C_3H_7OH propyl alcohol (1-propanol) (156, 194, 242, 427, 602, 606, 626, 661)

(118) C_3H_8O $CH_3CHOHCH_3$ isopropyl alcohol (2-propanol) (185, 189, 194, 242, 427, 602)

(119) $C_4H_{10}O$ C_4H_9OH butyl alcohol (1-butanol) (156, 350, 351, 427, 471, 602, 606, 626, 661)

(120) $C_4H_{10}O$ $(CH_3)_2CHCH_2OH$ isobutyl alcohol (2-methyl-1-propanol) (242, 602, 626)

(121) $C_4H_{10}O$ $C_2H_5CHOHCH_3$ sec-butyl alcohol (2-butanol) (373, 471, 602)

(122) $C_4H_{10}O$ $(CH_3)_3COH$ tert-butyl alcohol (2-methyl-2-propanol) (185, 189, 427, 471, 602, 626)

(123) $C_5H_{12}O$ $C_5H_{11}OH$ amyl alcohol (1-pentanol) (31, 186, 190, 291, 471, 661)

(124) $C_5H_{12}O$ $(CH_3)_2CHCH_2CH_2OH$ isoamyl alcohol (3-methyl-1-pentanol) (31, 186, 190, 242, 291, 471, 629)

(125) $C_5H_{12}O$ $C_3H_7CHOHCH_3$ sec-amyl alcohol (2-pentanol) (346, 347, 471)

(126) $C_5H_{12}O$ $(CH_3)_2COHC_2H_5$ tert-amyl alcohol (2-methyl-2-butanol) (185, 189, 346, 347, 471)

(127) $C_5H_{12}O$ $(C_2H_5)_2CHOH$ diethylcarbinol (3-pentanol) (346, 347, 471, 533)

(128) $C_5H_{12}O$ $C_2H_5CH(CH_3)CH_2OH$ sec-butylcarbinol (2-methyl-1-butanol) (288, 346, 347)

(129) $C_5H_{12}O$ $(CH_3)_3CCH_2OH$ tert-butylcarbinol (2,2-dimethyl-1-propanol) (346, 347, 471)

(130) $C_5H_{12}O$ $(CH_3)_2CHCH(CH_3)OH$ methylisopropylcarbinol (3-methyl-2-butanol) (346, 347)

(131) $C_6H_{14}O$ $(C_2H_5)_2(CH_3)COH$ diethylmethylcarbinol (3-methyl-3-pentanol) (551)

(132) $C_6H_{14}O$ $C_6H_{13}OH$ 1-hexanol (31, 661)

(133) $C_7H_{16}O$ $C_7H_{15}OH$ 1-heptanol (31, 661)

(134) $C_8H_{18}O$ $C_7H_{15}CH_2OH$ 1-octanol (31, 133, 471, 661)

(135) $C_8H_{18}O$ $C_6H_{13}CHOHCH_3$ 2-octanol (133, 471)

(136) $C_8H_{18}O$ $C_5H_{11}CHOHC_2H_5$ 3-octanol (133)

(137) $C_8H_{18}O$ $C_4H_9CHOHC_3H_7$ 4-octanol (133)

(138) $C_8H_{18}O$ $(CH_3)_2CH(CH_2)_2C(CH_3)OHCH_3$ 2,5-dimethyl-2-hexanol (10)

(139) $C_8H_{18}O$ $(CH_3)_2CHCH_2C(CH_3)OHC_2H_5$ 3,5-dimethyl-3-hexanol (10)

(140) $C_8H_{18}O$ $C_5H_{11}C(CH_3)OHCH_2$ 2-methyl-2-heptanol (133)

(141) $C_8H_{18}O$ $C_4H_9C(CH_3)OHC_2H_5$ 3-methyl-3-heptanol (133)

(142) $C_8H_{18}O$ $C_3H_7C(CH_3)OHC_3H_7$ 4-methyl-4-heptanol (133)

(143) $C_8H_{18}O$ $C_5H_{11}CH(CH_3)CH_2OH$ 2-methyl-1-heptanol (133)

(144) $C_8H_{18}O$ $C_3H_7CHOHCH_2CH(CH_3)CH_3$ 2-methyl-4-heptanol (133)

(145) $C_8H_{18}O$ $C_4H_9CH(CH_3)CHOHCH_3$ 3-methyl-2-heptanol (133)

(146) $C_8H_{18}O$ $C_3H_7CH(CH_3)CH_2CH_2CH_2OH$ 4-methyl-1-heptanol (133)

(147) $C_8H_{18}O$ $C_3H_7CH(CH_3)CH_2CHOHCH_3$ 4-methyl-2-heptanol (133)

(148) $C_8H_{18}O$ $C_3H_7CH(CH_3)CHOHC_2H_5$ 4-methyl-3-heptanol (133)

(149) $C_8H_{18}O$ $C_2H_5CH(CH_3)(CH_2)_3CH_2OH$ 5-methyl-1-heptanol (133)

(150) $C_8H_{18}O$ $C_2H_5CH(CH_3)(CH_2)_2CHOHCH_3$ 5-methyl-2-heptanol (133)

(151) $C_8H_{18}O$ $C_2H_5CH(CH_3)CH_2CHOHC_2H_5$ 5-methyl-3-heptanol (133)

(152) $C_8H_{18}O$ $CH_3CH(CH_3)(CH_2)_4CH_2OH$ 6-methyl-1-heptanol (133)

(153) $C_8H_{18}O$ $CH_3CH(CH_3)(CH_2)_3CHOHCH_3$ 6-methyl-2-heptanol (133)

(154) $C_8H_{18}O$ $CH_3CH(CH_3)(CH_2)_2CHOHC_2H_5$ 6-methyl-3-heptanol (133)

(155) $C_9H_{20}O$ $(CH_3)_2CHCH_2CH(CH_3)CHOHC_2H_5$ 4,6-dimethyl-3-heptanol (10)

(156) $C_9H_{20}O$ $(CH_3)_2CH(CH_2)_2C(CH_3)OHC_2H_5$ 3,6-dimethyl-3-heptanol (10)

(157) $C_9H_{20}O$ $(CH_3)_2CHCH_2C(CH_3)OHCH(CH_3)_2$ 2,3,5-trimethyl-3-hexanol (10)

(158) $C_9H_{20}O$ $C_9H_{19}OH$ nonyl alcohol (1-nonanol) (31, 661)

(159) $C_{10}H_{22}O$ $C_{10}H_{21}OH$ decyl alcohol (1-decanol) (661)

(160) $C_{10}H_{22}O$ $(CH_3)_2CHCH_2C(CH_3)OHCH_2CH(CH_3)_2$ 2,4,6-trimethyl-4-heptanol (10)

(161) $C_{10}H_{22}O$ $C_4H_9C(CH_3)OHCH_2CH(CH_3)_2$ 2,4-dimethyl-4-octanol (10)

(162) $C_{11}H_{24}O$ $C_{11}H_{23}OH$ undecyl alcohol (hendecyl alcohol) (661)

(163) $C_{11}H_{24}O$ $(CH_3)_2CH(CH_2)_2C(CH_3)OHCH_2CH(CH_3)_2$ 2,4,7-trimethyl-4-octanol (10)

(164) $C_{12}H_{26}O$ $C_{12}H_{25}OH$ dodecyl alcohol (1-dodecanol) (661)

b. Polyhydric alcohols and sugars

(165) C_2H_5ClO CH_2OHCH_2Cl ethylenechlorohydrin (320, 428)

(166) $C_2H_6O_2$ CH_2OHCH_2OH ethylene glycol (320, 350, 351, 428, 456, 595, 645)

(167) $C_3H_8O_2$ $CH_3CHOHCH_2OH$ α-propylene glycol (1,2-propanediol) (456)

(168) $C_3H_8O_3$ $CH_2OHCHOHCH_2OH$ glycerin (glycerol) (26, 28, 29, 122, 242, 294, 319, 417, 428, 553, 598, 616, 617, 645)

(169) $C_5H_{10}O_4$ $CH_2OHCHOHCH_2OCOCH_3$ glycerol acetate (598)

(170) $C_6H_{12}O_6$ $CH_2OH(CHOH)_4CHO$ glucose (386)

(171) $C_6H_{12}O_6$ $CH_2OH(CHOH)_4CHO$ galactose (386)

(172) $C_6H_{12}O_6$ $CH_2OH(CHOH)_3COCH_2OH$ fructose (386)

(173) $C_{12}H_{22}O_{11}$ $C_{12}H_{22}O_{11}$ sucrose (386, 516, 645)

(174) $C_{12}H_{22}O_{11} \cdot H_2O$ $C_{12}H_{22}O_{11} \cdot H_2O$ maltose (386)

(175) $C_{18}H_{32}O_{16} \cdot 5H_2O$ $C_{18}H_{32}O_{16} \cdot 5H_2O$ raffinose (386)

IV. Ethers

(176) C_2H_4O $\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}\!\!\!\Big\rangle O$ ethylene oxide (266, 409, 410)

(177) C_2H_6O CH_3OCH_3 dimethyl ether (173, 176, 266, 569)

(178) C_3H_5BrO $BrCH_2C\underset{\diagdown\,O\,\diagup}{H}CH_2$ bromomethylethylene oxide (409, 410)

(179) C_3H_5ClO $ClCH_2C\underset{\diagdown\,O\,\diagup}{H}CH_2$ chloromethylethylene oxide (409, 410)

(180) $C_3H_6O_2$ $HOCH_2C\underset{\diagdown\,O\,\diagup}{H}CH_2$ hydroxymethylethylene oxide (409, 410)

(181) $C_3H_8O_2$ $CH_2OHCH_2OCH_3$ ethylene glycol monomethyl ether (320)

(182) C_4H_7ClO $CH_2ClC\underset{\diagdown\,O\,\diagup}{H}CHCH_3$ α-chloromethyl-β-methylethylene oxide (409)

(183) C_4H_8O $C_2H_5C\underset{\diagdown\,O\,\diagup}{H}CH_2$ ethylethylene oxide (409, 410)

(184) C_4H_8O $\begin{matrix} CH_3 \\ \\ CH_3 \end{matrix}\!\!\!\Big\rangle C\underset{\diagdown\,O\,\diagup}{\text{—}}CH_2$ α,α-dimethylethylene oxide (409, 410)

(185) C_4H_8O $CH_3C\underset{\diagdown\,O\,\diagup}{H}CHCH_3$ α,β-dimethylethylene oxide (409)

(186) $C_4H_{10}O$ $C_2H_5OC_2H_5$ diethyl ether (25, 162, 166, 168, 170, 171, 192, 194, 242, 294, 452, 523, 529, 530, 561, 569, 597, 654)

(187) $C_4H_{10}O_2$ $CH_2OHCH_2OC_2H_5$ ethylene glycol monoethyl ether (320)

(188) $C_5H_{12}O_2$ $CH_2OHCH_2OC_3H_7$ ethylene glycol monopropyl ether (320)

(189) $C_6H_{14}O$ $C_3H_7OC_3H_7$ dipropyl ether (316)

(190) $C_6H_{14}O$ $(CH_3)_2CHOCH(CH_3)_2$ diisopropyl ether (316)

(191) $C_{10}H_{22}O$ $(C_5H_{11})_2O$ diamyl ether (316)

(192) $C_{10}H_{22}O$ $[(CH_3)_2CHCH_2CH_2]_2O$ diisoamyl ether (316)

V. Carbonyl compounds

a. Aldehydes

(193) CH_2O CH_2O formaldehyde (309, 348, 376, 485, 596, 597, 606)

(194) $(CH_2O)_x$ $(CH_2O)_x$ paraformaldehyde (309)

(195) C_2H_4O CH_3CHO acetaldehyde (155, 161, 348, 500, 627, 668)

(196) C_3H_6O C_2H_5CHO propionaldehyde (155, 161, 162, 166, 348)

(197) C_4H_8O C_3H_7CHO butyraldehyde (348, 456)

(198) C_4H_8O $(CH_3)_2CHCHO$ isobutyraldehyde (348)

(199) $C_4H_8O_2$ $CH_3CHOHCH_2CHO$ aldol (310)

(200) $C_5H_{10}O$ C_4H_9CHO valeraldehyde (348)

(201) $C_5H_{10}O$ $(CH_3)_2CHCH_2CHO$ isovaleraldehyde (348)

(202) $C_5H_{10}O$ $C_2H_5(CH_3)CHCHO$ *sec*-valeraldehyde (α-methylbu-tyraldehyde) (348)

(203) $C_5H_{10}O$ $(CH_3)_3CCHO$ *tert*-valeraldehyde (pivalaldehyde) (348)

(204) $C_6H_{12}O$ $C_5H_{11}CHO$ caproaldehyde (348)

(205) $C_6H_{12}O$ $(CH_3)_2CHCH_2CH_2CHO$ isocaproaldehyde (348)

(206) $C_6H_{12}O$ $C_2H_5(CH_3)_2CCHO$ *tert*-caproaldehyde (α,α-dimethyl-butyraldehyde) (348)

(207) $C_6H_{12}O_3$ $(C_2H_4O)_3$ paraldehyde (434, 500, 627)

(208) $C_7H_{14}O$ $C_6H_{13}CHO$ heptanal (enanthaldehyde) (348, 414)

(209) $C_8H_{16}O$ $C_7H_{15}CHO$ octanal (caprylaldehyde) (348)

(210) $C_9H_{18}O$ $C_8H_{17}CHO$ nonanal (pelargonaldehyde) (348)

(211) $C_{10}H_{20}O$ $C_9H_{19}CHO$ decanal (capraldehyde) (348)

(212) $C_{11}H_{22}O$ $C_{10}H_{21}CHO$ undecanal (undecylaldehyde) (90)

(213) $C_{12}H_{24}O$ $C_{11}H_{23}CHO$ dodecanal (lauraldehyde) (90)

(214) $C_{12}H_{24}O$ $CH_3(CH_2)_8CH(CH_3)CHO$ α-methylundecanal (α-meth-ylundecylaldehyde) (90)

1. Halogen derivatives of aldehydes

(215) C_2HCl_3O CCl_3CHO chloral (125, 173, 176, 490, 500, 595)

(216) $C_2H_2Cl_2O$ Cl_2HCCHO dichloroacetaldehyde (125)

(217) $C_2H_3Cl_3O_2$ $CCl_3CHO \cdot H_2O$ chloral hydrate (490, 500)

b. Ketones

(218) C_3H_6O CH_3COCH_3 acetone (152, 158, 163, 167, 170, 194, 206, 242, 294, 348, 500, 541, 561, 568, 574, 596, 597, 606, 644, 645, 646)

(219) $C_4H_6O_2$ $CH_3COCOCH_3$ diacetyl (298, 358)

(220) C_4H_8O $CH_3COC_2H_5$ methyl ethyl ketone (153, 159, 242, 348, 561, 597, 644)

(221) $C_5H_8O_2$ $CH_3COCH_2COCH_3$ acetylacetone (298, 354, 359)

(222) $C_5H_{10}O$ $C_2H_5COC_2H_5$ diethyl ketone (242, 348, 597, 644)

(223) $C_5H_{10}O$ $CH_3COC_3H_7$ methyl propyl ketone (242, 348, 359)

(224) $C_5H_{10}O$ $CH_3COCH(CH_3)_2$ methyl isopropyl ketone (348)

(225) $C_6H_{10}O_2$ $CH_3CO(CH_2)_2COCH_3$ acetonylacetone (2,4-hexane-dione) (298, 354)

(226) $C_6H_{10}O_2$ $CH_3COCH(CH_3)COCH_3$ methylacetylacetone (359)

(227) $C_6H_{12}O$ $CH_3COC_4H_9$ methyl butyl ketone (348)

(228) $C_6H_{12}O$ $CH_3COCH_2CH(CH_3)_2$ methyl isobutyl ketone (348)

(229) $C_6H_{12}O$ $CH_3COCH(CH_3)C_2H_5$ methyl *sec*-butyl ketone (348, 359)

(230) $C_6H_{12}O$ $CH_3COC(CH_3)_3$ methyl *tert*-butyl ketone (348)

(231) $C_6H_{12}O$ $C_2H_5COC_3H_7$ ethyl propyl ketone (445)

(232) $C_6H_{12}O$ $C_2H_5COCH(CH_3)_2$ ethyl isopropyl ketone (445)

(233) $C_7H_{12}O_2$ $CH_3COC(CH_3)_2COCH_3$ dimethylacetylacetone (3,3-dimethyl-2,4-pentanedione) (358, 359)

(234) $C_7H_{14}O$ $C_3H_7COC_3H_7$ dipropyl ketone (348)

(235) $C_7H_{14}O$ $(CH_3)_2CHCOCH(CH_3)_2$ diisopropyl ketone (348)

(236) $C_7H_{14}O$ $CH_3COC_5H_{11}$ methyl amyl ketone (348)

(237) $C_7H_{14}O$ $CH_3COC(CH_3)_2C_2H_5$ methyl *tert*-amyl ketone (3,3-dimethyl-2-pentanone) (348, 359)

(238) $C_7H_{14}O$ $C_2H_5COC_4H_9$ ethyl butyl ketone (445)
(239) $C_7H_{14}O$ $C_2H_5COCH_2CH(CH_3)_2$ ethyl isobutyl ketone (445)
(240) $C_8H_{16}O$ $CH_3COC_6H_{13}$ methyl hexyl ketone (348)
(241) $C_8H_{16}O$ $C_2H_5COC_5H_{11}$ ethyl amyl ketone (445)
(242) $C_8H_{16}O$ $C_2H_5CO(CH_2)_2CH(CH_3)_2$ ethyl isoamyl ketone (445)
(243) $C_9H_{18}O$ $C_2H_5COC_6H_{13}$ ethyl hexyl ketone (445)
(244) $C_9H_{18}O$ $C_2H_5CO(CH_2)_3CH(CH_3)_2$ ethyl isohexyl ketone (445)
(245) $C_9H_{18}O$ $(CH_3)_2CHCH_2COCH_2CH(CH_3)_2$ diisobutyl   ketone (348)
(246) $C_{11}H_{22}O$ $CH_3COC_9H_{19}$ methyl nonyl ketone (348)
(247) $C_{18}H_{36}O$ $C_2H_5COC_{15}H_{31}$ ethyl pentadecyl ketone (445)

1. Halogen derivatives of ketones

(248) $C_3H_4Cl_2O$ $Cl_2HCCOCH_3$ 1,1-dichloroacetone (125)
(249) C_3H_5ClO ClH_2CCOCH_3 chloroacetone (125)

c. Acyl halides

(250) C_2Cl_4O Cl_3CCOCl trichloroacetyl chloride (125)
(251) C_2HCl_3O $Cl_2HCCOCl$ dichloroacetyl chloride (125)
(252) $C_2H_2Cl_2O$ $CH_2ClCOCl$ chloroacetyl chloride (125, 173, 176)
(253) C_2H_3BrO CH_3COBr acetyl bromide (168, 171, 366)
(254) C_2H_3ClO CH_3COCl acetyl chloride (168, 171, 357, 592)
(255) C_3H_5BrO C_2H_5COBr propionyl bromide (366)
(256) C_3H_5ClO CH_3CH_2COCl propionyl chloride (357)
(257) C_4H_7ClO $CH_3(CH_2)_2COCl$ butyryl chloride (357)
(258) C_4H_7ClO $(CH_3)_2CHCOCl$ isobutyryl chloride (357)
(259) C_5H_9ClO $CH_3(CH_2)_3COCl$ valeryl chloride (357)
(260) C_5H_9ClO $(CH_3)_2CHCH_2COCl$ isovaleryl chloride (357)
(261) C_5H_9ClO $CH_3CH_2CH(CH_3)COCl$ α-methylbutyryl   chloride (357)
(262) C_5H_9ClO $(CH_3)_3CCOCl$ pivalyl chloride (357)
(263) $C_6H_{11}ClO$ $CH_3(CH_2)_4COCl$ caproyl chloride (357)
(264) $C_6H_{11}ClO$ $(CH_3)_2CH(CH_2)_2COCl$ isocaproyl chloride (357)
(265) $C_6H_{11}ClO$ $C_2H_5C(CH_3)_2COCl$ α,α-dimethylbutyryl   chloride (357)
(266) $C_7H_{10}Cl_2O_2$ $(C_2H_5)_2C(COCl)_2$ diethylmalonyl chloride (358)

VI. Monocarboxylic acids and their derivatives

a. Monocarboxylic acids

(267) $C_2D_4O_2$ CD_3COOD acetic acid-d_4 (19)

(268) CH_2O_2 $HCOOH$ formic acid (28, 48, 152, 158, 168, 171, 242, 294, 352, 428, 489, 535, 625)

(269) $C_2H_4O_2$ CH_3COOH acetic acid (19, 33, 152, 157, 158, 168, 170, 171, 194, 221, 237, 242, 248, 294, 330, 352, 378, 379, 380, 403, 490, 535, 546, 547, 548, 561, 597, 618, 645, 663)

(270) $C_3H_6O_2$ C_2H_5COOH propionic acid (152, 156, 158, 242, 352, 597, 618)

(271) $C_4H_8O_2$ C_3H_7COOH butyric acid (152, 156, 158, 242, 352, 618)

(272) $C_4H_8O_2$ $(CH_3)_2CHCOOH$ isobutyric acid (352, 373, 672)
(273) $C_5H_{10}O_2$ C_4H_9COOH valeric acid (352, 597)
(274) $C_5H_{10}O_2$ $(CH_3)_2CHCH_2COOH$ isovaleric acid (352, 597)
(275) $C_5H_{10}O_2$ $(CH_3)_3CCOOH$ pivalic acid (α,α-dimethylpropionic acid) (352)
(276) $C_5H_{10}O_2$ $C_2H_5CH(CH_3)COOH$ α-methylbutyric acid (352)
(277) $C_6H_{12}O_2$ $C_5H_{11}COOH$ caproic acid (352)
(278) $C_6H_{12}O_2$ $(CH_3)_2CHCH_2CH_2COOH$ isocaproic acid (352)
(279) $C_6H_{12}O_2$ $C_2H_5C(CH_3)_2COOH$ α,α-dimethylbutyric acid (352)
(280) $C_7H_{14}O_2$ $C_6H_{13}COOH$ enanthic acid (352)
(281) $C_8H_{16}O_2$ $C_7H_{15}COOH$ caprylic acid (352)
(282) $C_9H_{18}O_2$ $C_8H_{17}COOH$ pelargonic acid (352)
(283) $C_{10}H_{20}O_2$ $C_9H_{19}COOH$ capric acid (352)

b. Halogen derivatives of monocarboxylic acids

(284) $C_2HCl_3O_2$ CCl_3COOH trichloroacetic acid (248, 352, 490, 592, 664)
(285) $C_2H_2Cl_2O_2$ $CHCl_2COOH$ dichloroacetic acid (352, 456, 592, 664)
(286) $C_2H_3BrO_2$ $CH_2BrCOOH$ bromoacetic acid (124)
(287) $C_2H_3ClO_2$ $CH_2ClCOOH$ chloroacetic acid (248, 352, 490, 592, 664)

c. Ketonic derivatives of monocarboxylic acids

(288) $C_3H_4O_3$ $CH_3COCOOH$ pyruvic acid (168, 171, 354)

d. Anhydrides of monocarboxylic acids

(289) $C_4H_6O_3$ $(CH_3CO)_2O$ acetic anhydride (369, 490, 592)
(290) $C_6H_{10}O_3$ $(C_2H_5CO)_2O$ propionic anhydride (369)
(291) $C_8H_{14}O_3$ $(C_3H_7CO)_2O$ butyric anhydride (369)
(292) $C_8H_{14}O_3$ $[(CH_3)_2CHCO]_2O$ isobutyric anhydride (369)
(293) $C_{10}H_{18}O_3$ $[(CH_3)_2CHCH_2O]_2O$ isovaleric anhydride (369)
(294) $C_{12}H_{22}O_3$ $(C_5H_{11}CO)_2O$ caproic anhydride (369)

e. Esters of monocarboxylic acids

1. Esters

(295) $C_2H_4O_2$ $HCOOCH_3$ methyl formate (168, 171, 353, 488, 605)
(296) $C_3H_6O_2$ $HCOOC_2H_5$ ethyl formate (152, 156, 158, 248, 353, 485, 488)
(297) $C_3H_6O_2$ CH_3COOCH_3 methyl acetate (124, 152, 156, 158, 170, 194, 353, 488, 597, 605)
(298) $C_4H_8O_2$ $CH_3COOC_2H_5$ ethyl acetate (124, 152, 156, 158, 165, 194, 248, 353, 488, 490, 561, 597)
(299) $C_4H_8O_2$ $C_2H_5COOCH_3$ methyl propionate (316, 353, 488, 597, 605)
(300) $C_4H_8O_2$ $HCOOC_3H_7$ propyl formate (357, 488, 605)
(301) $C_4H_8O_2$ $HCOOCH(CH_3)_2$ isopropyl formate (357)
(302) $C_5H_{10}O_2$ $CH_3COOC_3H_7$ propyl acetate (124, 194, 488, 597)
(303) $C_5H_{10}O_2$ $CH_3COOCH(CH_3)_2$ isopropyl acetate (124)
(304) $C_5H_{10}O_2$ $C_2H_5COOC_2H_5$ ethyl propionate (152, 158, 353, 488, 561, 597, 605)

(305) $C_5H_{10}O_2$ $HCOOC_4H_9$ butyl formate (357, 456, 488)

(306) $C_5H_{10}O_2$ $HCOOCH_2CH(CH_3)_2$ isobutyl formate (357, 605)

(307) $C_5H_{10}O_2$ $C_3H_7COOCH_3$ methyl butyrate (353, 488)

(308) $C_5H_{10}O_2$ $HCOOCH(CH_3)C_2H_5$ *sec*-butyl formate (357)

(309) $C_5H_{10}O_2$ $(CH_3)_2CHCOOCH_3$ methyl isobutyrate (353)

(310) $C_6H_{12}O_2$ $C_2H_5COOC_3H_7$ propyl propionate (316, 456)

(311) $C_6H_{12}O_2$ $C_2H_5COOCH(CH_3)_2$ isopropyl propionate (316)

(312) $C_6H_{12}O_2$ $CH_3COOC_4H_9$ butyl acetate (124, 456, 488, 597, 605)

(313) $C_6H_{12}O_2$ $CH_3COOCH_2CH(CH_3)_2$ isobutyl acetate (124, 605)

(314) $C_6H_{12}O_2$ $C_3H_7COOC_2H_5$ ethyl butyrate (152, 158, 353, 488, 561)

(315) $C_6H_{12}O_2$ $(CH_3)_2CHCOOC_2H_5$ ethyl isobutyrate (353)

(316) $C_6H_{12}O_2$ $CH_3COOCH(CH_3)C_2H_5$ *sec*-butyl acetate (124)

(317) $C_6H_{12}O_2$ $HCOO(CH_2)_2CH(CH_3)_2$ isoamyl formate (168, 171, 357, 488, 597)

(318) $C_6H_{12}O_2$ $C_4H_9COOCH_3$ methyl valerate (353)

(319) $C_6H_{12}O_2$ $(CH_3)_2CHCH_2COOCH_3$ methyl isovalerate (353)

(320) $C_6H_{12}O_2$ $C_2H_5CH(CH_3)COOCH_3$ methyl α-methylbutyrate (353)

(321) $C_6H_{12}O_2$ $HCOOC_5H_{11}$ amyl formate (357)

(322) $C_6H_{12}O_2$ $(CH_3)_3CCOOCH_3$ methyl pivalate (353)

(323) $C_7H_{14}O_2$ $CH_3COOC_5H_{11}$ amyl acetate (124)

(324) $C_7H_{14}O_2$ $CH_3COO(CH_2)_2CH(CH_3)_2$ isoamyl acetate (124, 152, 158, 488)

(325) $C_7H_{14}O_2$ $C_2H_5COOC_4H_9$ butyl propionate (316)

(326) $C_7H_{14}O_2$ $C_2H_5COOCH_2CH(CH_3)_2$ isobutyl propionate (316)

(327) $C_7H_{14}O_2$ $C_4H_9COOC_2H_5$ ethyl valerate (353)

(328) $C_7H_{14}O_2$ $(CH_3)_2CHCH_2COOC_2H_5$ ethyl isovalerate (353)

(329) $C_7H_{14}O_2$ $C_2H_5CH(CH_3)COOC_2H_5$ ethyl α-methylbutyrate (353)

(330) $C_7H_{14}O_2$ $(CH_3)_3CCOOC_2H_5$ ethyl pivalate (353)

(331) $C_7H_{14}O_2$ $C_5H_{11}COOCH_3$ methyl caproate (353)

(332) $C_7H_{14}O_2$ $(CH_3)_2CH(CH_2)_2COOCH_3$ methyl isocaproate (353)

(333) $C_7H_{14}O_2$ $C_2H_5C(CH_3)(CH_3)COOCH_3$ methyl α,α-dimethylbutyrate (353)

(334) $C_8H_{16}O_2$ $C_2H_5COOC_5H_{11}$ amyl propionate (316)

(335) $C_8H_{16}O_2$ $C_2H_5COO(CH_2)_2CH(CH_3)_2$ isoamyl propionate (316, 456, 605)

(336) $C_8H_{16}O_2$ $C_5H_{11}COOC_2H_5$ ethyl caproate (353)

(337) $C_8H_{16}O_2$ $(CH_3)_2CH(CH_2)_2COOC_2H_5$ ethyl isocaproate (353)

(338) $C_8H_{16}O_2$ $C_2H_5C(CH_3)(CH_3)COOC_2H_5$ ethyl α,α-dimethyl-butyrate (353)

(339) $C_8H_{16}O_2$ $C_6H_{13}COOCH_3$ methyl enanthate (353)

(340) $C_9H_{18}O_2$ $C_6H_{13}COOC_2H_5$ ethyl enanthate (353)

(341) $C_9H_{18}O_2$ $C_7H_{15}COOCH_3$ methyl caprylate (353)

(342) $C_{10}H_{20}O_2$ $C_7H_{15}COOC_2H_5$ ethyl caprylate (353)

(343) $C_{10}H_{20}O_2$ $C_8H_{17}COOCH_3$ methyl pelargonate (353)

(344) $C_{11}H_{22}O_2$ $C_9H_{19}COOCH_3$ methyl caprate (353)

2. Halogen derivatives of esters

(345) $C_2H_3ClO_2$ $ClCOOCH_3$ methyl *chloroformate* (357)

(346) $C_3H_3Cl_3O_2$ $Cl_3CCOOCH_3$ methyl trichloroacetate (124)

(347) $C_3H_4Cl_2O_2$ $CHCl_2COOCH_3$ methyl dichloroacetate (124)
(348) $C_3H_5BrO_2$ $CH_2BrCOOCH_3$ methyl bromoacetate (124, 631)
(349) $C_3H_5ClO_2$ $ClCOOC_2H_5$ ethyl chloroformate (173, 176, 357)
(350) $C_3H_5ClO_2$ $CH_2ClCOOCH_3$ methyl chloroacetate (124)
(351) $C_4H_5Cl_3O_2$ $CCl_3COOC_2H_5$ ethyl trichloroacetate (124)
(352) $C_4H_6Cl_2O_2$ $CHCl_2COOC_2H_5$ ethyl dichloroacetate (124)
(353) $C_4H_7BrO_2$ $CH_2BrCOOC_2H_5$ ethyl bromoacetate (124)
(354) $C_4H_7ClO_2$ $CH_2ClCOOC_2H_5$ ethyl chloroacetate (124, 456, 485)
(355) $C_4H_7ClO_2$ $ClCOOC_3H_7$ propyl chloroformate (357)
(356) $C_5H_7Cl_3O_2$ $CCl_3COOC_3H_7$ propyl trichloroacetate (124)
(357) $C_5H_7Cl_3O_2$ $CCl_3COOCH(CH_3)_2$ isopropyl trichloroacetate (124)
(358) $C_5H_8Cl_2O_2$ $CHCl_2COOC_3H_7$ propyl dichloroacetate (124)
(359) $C_5H_8Cl_2O_2$ $CHCl_2COOCH(CH_3)_2$ isopropyl dichloroacetate (124)
(360) $C_5H_9BrO_2$ $CH_2BrCOOC_3H_7$ propyl bromoacetate (124)
(361) $C_5H_9BrO_2$ $CH_2BrCOOCH(CH_3)_2$ isopropyl bromoacetate (124)
(362) $C_5H_9ClO_2$ $CH_2ClCOOC_3H_7$ propyl chloroacetate (124)
(363) $C_5H_9ClO_2$ $CH_2ClCOOCH(CH_3)_2$ isopropyl chloroacetate (124)
(364) $C_5H_9ClO_2$ $ClCOOCH_2CH(CH_3)_2$ isobutyl chloroformate (357)
(365) $C_6H_9Cl_3O_2$ $CCl_3COOC_4H_9$ butyl trichloroacetate (124)
(366) $C_6H_{10}Cl_2O_2$ $CHCl_2COOC_4H_9$ butyl dichloroacetate (124)
(367) $C_6H_{11}BrO_2$ $CH_2BrCOOC_4H_9$ butyl bromoacetate (124)
(368) $C_6H_{11}ClO_2$ $ClCOOCH_2CH_2CH(CH_3)_2$ isoamyl   chloroformate (357)
(369) $C_6H_{11}ClO_2$ $CH_2ClCOOC_4H_9$ butyl chloroacetate (124)
(370) $C_7H_{11}Cl_3O_2$ $CCl_3COOC_5H_{11}$ amyl trichloroacetate (124)
(371) $C_7H_{12}Cl_2O_2$ $CHCl_2COOC_5H_{11}$ amyl dichloroacetate (124)
(372) $C_7H_{13}ClO_2$ $CH_2ClCOOC_5H_{11}$ amyl chloroacetate (124)

3. Ketonic derivatives of esters

(373) $C_4H_6O_3$ $CH_3COCOOCH_3$ methyl pyruvate (358)
(374) $C_5H_8O_3$ $CH_3COCH_2COOCH_3$ methyl acetoacetate (358, 444)
(375) $C_5H_8O_3$ $CH_3COCOOC_2H_5$ ethyl pyruvate (358, 366)
(376) $C_6H_{10}O_3$ $CH_3COCH(CH_3)COOCH_3$ methyl α-methylacetoacetate (444)
(377) $C_6H_{10}O_3$ $CH_3COCH_2COOC_2H_5$ ethyl acetoacetate (keto) (165, 358, 485)
(378) $C_6H_{10}O_3$ $CH_3C(OH)=CHCOOC_2H_5$ ethyl acetoacetate (enol) (165, 485)
(379) $C_6H_{10}O_3$ $CH_3CO(CH_2)_2COOCH_3$ methyl levulinate (354)
(380) $C_7H_{12}O_3$ $CH_3COCH(CH_3)COOC_2H_5$ ethyl α-methylacetoacetate (358, 444)
(381) $C_7H_{12}O_3$ $CH_3CO(CH_2)_2COOC_2H_5$ ethyl levulinate (354)
(382) $C_7H_{12}O_3$ $CH_3COCH(C_2H_5)COOCH_3$ methyl α-ethylacetoacetate (444)
(383) $C_7H_{12}O_3$ $CH_3COC(CH_3)_2COOCH_3$ methyl α,α-dimethylacetoacetate (354, 358)
(384) $C_8H_{14}O_3$ $CH_3COCH(C_2H_5)COOC_2H_5$ ethyl α-ethylacetoacetate (444)
(385) $C_8H_{14}O_3$ $CH_3COC(CH_3)_2COOC_2H_5$ ethyl α,α-dimethylacetoacetate (358)

(386) $C_9H_{16}O_3$ $CH_3COCH(CH_2CH(CH_3)_2)COOCH_3$ methyl α-iso-amylacetoacetate (444)

(387) $C_{10}H_{18}O_3$ $CH_3COCH(C_4H_9)COOC_2H_5$ ethyl α-butylacetoace-tate (444)

(388) $C_{11}H_{20}O_3$ $CH_3COCH(CH_2CH_2CH(CH_3)_2)COOC_2H_5$ ethyl α-iso-amylacetoacetate (444)

f. Salts of monocarboxylic acids

(389) $CHNaO_2$ HCOONa   sodium formate (248)

(390) $C_2Cl_3NaO_2$ CCl_3COONa sodium trichloroacetate (248)

(391) $C_2H_2ClNaO_2$ $CH_2ClCOONa$ sodium chloroacetate (248)

(392) C_2H_3NaO CH_3COONa sodium acetate (162, 166, 248)

(393) $C_2H_7NO_2$ CH_3COONH_4 ammonium acetate (162, 166, 192, 376)

(394) $C_4H_6CdO_4$ $(CH_3COO)_2Cd$ cadmium acetate (376)

(395) $C_4H_6O_4Pb$ $(CH_3COO)_2Pb$ lead acetate (376)

(396) $C_4H_6O_4Zn$ $(CH_3COO)_2Zn$ zinc acetate (163, 167, 376)

VII. Dicarboxylic acids and their derivatives

a. Dicarboxylic acids

(397) $C_2H_2O_4$ $(COOH)_2$ oxalic acid (313, 376, 536)

(398) $C_3H_4O_4$ $CH_2(COOH)_2$ malonic acid (248)

(399) $C_4H_6O_6$ $HOOC(CHOH)_2COOH$ tartaric acid (502)

(400) $C_6H_8O_7$ $HOOCC(OH)(CH_2COOH)_2$ citric acid (476)

b. Anhydrides of dicarboxylic acids

(401) $C_4H_4O_3$

$$\begin{array}{c} O \\ \parallel \\ H_2C-C \\ | \quad\quad >O \\ H_2C-C \\ \backslash\backslash \\ O \end{array}$$ succinic anhydride (369)

(402) $C_5H_6O_3$

$$\begin{array}{c} O \\ \parallel \\ CH_3-CH-C \\ | \quad\quad >O \\ CH_2-C \\ \backslash\backslash \\ O \end{array}$$ methylsuccinic anhydride (369)
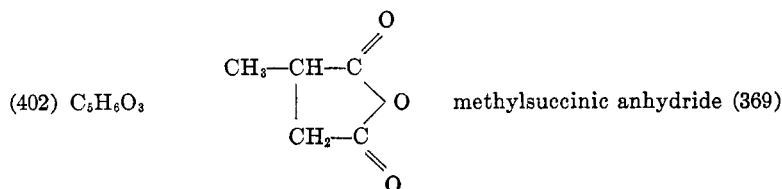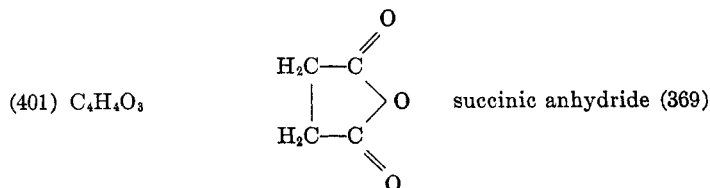
c. Esters of dicarboxylic acids

(403) $C_3H_6O_3$ $(CH_3O)_2CO$ dimethyl carbonate (168, 171, 354)

(404) $C_4H_6O_4$ $CH_3OOCCOOCH_3$ dimethyl oxalate (354)

(405) $C_5H_8O_4$ $CH_3OOCCH_2COOCH_3$ dimethyl malonate (369)

(406) $C_5H_{10}O_3$ $(C_2H_5O)_2CO$ diethyl carbonate (168, 171, 354)

(407) $C_6H_{10}O_4$ $C_2H_5OOCCOOC_2H_5$ diethyl oxalate (163, 167, 354, 592)

(408) $C_6H_{10}O_4$ $CH_3OOC(CH_2)_2COOCH_3$ dimethyl succinate (354)

(409) $C_7H_{10}O_5$ $(CH_3OOCCH_2)_2CO$ dimethyl   acetonedicarboxylate (358)

(410) $C_7H_{12}O_4$ $C_2H_5OOCCH_2COOC_2H_5$ diethyl malonate (163, 167, 248, 369, 485)

(411) $C_8H_{14}O_4$ $C_2H_5OOC(CH_2)_2COOC_2H_5$ diethyl succinate (163, 167, 354)

(412) $C_8H_{14}O_4$ $C_2H_5OOCCH(CH_3)COOC_2H_5$ diethyl methylmalonate (358)

(413) $C_8H_{14}O_4$ $C_2H_5OOC(CHOH)_2COOC_2H_5$ ethyl tartrate (502)

(414) $C_9H_{14}O_6$ $CH_3OOCCH_2CH(COOCH_3)CH_2COOCH_3$ trimethyl tricarballylate (354)

(415) $C_9H_{16}O_4$ $C_2H_5OOCC(CH_3)(CH_3)COOC_2H_5$ diethyl dimethylmalonate (358)

(416) $C_{10}H_{16}O_6$ $HC(COOC_2H_5)_3$ triethyl methanetricarboxylate (354)

(417) $C_{12}H_{18}O_6$
$$CH_3COCHCOOC_2H_5 \atop \overset{|}{CH_3COCHCOOC_2H_5}$$
diethyl diacetylsuccinate (358)

(418) $C_{13}H_{20}O_8$ $C(COOC_2H_5)_4$ tetraethyl methanetetracarboxylate (354)

d. Salts of dicarboxylic acids

(419) $C_3H_2O_4Na_2$ $NaOOCCH_2COONa$ sodium malonate (248)

(420) $C_4H_4Cs_2O_6$ $CsOOC(CHOH)_2COOCs$ cesium tartrate (502)

(421) $C_4H_4KNaO_6 \cdot 4H_2O$ $KOOC(CHOH)_2COONa$ Rochelle salt (potassium sodium tartrate) (393, 476)

(422) $C_4H_4K_2O_6$ $KOOC(CHOH)_2COOK$ potassium tartrate (502)

(423) $C_4H_4Li_2O_6$ $LiOOC(CHOH)_2COOLi$ lithium tartrate (502)

(424) $C_4H_4Na_2O_6$ $NaOOC(CHOH)_2COONa$ sodium tartrate (502)

(425) $C_4H_4O_6Rb_2$ $RbOOC(CHOH)_2COORb$ rubidium tartrate (502)

(426) $C_4H_{12}N_2O_6$ $NH_4OOC(CHOH)_2COONH_4$ ammonium tartrate (502)

VIII. Cyano compounds

a. Cyano derivatives of hydrocarbons (nitriles)

(427) CHN HCN hydrogen cyanide (44, 144, 145, 148, 165, 330, 400, 625)

(428) C_2N_2 $(CN)_2$ cyanogen (501)

(429) C_2H_3N CH_3CN acetonitrile (145, 148, 163, 167, 320, 400, 485, 498, 668)

(430) C_3H_5N C_2H_5CN propionitrile (169, 172, 320)

(431) $C_4H_4N_2$ CH_2CNCH_2CN succinonitrile (145, 148)

(432) C_4H_7N C_3H_7CN butyronitrile (145, 148, 320)

(433) C_5H_9N C_4H_9CN valeronitrile (145, 148)

(434) C_5H_9N $(CH_3)_2CHCH_2CN$ isovaleronitrile (145, 148)

(435) $C_6H_{11}N$ $(CH_3)_2CHCH_2CH_2CN$ isocapronitrile (145, 148)

b. Cyano derivatives of halogen-substituted hydrocarbons

(436) C_2Cl_3N Cl_3CCN trichloroacetonitrile (125)

(437) C_2HCl_2N Cl_2HCCN dichloroacetonitrile (125)

(438) C_2H_2ClN ClH_2CCN chloroacetonitrile (125)

c. Cyano derivatives of acids

(439) $C_3H_3O_2N$ $CH_2CNCOOH$ cyanoacetic acid (145, 148)

d. Cyano derivatives of esters

(440) $C_4H_5O_2N$ $CH_2CNCOOCH_3$ methyl cyanoacetate (500)

(441) $C_5H_7O_2N$ $CH_2CNCOOC_2H_5$ ethyl cyanoacetate (162, 166)

e. Isocyanides

(442) C_2H_3N CH_3NC methyl isocyanide (145, 148, 400)

(443) C_3H_5N C_2H_5NC ethyl isocyanide (145, 148)

f. Thiocyanates

(444) C_2H_3NS CH_3SCN methyl thiocyanate (501)

(445) C_3H_5NS C_2H_5SCN ethyl thiocyanate (145, 148)

g. Isothiocyanates

(446) C_3H_5NS C_2H_5NCS ethyl isothiocyanate (145, 148)

(447) C_5H_9NS $(CH_3)_2CHCH_2NCS$ isobutyl isothiocyanate (145, 148)

h. Isocyanates

(448) C_2H_3NO CH_3NCO methyl isocyanate (371)

(449) C_3H_5NO C_2H_5NCO ethyl isocyanate (336, 371)

(450) C_4H_7NO $(CH_3)_2CHNCO$ isopropyl isocyanate (336, 371)

IX. Sulfur compounds

a. Mercaptans

(451) CH_4S CH_3SH methyl mercaptan (620, 625)

(452) C_2H_6S C_2H_5SH ethyl mercaptan (620)

(453) C_3H_8S C_3H_7SH propyl mercaptan (620)

(454) C_3H_8S $(CH_3)_2CHSH$ isopropyl mercaptan (185, 189)

(455) $C_4H_{10}S$ C_4H_9SH butyl mercaptan (620)

(456) $C_4H_{10}S$ $(CH_3)_2CHCH_2SH$ isobutyl mercaptan (373, 620)

(457) $C_4H_{10}S$ $C_2H_5CH(CH_3)SH$ *sec*-butyl mercaptan (346, 347)

(458) $C_4H_{10}S$ $(CH_3)_3CSH$ *tert*-butyl mercaptan (346, 347)

(459) $C_5H_{12}S$ $CH_3(CH_2)_4SH$ amyl mercaptan (140, 186, 190)

(460) $C_5H_{12}S$ $(CH_3)_2CHCH_2CH_2SH$ isoamyl mercaptan (186, 190, 593, 620)

(461) $C_5H_{12}S$ $(CH_3)_2C(SH)C_2H_5$ *tert*-amyl mercaptan (346, 347)

(462) $C_6H_{14}S$ $CH_3(CH_2)_5SH$ hexyl mercaptan (140)

(463) $C_7H_{16}S$ $CH_3(CH_2)_6SH$ heptyl mercaptan (140)

b. Thioethers

(464) C_2H_6S CH_3SCH_3 dimethyl sulfide (419, 437, 623)

(465) $C_2H_6S_2$ CH_3SSCH_3 dimethyl disulfide (90, 437, 623)

(466) $C_2H_6S_3$ CH_3SSSCH_3 dimethyl trisulfide (90, 268)

(467) C_3H_8S $CH_3SC_2H_5$ methyl ethyl sulfide (419, 437)

(468) $C_4H_{10}S$ $C_2H_5SC_2H_5$ diethyl sulfide (419, 437, 591, 593, 623)

(469) $C_4H_{10}S_2$ $C_2H_5SSC_2H_5$ diethyl disulfide (90, 437, 623)

(470) $C_4H_{10}S_3$ $C_2H_5SSSC_2H_5$ diethyl trisulfide (90, 268)

(471) $C_4H_{10}S_4$ $C_2H_5SSSSC_2H_5$ diethyl tetrasulfide (90)

(472) $C_6H_{14}S$ $C_3H_7SC_3H_7$ dipropyl sulfide (593, 623)

(473) $C_8H_{18}S$ $C_4H_9SC_4H_9$ dibutyl sulfide (623)

(474) $C_8H_{18}S$ $[(CH_3)_2CHCH_2]_2S$ diisobutyl sulfide (593, 623)

c. Esters of sulfurous acid

(475) $C_2H_6O_2S$ $(CH_3O)_2SO$ dimethyl sulfite (419, 437)
(476) $C_4H_{10}O_3S$ $(C_2H_5O)_2SO$ diethyl sulfite (419, 437, 475)

d. Thio acids

(477) C_2H_4OS CH_3COSH thioacetic acid (366, 593)
(478) $C_2H_4O_2S$ $CH_2OHCOSH$ thioglycolic acid (593)
(479) C_3H_6OS C_2H_5COSH thiopropionic acid (366)

X. *Nitrogen compounds*

a. Amines, amides, imides, and oximes

1. Amines

(480) CH_5N CH_3NH_2 methylamine (116, 117, 168, 171, 626)
(481) C_2H_7N $C_2H_5NH_2$ ethylamine (168, 171, 626)
(482) C_2H_7N $(CH_3)_2NH$ dimethylamine (169, 172, 173, 176)
(483) $C_2H_8N_2$ $NH_2CH_2CH_2NH_2$ ethylenediamine (173, 176, 350, 351)
(484) C_3H_9N $(CH_3)_3N$ trimethylamine (173, 176)
(485) C_3H_9N $C_3H_7NH_2$ propylamine (173, 176)
(486) C_3H_9N $(CH_3)_2CHNH_2$ isopropylamine (185, 189)
(487) $C_4H_{11}N$ $(CH_3)_2CHCH_2NH_2$ isobutylamine (373)
(488) $C_4H_{11}N$ $(C_2H_5)_2NH$ diethylamine (173, 176)
(489) $C_4H_{11}N$ $C_4H_9NH_2$ butylamine (32, 350, 351)
(490) $C_4H_{11}N$ $C_2H_5CH(CH_3)NH_2$ *sec*-butylamine (32, 346, 347)
(491) $C_5H_{13}N$ $CH_3(CH_2)_4NH_2$ amylamine (186, 190)
(492) $C_5H_{13}N$ $(CH_3)_2CH(CH_2)_2NH_2$ isoamylamine (186, 190)
(493) $C_6H_{15}N$ $(C_2H_5)_3N$ triethylamine (173, 176, 358, 359, 626)
(494) $C_7H_{17}N$ $C_7H_{15}NH_2$ heptylamine (32)
(495) NH_3O NH_2OH hydroxylamine (428)
(496) N_2H_4 NH_2NH_2 hydrazine (325, 326, 582)
(497) N_2H_6O $NH_2NH_2 \cdot H_2O$ hydrazine hydrate (326, 485, 582)

2. Amides

(498) CH_2ClNO $ClCONH_2$ chloroformamide (366)
(499) CH_3NO $HCONH_2$ formamide (162, 166, 173, 176, 366, 594)
(500) CH_4N_2O NH_2CONH_2 urea (366, 376, 485, 594)
(501) CH_5ClN_2O $NH_2CONH_2 \cdot HCl$ urea hydrochloride (377)
(502) $C_2H_4N_4$ $NH_2C(=NH)NHCN$ dicyanodiamide (173, 176)
(503) C_2H_5NO CH_3CONH_2 acetamide (162, 166, 366, 594)
(504) $C_3H_5NO_2$ $CH_3COCONH_2$ pyruvamide (366)
(505) C_3H_7NO $C_2H_5CONH_2$ propionamide (366)
(506) $C_3H_7NO_2$ $C_2H_5OCONH_2$ ethyl urethan (366)
(507) $C_4H_9NO_2$ $C_3H_7OCONH_2$ propyl urethan (366)

3. Imides

(508) $C_4H_5NO_2$

succinimide (369)

4. Oximes

(509) C_4H_9NO $CH_3C(=NOH)C_2H_5$ ethyl methyl ketoxime (87, 88)

(510) $C_5H_{11}NO$ $CH_3C(=NOCH_3)C_2H_5$ ethyl methyl ketoxime O-methyl ether (87, 88)

(511) $C_5H_{11}NO$ $CH_3C(=NOH)C_3H_7$ methyl propyl ketoxime (87, 88)

(512) $C_6H_{13}NO$ $CH_3C(=NOH)C_4H_9$ methyl butyl ketoxime (87, 88)

b. Nitro compounds

(513) CBr_3NO_2 CBr_3NO_2 bromopicrin (442)

(514) CCl_3NO_2 CCl_3NO_2 chloropicrin (430, 442)

(515) CHN_3O_9 $CH(NO_3)_3$ trinitromethane (430)

(516) CH_3NO_2 CH_3NO_2 nitromethane (151, 168, 171, 242, 430, 498)

(517) $CH_4N_2O_2$ CH_3NHNO_2 methylnitramine (173, 176)

(518) $C_2H_5NO_2$ $C_2H_5NO_2$ nitroethane (151)

(519) $C_3H_7NO_2$ $C_3H_7NO_2$ nitropropane (151)

(520) $C_4H_9NO_2$ $C_4H_9NO_2$ nitrobutane (151)

(521) $C_5H_{11}NO_2$ $C_5H_{11}NO_2$ nitropentane (151)

(522) CN_4O_8 $C(NO_2)_4$ tetranitromethane (242, 430, 442)

c. Nitrites

(523) CH_3NO_2 CH_3ONO methyl nitrite (151, 170)

(524) $C_2H_5NO_2$ C_2H_5ONO ethyl nitrite (151)

(525) $C_3H_7NO_2$ C_3H_7ONO propyl nitrite (151)

(526) $C_4H_9NO_2$ C_4H_9ONO butyl nitrite (151)

(527) $C_4H_9NO_2$ $(CH_3)_2CHCH_2ONO$ isobutyl nitrite (373)

(528) $C_5H_{11}NO_2$ $(CH_3)_2CH(CH_2)_2ONO$ isoamyl nitrite (151)

d. Nitrates

(529) CH_3NO_3 CH_3ONO_2 methyl nitrate (151, 240, 241, 429)

(530) $C_2H_5NO_3$ $C_2H_5ONO_2$ ethyl nitrate (151, 241, 429)

(531) $C_3H_7NO_3$ $C_3H_7ONO_2$ propyl nitrate (151, 241, 429)

(532) $C_3H_7NO_3$ $(CH_3)_2CHONO_2$ isopropyl nitrate (241)

(533) $C_4H_9NO_3$ $(CH_3)_2CHCH_2ONO_2$ isobutyl nitrate (373)

(534) $C_4H_9NO_3$ $C_4H_9ONO_2$ butyl nitrate (151, 429)

(535) $C_4H_9NO_3$ $C_2H_5CH(CH_3)ONO_2$ sec-butyl nitrate (241)

(536) $C_5H_{11}NO_3$ $C_5H_{11}ONO_2$ amyl nitrate (429, 592)

(537) $C_5H_{11}NO_3$ $(CH_3)_2CH(CH_2)_2ONO_2$ isoamyl nitrate (241, 592)

(538) $C_6H_{13}NO_3$ $C_6H_{13}ONO_2$ hexyl nitrate (429)

(539) $C_7H_{15}NO_3$ $C_7H_{15}ONO_2$ heptyl nitrate (429)

(540) $C_9H_{19}NO_3$ $C_9H_{19}ONO_2$ nonyl nitrate (431)

(541) $C_{10}H_{21}NO_3$ $C_{10}H_{21}ONO_2$ decyl nitrate (431)

(542) $C_{12}H_{25}NO_3$ $C_{12}H_{25}ONO_2$ dodecyl nitrate (431)

XI. Metallo derivatives of hydrocarbons

(543) CH_3BrMg CH_3MgBr methylmagnesium bromide (129)

(544) CH_3IMg CH_3MgI methylmagnesium iodide (129)

(545) C_2H_6Hg $Hg(CH_3)_2$ mercury dimethyl (269)

(546) C_2H_6Zn $Zn(CH_3)_2$ zinc dimethyl (269, 619)

(547) C_3H_9Bi $Bi(CH_3)_3$ bismuth trimethyl (269)

(548) $C_4H_{10}Hg$ $Hg(C_2H_5)_2$ mercury diethyl (269)
(549) $C_4H_{10}Zn$ $Zn(C_2H_5)_2$ zinc diethyl (269, 619)
(550) $C_4H_{12}O_4Si$ $SiO_4(CH_3)_4$ methyl orthosilicate (560)
(551) $C_4H_{12}Pb$ $Pb(CH_3)_4$ lead tetramethyl (210)
(552) $C_4H_{12}Si$ $Si(CH_3)_4$ silicon tetramethyl (533)
(553) $C_4H_{12}Sn$ $Sn(CH_3)_4$ tin tetramethyl (269)
(554) C_4NiO_4 $Ni(CO)_4$ nickel carbonyl (210, 649)
(555) C_5FeO_5 $Fe(CO)_5$ iron carbonyl (210)
(556) $C_6H_{18}O_7Si_2$ $Si_2O_7(CH_3)_6$ methyl ester of silicic (dimeric) acid (560)
(557) $C_8H_{20}Pb$ $Pb(C_2H_5)_4$ lead tetraethyl (209, 210, 269)
(558) $C_8H_{24}O_{10}Si_3$ $Si_3O_{10}(CH_3)_8$ methyl ester of silicic (trimeric) acid (560)
(559) $C_{22}H_{66}O_{30}Si_{10}$ $Si_{10}O_{30}(CH_3)_{22}$ methyl ester of silicic (decameric) acid (560)

B. UNSATURATED COMPOUNDS

I. Hydrocarbons

a. Olefins

(560) C_2H_4 $CH_2{=}CH_2$ ethylene (99, 194, 195, 196, 197, 205, 405, 411, 650)
(561) C_3H_6 $CH_3CH{=}CH_2$ propylene (propene) (69, 99)
(562) C_4H_8 $C_2H_5CH{=}CH_2$ butylene (1-butene) (99)
(563) C_5H_{10} $C_3H_7CH{=}CH_2$ amylene (1-pentene) (73, 97, 99, 508)
(564) C_5H_{10} $C_2H_5CH{=}CHCH_3$ 2-pentene (508)
(565) C_5H_{10} $(CH_3)_2C{=}CHCH_3$ trimethylethylene (2-methyl-2-butene) (106, 232)
(566) C_5H_{10} $(CH_3)_2CHCH{=}CH_2$ 3-methyl-1-butene (635)
(567) C_6H_{12} $C_4H_9CH{=}CH_2$ 1-hexene (97, 99, 406, 508, 544)
(568) C_6H_{12} $(CH_3)_2C{=}C(CH_3)_2$ tetramethylethylene (300, 508, 544)
(569) C_6H_{12} $C_3H_7CH{=}CHCH_3$ cis-2-hexene (508, 544)
(570) C_6H_{12} $C_3H_7CH{=}CHCH_3$ trans-2-hexene (508, 544)
(571) C_6H_{12} $(CH_3)_2CHCH{=}CHCH_3$ cis-4-methyl-2-pentene (281, 508, 544)
(572) C_6H_{12} $(CH_3)_2CHCH{=}CHCH_3$ trans-4-methyl-2-pentene (508, 544)
(573) C_6H_{12} $C_2H_5C(CH_3){=}CHCH_3$ 3-methyl-2-pentene (508, 544, 551)
(574) C_6H_{12} $C_2H_5CH{=}C(CH_3)_2$ 2-methyl-2-pentene (508, 544)
(575) C_7H_{14} $C_5H_{11}CH{=}CH_2$ 1-heptene (97, 99, 406)
(576) C_8H_{16} $C_6H_{13}CH{=}CH_2$ 1-octene (97, 99)
(577) C_8H_{16} $CH_3C(CH_3)_2CH{=}C(CH_3)_2$ 2,4,4-trimethyl-2-pentene (533)
(578) C_8H_{16} $C_5H_{11}CH{=}CHCH_3$ 2-octene (281)
(579) C_8H_{16} $CH_3C(CH_3)_2CH_2C(CH_3){=}CH_2$ 2,4,4-trimethyl-1-pentene (533)
(580) C_8H_{16} $CH_3CH(CH_3)CH_2C(CH_3){=}CHCH_3$ 3,5-dimethyl-2-hexene (10)
(581) C_8H_{16} $(CH_3)_2CHCH_2CH{=}C(CH_3)CH_3$ 2,5-dimethyl-2-hexene (10)

(582) C_9H_{18} $C_6H_{13}C(CH_3)$=CH_2 2-methyl-1-octene (273, 282)
(583) C_9H_{18} $C_5H_{11}CH$=$C(CH_3)_2$ 2-methyl-2-octene (273, 282)
(584) C_9H_{18} $C_7H_{15}CH$=CH_2 1-nonene (97, 99)
(585) C_9H_{18} $C_6H_{13}CH$=$CHCH_3$ 2-nonene (281)
(586) C_9H_{18} $C_5H_{11}C(CH_3)$=$CHCH_3$ 3-methyl-2-octene (282)
(587) C_9H_{18} $(CH_3)_2CHCH_2C(CH_3)$=CHC_2H_5 4,6-dimethyl-3-heptene (10)
(588) C_9H_{18} $(CH_3)_2CH(CH_2)_2C(CH_3)$=$CHCH_3$ 3,6-dimethyl-2-heptene (10)
(589) C_9H_{18} $(CH_3)_2CHCH_2C(CH_3)$=$C(CH_3)_2$ 2,3,5-trimethyl-2-hexene (10)
(590) $C_{10}H_{20}$ $C_6H_{13}C(C_2H_5)$=CH_2 2-ethyl-1-octene (273)
(591) $C_{10}H_{20}$ $C_6H_{13}C(CH_3)$=$CHCH_3$ 3-methyl-2-nonene (273)
(592) $C_{10}H_{20}$ $C_5H_{11}CH$=$C(CH_3)C_2H_5$ 3-methyl-3-nonene (273)
(593) $C_{10}H_{20}$ $C_4H_9CH(CH_3)CH$=$C(CH_3)_2$ 2,4-dimethyl-2-octene (10)
(594) $C_{10}H_{20}$ $(CH_3)_2CHCH_2C(CH_3)$=$CHCH(CH_3)_2$ 2,4,6-trimethyl-3-heptene (10)
(595) $C_{11}H_{22}$ $(CH_3)_2CHCH_2CH$=$C(CH_3)CH_2CH(CH_3)_2$ 2,4,7-trimethyl-4-octene (10)
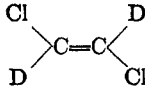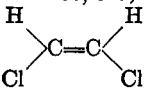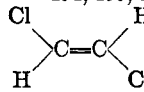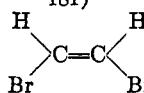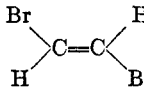
b. Diolefins

(596) C_3H_4 CH_2=C=CH_2 allene (105, 106, 116, 37?)
(597) C_4H_6 CH_2=C=$CHCH_3$ methylallene (1,2-butadiene) (106)
(598) C_4H_6 CH_2=$CHCH$=CH_2 butadiene (1,3-butadiene) (165)
(599) C_5H_8 CH_2=$CHCH_2CH$=CH_2 1,4-pentadiene (508)
(600) C_5H_8 $(CH_3)_2C$=C=CH_2 1,1-dimethylallene (3-methyl-1,2-butadiene) (105, 106)
(601) C_5H_8 CH_3CH=C=$CHCH_3$ 1,3-dimethylallene (2,3-pentadiene) (371)
(602) C_5H_8 CH_3CH=$CHCH$=CH_2 1,3-pentadiene (piperylene) (165)
(603) C_5H_8 CH_2=$C(CH_3)CH$=CH_2 3-methyl-1,3-butadiene (isoprene) (100,106, 165, 580)
(604) C_5H_8 CH_2=C=CHC_2H_5 ethylallene (1,2-pentadiene) (371)
(605) $(C_5H_8)x$ $(C_5H_8)x$ rubber (246)
(606) C_6H_{10} C_3H_7CH=C=CH_2 propylallene (1,2-hexadiene) (105, 106)
(607) C_6H_{10} CH_2=$CHCH_2CH_2CH$=CH_2 1,5-hexadiene (508)
(608) C_6H_{10} CH_2=$C(CH_3)C(CH_3)$=CH_2 2,3-dimethyl-1,3-butadiene (165)
(609) C_7H_{12} C_4H_9CH=C=CH_2 butylallene (1,2-heptadiene) (105, 106)
(610) $C_{40}H_{56}$ lycopene (228)

II. Halogen derivatives of hydrocarbons

a. Chlorine derivatives

(611) $C_2D_2Cl_2$

$$\underset{Cl}{\overset{D}{>}}C=C\underset{Cl}{\overset{D}{<}}$$

cis-1,2-dichloroethylene-d_2 (609)

(612) $C_2D_2Cl_2$

$$\begin{matrix} Cl & & D \\ & \diagdown C{=}C \diagup & \\ D & & Cl \end{matrix}$$
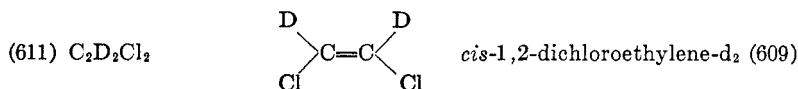
trans-1,2-dichloroethylene-d_2 (609)

(613) C_2Cl_4 $CCl_2{=}CCl_2$ tetrachloroethylene (162, 166, 456, 518, 519, 595)

(614) C_2HCl_3 $CCl_2{=}CHCl$ trichloroethylene (72, 162, 166, 294)

(615) $C_2H_2Cl_2$ $CHCl{=}CHCl$ 1,2-dichloroethylene (mixt.) (68, 162, 166, 519)

(616) $C_2H_2Cl_2$

$$\begin{matrix} H & & H \\ & \diagdown C{=}C \diagup & \\ Cl & & Cl \end{matrix}$$

1,2-dichloroethylene (*cis*) (72, 77, 78, 494, 495, 496, 600, 608, 609)

(617) $C_2H_2Cl_2$

$$\begin{matrix} Cl & & H \\ & \diagdown C{=}C \diagup & \\ H & & Cl \end{matrix}$$

1,2-dichloroethylene (*trans*) (72, 77, 78, 494, 495, 496, 600, 608, 609)

(618) C_2H_3Cl $CH_2{=}CHCl$ vinyl chloride (99, 495, 496, 642)

(619) C_3H_5Cl $CH_2{=}CHCH_2Cl$ allyl chloride (3-chloro-1-propene) (57, 99, 162, 166, 297, 495, 496, 500, 554, 578, 642)

(620) C_3H_5Cl $CHCl{=}CHCH_3$ 1-chloropropylene (1-chloro-1-propene) (495, 496, 642)

(621) C_3H_5Cl $CH_2{=}CClCH_3$ 2-chloropropylene (2-chloro-1-propene) (495, 496, 642)

(622) $C_4H_6Cl_2$ $CH_3CH{=}CHCHCl_2$ 1,1-dichloro-2-butene (333)

(623) $C_4H_6Cl_2$ $CH_3CHClCH{=}CHCl$ 1,3-dichloro-1-butene (333)

(624) C_4H_7Cl $CH_2ClCH{=}CHCH_3$ 1-chloro-2-butene (crotyl chloride) (281)

b. Bromine derivatives

(625) $C_2H_2Br_2$ $CHBr{=}CHBr$ 1,2-dibromoethylene (mixt.) (134, 180, 181)

(626) $C_2H_2Br_2$

$$\begin{matrix} H & & H \\ & \diagdown C{=}C \diagup & \\ Br & & Br \end{matrix}$$

1,2-dibromoethylene (*cis*) (180, 181)

(627) $C_2H_2Br_2$

$$\begin{matrix} Br & & H \\ & \diagdown C{=}C \diagup & \\ H & & Br \end{matrix}$$

1,2-dibromoethylene (*trans*) (180, 181)

(628) C_2H_3Br $CH_2{=}CHBr$ vinyl bromide (99)

(629) $C_3H_4Br_2$ $CH_2{=}CBrCH_2Br$ 2,3-dibromo-1-propene (371, 409)

(630) C_3H_5Br $CH_2{=}CHCH_2Br$ allyl bromide (57, 99, 162, 166, 295)

(631) $C_4H_6Br_2$ $CH_3CH{=}CBrCH_2Br$ 1,2-dibromo-2-butene (282)

(632) C_4H_7Br $CH_3CH{=}CHCH_2Br$ 2-butenyl bromide (*cis-trans*) (1-bromo-2-butene) (283, 284)

(633) C_4H_7Br $CH_2{=}CHCHBrCH_3$ methylallyl bromide (3-bromo-1-butene) (283, 284)

(634) C_4H_7Br $CH_3CBr{=}CHCH_3$ 2-bromo-2-butene (282)

(635) C_5H_9Br $(CH_3)_2C{=}CBrCH_3$ bromomethylbutene (2-bromo-3-methyl-2-butene) (106)

III. Alcohols

(636) C_3H_5ClO $CHCl=CHCH_2OH$ 3-chloro-2-propen-1-ol (333)

(637) C_3H_6O $CH_2=CHCH_2OH$ allyl alcohol (2-propen-1-ol) (69, 99, 163, 167, 242, 629)

(638) C_4H_8O $CH_3CH=CHCH_2OH$ crotonyl alcohol (2-buten-1-ol) (283, 284)

(639) C_4H_8O $CH_2=CHCH(CH_3)OH$ methylallyl alcohol (3-buten-2-ol) (99, 283, 284)

(640) $C_5H_{10}O$ $CH_2=CHCH(C_2H_5)OH$ ethylallyl alcohol (1-penten-3-ol) (283, 371)

(641) $C_5H_{10}O$ $CH_3CH=C(CH_3)CH_2OH$ methylcrotonyl alcohol (2-methyl-2-buten-1-ol) (288)

(642) $C_{10}H_{18}O$ $(CH_3)_2C=CHCH_2CH_2C(OH)(CH_3)CH=CH_2$ linalool (86)

(643) $C_{10}H_{18}O$ $(CH_3)_2C=CHCH_2CH_2C(CH_3)=CHCH_2OH$ geraniol and nerol (86, 302)

(644) $C_{10}H_{20}O$ $CH_2OHCH_2CH(CH_3)(CH_2)_3C(CH_3)=CH_2$ citronellol (86, 273, 469, 470)

(645) $C_{10}H_{20}O$ $CH_2OHCH_2CH(CH_3)(CH_2)_2CH=C(CH_3)_2$ rhodinol (86, 273, 469, 470)

IV. Ethers

a. Halogen derivatives of ethers

(646) $C_6H_{11}ClO$ $CH_3CH(OC_2H_5)CH=CHCl$ 1-chloro-3-ethoxy-1-butene (333)

V. Carbonyl compounds

a. Aldehydes

(647) C_3H_4O $CH_2=CHCHO$ acrolein (99, 100)

(648) C_4H_6O $CH_3CH=CHCHO$ crotonaldehyde (283, 284, 310, 366)

(649) C_4H_6O $CH_3CH=CHCHO$ *trans*-crotonaldehyde (100)

(650) $C_6H_{10}O$ $C_2H_5CH=C(CH_3)CHO$ α-methyl-α-pentenaldehyde (282)

(651) $C_{10}H_{16}O$ $(CH_3)_2C=CH(CH_2)_2C(CH_3)=CHCHO$ citral (86)

(652) $C_{10}H_{18}O$ $CH_2=C(CH_3)(CH_2)_3CH(CH_3)CH_2CHO$ citronellal (86, 470)

(653) $C_{11}H_{20}O$ $C_8H_{17}CH=CHCHO$ undecylenaldehyde (90)

b. Ketones

(654) C_5H_8O $CH_3CH=CHCOCH_3$ ethylideneacetone (366)

(655) $C_6H_{10}O$ $(CH_3)_2C=CHCOCH_3$ mesityl oxide (354, 359)

(656) $C_9H_{14}O$ $\begin{matrix} CH_3 \\ \\ CH_3 \end{matrix}\Big> C=CHCOCH=C \Big< \begin{matrix} CH_3 \\ \\ CH_3 \end{matrix}$ phorone (90)

c. Acyl halides

(657) C_4H_5ClO $CH_3CH=CHCOCl$ crotonyl chloride (366)

VI. Monocarboxylic acids

a. Monocarboxylic acids

(658) $C_3H_4O_2$ $CH_2{=}CHCOOH$ acrylic acid (99)

(659) $C_4H_6O_2$
$$\begin{array}{c} HCCOOH \\ \| \\ H_3CCH \end{array}$$
crotonic acid (trans) (180, 181)

(660) $C_4H_6O_2$
$$\begin{array}{c} HCCOOH \\ \| \\ HCCH_3 \end{array}$$
crotonic acid (cis) (180, 181)

(661) $C_{10}H_{18}O_2$ $CH_2{=}C(CH_3)(CH_2)_3CH(CH_3)CH_2COOH$ citronellic acid (470)

b. Halogen derivatives of monocarboxylic acids

(662) $C_4H_5ClO_2$

$$\begin{array}{cc} H_3C & H \\ \diagdown & \diagup \\ C{=}C & \\ \diagup & \diagdown \\ Cl & COOH \end{array}$$
β-chlorocrotonic acid (trans) (180, 181)

(663) $C_4H_5ClO_2$

$$\begin{array}{cc} Cl & H \\ \diagdown & \diagup \\ C{=}C & \\ \diagup & \diagdown \\ H_3C & COOH \end{array}$$
β-chlorocrotonic acid (cis) (180, 181)

c. Esters of monocarboxylic acids

(664) $C_4H_6O_2$ $CH_2{=}CHCOOCH_3$ methyl acrylate (366)

(665) $C_4H_7ClO_2$ $CH_3COOCH_2CH{=}CHCl$ γ-chloroallyl acetate (333)

(666) $C_5H_8O_2$

$$\begin{array}{cc} H_3C & H \\ \diagdown & \diagup \\ C{=}C & \\ \diagup & \diagdown \\ H & COOCH_3 \end{array}$$
methyl crotonate (trans) (180, 181)

(667) $C_5H_8O_2$ $CH_3COOCH_2CH{=}CH_2$ allyl acetate (508)

(668) $C_5H_8O_2$

$$\begin{array}{cc} H & H \\ \diagdown & \diagup \\ C{=}C & \\ \diagup & \diagdown \\ H_3C & COOCH_3 \end{array}$$
methyl crotonate (cis) (180, 181)

(669) $C_6H_9ClO_2$ $CH_3C(Cl){=}CHCOOC_2H_5$ ethyl β-chlorocrotonate (366)

(670) $C_6H_{10}O_2$ $CH_3COOCH(CH_3)CH{=}CH_2$ methylvinylcarbinol acetate (α-methylallyl acetate) (283)

(671) $C_6H_{10}O_2$ $CH_3CH{=}CHCOOC_2H_5$ ethyl crotonate (366)

(672) $C_6H_{10}O_2$ $CH_3COOCH_2CH{=}CHCH_3$ crotonyl acetate (283, 284)

(673) $C_6H_{10}O_2$ $(CH_3)_2C{=}CHCOOCH_3$ methyl β,β-dimethylacrylate (354)

(674) $C_6H_{10}O_3$ $CH_3C(OH){=}CHCOOC_2H_5$ ethyl acetoacetate (enol) (165, 485)

(675) $C_7H_{12}O_2$ $CH_3COOCH_2C(CH_3){=}CHCH_3$ β-methylcrotonyl acetate (288)

(676) $C_8H_{14}O_3$ $CH_3C(OC_2H_5){=}CHCOOC_2H_5$ ethyl β-ethoxycrotonate (358)

VII. Esters of aminocarboxylic acids
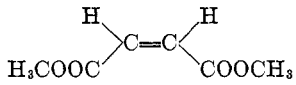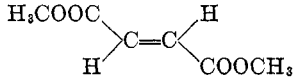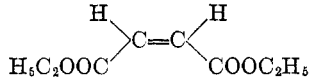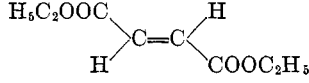
(677) $C_6H_{11}NO_2$ $CH_3C(NH_2){=}CHCOOC_2H_5$ ethyl β-aminocrotonate (358)

(678) $C_7H_{13}NO_2$ $CH_3C(NHCH_3){=}CHCOOC_2H_5$ ethyl β-methylaminocrotonate (358)

(679) $C_8H_{15}NO_2$ $CH_3C[N(CH_3)_2]{=}CHCOOC_2H_5$ ethyl-β-dimethylaminocrotonate (358)

VIII. Dicarboxylic acids

a. Anhydrides of dicarboxylic acids

(680) $C_4H_2O_3$

$$\begin{array}{c} HC-C \diagup^O \\ \| \quad \diagdown O \\ HC-C \diagdown_O \end{array}$$ maleic anhydride (369)
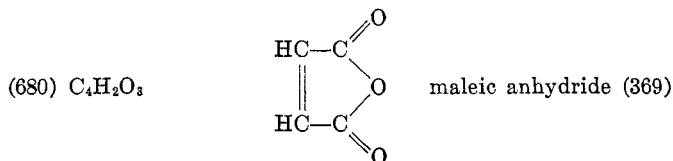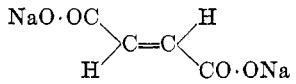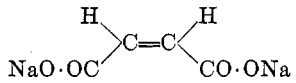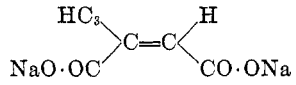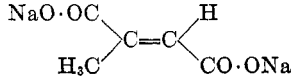
b. Esters of dicarboxylic acids

(681) $C_6H_8O_4$

$$\begin{array}{c} H \quad\quad H \\ \diagdown C{=}C \diagup \\ H_3COOC \diagup \quad\quad \diagdown COOCH_3 \end{array}$$ dimethyl maleate (180, 181, 369)

(682) $C_6H_8O_4$

$$\begin{array}{c} H_3COOC \quad\quad H \\ \diagdown C{=}C \diagup \\ H \diagup \quad\quad \diagdown COOCH_3 \end{array}$$ dimethyl fumarate (180, 181)

(683) $C_8H_{12}O_4$

$$\begin{array}{c} H \quad\quad H \\ \diagdown C{=}C \diagup \\ H_5C_2OOC \diagup \quad\quad \diagdown COOC_2H_5 \end{array}$$ diethyl maleate (180, 181, 231)

(684) $C_8H_{12}O_4$

$$\begin{array}{c} H_5C_2OOC \quad\quad H \\ \diagdown C{=}C \diagup \\ H \diagup \quad\quad \diagdown COOC_2H_5 \end{array}$$ diethyl fumarate (180, 181, 231)

(685) $C_{12}H_{18}O_6$ $C_2H_5OOCCH_2C(COOC_2H_5){=}CHCOOC_2H_5$ triethyl aconitate (354)

c. Salts of dicarboxylic acids

(686) $C_4H_2Na_2O_4$

$$\begin{array}{c} NaO{\cdot}OC \quad\quad H \\ \diagdown C{=}C \diagup \\ H \diagup \quad\quad \diagdown CO{\cdot}ONa \end{array}$$ disodium fumarate (603)

(687) $C_4H_2Na_2O_4$

$$\begin{array}{c} H \quad\quad H \\ \diagdown C{=}C \diagup \\ NaO{\cdot}OC \diagup \quad\quad \diagdown CO{\cdot}ONa \end{array}$$ disodium maleate (603)

(688) $C_5H_4Na_2O_4$

$$\begin{array}{c} HC_3 \quad\quad H \\ \diagdown C{=}C \diagup \\ NaO{\cdot}OC \diagup \quad\quad \diagdown CO{\cdot}ONa \end{array}$$ disodium citraconate (603)

(689) $C_5H_4Na_2O_4$

$$\begin{array}{c} NaO{\cdot}OC \quad\quad H \\ \diagdown C{=}C \diagup \\ H_3C \diagup \quad\quad \diagdown CO{\cdot}ONa \end{array}$$ disodium mesaconate (603)

IX. Cyano compounds

(690) C_4H_5N CH_2=$CHCH_2CN$ vinyl acetonitrile (306)

(691) C_4H_5N

$$CH_3\diagdown \atop H\diagup C{=}C{\diagup H \atop \diagdown CN}$$

crotononitrile (*trans*) (306)

(692) C_4H_5N

$$CH_3\diagdown \atop H\diagup C{=}C{\diagup CN \atop \diagdown H}$$

crotononitrile (*cis*) (306)

(693) C_4H_5N CH_2=$CHCH_2NCS$ allyl isothiocyanate (162, 166, 592)

X. Thioethers

(694) C_4H_6S $(CH_2$=$CH)_2S$ divinyl sulfide (69, 89, 94)

(695) $C_6H_{10}S$ $(CH_2$=$CHCH_2)_2S$ diallyl sulfide (69, 89, 94, 591, 593, 623, 625)

XI. Amides

(696) $C_6H_{11}NO$ CH_3CH=$CHCON(CH_3)_2$ N,N-dimethylcrotonamide (366)

XII. Acetylenic compounds

a. Hydrocarbons

(697) C_2DH $CH{\equiv}CD$ acetylene-d (583)

(698) C_2D_2 $DC{\equiv}CD$ acetylene-d_2 (252, 254, 256, 455, 583)

(699) C_2H_2 $CH{\equiv}CH$ acetylene (45, 46, 194, 195, 196, 197, 200, 252, 255, 303, 411, 455, 476, 555, 615)

(700) C_3H_4 $CH_3C{\equiv}CH$ methylacetylene (propine) (250, 251)

(701) C_4H_4 CH_2=$CHC{\equiv}CH$ vinylacetylene (1-buten-3-ine) (251)

(702) C_4H_6 $CH_3C{\equiv}CCH_3$ dimethylacetylene (2-butine) (251, 275, 280)

(703) C_5H_8 $C_2H_5C{\equiv}CCH_3$ methylethylacetylene (2-pentine) (275, 280)

(704) C_6H_{10} $C_4H_9C{\equiv}CH$ butylacetylene (1-hexine) (102, 103)

(705) C_6H_{10} $C_3H_7C{\equiv}CCH_3$ methylpropylacetylene (2-hexine) (275 280)

(706) C_6H_{10} $(CH_3)_2CHCH_2C{\equiv}CH$ isobutylacetylene (4-methyl-1-pentine) (280)

(707) C_7H_{12} $C_5H_{11}C{\equiv}CH$ amylacetylene (1-heptine) (102, 103)

(708) C_7H_{12} $C_4H_9C{\equiv}CCH_3$ methylbutylacetylene (2-heptine) (275, 280)

(709) C_8H_{14} $C_6H_{13}C{\equiv}CH$ hexylacetylene (1-octine) (102, 103)

(710) C_8H_{14} $C_5H_{11}C{\equiv}CCH_3$ methylamylacetylene (2-octine) (102, 103, 274, 280)

(711) C_9H_{12} $HC{\equiv}C(CH_2)_5C{\equiv}CH$ 1,8-nonadiine (280)

(712) C_9H_{16} $C_5H_{11}C{\equiv}CC_2H_5$ ethylamylacetylene (3-nonine) (274)

(713) C_9H_{16} $C_6H_{13}C{\equiv}CCH_3$ methylhexylacetylene (2-nonine) (274, 280)

(714) $C_{10}H_{18}$ $C_5H_{11}C{\equiv}CC_3H_7$ propylamylacetylene (4-decine) (274)

(715) $C_{10}H_{18}$ $C_6H_{13}C{\equiv}CC_2H_5$ ethylhexylacetylene (3-decine) (274)

(716) $C_{11}H_{20}$ $C_5H_{11}C{\equiv}CC_4H_9$ butylamylacetylene   (5-undecine)
(274)

(717) $C_{11}H_{20}$ $C_6H_{13}C{\equiv}CC_3H_7$ propylhexylacetylene   (4-undecine)
(274)

(718) $C_{12}H_{22}$ $C_6H_{13}C{\equiv}CC_4H_9$ butylhexylacetylene   (5-dodecine)
(274)

b. Halogen derivatives

(719) C_2I_2 $CI{\equiv}CI$ diiodoacetylene (254)

c. Alcohols

(720) C_3H_4O $CH{\equiv}CCH_2OH$ propargyl alcohol (277, 280)

(721) C_5H_8O $CH{\equiv}CC(CH_3)_2OH$ dimethylpropargyl alcohol (2-methyl-3-butin-2-ol) (102, 103)

(722) $C_8H_{14}O$ $C_5H_{11}C{\equiv}CCH_2OH$ 2-octin-1-ol (276)

(723) $C_9H_{16}O$ $C_6H_{13}C{\equiv}CCH_2OH$ 2-nonin-1-ol (276)

(724) $C_{10}H_{18}O$ $C_5H_{11}C{\equiv}CCHOHCH_3$ 3-nonin-2-ol (276)

(725) $C_{10}H_{18}O$ $C_5H_{11}C{\equiv}CC(OH)(CH_3)CH_3$ 2-methyl-3-nonin-2-ol (280)

(726) $C_{10}H_{18}O$ $C_6H_{13}C{\equiv}CCHOHCH_3$ 3-decin-2-ol (276, 280)

(727) $C_{11}H_{20}O$ $C_5H_{11}C{\equiv}CC(OH)(CH_3)C_2H_5$ 3-methyl-4-decin-3-ol (280)

(728) $C_{14}H_{24}O$ $(C_5H_{11}C{\equiv}C)_2CHOH$ diheptinylcarbinol (280)

(729) $C_{22}H_{34}O$ $(C_5H_{11}C{\equiv}C)_3COH$ triheptinylcarbinol (280)

d. Ethers

(730) C_4H_4O $HC{\equiv}CCH\ CH_2$ 3,4-epoxy-1-butine (280, 409, 410)
                               O

(731) C_4H_6O $CH{\equiv}CCH_2OCH_3$ 3-methoxy-1-propine (277, 280)

(732) C_5H_5ClO $CH{\equiv}CC\ H\ CHCH_2Cl$ 3,4-epoxy-5-chloro-1-pentine (280, 409)
                               O

(733) $C_6H_6O_2$ $CH_2CHC{\equiv}CCHCH_2$ 1,2,5,6-diepoxy-3-hexine (280, 409, 410)
                    O   O

(734) $C_9H_{16}O$ $C_5H_{11}C{\equiv}CCH_2OCH_3$ 1-methoxy-2-octine (277, 280)

(735) $C_{10}H_{18}O$ $C_6H_{13}C{\equiv}CCH_2OCH_3$ 1-methoxy-2-nonine (277, 280)

(736) $C_{10}H_{18}O$ $C_5H_{11}C{\equiv}CCH(OCH_3)CH_3$ 2-methoxy-3-nonine (277, 280)

(737) $C_{11}H_{20}O$ $C_5H_{11}C{\equiv}CC(OCH_3)(CH_3)_2$ 2-methoxy-2-methyl-3-nonine (280)

(738) $C_{11}H_{22}O$ $C_5H_{11}C{\equiv}CC(OCH_3)(CH_3)C_2H_5$ 3-methoxy-3-methyl-4-decine (280)
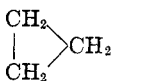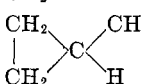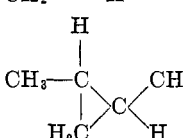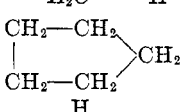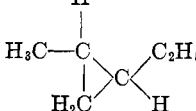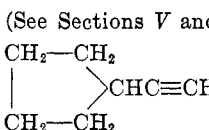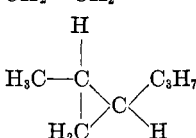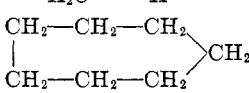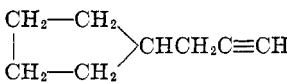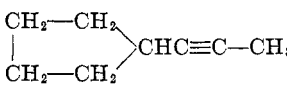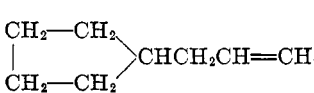
e. Esters of acetylenic acids

(739) $C_9H_{14}O_2$ $C_5H_{11}C{\equiv}CCOOCH_3$ methyl α-octinoate (102, 103)

(740) $C_{10}H_{16}O_2$ $C_6H_{13}C{\equiv}CCOOCH_3$ methyl α-noninoate (280)

Part II. Cyclic Compounds

A. Alicyclic Compounds

I. Cycloparaffins

(741) C_3H_6
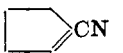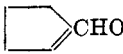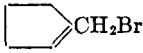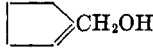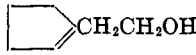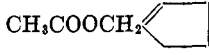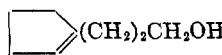
$$\begin{array}{c} CH_2 \\ | \quad\diagdown CH_2 \\ CH_2 \end{array}$$
cyclopropane (54, 118, 349, 406, 407, 650, 668)

(742) C_4H_8

$$\begin{array}{c} CH_2 \quad CH_3 \\ | \quad\diagdown C\diagup \\ CH_2 \quad H \end{array}$$
methylcyclopropane (118, 407)

(743) C_5H_{10}

$$\begin{array}{c} H \\ | \\ CH_3-C \quad CH_3 \\ | \quad\diagdown C\diagup \\ H_2C \quad H \end{array}$$
1, 2-dimethylcyclopropane (407)

(744) C_5H_{10}

$$\begin{array}{c} CH_2-CH_2 \\ | \quad\quad\diagdown CH_2 \\ CH_2-CH_2 \end{array}$$
cyclopentane (118, 634, 635, 636)

(745) C_6H_{12}

$$\begin{array}{c} H \\ | \\ H_3C-C \quad C_2H_5 \\ | \quad\diagdown C\diagup \\ H_2C \quad H \end{array}$$
1-methyl-2-ethylcyclopropane (406, 407)

(746) C_6H_{12}

$$\begin{array}{c} CH_2-CH_2 \quad CH_3 \\ | \quad\quad\diagdown C\diagup \\ CH_2-CH_2 \quad H \end{array}$$
methylcyclopentane (118)

C_6H_{12} (See Sections *V* and *VI* for cyclohexane and derivatives)

(747) C_7H_{10}

$$\begin{array}{c} CH_2-CH_2 \\ | \quad\quad\diagdown CHC\equiv CH \\ CH_2-CH_2 \end{array}$$
cyclopentylacetylene (278, 280)

(748) C_7H_{14}

$$\begin{array}{c} H \\ | \\ H_3C-C \quad C_3H_7 \\ | \quad\diagdown C\diagup \\ H_2C \quad H \end{array}$$
1-methyl-2-propylcyclopropane (407)

(749) C_7H_{14}

$$\begin{array}{c} CH_2-CH_2-CH_2 \\ | \quad\quad\quad\quad\diagdown CH_2 \\ CH_2-CH_2-CH_2 \end{array}$$
cycloheptane (118)

(750) C_8H_{12}

$$\begin{array}{c} CH_2-CH_2 \\ | \quad\quad\diagdown CHCH_2C\equiv CH \\ CH_2-CH_2 \end{array}$$
3-cyclopentyl-1-propine (279, 280)

(751) C_8H_{12}

$$\begin{array}{c} CH_2-CH_2 \\ | \quad\quad\diagdown CHC\equiv C-CH_3 \\ CH_2-CH_2 \end{array}$$
1-cyclopentyl-1-propine (methylcyclopentyl-acetylene) (278, 280)

(752) C_8H_{14}

$$\begin{array}{c} CH_2-CH_2 \\ | \quad\quad\diagdown CHCH_2CH= CH_2 \\ CH_2-CH_2 \end{array}$$
3-cyclopentyl-1-propene (508)

(753) C_8H_{16}

$$\begin{array}{c} CH_2-CH_2-CH_2 \\ | \qquad\qquad\qquad C \\ CH_2-CH_2-CH_2 \end{array}\!\!\Big\langle\begin{array}{c} CH_3 \\ H \end{array}$$

methylcycloheptane (118)

(754) C_8H_{16}

$$\begin{array}{c} CH_2------CH_2------CH_2 \\ | \qquad\qquad\qquad\qquad\qquad\qquad CH_2 \\ CH_2-CH_2-CH_2-CH_2 \end{array}$$

cyclooctane (118)

(755) C_9H_{10}

$$\begin{array}{c} CH_2-CH-C_6H_5 \\ \diagdown \quad \diagup \\ CH_2 \end{array}$$

phenylcyclopropane (404, 405, 407)

(756) C_9H_{14}

$$\begin{array}{c} CH_2-CH_2 \\ | \qquad\qquad \diagdown CHCH_2C\equiv CCH_3 \\ CH_2-CH_2 \end{array}$$

1-cyclopentyl-2-butine (279, 280)

(757) C_9H_{16}

$$\begin{array}{c} CH_2-CH_2 \\ | \qquad\qquad \diagdown CHCH_2CH=CHCH_3 \\ CH_2-CH_2 \end{array}$$

1-cyclopentyl-2-butene (281)

(758) C_9H_{18}

$$\begin{array}{c} CH_2------CH_2------CH_2 \\ | \qquad\qquad\qquad\qquad\qquad\qquad C \\ CH_2-CH_2-CH_2-CH_2 \end{array}\!\!\Big\langle\begin{array}{c} CH_3 \\ H \end{array}$$

methylcyclooctane (118)

(759) $C_{15}H_{14}$

$$\begin{array}{c} CH_2-CH-C_6H_5 \\ \diagdown \quad \diagup \\ CH-C_6H_5 \end{array}$$

1,2-diphenylcyclopropane (407)

II. Derivatives of cycloparaffins

(760) C_5H_8O

═O   cyclopentanone (89, 504)

(761) $C_5H_{10}O$

$\overset{H}{-}$OH   cyclopentanol (505)

(762) $C_6H_{10}O$

═O   2-methylcyclopentanone (504)
CH_3

(763) $C_6H_{10}O$

H_3C ═O   3-methylcyclopentanone (504)

(764) $C_6H_{10}O$

$\overset{H}{-}$CHO   cyclopentanealdehyde (506)

(765) $C_8H_{13}Br$

$\overset{H}{-}CH_2CBr=CH_2$ 3-cyclopentyl-2-bromo-1-propene (280, 508)

(766) $C_9H_{14}O$

$\overset{H}{-}CH_2C\equiv CCH_2OH$ 4-cyclopentyl-2-butin-1-ol (279, 280)

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* ⬠ represents
$$\begin{array}{c} H_2C-CH_2 \\ | \qquad\qquad \diagdown C \\ H_2C-CH_2 \end{array}$$

(767) $C_{10}H_{16}O$ H / —CH$_2$C≡CCHOHCH$_3$ 5-cyclopentyl-3-pentin-2-ol (279, 280)

(768) $C_{10}H_{16}O$ H / —CH$_2$C≡CCH$_2$OCH$_3$ 1-methoxy-4-cyclopentyl-2-butine (279, 280)

(769) $C_{11}H_{18}O$ H / —CH$_2$C≡CCH(OCH$_3$)CH$_3$ 2-methoxy-5-cyclopentyl-3-pentine (279, 280)
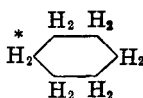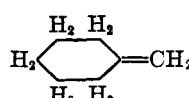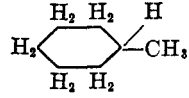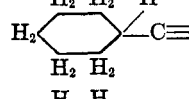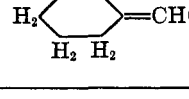
III. Cycloölefins

(770) C_5H_6 cyclopentadiene (601)

(771) C_5H_8 cyclopentene (69, 260, 505, 508, 636)

C_6H_{10} (See sections VII and VIII for cyclohexenes and derivatives)

(772) C_6H_{10} CH$_3$ 1-methyl-Δ¹-cyclopentene (261, 506, 508)

(773) C_7H_{12} C$_2$H$_5$ 1-ethyl-Δ¹-cyclopentene (261, 506)

(774) C_7H_{12} H$_2$C—CH$_2$—CH$_2$ / H$_2$C—CH$_2$—CH⟩CH   cycloheptene (suberene) (260)

(775) C_8H_{14} CH$_2$CH$_2$CH$_2$ / CH$_2$CH$_2$CH⟩CCH$_3$ 1-methyl-Δ¹-cycloheptene (261)

(776) C_8H_{14} H$_2$C—CH$_2$—CH$_2$—CH$_2$ / H$_2$C—CH$_2$——CH⟩CH   cycloöctene (260)

(777) $C_{10}H_{12}$ [ ]$_2$ dicyclopentadiene (601)

(778) $C_{11}H_{12}$ C$_6$H$_5$ 1-phenyl-Δ¹-cyclopentene (506)

(779) $C_{11}H_{14}$ CH$_2$C$_6$H$_5$ 1-benzyl-Δ¹-cyclopentene (507, 508)

(780) $C_{15}H_{24}$ CH / C$_{12}$H$_{20}$ ‖ \ C—CH$_3$ cedrene (423)

IV. *Derivatives of cycloölefins*

(781) C_6H_7N ⬡>CN   1-cyano-Δ^1-cyclopentene (505, 508)

(782) C_6H_8O ⬡>CHO   cyclopentenealdehyde (506, 508)

(783) C_6H_9Br ⬡>CH_2Br 1-bromomethyl-Δ^1-cyclopentene (507)

(784) $C_6H_{10}O$ ⬡>CH_2OH Δ^1-cyclopentenylcarbinol (505, 508)

(785) $C_7H_{10}O_2$ ⬡>$COOCH_3$ methyl Δ^1-cyclopentenecarboxylate (506, 508)

(786) $C_7H_{12}O$ ⬡>CH_2CH_2OH Δ^1-cyclopentenylethanol (505, 508)

(787) $C_8H_{12}O_2$ CH_3COOCH_2<⬡ Δ^1-cyclopentenylcarbinol acetate (507)

(788) $C_8H_{14}O$ ⬡>$(CH_2)_2CH_2OH$ Δ^1-cyclopentenylpropanol (505, 508)

V. *Cyclohexanes*
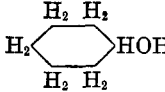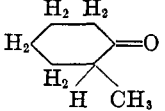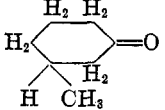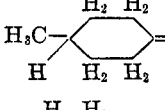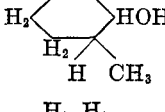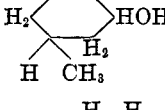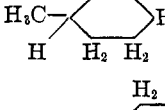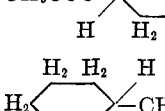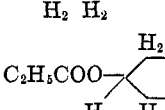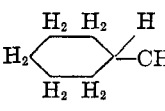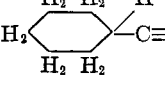
(789) C_6H_{12} H_2, H_2 / H_2 ⬡ H_2 / H_2, H_2 cyclohexane (6, 7, 41, 54, 117, 118, 194, 242, 259, 260, 290, 381, 404, 472, 498, 534, 564, 573, 606, 634, 635, 636, 661)

(790) C_7H_{12} H_2, H_2 / H_2 ⬡ =CH_2 / H_2, H_2 methylenecyclohexane (302)

(791) C_7H_{14} H_2, H_2, H / H_2 ⬡ —CH_3 / H_2, H_2 methylcyclohexane (6, 7, 118, 259, 472)

(792) C_8H_{12} H_2, H_2, H / H_2 ⬡ —C≡CH / H_2, H_2 cyclohexylacetylene (278)

(793) C_8H_{14} H_2, H_2 / H_2 ⬡ =$CHCH_3$ / H_2, H_2 ethylidenecyclohexane (302)

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* ⟨⬡⟩ represents C<$\begin{smallmatrix} C-C \\ C-C \end{smallmatrix}$>$C$

(794) C_8H_{16} [cyclohexane ring with H_2 H_2 / H_2 / H_2 H_2 and $(CH_3)_2$]   1,1-dimethylcyclohexane (441)

(795) C_8H_{16} [cyclohexane ring with H_2 H_2 H / H_2 / H CH_3 and —CH_3]   1,2-dimethylcyclohexane (*cis* or *trans*) (259, 402, 439, 440)

(796) C_8H_{16} [cyclohexane ring with H_2 H_2 H / H_2 / H CH_3 and —CH_3]   1,3-dimethylcyclohexane (*cis* or *trans*) (6, 7, 259, 441, 472)

(797) C_8H_{16} [cyclohexane ring, H_3C— and —CH_3, with H H_2 H_2 H / H_2 H_2]   1,4-dimethylcyclohexane (*cis* or *trans*) (6, 7, 259, 441)

(798) C_9H_{14} [cyclohexane ring with H_2 H_2 H / H_2 H_2 and —$C\equiv CCH_3$]   methylcyclohexylacetylene (1-cyclohexyl-1-propine) (278, 280)

(799) C_9H_{16} [cyclohexane ring with H_2 H_2 H / H_2 H_2 and —$CH_2CH=CH_2$]   3-cyclohexyl-1-propene (508)

(800) C_9H_{16} [cyclohexane ring with H_2 H_2 / H_2 H_2 and $=C(CH_3)_2$]   isopropylidenecyclohexane (302)

(801) $C_{10}H_{16}$ [cyclohexane ring with H_2 H_2 H / H_2 H_2 and —$CH_2C\equiv CCH_3$]   1-cyclohexyl-2-butine (278, 280)

(802) $C_{12}H_{22}$ [cyclohexane ring with H_2 H_2 H / H_2 H_2 and —$(CH_2)_3CH=CHCH_3$]   6-cyclohexyl-2-hexene (281)

(803) $C_{13}H_{16}$ [cyclohexane ring with H_2 H_2 / H_2 H_2 and $=CHC_6H_5$]   benzalcyclohexane (517)

(804) $C_{14}H_{26}$ [two cyclohexane rings joined by —CH_2CH_2—, with H_2 H_2 H ... H H_2 H_2 / H_2 H_2 ... H_2 H_2]   1,2-dicyclohexyl-ethane (89)

VI. Derivatives of cyclohexane

(805) $C_6H_{10}O$ [cyclohexane ring with H_2 H_2 / H_2 H_2 and $=O$]   cyclohexanone (208, 472, 504)

(806) $C_6H_{12}O$ cyclohexanol (456, 472, 498)

(807) $C_7H_{12}O$ 2-methylcyclohexanone (472, 504)

(808) $C_7H_{12}O$ 3-methylcyclohexanone (472, 504)

(809) $C_7H_{12}O$ 4-methylcyclohexanone (472, 504)

(810) $C_7H_{14}O$ 2-methylcyclohexanol (472)

(811) $C_7H_{14}O$ 3-methylcyclohexanol (472)

(812) $C_7H_{14}O$ 4-methylcyclohexanol (472)

(813) $C_8H_{14}O_2$ cyclohexyl acetate (472)

(814) $C_9H_{15}Br$ 3-cyclohexyl-2-bromo-1-propene (508)

(815) $C_9H_{16}O_2$ cyclohexyl propionate (472)

(816) $C_{10}H_{16}O$ 4-cyclohexyl-2-butin-1-ol (276, 280)

(817) $C_{10}H_{16}O$ 1-cyclohexyl-1-butin 3-ol (278, 280)

(818) $C_{11}H_{18}O$

H_2 H_2 H
H_2⟨⟩—$CH_2C\equiv CCHOHCH_3$ 5-cyclohexyl-3-
H_2 H_2 pentin-2-ol
                                                            (276, 280)

(819) $C_{11}H_{18}O$

H_2 H_2 H
H_2⟨⟩—$CH_2C\equiv CCH_2OCH_3$ 1-cyclohexyl-4-
H_2 H_2 methoxy-2-
                                                            butine (277, 280)

(820) $C_{12}H_{20}O$

H_2 H_2 H
H_2⟨⟩—$CH_2C\equiv CCH(OCH_3)CH_3$ 1-cyclohexyl-4-
H_2 H_2 methoxy-2-
                                                            pentine
                                                            (277, 280)

(821) $C_{12}H_{20}O$

H_2 H_2 H
H_2⟨⟩—$CH_2C\equiv CC(OH)(CH_3)_2$ 5-cyclohexyl-2-
H_2 H_2 methyl-3-
                                                            pentin-2-ol
                                                            (280)

(822) $C_{13}H_{16}O_2$

H_2 H_2
C_6H_5COO—⟨⟩H_2 cyclohexyl benzoate (420)
H H_2 H_2
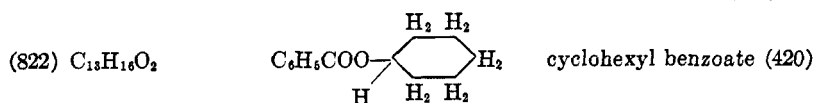
VII. Cyclohexenes

(823) C_6H_{10}

H_2 H_2
H_2⟨⟩H cyclohexene (6, 7, 8, 260, 404, 405, 456,
H_2 H 472, 634, 635, 636, 661)

(824) C_7H_{12}

H_2 H_2
H_2⟨⟩CH_3 1-methyl-Δ^1-cyclohexene (261)
H_2 H

(825) C_7H_{12}

H_2 H_2 H
H⟨⟩—CH_3 1-methyl-Δ^3-cyclohexene (261)
H H_2

(826) C_8H_{14}

H_2 H_2
H_2⟨⟩C_2H_5 1-ethyl-Δ^1-cyclohexene (261)
H_2 H

(827) C_8H_{14}

H H_2 H_2
H_3C—⟨⟩CH_3 1,4-dimethyl-Δ^1-cyclohexene (261)
H_2 H

(828) C_8H_{14}

H_2 H_2
H_2⟨⟩CH_3 1,2-dimethyl-Δ^1-cyclohexene (302)
H_2 CH_3

(829) C_9H_{16}

H_2 H_2 H
H_3C⟨⟩—CH_3 1,3,4-trimethyl-Δ^3-cyclohexene
CH_3 H_2 (261)

VIII. Derivatives of cyclohexenes

(830) $C_7H_{10}O$ 1-methyl-Δ^1-cyclohexen-6-one (508)

(831) $C_7H_{12}O$ 1-methyl-Δ^1-cyclohexen-6-ol (508)

(832) $C_8H_{14}O$ 1-ethyl-Δ^1-cyclohexen-6-ol (288)

(833) $C_9H_{16}O$ 1-methyl-6-ethoxy-Δ^1-cyclohexene (508)

(834) $C_{10}H_{16}O_2$ 1-ethyl-Δ^1-cyclohexen-6-ol acetate (288)

IX. Cyclohexadienes

(835) C_6H_8 1,3-cyclohexadiene (8, 90, 92, 370, 461)

(836) C_6H_8 1,4-cyclohexadiene (8, 370)
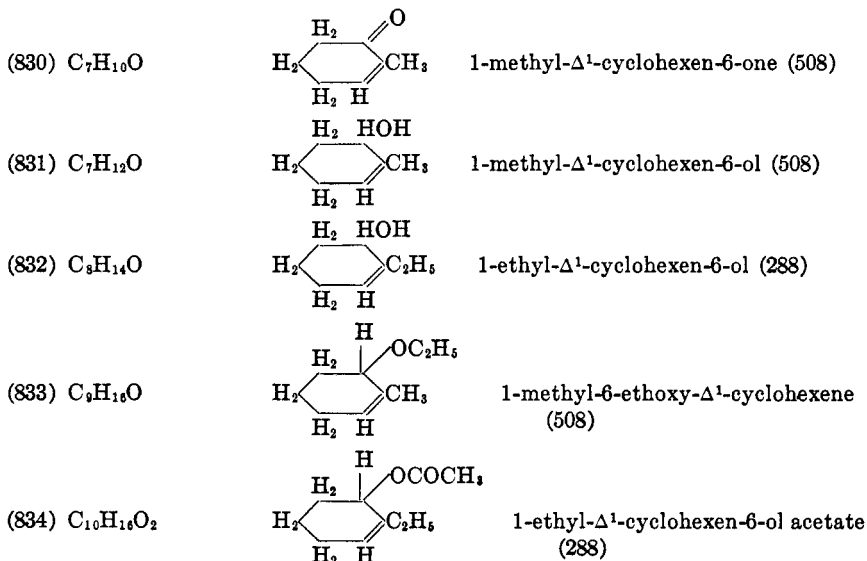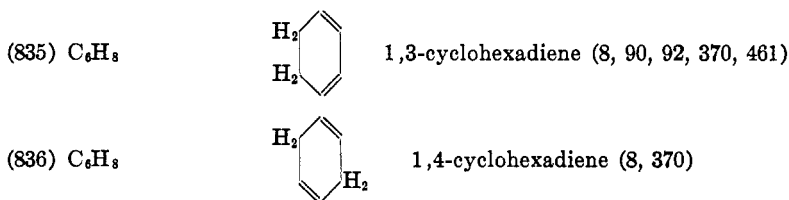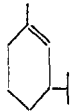
X. Terpenes, polycyclic terpenes, and terpene derivatives

a. Terpenes and terpenoids

(837) $C_{10}H_{14}$ *p*-cymene (215, 216, 217, 218, 456)

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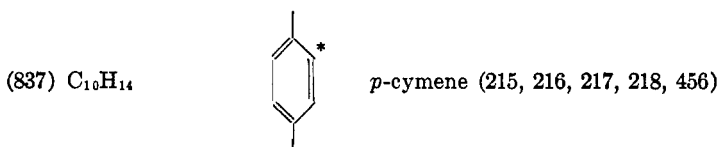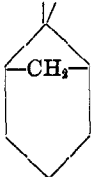
* ⬡ is the cyclohexane ring. In the unsaturated derivatives, the unsaturation is indicated by double bonds. A single bond extending from the ring represents a CH_3 group, while a $=CH_2$ is indicated by a double bond attached to the ring. —⊥ represents —$CH(CH_3)_2$. ⊥ represents —$C(=CH_2)CH_3$. A straight line at the midpoint of which two other lines meet represents H_3C—C—CH_3.

(838) $C_{10}H_{16}$ *dl*-limonene (dipentene) (82, 97, 215, 216, 217, 218, 220, 404, 405, 580)

(839) $C_{10}H_{16}$ α-phellandrene (215, 216, 217)

(840) $C_{10}H_{16}$ β-phellandrene (215, 216, 217)

(841) $C_{10}H_{16}$ α-terpinene (218, 220)

(842) $C_{10}H_{16}$ γ-terpinene (218, 220)

(843) $C_{10}H_{16}$ terpinolene (218, 220)

(844) $C_{10}H_{16}$ =CH₂   α-pyronene (211)

(845) $C_{10}H_{16}$ β-pyronene (211)

(846) $C_{10}H_{16}$ sylvestrene (217)

(847) $C_{10}H_{18}$ Δ³-menthene (76, 82, 218, 404)

(848) $C_{10}H_{18}$ carvomenthene (215, 216, 217, 404, 405)

(849) $C_{10}H_{18}$ Δ^1-m-menthene (217)

(850) $C_{10}H_{20}$ menthane (82, 215, 216, 217)

(851) $C_{40}H_{56}$ α- and β-carotene (228)

b. Polycyclic terpenes

(852) C_9H_{16} nopinane (212, 213, 216)

(853) $C_{10}H_{16}$ sabinene (82, 473)

(854) $C_{10}H_{16}$ α-thujene (473)

(855) $C_{10}H_{16}$ dl-Δ^3-carene (212, 213, 216, 219, 473)

(856) $C_{10}H_{16}$ Δ^4-carene (473)

(857) $C_{10}H_{16}$ dl-α-pinene (56, 76, 80, 82, 199, 212, 213, 216, 219, 328, 473, 598)

(858) $C_{10}H_{16}$ β-pinene (nopinene) (212, 213, 216, 219)

(859) $C_{10}H_{16}$ CH₂   camphene (212, 213, 216)

(860) $C_{10}H_{18}$ camphane (212, 213, 216, 218)

(861) $C_{10}H_{18}$ pinane (82, 212, 213, 216)
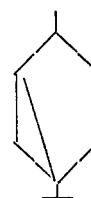
(862) $C_{10}H_{18}$ sabinane (thujane) (82)
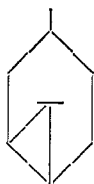
(863) $C_{10}H_{18}$ carane (212, 213, 216)

c. Terpene derivatives
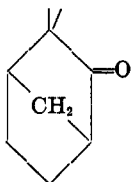
(864) $C_9H_{14}O$ camphenilone (208)
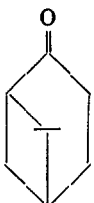
(865) $C_9H_{14}O$ nopinone (208)
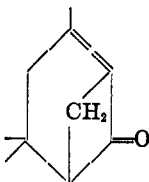
(866) $C_{10}H_{14}O$ verbenone (208)
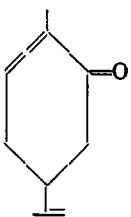
(867) $C_{10}H_{14}O$ carvone (66, 86, 208)
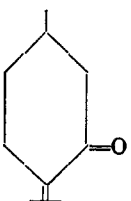
(868) $C_{10}H_{16}O$ pulegone (86, 208)
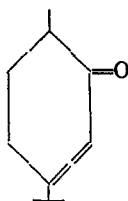
(869) $C_{10}H_{16}O$　　　carvenone (carveol) (86, 208)
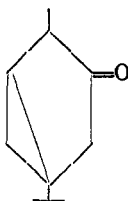
(870) $C_{10}H_{16}O$　　　β-thujone (86, 208)
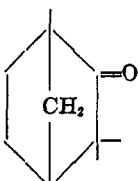
(871) $C_{10}H_{16}O$　　　CH₂　　　fenchone (86, 208)
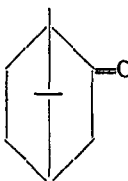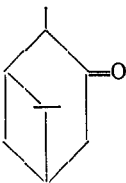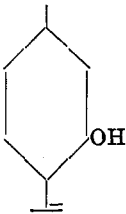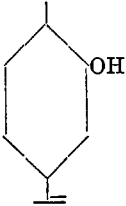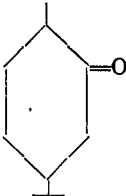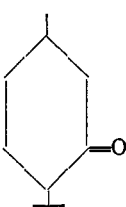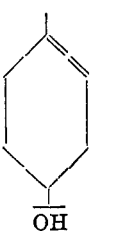
(872) $C_{10}H_{16}O$　　　camphor (208)
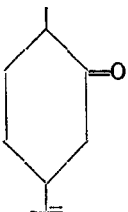
(873) $C_{10}H_{16}O$　　　dihydrocarvone (208)
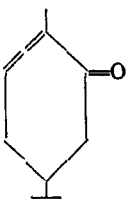
(874) $C_{10}H_{16}O$　　　carvotanacetone (208)

(875) $C_{10}H_{16}O$ pinocamphone (208)

(876) $C_{10}H_{18}O$ isopulegol (66, 67)

(877) $C_{10}H_{18}O$ dihydrocarvenone (dihydrocarveol) (66, 67)

(878) $C_{10}H_{18}O$ tetrahydrocarvone (66, 208)

(879) $C_{10}H_{18}O$ menthone (86, 208)

(880) $C_{10}H_{18}O$ α-terpineol (66, 67, 86)
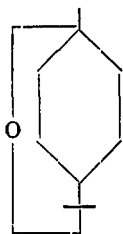
(881) $C_{10}H_{18}O$ eucalyptol (cineole) (86, 218, 220)
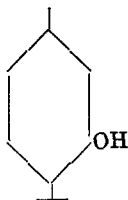
(882) $C_{10}H_{20}O$ menthol (66, 67)
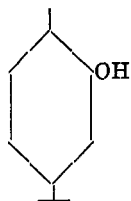
(883) $C_{10}H_{20}O$ carvomenthol (66, 67)
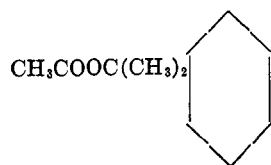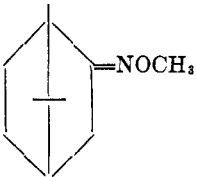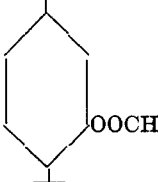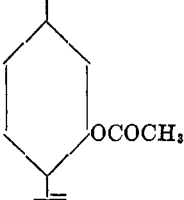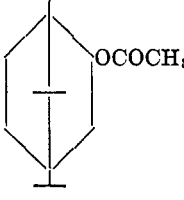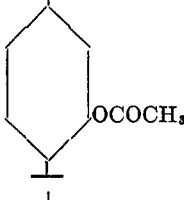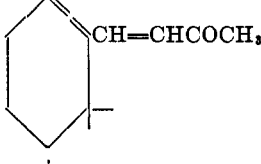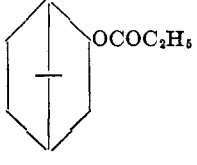
(884) $C_{10}H_{20}O_2$ $CH_3COOC(CH_3)_2$ terpenyl acetate (67)
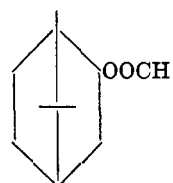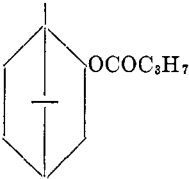
(885) $C_{11}H_{18}O_2$ bornyl and isobornyl formate (66, 67)
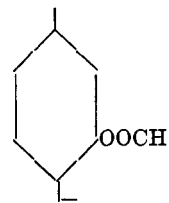
(886) $C_{11}H_{18}O_2$ isopulegyl formate (66, 67)

(887) $C_{11}H_{19}NO$ camphor O-methyloxime (87, 88)

(888) $C_{11}H_{20}O_2$ menthyl formate (66, 67)

(889) $C_{12}H_{20}O_2$ isopulegyl acetate (66, 67)

(890) $C_{12}H_{20}O_2$ bornyl and isobornyl acetate (66, 67)

(891) $C_{12}H_{22}O_2$ menthyl acetate (66, 67)

(892) $C_{13}H_{20}O$ β-ionone (228)

(893) $C_{13}H_{22}O_2$ bornyl and isobornyl propionate (66, 67)

(894) $C_{14}H_{24}O_2$ bornyl and isobornyl butyrate (66 67)

(895) $C_{40}H_{56}O_2$ leaf xanthophyll (228)

B. AROMATIC COMPOUNDS

I. Benzene and monosubstitution derivatives

a. Hydrocarbons

(896) C_6D_6 C_6D_6 benzene-d_6 (18, 334, 466, 660)
(897) C_6HD_5 C_6HD_5 benzene-d_5 (334)
(898) C_6H_5D C_6H_5D benzene-d (18, 334)
(899) C_6H_6 C_6H_6 benzene (6, 7, 23, 24, 27, 28, 40, 41, 42, 48, 51, 54, 55, 58, 61, 70, 108, 109, 112, 113, 117, 119, 121, 122, 129, 136, 137, 139, 141, 143, 153, 155, 156, 157, 158, 159, 161, 170, 192, 194, 196, 201, 204, 221, 226, 227, 235, 236, 237, 242, 247, 271, 286, 291, 292, 293, 321, 322, 334, 381, 394, 415, 433, 434, 435, 438, 452, 459, 465, 475, 512, 515, 519, 523, 524, 526, 534, 537, 543, 546, 547, 555, 556, 561, 564, 566, 572, 573, 575, 576, 577, 578, 579, 587, 624, 625, 634, 635, 636, 639, 640, 641, 647, 648, 650, 654, 655, 657, 658, 659, 660, 661; also 272)
(900) C_7H_8 $C_6H_5CH_3$ toluene (6, 7, 117, 136, 137, 139, 141, 156, 157, 158, 192, 194, 196, 237, 242, 291, 292, 293, 321, 322, 355, 394, 396, 435, 475, 500, 519, 523, 526, 543, 561, 578, 587, 624, 659)
(901) C_8H_6 $C_6H_5C{\equiv}CH$ phenylacetylene (100, 102, 103)
(902) C_8H_8 $C_6H_5CH{=}CH_2$ phenylethylene (styrene) (99, 100, 404, 405, 559)
(903) $(C_8H_8)_x$ $(C_8H_8)_x$ polystyrene (559)
(904) C_8H_{10} $C_6H_5CH_2CH_3$ ethylbenzene (6, 7, 155, 161, 242, 292, 559)
(905) C_9H_8 $C_6H_5C{\equiv}CCH_3$ methylphenylacetylene (100, 102, 103, 274, 280)
(906) C_9H_8 $C_6H_5CH_2C{\equiv}CH$ benzylacetylene (102, 103)
(907) C_9H_{10} $C_6H_5CH_2CH{=}CH_2$ benzylethylene (3-phenyl-1-propene) (69, 97, 99, 404, 405)
(908) C_9H_{10} $C_6H_5CH{=}CHCH_3$ isoallylbenzene (1-phenyl-1-propene) (69, 281, 404, 405)
(909) C_9H_{10} $C_6H_5CH{=}CHCH_3$ isoallylbenzene (*cis*) (100)
(910) C_9H_{10} $C_6H_5CH{=}CHCH_3$ isoallylbenzene (*trans*) (100)
(911) C_9H_{12} $C_6H_5C_3H_7$ propylbenzene (6)
(912) $C_{10}H_{10}$ $C_6H_5C{\equiv}CC_2H_5$ ethylphenylacetylene (274)
(913) $C_{10}H_{12}$ $C_6H_5CH{=}C(CH_3)_2$ β,β-dimethylstyrene (2-methyl-1-phenyl-1-propene) (517, 551)

(914) $C_{10}H_{14}$ $C_6H_5C_4H_9$ butylbenzene (6, 7)

(915) $C_{11}H_{10}$ $C_6H_5C\equiv CCH_2CH=CH_2$ allylphenylacetylene (97, 99)

(916) $C_{11}H_{12}$ $C_6H_5C\equiv CC_3H_7$ propylphenylacetylene (274)

(917) $C_{11}H_{16}$ $C_6H_5C_5H_{11}$ amylbenzene (6)

(918) $C_{13}H_{12}$ $C_6H_5CH_2C_6H_5$ diphenylmethane (140, 180, 181, 207)

(919) $C_{14}H_{10}$ $C_6H_5C\equiv CC_6H_5$ tolane (180, 181)

(920) $C_{14}H_{12}$ $C_6H_5CH=CHC_6H_5$ stilbene (*cis*) (180, 181)

(921) $C_{14}H_{12}$ $C_6H_5CH=CHC_6H_5$ stilbene (*trans*) (180, 181)

(922) $C_{14}H_{14}$ $C_6H_5CH_2CH_2C_6H_5$ dibenzyl (180, 181)

b. Halogen derivatives

1. Fluorine derivatives

(923) C_6H_5F C_6H_5F fluorobenzene (138, 265, 355, 463, 464)

2. Chlorine derivatives

(924) C_6H_5Cl C_6H_5Cl chlorobenzene (57, 69, 129, 153, 157, 159, 187, 191, 237, 294, 395, 462, 465, 519, 561, 573, 587, 625, 654)

(925) $C_7H_5Cl_3$ $C_6H_5CCl_3$ benzotrichloride (168, 171, 500)

(926) C_7H_7Cl $C_6H_5CH_2Cl$ benzyl chloride (129, 155, 205, 500)

(927) C_8H_5Cl $C_6H_5C\equiv CCl$ 1-chloro-2-phenylacetylene (102, 103)

3. Bromine derivatives

(928) C_6H_5Br C_6H_5Br bromobenzene (57, 102, 117, 153, 157, 159, 237, 355, 462, 498, 510, 587, 625, 659)

(929) C_8H_7Br $C_6H_5CH=CHBr$ 1-bromo-2-phenylethylene (508)

(930) C_9H_9Br $C_6H_5CH_2CBr=CH_2$ 2-bromo-2-benzylethylene (404, 405)

4. Iodine derivatives

(931) C_6H_5I C_6H_5I iodobenzene (153, 159, 174, 177, 462, 587)

c. Hydroxyl derivatives

(932) C_6H_6O C_6H_5OH phenol (136, 137, 153, 159, 237, 242, 355, 500)

(933) C_7H_8O $C_6H_5CH_2OH$ benzyl alcohol (155, 161, 320)

(934) $C_8H_{10}O$ $C_6H_5CHOHCH_3$ methylphenylcarbinol (421)

(935) C_9H_8O $C_6H_5C\equiv CCH_2OH$ 3-phenyl-2-propin-1-ol (276, 280)

(936) $C_{10}H_{10}O$ $C_6H_5C\equiv CCHOHCH_3$ 4-phenyl-3-butin-2-ol (276, 280)

(937) $C_{10}H_{14}O$ $(C_6H_5CH_2)C(CH_3)_2OH$ dimethylbenzylcarbinol (551)

(938) $C_{13}H_{12}O$ $(C_6H_5)_2CHOH$ diphenylcarbinol (207)

d. Ethers

(939) C_7H_8O $C_6H_5OCH_3$ methyl phenyl ether (anisole) (153, 159, 237, 242, 362, 480, 561)

(940) $C_{10}H_{10}O$ $C_6H_5C\equiv CCH_2OCH_3$ 3-methoxy-1-phenyl-1-propine (277, 280)

(941) $C_{11}H_{12}O$ $C_6H_5C\equiv CCH(OCH_3)CH_3$ 3-methoxy-1-phenyl-1-butine (277, 280)

(942) $C_{12}H_{10}O$ $C_6H_5OC_6H_5$ diphenyl ether (173, 176, 207, 659)

(943) $C_{12}H_{17}O$ $C_6H_5C\equiv CC(OCH_3)(CH_3)_2$ 3-methoxy-3-methyl-1-phenyl-1-butine (280)

(944) $C_{14}H_{10}O_4$ $C_6H_5CO\cdot O\cdot O\cdot OCC_6H_5$ benzoyl peroxide (369)

e. Carbonyl compounds

1. Aldehydes

(945) C_7H_6O C_6H_5CHO benzaldehyde   (5, 28, 136, 137, 153, 159, 294, 361, 414, 485, 486, 500, 561, 627)

(946) C_8H_8O $C_6H_5CH_2CHO$ phenylacetaldehyde (90, 361)

(947) C_9H_8O $C_6H_5CH=CHCHO$ cinnamaldehyde (361, 369)

(948) C_9H_8O $C_6H_5CH=CHCHO$ cinnamaldehyde (*trans*) (100)

2. Ketones

(949) C_8H_8O $C_6H_5COCH_3$ acetophenone (153, 155, 159, 242, 361, 561)

(950) $C_9H_{10}O$ $C_6H_5COC_2H_5$ propiophenone (ethyl phenyl ketone) (361)

(951) $C_9H_{10}O$ $C_6H_5CH_2COCH_3$ methyl benzyl ketone (361)

(952) $C_{10}H_{10}O$ $C_6H_5CH=CHCOCH_3$ benzalacetone (359, 361)

(953) $C_{10}H_{10}O$ $CH_3CH=CHCOC_6H_5$ ethylideneacetophenone (366)

(954) $C_{10}H_{12}O$ $C_6H_5CH_2COC_2H_5$ ethyl benzyl ketone (361)

(955) $C_{11}H_{12}O_2$ $C_6H_5COCH_2COC_2H_5$ benzoylpropionylmethane (359)

(956) $C_{13}H_{10}O$ $C_6H_5COC_6H_5$ benzophenone (155, 161, 361, 375, 594)

(957) $C_{14}H_{10}O_2$ $C_6H_5COCOC_6H_5$ benzil (358)

(958) $C_{14}H_{12}O$ $C_6H_5CH_2COC_6H_5$ desoxybenzoin (361)

(959) $C_{15}H_{12}O$ $C_6H_5CH=CHCOC_6H_5$ benzalacetophenone (361)

(960) $C_{15}H_{12}O$ $C_6H_5COCH_2COC_6H_5$ dibenzoylmethane (359)

3. Acyl halides

(961) C_7H_5BrO C_6H_5COBr benzoyl bromide (361)

(962) C_7H_5ClO C_6H_5COCl benzoyl chloride (155, 161, 361, 420, 561, 592)

(963) C_8H_7ClO $C_6H_5COCH_2Cl$ phenacyl chloride (361)

(964) C_8H_7ClO $C_6H_5CH_2COCl$ phenylacetyl chloride (361)

(965) C_9H_7ClO $C_6H_5CH=CHCOCl$ cinnamoyl chloride (361)

f. Acids

(966) $C_7H_6O_2$ C_6H_5COOH benzoic acid (163, 167, 168, 170, 171, 352)

(967) C_7H_6OS C_6H_5COSH thiobenzoic acid (361)

(968) $C_8H_8O_2$ $C_6H_5CH_2COOH$ phenylacetic acid (361)

(969) $C_9H_6O_2$ $C_6H_5C\equiv CCOOH$ phenylpropiolic acid (361)

(970) $C_9H_8O_2$ $C_6H_5CH=CHCOOH$ cinnamic acid (361)

g. Anhydrides of acids

(971) $C_{14}H_{10}O_3$ $(C_6H_5CO)_2O$ benzoic anhydride (369)

h. Esters

(972) $C_8H_8O_2$ $C_6H_5COOCH_3$ methyl benzoate (163, 167, 355, 369, 420)

(973) $C_8H_8O_2$ $CH_3COOC_6H_5$ phenyl acetate (420)

(974) $C_9H_9BrO_2$ $C_6H_5CHBrCOOCH_3$ methyl phenylbromoacetate (631)

(975) $C_9H_9ClO_2$ $CH_2ClCOOCH_2C_6H_5$ benzyl chloroacetate (456)

(976) $C_9H_{10}O_2$ $C_6H_5COOC_2H_5$ ethyl benzoate (163, 167, 248, 355, 420)

(977) $C_9H_{10}O_2$ $CH_3COOCH_2C_6H_5$ benzyl acetate (456)

(978) $C_9H_{10}O_2$ $C_6H_5CH_2COOCH_3$ methyl phenylacetate (361, 421)
(979) $C_{10}H_{10}O_2$ $C_6H_5CH=CHCOOCH_3$ methyl cinnamate (361)
(980) $C_{10}H_{10}O_3$ $C_6H_5COCOOC_2H_5$ ethyl benzoylformate (359)
(981) $C_{10}H_{12}O_2$ $C_3H_7COOC_6H_5$ phenyl butyrate (420)
(982) $C_{10}H_{12}O_2$ $C_6H_5COOC_3H_7$ propyl benzoate (420)
(983) $C_{10}H_{12}O_2$ $C_6H_5COOCH(CH_3)_2$ isopropyl benzoate (420)
(984) $C_{10}H_{12}O_2$ $C_6H_5CH_2COOC_2H_5$ ethyl phenylacetate (361, 421)
(985) $C_{11}H_{10}O_2$ $C_6H_5C{\equiv}CCOOC_2H_5$ ethyl phenylpropiolate (361)
(986) $C_{11}H_{12}O_2$ $C_6H_5CH=CHCOOC_2H_5$ ethyl cinnamate (359, 361, 369, 421)
(987) $C_{11}H_{12}O_3$ $C_6H_5COCH_2COOC_2H_5$ ethyl benzoylacetate (359)
(988) $C_{11}H_{14}O_2$ $C_6H_5COOC_4H_9$ butyl benzoate (420)
(989) $C_{11}H_{14}O_2$ $C_6H_5COOCH_2CH(CH_3)_2$ isobutyl benzoate (420)
(990) $C_{11}H_{14}O_2$ $C_6H_5CH_2CH_2COOC_2H_5$ ethyl hydrocinnamate (90, 361, 421)
(991) $C_{12}H_{14}O_2$ $C_6H_5CH=CHCOOCH(CH_3)_2$ isopropyl cinnamate (421)
(992) $C_{12}H_{16}O_2$ $C_6H_5COO(CH_2)_2CH(CH_3)_2$ isoamyl benzoate (420)
(993) $C_{14}H_{12}O_2$ $C_6H_5COOC_6H_4CH_3$ o-tolyl benzoate (420)
(994) $C_{15}H_{22}O_2$ $C_6H_5COOC_8H_{17}$ octyl benzoate (420)

i. Salts

(995) $C_7H_5NaO_2$ C_6H_5COONa sodium benzoate (248)

j. Cyano derivatives

(996) C_7H_5N C_6H_5CN benzonitrile (155, 161, 355, 500, 561)
(997) C_7H_5NO C_6H_5NCO phenyl isocyanate (145, 148)
(998) C_7H_5NS C_6H_5NCS phenyl isothiocyanate (145, 148, 485, 501)
(999) C_8H_7N $C_6H_5CH_2CN$ benzyl cyanide (169, 172, 320, 500)

k. Mercaptans and sulfides

(1000) C_6H_6S C_6H_5SH phenyl mercaptan (620)
(1001) $C_{12}H_{10}S$ $C_6H_5SC_6H_5$ diphenyl sulfide (207)
(1002) $C_{12}H_{10}S_2$ $C_6H_5SSC_6H_5$ diphenyl disulfide (659)
(1003) $C_{14}H_{14}S$ $C_6H_5CH_2SCH_2C_6H_5$ dibenzyl sulfide (593)

l. Sulfonic acids

(1004) $C_6H_5ClSO_2$ $C_6H_5SO_2Cl$ benzenesulfonyl chloride (475)
(1005) $C_6H_6SO_3$ $C_6H_5SO_2OH$ benzenesulfonic acid (475)

m. Amines, amides, imides, and oximes

(1006) C_6H_7N $C_6H_5NH_2$ aniline (74, 117, 153, 159, 173, 176, 239, 485)
(1007) $C_6H_8N_2$ $C_6H_5NHNH_2$ phenylhydrazine (485)
(1008) C_7H_7NO $C_6H_5CH=NOH$ benzaldoxime (87, 88)
(1009) C_7H_7NO $C_6H_5CONH_2$ benzamide (361)
(1010) $C_7H_8N_2O_2$ $C_6H_5N(CH_3)NO_2$ methylphenylnitramine (173, 176)
(1011) C_7H_9N $C_6H_5CH_2NH_2$ benzylamine (168, 171)
(1012) C_7H_9N $C_6H_5NHCH_3$ methylaniline (239)
(1013) C_8H_8NNaO $C_6H_5C(CH_3)=NONa$ acetophenone oxime (Na salt) (87, 88)

(1014) C_8H_9NO $C_6H_5NHCOCH_3$ acetanilide (594)
(1015) C_8H_9NO $C_6H_5C(CH_3)=NOH$ acetophenone oxime (87, 88)
(1016) $C_8H_{11}N$ $C_6H_5N(CH_3)_2$ dimethylaniline (74, 155, 161, 239)
(1017) $C_{10}H_{15}N$ $C_6H_5N(C_2H_5)_2$ diethylaniline (239)
(1018) $C_{11}H_{13}NO$ $C_6H_5CH=CHCOCON(CH_3)_2$ N,N-dimethylcinnamide (361)
(1019) $C_{12}H_{11}N$ $(C_6H_5)_2NH$ diphenylamine (173, 176)
(1020) $C_{13}H_{11}N$ $C_6H_5N=CHC_6H_5$ benzalaniline (84)

n. Nitro derivatives

(1021) $C_6H_5NO_2$ $C_6H_5NO_2$ nitrobenzene (7, 116, 117, 135, 136, 137, 153, 159, 170, 237, 242, 308, 403, 543, 548, 565, 574, 625, 651)
(1022) $C_7H_6NNaO_2$ $C_6H_5CH=NOONa$ *aci*-phenylnitromethane (Na salt) (151)
(1023) $C_7H_7NO_2$ $C_6H_5CH_2NO_2$ phenylnitromethane (151)

o. Metallo derivatives

(1024) $C_{12}H_{10}Hg$ $(C_6H_5)_2Hg$ mercury diphenyl (207)
(1025) $C_{12}H_{10}Se$ $(C_6H_5)_2Se$ selenium diphenyl (207)

II. *Disubstituted derivatives of benzene*

a. Hydrocarbons

(1026) C_8H_{10} $CH_3C_6H_4CH_3$ xylene (60, 142, 153, 159, 194, 242, 294, 332, 654)
(1027) C_8H_{10} $CH_3C_6H_4CH_3$ *o*-xylene (6, 8, 93, 142, 153, 156, 157, 159, 242, 355, 659)
(1028) C_8H_{10} $CH_3C_6H_4CH_3$ *m*-xylene (8, 142, 153, 156, 157, 159, 242, 355, 561, 659)
(1029) C_8H_{10} $CH_3C_6H_4CH_3$ *p*-xylene (6, 7, 8, 142, 153, 156, 157, 159, 242, 355, 659)
(1030) $C_{10}H_{10}$ $C_6H_4(CH=CH_2)_2$ *o*-divinylbenzene (508)
(1031) $C_{10}H_{14}$ $C_6H_4(C_2H_5)_2$ diethylbenzene (mixt.) (6)
      $C_{10}H_{14}$ cymene (see terpenes)
(1032) $C_{12}H_{14}$ $C_6H_4(CH=CHCH_3)_2$ *o*-diisoallylbenzene (508)

b. Halogen derivatives

(1033) C_6H_4BrCl ClC_6H_4Br *o*-chlorobromobenzene (367, 368)
(1034) C_6H_4BrCl ClC_6H_4Br *m*-chlorobromobenzene (367, 368)
(1035) C_6H_4BrCl ClC_6H_4Br *p*-chlorobromobenzene (367, 368)
(1036) $C_6H_4BrNO_2$ $BrC_6H_4NO_2$ *o*-bromonitrobenzene (554)
(1037) $C_6H_4BrNO_2$ $BrC_6H_4NO_2$ *m*-bromonitrobenzene (554)
(1038) $C_6H_4BrNO_2$ $BrC_6H_4NO_2$ *p*-bromonitrobenzene (554)
(1039) $C_6H_4Cl_2$ ClC_6H_4Cl dichlorobenzene (mixt.) (153, 159, 454)
(1040) $C_6H_4Cl_2$ ClC_6H_4Cl *o*-dichlorobenzene (153, 159, 187, 191, 454, 465, 584)
(1041) $C_6H_4Cl_2$ ClC_6H_4Cl *m*-dichlorobenzene (163, 167, 187, 191, 454, 465, 584)
(1042) $C_6H_4Cl_2$ ClC_6H_4Cl *p*-dichlorobenzene (153, 159, 187, 191, 286, 454, 465, 584)

(1043) C_6H_4ClF ClC_6H_4F *o*-chlorofluorobenzene (367, 368)
(1044) C_6H_4ClF ClC_6H_4F *m*-chlorofluorobenzene (367, 368)
(1045) C_6H_4ClI ClC_6H_4I *o*-chloroiodobenzene (367, 368)
(1046) C_6H_4ClI ClC_6H_4I *m*-chloroiodobenzene (367, 368)
(1047) C_6H_4ClI ClC_6H_4I *p*-chloroiodobenzene (367, 368)
(1048) $C_6H_4ClNO_2$ $ClC_6H_4NO_2$ *o*-chloronitrobenzene (554)
(1049) $C_6H_4ClNO_2$ $ClC_6H_4NO_2$ *m*-chloronitrobenzene (554)
(1050) $C_6H_4ClNO_2$ $ClC_6H_4NO_2$ *p*-chloronitrobenzene (554)
(1051) C_6H_5ClO ClC_6H_4OH *o*-chlorophenol (309, 367, 368, 543)
(1052) C_6H_5ClO ClC_6H_4OH *m*-chlorophenol (367, 368)
(1053) C_6H_5ClO ClC_6H_4OH *p*-chlorophenol (367, 368)
(1054) C_6H_6ClN $ClC_6H_4NH_2$ *o*-chloroaniline (367, 368)
(1055) C_6H_6ClN $ClC_6H_4NH_2$ *m*-chloroaniline (367, 368)
(1056) C_6H_6ClN $ClC_6H_4NH_2$ *p*-chloroaniline (367, 368)
(1057) C_7H_4ClN ClC_6H_4CN *o*-chlorobenzonitrile (367, 368)
(1058) C_7H_4ClN ClC_6H_4CN *m*-chlorobenzonitrile (367, 368)
(1059) C_7H_4ClN ClC_6H_4CN *p*-chlorobenzonitrile (367, 368)
(1060) C_7H_5ClO ClC_6H_4CHO *o*-chlorobenzaldehyde (90)
(1061) C_7H_5ClO ClC_6H_4CHO *m*-chlorobenzaldehyde (90)
(1062) C_7H_5ClO ClC_6H_4CHO *p*-chlorobenzaldehyde (90)
(1063) C_7H_7Br $BrC_6H_4CH_3$ *o*-bromotoluene (355)
(1064) C_7H_7Br $BrC_6H_4CH_3$ *m*-bromotoluene (355)
(1065) C_7H_7Br $BrC_6H_4CH_3$ *p*-bromotoluene (355)
(1066) C_7H_7F $FC_6H_4CH_3$ *o*-fluorotoluene (355)
(1067) C_7H_7F $FC_6H_4CH_3$ *m*-fluorotoluene (355)
(1068) C_7H_7F $FC_6H_4CH_3$ *p*-fluorotoluene (355)
(1069) C_7H_7I $IC_6H_4CH_3$ *o*-iodotoluene (355)
(1070) C_7H_7I $IC_6H_4CH_3$ *m*-iodotoluene (355)
(1071) C_7H_7I $IC_6H_4CH_3$ *p*-iodotoluene (355)
(1072) C_7H_8Cl $ClC_6H_4CH_3$ *o*-chlorotoluene (316, 355, 554)
(1073) C_7H_8Cl $ClC_6H_4CH_3$ *m*-chlorotoluene (316, 355, 554)
(1074) C_7H_8Cl $ClC_6H_4CH_3$ *p*-chlorotoluene (316, 355, 554)
(1075) $C_8H_8Br_2$ $C_6H_4(CH_2Br)_2$ xylene dibromide (449)
(1076) $C_9H_9ClO_2$ $ClC_6H_4COOC_2H_5$ ethyl *o*-chlorobenzoate (90)
(1077) $C_9H_9ClO_2$ $ClC_6H_4COOC_2H_5$ ethyl *m*-chlorobenzoate (90)
(1078) $C_9H_9ClO_2$ $ClC_6H_4COOC_2H_5$ ethyl *p*-chlorobenzoate (90)
(1079) $C_9H_9BrO_2$ $BrC_6H_4COOC_2H_5$ ethyl *o*-bromobenzoate (90)
(1080) $C_9H_9BrO_2$ $BrC_6H_4COOC_2H_5$ ethyl *m*-bromobenzoate (90)
(1081) $C_9H_9BrO_2$ $BrC_6H_4COOC_2H_5$ ethyl *p*-bromobenzoate (90)
(1082) $C_9H_9IO_2$ $IC_6H_4COOC_2H_5$ ethyl *o*-iodobenzoate (90)
(1083) $C_9H_9IO_2$ $IC_6H_4COOC_2H_5$ ethyl *m*-iodobenzoate (90)
(1084) $C_9H_9IO_2$ $IC_6H_4COOC_2H_5$ ethyl *p*-iodobenzoate (90)

c. Hydroxyl derivatives

(1085) C_6H_5ClO ClC_6H_4OH *o*-chlorophenol (309, 351, 367, 368, 543)
(1086) C_6H_5ClO ClC_6H_4OH *m*-chlorophenol (351, 367, 368)
(1087) C_6H_5ClO ClC_6H_4OH *p*-chlorophenol (351, 367, 368)
(1088) $C_6H_6O_2$ HOC_6H_4OH catechol (*o*-dihydroxybenzene) (362)
(1089) $C_6H_6O_2$ HOC_6H_4OH resorcinol (*m*-dihydroxybenzene) (298, 354, 362)

(1090) $C_6H_6O_2$ HOC$_6$H$_4$OH   hydroquinone (*p*-dihydroxybenzene) (362)

(1091) $C_7H_6O_2$ HOC$_6$H$_4$CHO   salicylaldehyde (o-hydroxybenzaldehyde) (627)

(1092) $C_7H_6O_2$ HOC$_6$H$_4$CHO   *m*-hydroxybenzaldehyde (90)

(1093) $C_7H_6O_2$ HOC$_6$H$_4$CHO   *p*-hydroxybenzaldehyde (90)

(1094) C_7H_8O CH$_3$C$_6$H$_4$OH   *o*-cresol (355)

(1095) C_7H_8O CH$_3$C$_6$H$_4$OH   *m*-cresol (355)

(1096) C_7H_8O CH$_3$C$_6$H$_4$OH   *p*-cresol (355)

(1097) $C_8H_8O_3$ HOC$_6$H$_4$COOCH$_3$ methyl salicylate (421)

(1098) $C_9H_{10}O_3$ HOC$_6$H$_4$COOC$_2$H$_5$ ethyl salicylate (421)

(1099) $C_{13}H_{10}O_3$ HOC$_6$H$_4$COOC$_6$H$_5$ phenyl salicylate (salol) (534, 625, 628)

d. Ethers

(1100) $C_8H_{10}O$ CH$_3$C$_6$H$_4$OCH$_3$ *o*-cresyl methyl ether (316)

(1101) $C_8H_{10}O$ CH$_3$C$_6$H$_4$OCH$_3$ *m*-cresyl methyl ether (316)

(1102) $C_8H_{10}O$ CH$_3$C$_6$H$_4$OCH$_3$ *p*-cresyl methyl ether (316)

(1103) $C_8H_{10}O_2$ H$_3$COC$_6$H$_4$OCH$_3$ *o*-dimethoxybenzene (veratrole) (362)

(1104) $C_8H_{10}O_2$ H$_3$COC$_6$H$_4$OCH$_3$ *m*-dimethoxybenzene (362)

(1105) $C_8H_{10}O_2$ H$_3$COC$_6$H$_4$OCH$_3$ *p*-dimethoxybenzene (362)

(1106) $C_{10}H_{12}O$ CH$_3$O—⟨ ⟩—CH=CHCH$_3$ anethole (299, 301)

e. Aldehydes

(1107) C_7H_5ClO ClC$_6$H$_4$CHO   *o*-chlorobenzaldehyde (90)

(1108) C_7H_5ClO ClC$_6$H$_4$CHO   *m*-chlorobenzaldehyde (90)

(1109) C_7H_5ClO ClC$_6$H$_4$CHO   *p*-chlorobenzaldehyde (90)

(1110) $C_7H_5NO_3$ NO$_2$C$_6$H$_4$CHO   *o*-nitrobenzaldehyde (151)

(1111) $C_7H_5NO_3$ NO$_2$C$_6$H$_4$CHO   *m*-nitrobenzaldehyde (151)

(1112) $C_7H_5NO_3$ NO$_2$C$_6$H$_4$CHO   *p*-nitrobenzaldehyde (151)

(1113) $C_7H_6O_2$ HOC$_6$H$_4$CHO   salicylaldehyde (o-hydroxybenzaldehyde) (627)

(1114) $C_7H_6O_2$ HOC$_6$H$_4$CHO   *m*-hydroxybenzaldehyde (90)

(1115) $C_7H_6O_2$ HOC$_6$H$_4$CHO   *p*-hydroxybenzaldehyde (90)

(1116) C_8H_8O CH$_3$C$_6$H$_4$CHO   *o*-tolualdehyde (90)

(1117) C_8H_8O CH$_3$C$_6$H$_4$CHO   *m*-tolualdehyde (90)

(1118) C_8H_8O CH$_3$C$_6$H$_4$CHO   *p*-tolualdehyde (90)

(1119) $C_8H_8O_2$ CH$_3$OC$_6$H$_4$CHO   *p*-anisaldehyde (627)

(1120) $C_{10}H_{12}O$ (CH$_3$)$_2$CHC$_6$H$_4$CHO   cuminaldehyde (90)

f. Acids

(1121) $C_7H_5NO_4$ NO$_2$C$_6$H$_4$COOH   *o*-nitrobenzoic acid (69, 151)

(1122) $C_7H_5NO_4$ NO$_2$C$_6$H$_4$COOH   *m*-nitrobenzoic acid (69, 151)

(1123) $C_7H_5NO_4$ NO$_2$C$_6$H$_4$COOH   *p*-nitrobenzoic acid (69, 151)

g. Anhydrides of acids

(1124) $C_8H_4O_3$ phthalic anhydride (369)
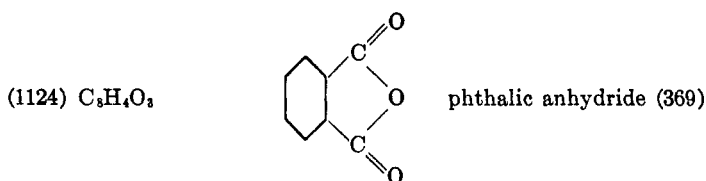
h. Esters

(1125) $C_8H_8O_3$ $HOC_6H_4COOCH_3$ methyl salicylate (421)
(1126) $C_9H_9BrO_2$ $BrC_6H_4COOC_2H_5$ ethyl o-bromobenzoate (90)
(1127) $C_9H_9BrO_2$ $BrC_6H_4COOC_2H_5$ ethyl m-bromobenzoate (90)
(1128) $C_9H_9BrO_2$ $BrC_6H_4COOC_2H_5$ ethyl p-bromobenzoate (90)
(1129) $C_9H_9IO_2$ $IC_6H_4COOC_2H_5$ ethyl o-iodobenzoate (90)
(1130) $C_9H_9IO_2$ $IC_6H_3COOC_2H_5$ ethyl m-iodobenzoate (90)
(1131) $C_9H_9IO_2$ $IC_6H_4COOC_2H_5$ ethyl p-iodobenzoate (90)
(1132) $C_9H_9ClO_2$ $ClC_6H_4COOC_2H_5$ ethyl o-chlorobenzoate (90)
(1133) $C_9H_9ClO_2$ $ClC_6H_4COOC_2H_6$ ethyl m-chlorobenzoate (90)
(1134) $C_9H_9ClO_2$ $ClC_6H_4COOC_2H_5$ ethyl p-chlorobenzoate (90)
(1135) $C_9H_{10}O_2$ $CH_3C_6H_4COOCH_3$ methyl o-toluate (355, 420)
(1136) $C_9H_{10}O_2$ $CH_3C_6H_4COOCH_3$ methyl m-toluate (355)
(1137) $C_9H_{10}O_2$ $CH_3C_6H_4COOCH_3$ methyl p-toluate (355)
(1138) $C_9H_{10}O_3$ $HOC_6H_4COOC_2H_5$ ethyl salicylate (421)
(1139) $C_{10}H_{10}O_4$ $CH_3OOCC_6H_4COOCH_3$ dimethyl phthalate (369, 421)
(1140) $C_{10}H_{12}O_2$ $CH_3C_6H_4COOC_2H_5$ ethyl o-toluate (355)
(1141) $C_{10}H_{12}O_2$ $CH_3C_6H_4COOC_2H_5$ ethyl m-toluate (355)
(1142) $C_{10}H_{12}O_2$ $CH_3C_6H_4COOC_2H_5$ ethyl p-toluate (355)
(1143) $C_{12}H_{14}O_2$ $C_6H_4(COOC_2H_5)_2$ diethyl phthalate (369, 421)
(1144) $C_{12}H_{14}O_4$ $H_5C_2OOCC_6H_4COOC_2H_5$ diethyl isophthalate (90)
(1145) $C_{12}H_{14}O_4$ $H_5C_2OOCC_6H_4COOC_2H_5$ diethyl terephthalate (90)
(1146) $C_{13}H_{10}O_3$ $HOC_6H_4COOC_6H_5$ phenyl salicylate (534, 625, 628)
(1147) $C_{14}H_{12}O_2$ $C_6H_5COOC_6H_4CH_3$ o-tolyl benzoate (420)

i. Cyano derivatives

(1148) C_7H_4ClN ClC_6H_4CN o-chlorobenzonitrile (351, 367, 368)
(1149) C_7H_4ClN ClC_6H_4CN m-chlorobenzonitrile (351, 367, 368)
(1150) C_7H_4ClN ClC_6H_4CN p-chlorobenzonitrile (351, 367, 368)
(1151) C_8H_7N $CH_3C_6H_4CN$ o-tolunitrile (145, 148, 355)
(1152) C_8H_7N $CH_3C_6H_4CN$ m-tolunitrile (355)
(1153) C_8H_7N $CH_3C_6H_4CN$ p-tolunitrile (355)
(1154) C_8H_7NS $CH_3C_6H_4NCS$ p-tolyl isothiocyanate (145, 148)

j. Sulfonic acids

(1155) $C_7H_8SO_3$ $CH_3C_6H_4SO_2OH$ toluene-p-sulfonic acid (475)

k. Amines and oximes

(1156) C_6H_6ClN $ClC_6H_4NH_2$ o-chloroaniline (351, 367, 368)
(1157) C_6H_6ClN $ClC_6H_4NH_2$ m-chloroaniline (351, 367, 368)
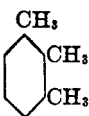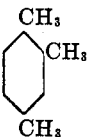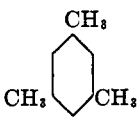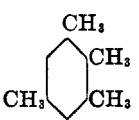
(1158) C_6H_6ClN $ClC_6H_4NH_2$ p-chloroaniline (351, 367, 368)
(1159) C_7H_6ClNO $ClC_6H_4CH=NOH$ o-chlorobenzaldoxime (87, 88)
(1160) C_7H_9N $CH_3C_6H_4NH_2$ o-toluidine (239, 355, 454)
(1161) C_7H_9N $CH_3C_6H_4NH_2$ m-toluidine (239, 355, 454)
(1162) C_7H_9N $CH_3C_6H_4NH_2$ p-toluidine (239, 355, 454)
(1163) $C_{13}H_{10}ClN$. $C_6H_5CH=NC_6H_4Cl$ benzal p-chloroaniline (84)
(1164) $C_{13}H_{10}ClN$ $ClC_6H_4CH=NC_6H_5$ p-chlorobenzalaniline (84)
(1165) $C_{13}H_{11}N$ $C_6H_5N=CHC_6H_5$ benzalaniline (84)
(1166) $C_{14}H_{13}NO$ $C_6H_5CONHC_6H_4CH_3$ benzoyl p-toluidine (84)
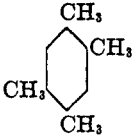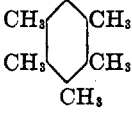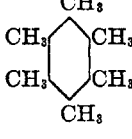
1. Nitro derivatives

(1167) $C_6H_4BrNO_2$ $BrC_6H_4NO_2$ o-bromonitrobenzene (554)
(1168) $C_6H_4BrNO_2$ $BrC_6H_4NO_2$ m-bromonitrobenzene (554)
(1169) $C_6H_4BrNO_2$ $BrC_6H_4NO_2$ p-bromonitrobenzene (554)
(1170) $C_6H_4ClNO_2$ $ClC_6H_4NO_2$ o-chloronitrobenzene (554)
(1171) $C_6H_4ClNO_2$ $ClC_6H_4NO_2$ m-chloronitrobenzene (554)
(1172) $C_6H_4ClNO_2$ $ClC_6H_4NO_2$ p-chloronitrobenzene (554)
(1172A) $C_7H_5NO_3$ $NO_2C_6H_4CHO$ o-nitrobenzaldehyde (151)
(1173) $C_7H_5NO_3$ $NO_2C_6H_4CHO$ m-nitrobenzaldehyde (151)
(1174) $C_7H_5NO_3$ $NO_2C_6H_4CHO$ p-nitrobenzaldehyde (151)
(1175) $C_7H_5NO_4$ $NO_2C_6H_4COOH$ o-nitrobenzoic acid (69, 151)
(1176) $C_7H_5NO_4$ $NO_2C_6H_4COOH$ m-nitrobenzoic acid (69, 151)
(1177) $C_7H_5NO_4$ $NO_2C_6H_4COOH$ p-nitrobenzoic acid (69, 151)
(1178) $C_7H_7NO_2$ $NO_2C_6H_4CH_3$ nitrotoluene (151, 242, 454, 543)
(1179) $C_7H_7NO_2$ $NO_2C_6H_4CH_3$ o-nitrotoluene (69, 151, 242, 316, 454)
(1180) $C_7H_7NO_2$ $NO_2C_6H_4CH_3$ m-nitrotoluene (69, 151, 242, 316, 454)
(1181) $C_7H_7NO_2$ $NO_2C_6H_4CH_3$ p-nitrotoluene (69, 151, 242, 316, 454)
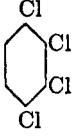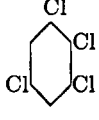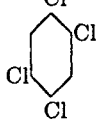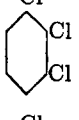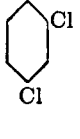
III. Tri-, tetra-, penta-, and hexa-substitution derivatives of benzene
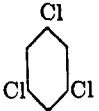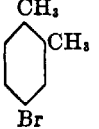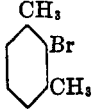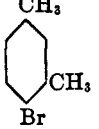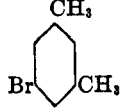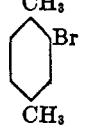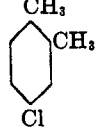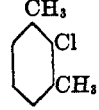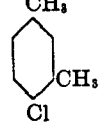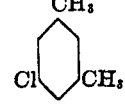
a. Hydrocarbons
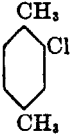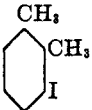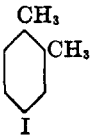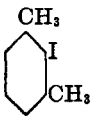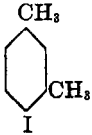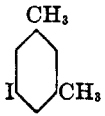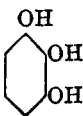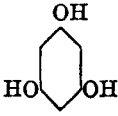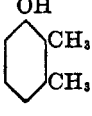
(1182) C_9H_{12} 1,2,3-trimethylbenzene (362)

(1183) C_9H_{12} 1,2,4-trimethylbenzene (362)

(1184) C_9H_{12} 1,3,5-trimethylbenzene (mesitylene) (6, 8, 367, 625, 627)

(1185) $C_{10}H_{14}$ 1,2,3,5-tetramethylbenzene (362)
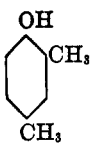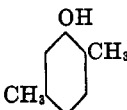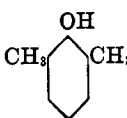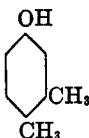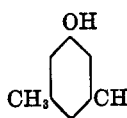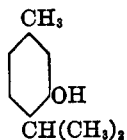
(1186) $C_{10}H_{14}$ 1,2,4,5-tetramethylbenzene (362)

(1187) $C_{11}H_{16}$ pentamethylbenzene (362)

(1188) $C_{12}H_{18}$ hexamethylbenzene (362, 463)

(1189) $C_{12}H_{18}$ $C_6H_3(C_2H_5)_3$ triethylbenzene (mixt.) (6)

(1190) $C_{14}H_{22}$ $C_6H_2(C_2H_5)_4$ tetraethylbenzene (mixt.) (6)

b. Halogen derivatives
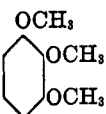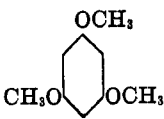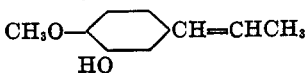
(1191) C_6Cl_6 C_6Cl_6 hexachlorobenzene (187, 191, 463, 465)

(1192) C_6HCl_5 C_6HCl_5 pentachlorobenzene (187, 191, 463)

(1193) $C_6H_2Cl_4$ 1,2,3,4-tetrachlorobenzene (187, 191)

(1194) $C_6H_2Cl_4$ 1,2,3,5-tetrachlorobenzene (69, 187, 191)

(1195) $C_6H_2Cl_4$ 1,2,4,5-tetrachlorobenzene (187, 191, 463)

(1196) $C_6H_3Cl_3$ 1,2,3-trichlorobenzene (187, 191, 465)

(1197) $C_6H_3Cl_3$ 1,2,4-trichlorobenzene (187, 191, 456, 463, 465)

(1198) $C_6H_3Cl_3$

1,3,5-trichlorobenzene (187, 191, 465)

(1199) C_8H_9Br

1,2-dimethyl-4-bromobenzene (360)

(1200) C_8H_9Br

1,3-dimethyl-2-bromobenzene (360)

(1201) C_8H_9Br

1,3-dimethyl-4-bromobenzene (360)

(1202) C_8H_9Br

1,3-dimethyl-5-bromobenzene (360)

(1203) C_8H_9Br

1,4-dimethyl-2-bromobenzene (360)

(1204) C_8H_9Cl

1,2-dimethyl-4-chlorobenzene (360)

(1205) C_8H_9Cl

1,3-dimethyl-2-chlorobenzene (360)

(1206) C_8H_9Cl

1,3-dimethyl-4-chlorobenzene (360)

(1207) C_8H_9Cl

1,3-dimethyl-5-chlorobenzene (360)
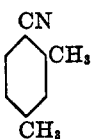
(1208) C_8H_9Cl 1,4-dimethyl-2-chlorobenzene (360)

(1209) C_8H_9I 1,2-dimethyl-3-iodobenzene (360)

(1210) C_8H_9I 1,2-dimethyl-4-iodobenzene (360)

(1211) C_8H_9I 1,3-dimethyl-2-iodobenzene (360)

(1212) C_8H_9I 1,3-dimethyl-4-iodobenzene (360)

(1213) C_8H_9I 1,3-dimethyl-5-iodobenzene (360)

(1214) C_8H_9I 1,4-dimethyl-2-iodobenzene (360)

c. Hydroxyl derivatives

(1215) $C_6H_6O_3$ pyrogallol (362)

(1216) $C_6H_6O_3$ phloroglucinol (362)

(1217) $C_8H_{10}O$ 1,2,3-xylenol (184, 188)

(1218) $C_8H_{10}O$

OH
CH₃
CH₃
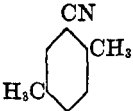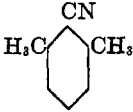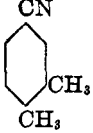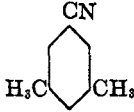
1,2,4-xylenol (184, 188)

(1219) $C_8H_{10}O$

OH
CH₃
CH₃

1,2,5-xylenol (184, 188)

(1220) $C_8H_{10}O$

OH
CH₃   CH₃

1,2,6-xylenol (184, 188)

(1221) $C_8H_{10}O$

OH
CH₃
CH₃

1,3,4-xylenol (184, 188)

(1222) $C_8H_{10}O$

OH
CH₃   CH₃

1,3,5-xylenol (184, 188)

(1223) $C_{10}H_{14}O$

CH₃
OH
CH(CH₃)₂

thymol (628)

d. Ethers
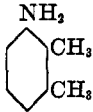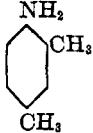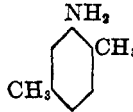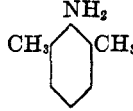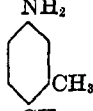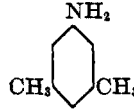
(1224) $C_9H_{12}O_3$

OCH₃
OCH₃
OCH₃

1,2,3-trimethoxybenzene (362)

(1225) $C_9H_{12}O_3$

OCH₃
CH₃O   OCH₃

1,3,5-trimethoxybenzene (362)

(1226) $C_{10}H_{12}O_2$

CH₃O—⟨ ⟩—CH=CHCH₃   isoeugenol (300, 301)
HO

e. Cyano derivatives

(1227) C_9H_9N

CN
CH₃
CH₃

2,4-dimethylbenzonitrile (360)
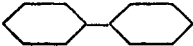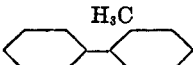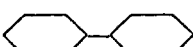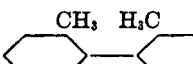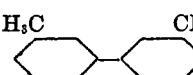
(1228) C_9H_9N 2,5-dimethylbenzonitrile (360)

(1229) C_9H_9N 2,6-dimethylbenzonitrile (360)

(1230) C_9H_9N 3,4-dimethylbenzonitrile (360)

(1231) C_9H_9N 3,5-dimethylbenzonitrile (360)

f. Amino derivatives
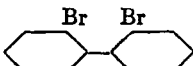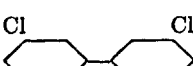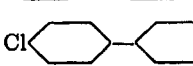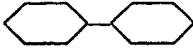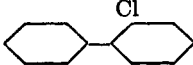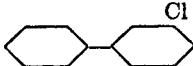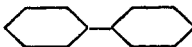
(1232) $C_8H_{11}N$ 1,2,3-xylidine (184, 188)

(1233) $C_8H_{11}N$ 1,2,4-xylidine (184, 188)

(1234) $C_8H_{11}N$ 1,2,5-xylidine (184, 188)

(1235) $C_8H_{11}N$ 1,2,6-xylidine (184, 188, 239)

(1236) $C_8H_{11}N$ 1,3,4-xylidine (184, 188)

(1237) $C_8H_{11}N$ 1,3,5-xylidine (184, 188, 239)

IV. Diphenyl and derivatives of diphenyl
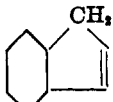
a. Hydrocarbons
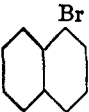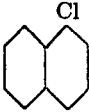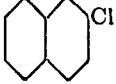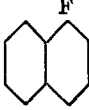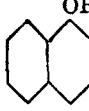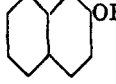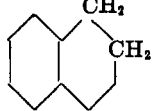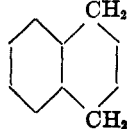
(1238) $C_{12}H_{10}$ diphenyl (163, 167, 207, 658, 659)

(1239) $C_{13}H_{12}$ 2-methyldiphenyl (89)

(1240) $C_{13}H_{12}$ 3-methyldiphenyl (89)

(1241) $C_{13}H_{12}$ 4-methyldiphenyl (89)

(1242) $C_{14}H_{14}$ 2,2'-dimethyldiphenyl (89)

(1243) $C_{14}H_{14}$ 3,3'-dimethyldiphenyl (89)

b. Halogen derivatives

(1244) $C_{12}H_8Br_2$ 2,2'-dibromodiphenyl (90)

(1245) $C_{12}H_8Cl_2$ 3,3'-dichlorodiphenyl (89)

(1246) $C_{12}H_8Cl_2$ 4,4'-dichlorodiphenyl (89)

(1247) $C_{12}H_9Br$ 4-bromodiphenyl (89)

(1248) $C_{12}H_9Cl$ 2-chlorodiphenyl (89)

(1249) $C_{12}H_9Cl$ 3-chlorodiphenyl (89)

(1250) $C_{12}H_9Cl$ 4-chlorodiphenyl (89)

V. Polycyclic compounds

(1251) C_9H_8 indene (89, 258, 299)

(1252) $C_{10}H_7Br$ 1-bromonaphthalene (258, 671)

(1253) $C_{10}H_7Br$ 2-bromonaphthalene (174, 177, 258)

(1254) $C_{10}H_7Cl$ 1-chloronaphthalene (258, 671)

(1255) $C_{10}H_7Cl$ 2-chloronaphthalene (258, 671)

(1256) $C_{10}H_7F$ 1-fluoronaphthalene (258)

(1257) $C_{10}H_8$ naphthalene (22, 153, 159, 258, 287, 343, 438, 498, 671)

(1258) $C_{10}H_8O$ 1-naphthol (258)

(1259) $C_{10}H_8O$ 2-naphthol (258)

(1260) $C_{10}H_8S$ 1-naphthyl mercaptan (258)

(1261) $C_{10}H_8S$ 2-naphthyl mercaptan (258)

(1262) $C_{10}H_{10}$ 1,2-dihydronaphthalene (69, 299)

(1263) $C_{10}H_{10}$ 1,4-dihydronaphthalene (69, 85, 299)

(1264) $C_{10}H_{12}$

$\begin{array}{c} CH_2 \\ CH_2 \\ CH_2 \\ CH_2 \end{array}$

1,2,3,4-tetrahydronaphthalene (81, 457, 458)

(1265) $C_{10}H_{18}$

$\begin{array}{cc} H_2 & H_2 \\ H_2 & H_2 \\ H_2 & H_2 \\ H_2 & H_2 \end{array}$

decahydronaphthalene (81, 457, 458)

(1266) $C_{11}H_7N$

CN

1-naphthyl cyanide (258)

(1267) $C_{11}H_7N$

CN

2-naphthyl cyanide (258)

(1268) $C_{11}H_7NO$

NCO

2-naphthyl isocyanate (145, 148)

(1269) $C_{11}H_{10}$

CH₃

1-methylnaphthalene (258, 671)

(1270) $C_{11}H_{10}$

CH₃

2-methylnaphthalene (258, 671)

C. HETEROCYCLIC COMPOUNDS

I. Monocyclic compounds

a. Compounds containing ring oxygen

(1271) C_4H_4O

$\begin{array}{cc} HC & CH \\ \| & \| \\ HC & CH \\ & O \end{array}$

furan (69, 70, 91, 257, 426, 517)

(1272) C_4H_5NO

$\begin{array}{cc} HC & CH \\ \| & \| \\ HC & CNH_2 \\ & O \end{array}$

2-furylamine (69, 91)

(1273) $C_4H_8O_2$

$$\begin{array}{c} CH_2\text{---}CH_2 \\ O \qquad\qquad O \\ CH_2\text{---}CH_2 \end{array}$$
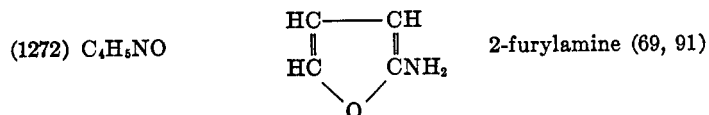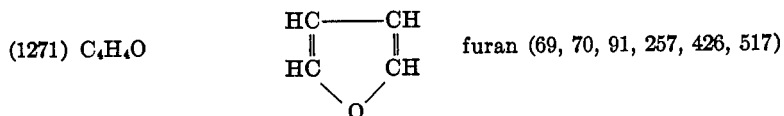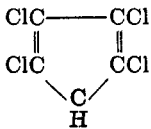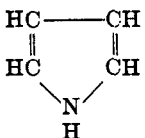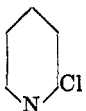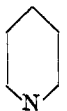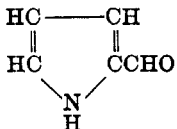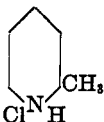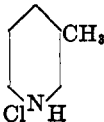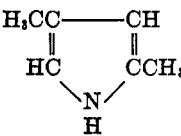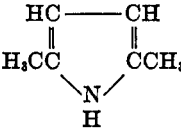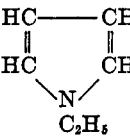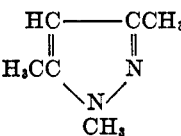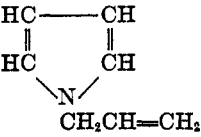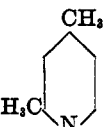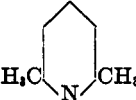
dioxane (630, 652)

(1274) $C_5H_3ClO_2$

$$\begin{array}{c} HC\text{-----}CH \\ \| \qquad \| \\ HC \qquad CCOCl \\ O \end{array}$$

2-furoyl chloride (422)

(1275) $C_5H_4O_2$

$$\begin{array}{c} HC\text{-----}CH \\ \| \qquad \| \\ HC \qquad CCHO \\ O \end{array}$$

2-furaldehyde (furfural) (91, 257, 369, 414, 422, 426)

(1276) C_5H_6O

$$\begin{array}{c} HC\text{-----}CH \\ \| \qquad \| \\ HC \qquad CCH_3 \\ O \end{array}$$

2-methylfuran (422, 426)

(1277) $C_5H_6O_2$

$$\begin{array}{c} HC\text{-----}CH \\ \| \qquad \| \\ HC \qquad CCH_2OH \\ O \end{array}$$

2-furylcarbinol (69, 422, 426, 517)

(1278) $C_5H_{10}O_2$

$$\begin{array}{c} H_2C\text{-----}CH_2 \\ | \qquad | \\ H_2C \qquad CHCH_2OH \\ O \end{array}$$

tetrahydro-2-furylcarbinol (422)

(1279) $C_6H_6O_3$

$$\begin{array}{c} HC\text{-----}CH \\ \| \qquad \| \\ HC \qquad CCOOCH_3 \\ O \end{array}$$

methyl 2-furoate (methyl pyro-mucate) (422)

(1280) C_6H_8O

$$\begin{array}{c} HC\text{-----}CH \\ \| \qquad \| \\ H_3CC \qquad CCH_3 \\ O \end{array}$$

2,5-dimethylfuran (69, 91)

(1281) $C_6H_{10}O_3$

$$\begin{array}{c} CH_3CH\text{---}C\text{=}O \\ | \qquad | \\ O \qquad O \\ C \\ (CH_3)_2 \end{array}$$

acetone lactic acid (479)

(1282) $C_7H_6O_3$

$$\begin{array}{c} HC\text{-----}CH \\ \| \qquad \| \\ HC \qquad CCH\text{=}CHCOOH \\ O \end{array}$$

2-furylacrylic acid (422)

(1283) $C_7H_8O_3$

$$\begin{array}{cc} HC\!\!-\!\!-\!\!-\!\!CH \\ \| \quad\quad \| \\ HC \quad\quad CCOOC_2H_5 \\ \diagdown\ \diagup \\ O \end{array}$$
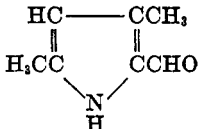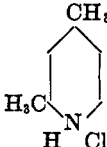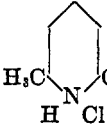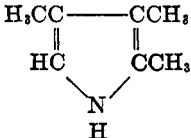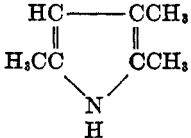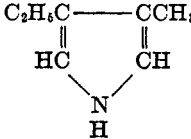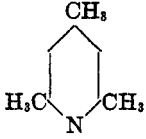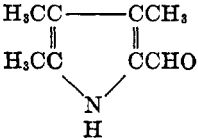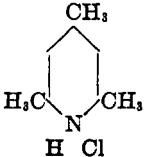
ethyl 2-furoate (ethyl pyro-mucate) (91, 422)

(1284) $C_7H_8O_3$

$$\begin{array}{cc} HC\!\!-\!\!-\!\!-\!\!CH \\ \| \quad\quad \| \\ HC \quad\quad CCH_2OOCCH_3 \\ \diagdown\ \diagup \\ O \end{array}$$

2-furylcarbinol acetate (422)

(1285) $C_9H_{10}O_3$

$$\begin{array}{cc} HC\!\!-\!\!-\!\!-\!\!CH \\ \| \quad\quad \| \\ HC \quad\quad CCH\!\!=\!\!CHCOOC_2H_5 \\ \diagdown\ \diagup \\ O \end{array}$$

ethyl 2-furylacrylate (422)

(1286) $C_9H_{16}O_3$

$$\begin{array}{c} (CH_3)_2CHCH_2CH\!\!-\!\!-\!\!C\!\!=\!\!O \\ |\quad\quad\quad | \\ O\quad\quad\ \ O \\ \diagdown\ \diagup \\ C \\ (CH_3)_2 \end{array}$$

acetone leuicic acid (479)
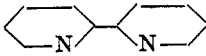
b. Compounds containing ring nitrogen

(1287) C_4HCl_4N

$$\begin{array}{cc} ClC\!\!-\!\!-\!\!-\!\!CCl \\ \| \quad\quad \| \\ ClC \quad\quad CCl \\ \diagdown\ \diagup \\ C \\ H \end{array}$$

tetrachloropyrrole (96)

(1288) C_4H_5N

$$\begin{array}{cc} HC\!\!-\!\!-\!\!-\!\!CH \\ \| \quad\quad \| \\ HC \quad\quad CH \\ \diagdown\ \diagup \\ N \\ H \end{array}$$

pyrrole (69, 70, 91, 95, 619, 625)

(1289) C_5H_4ClN

2-chloropyridine (462)

(1290) C_5H_5N

pyridine (75, 129, 242, 359, 378, 379, 480, 498, 621, 625, 645)

(1291) C_5H_5NO

$$\begin{array}{cc} HC\!\!-\!\!-\!\!-\!\!CH \\ \| \quad\quad \| \\ HC \quad\quad CCHO \\ \diagdown\ \diagup \\ N \\ H \end{array}$$

2-pyrrolealdehyde (96)

(1292) C_5H_6NO

$$\begin{array}{c} HC\!\!-\!\!-\!\!CH \\ \| \quad \| \\ HC \quad CCH\!\!=\!\!NOH \\ \diagdown N \diagup \\ H \end{array}$$

2-pyrrolealdoxime (96)

(1293) C_5H_7N

$$\begin{array}{c} HC\!\!-\!\!-\!\!CH \\ \| \quad \| \\ HC \quad CH \\ \diagdown N \diagup \\ CH_3 \end{array}$$

1-methylpyrrole (95, 96)

(1294) C_5H_7N

$$\begin{array}{c} HC\!\!-\!\!-\!\!CH \\ \| \quad \| \\ HC \quad CCH_3 \\ \diagdown N \diagup \\ H \end{array}$$

2-methylpyrrole (95)

(1295) $C_5H_{11}N$

$$\begin{array}{c} H_2 \quad H_2 \\ C\!\!-\!\!C \\ H_2C \qquad NH \\ C\!\!-\!\!C \\ H_2 \quad H_2 \end{array}$$

piperidine (73, 75, 568)

(1296) $C_5H_{11}N$

$$\begin{array}{c} H_2C\!\!-\!\!-\!\!CH_2 \\ | \qquad | \\ H_2C \quad CHCH_3 \\ \diagdown N \diagup \\ H \end{array}$$

2-methylpyrrolidine (95)

(1297) C_6H_7N

2-methylpyridine (α-picoline) (89, 480)

(1298) C_6H_7N

3-methylpyridine (β-picoline) (89)

(1299) C_6H_7NO

$$\begin{array}{c} HC\!\!-\!\!-\!\!CH \\ \| \quad \| \\ HC \quad CH \\ \diagdown N \diagup \\ COCH_3 \end{array}$$

1-acetylpyrrole (95)

(1300) C_6H_7NO

$$\begin{array}{c} HC\!\!-\!\!-\!\!CH \\ \| \quad \| \\ HC \quad CCOCH_3 \\ \diagdown N \diagup \\ H \end{array}$$

2-acetylpyrrole (96)

(1301) C_6H_8ClN 2-methylpyridine hydrochyloride (89)

(1302) C_6H_8ClN 3-methylpyridine hydrochloride (89)

(1303) C_6H_9N 2,4-dimethylpyrrole (96)

(1304) C_6H_9N 2,5-dimethylpyrrole (96)

(1305) C_6H_9N 1-ethylpyrrole (90)

(1306) $C_6H_{10}N_2$ 1,3,5-trimethylpyrazole (89)

(1307) $C_6H_{12}N_4$ $C_6H_{12}N_4$ hexamine (hexamethylenetetramine) (376)

(1308) $C_6H_{13}ClN_4$ $C_6H_{13}ClN_4$ hexamine hydrochloride (377)

(1309) C_7H_9N 1-allylpyrrole (69, 89)

(1310) C_7H_9N 2,4-dimethylpyridine (89)

(1311) C_7H_9N 2,6-dimethylpyridine (89)

(1312) C_7H_9NO

$$
\begin{array}{ccc}
HC & \!\!\!\!-\!\!\!\!- & CCH_3 \\
\| & & \| \\
H_3CC & & CCHO \\
& N & \\
& H &
\end{array}
$$

3,5-dimethyl-2-pyrrolealdehyde (96)

(1313) $C_7H_{10}ClN$

CH_3 ... H_3C ... N ... H Cl

2,4-dimethylpyridine hydrochloride (89)

(1314) $C_7H_{10}ClN$

H_3C ... N ... CH_3 ... H Cl

2,6-dimethylpyridine hydrochloride (89)

(1315) $C_7H_{11}N$

$$
\begin{array}{ccc}
H_3CC & \!\!\!\!-\!\!\!\!- & CCH_3 \\
\| & & \| \\
HC & & CCH_3 \\
& N & \\
& H &
\end{array}
$$

2,3,4-trimethylpyrrole (96)

(1316) $C_7H_{11}N$

$$
\begin{array}{ccc}
HC & \!\!\!\!-\!\!\!\!- & CCH_3 \\
\| & & \| \\
H_3CC & & CCH_3 \\
& N & \\
& H &
\end{array}
$$

2,3,5-trimethylpyrrole (96)

(1317) $C_7H_{11}N$

$$
\begin{array}{ccc}
C_2H_5C & \!\!\!\!-\!\!\!\!- & CCH_3 \\
\| & & \| \\
HC & & CH \\
& N & \\
& H &
\end{array}
$$

3-methyl-4-ethylpyrrole (opsopyrrole) (95)

(1318) $C_8H_{11}N$

CH_3 ... H_3C ... CH_3 ... N

2,4,6-trimethylpyridine (89)

(1319) $C_8H_{11}NO$

$$
\begin{array}{ccc}
H_3CC & \!\!\!\!-\!\!\!\!- & CCH_3 \\
\| & & \| \\
H_3CC & & CCHO \\
& N & \\
& H &
\end{array}
$$

3,4,5-trimethyl-2-pyrrolealdehyde (90)

(1320) $C_8H_{12}ClN$

CH_3 ... H_3C ... CH_3 ... N ... H Cl

2,4,6-trimethylpyridine hydrochloride (89)

(1321) $C_8H_{13}N$

$$\begin{array}{ccc} CH_3C\!\!-\!\!-\!\!-\!\!-CC_2H_5 \\ \| \qquad\quad \| \\ HC \qquad CCH_3 \\ \diagdown\ \ \diagup \\ N \\ | \\ H \end{array}$$

2,4-dimethyl-3-ethylpyrrole (kryptopyrrole) (95)

(1322) $C_8H_{13}N$

$$\begin{array}{ccc} HC\!\!-\!\!-\!\!-\!\!-CC_2H_5 \\ \| \qquad\quad \| \\ H_3CC \qquad CCH_3 \\ \diagdown\ \ \diagup \\ N \\ | \\ H \end{array}$$

2,5-dimethyl-3-ethylpyrrole (89)

(1323) $C_8H_{13}N$

$$\begin{array}{ccc} HC\!\!-\!\!-\!\!-\!\!-CH \\ \| \qquad\quad \| \\ H_3CC \qquad CCH_3 \\ \diagdown\ \ \diagup \\ N \\ | \\ C_2H_5 \end{array}$$

2,5-dimethyl-1-ethylpyrrole (89)

(1324) $C_9H_8N_2$

$$\begin{array}{ccc} HC\!\!-\!\!-\!\!-\!\!-CH \\ \| \qquad\quad \| \\ HC \qquad N \\ \diagdown\ \ \diagup \\ N \\ | \\ C_6H_5 \end{array}$$

1-phenylpyrazole (89)

(1325) $C_9H_{13}NO$

$$\begin{array}{ccc} C_2H_5C\!\!-\!\!-\!\!-\!\!-CCH_3 \\ \| \qquad\quad \| \\ H_3CC \qquad CCHO \\ \diagdown\ \ \diagup \\ N \\ | \\ H \end{array}$$

3,5-dimethyl-4-ethyl-2-pyrrole-aldehyde (90)

(1326) $C_9H_{15}N$

$$\begin{array}{ccc} HC\!\!-\!\!-\!\!-\!\!-CH \\ \| \qquad\quad \| \\ H_5C_2C \qquad CC_2H_5 \\ \diagdown\ \ \diagup \\ N \\ | \\ CH_3 \end{array}$$

1-methyl-2,5-diethylpyrrole (90)

(1327) $C_9H_{15}N$

$$\begin{array}{ccc} H_3CC\!\!-\!\!-\!\!-\!\!-CC_3H_7 \\ \| \qquad\quad \| \\ HC \qquad CCH_3 \\ \diagdown\ \ \diagup \\ N \\ | \\ H \end{array}$$

2,4-dimethyl-3-propylpyrrole (95)

(1328) $C_{10}H_8N_2$

α,α-dipyrridyl (89)

(1329) $C_{15}H_{20}N_2O$

$$\begin{array}{cccc} HC\!\!-\!\!-\!\!-\!\!-CC_2H_5 & H_5C_2C\!\!-\!\!-\!\!-\!\!-CH \\ \| \qquad\quad \| & \| \qquad\quad \| \\ H_3CC \qquad C\!\!-\!\!-C\!\!-\!\!-C \qquad CCH_3 \\ \diagdown\ \ \diagup \ \ \| \ \ \diagdown\ \ \diagup \\ N \qquad O \qquad N \\ | \qquad\qquad\quad | \\ H \qquad\qquad\quad H \end{array}$$

3,3'-diethyl-5,5'-dimethyl-2,2'-dipyrryl ketone (96)

(1330) $C_{15}H_{20}N_2O$

$$\begin{array}{c}\text{HC}\underline{\hspace{1cm}}\text{CCH}_3 \quad \text{H}_3\text{CC}\underline{\hspace{1cm}}\text{CH} \\ \| \qquad \| \qquad \| \qquad \| \\ \text{H}_5\text{C}_2\text{C} \quad \text{C}\underline{\hspace{0.5cm}}\text{C}\underline{\hspace{0.5cm}}\text{C} \quad \text{CC}_2\text{H}_5 \\ \diagdown\text{N}\diagup \quad \| \quad \diagdown\text{N}\diagup \\ \qquad \text{H} \qquad \text{O} \qquad \text{H}\end{array}$$

3,3'-dimethyl-5,5'-diethyl-2,2'-dipyrryl ketone (96)

(1331) $C_{19}H_{28}N_2O$

$$\begin{array}{c}\text{H}_7\text{C}_3\text{C}\underline{\hspace{1cm}}\text{CCH}_3 \quad \text{H}_3\text{CC}\underline{\hspace{1cm}}\text{CC}_3\text{H}_7 \\ \| \qquad \| \qquad \| \qquad \| \\ \text{H}_3\text{CC} \quad \text{C}\underline{\hspace{0.5cm}}\text{C}\underline{\hspace{0.5cm}}\text{C} \quad \text{CCH}_3 \\ \diagdown\text{N}\diagup \quad \| \quad \diagdown\text{N}\diagup \\ \qquad \text{H} \qquad \text{O} \qquad \text{H}\end{array}$$

3,3'-dimethyl-5,5'-dimethyl-4,4'-dipropyl-2,2'-dipyrryl ketone (96)
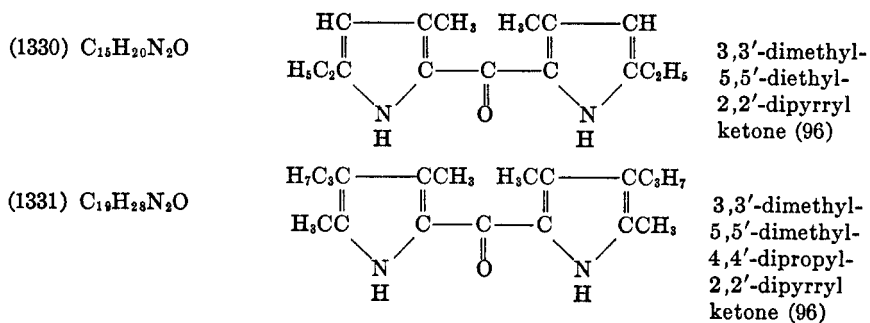
c. Compounds containing ring oxygen and nitrogen

(1332) $C_4H_6N_2O$

$$\begin{array}{c}\text{N}\underline{\hspace{1cm}}\text{N} \\ \| \qquad \| \\ \text{H}_3\text{CC} \qquad \text{CCH}_3 \\ \diagdown\text{O}\diagup\end{array}$$

2,5-dimethyloxdiazole (446, 447)

(1333) $C_4H_6N_2O$

$$\begin{array}{c}\text{H}_3\text{CC}\underline{\hspace{1cm}}\text{CCH}_3 \\ \| \qquad \| \\ \text{N} \qquad \text{N} \\ \diagdown\text{O}\diagup\end{array}$$

3,4-dimethylfurazan (446, 447)

(1334) $C_5H_8N_2O$

$$\begin{array}{c}\text{H}_3\text{CC}\underline{\hspace{1cm}}\text{CC}_2\text{H}_5 \\ \| \qquad \| \\ \text{N} \qquad \text{N} \\ \diagdown\text{O}\diagup\end{array}$$

4-methyl-3-ethylfurazan (446, 447)

(1335) $C_9H_8N_2O$

$$\begin{array}{c}\text{C}_6\text{H}_5\text{C}\underline{\hspace{1cm}}\text{CCH}_3 \\ \| \qquad \| \\ \text{N} \qquad \text{N} \\ \diagdown\text{O}\diagup\end{array}$$

3-methyl-4-phenylfurazan (443)

(1336) $C_9H_8N_2O$

$$\begin{array}{c}\text{N}\underline{\hspace{1cm}}\text{N} \\ \| \qquad \| \\ \text{C}_6\text{H}_5\text{C} \qquad \text{CCH}_3 \\ \diagdown\text{O}\diagup\end{array}$$

2-methyl-5-phenyloxdiazole (443)

(1337) $C_9H_8N_2O$

$$\begin{array}{c}\text{N}\underline{\hspace{1cm}}\text{CC}_6\text{H}_5 \\ \| \qquad \| \\ \text{H}_3\text{CC} \qquad \text{N} \\ \diagdown\text{O}\diagup\end{array}$$

5-methyl-3-phenylazoxime (443)

(1338) $C_9H_8N_2O$

$$\begin{array}{c}\text{N}\underline{\hspace{1cm}}\text{CCH}_3 \\ \| \qquad \| \\ \text{C}_6\text{H}_5\text{C} \qquad \text{N} \\ \diagdown\text{O}\diagup\end{array}$$

3-methyl-5-phenylazoxime (443)

(1339) $C_{14}H_{10}N_2O$

$$\begin{array}{c}\text{C}_6\text{H}_5\text{C}\underline{\hspace{1cm}}\text{CC}_6\text{H}_5 \\ \| \qquad \| \\ \text{N} \qquad \text{N} \\ \diagdown\text{O}\diagup\end{array}$$

3,4-diphenylfurazan (443)

(1340) $C_{14}H_{10}N_2O$

$$\begin{array}{c} N\text{------}N \\ \parallel \quad\quad \parallel \\ C_6H_5C \quad\quad CC_6H_5 \\ \diagdown \quad \diagup \\ O \end{array}$$

2,5-diphenyloxdiazole (443)

(1341) $C_{14}H_{10}N_2O$

$$\begin{array}{c} N\text{------}CC_6H_5 \\ \parallel \quad\quad \parallel \\ C_6H_5C \quad\quad N \\ \diagdown \quad \diagup \\ O \end{array}$$

3,5-diphenylazoxime (443)

d. Compounds containing ring sulfur

(1342) C_4HCl_3S

$$\begin{array}{c} HC\text{------}CCl \\ \parallel \quad\quad \parallel \\ ClC \quad\quad CCl \\ \diagdown \quad \diagup \\ S \end{array}$$

2,3,5-trichlorothiophene (91)

(1343) $C_4H_2Br_2S$

$$\begin{array}{c} HC\text{------}CH \\ \parallel \quad\quad \parallel \\ BrC \quad\quad CBr \\ \diagdown \quad \diagup \\ S \end{array}$$

2,5-dibromothiophene (91)

(1344) C_4H_4S

$$\begin{array}{c} HC\text{------}CH \\ \parallel \quad\quad \parallel \\ HC \quad\quad CH \\ \diagdown \quad \diagup \\ S \end{array}$$

thiophene (48, 61, 69, 91, 94, 619, 625, 628)

(1345) C_5H_6S

$$\begin{array}{c} HC\text{------}CH \\ \parallel \quad\quad \parallel \\ HC \quad\quad CCH_3 \\ \diagdown \quad \diagup \\ S \end{array}$$

2-methylthiophene (91)

II. *Polycyclic compounds*

(1346) $C_8H_4KNO_2$

potassium phthalimide (369)

(1347) $C_8H_6O_2$

phthalide (369)

(1348) $C_8H_6O_3$

piperonal (90)
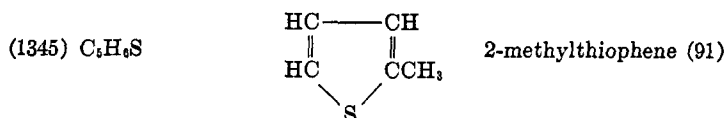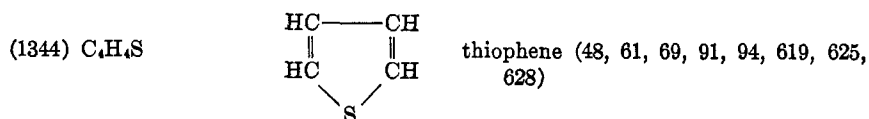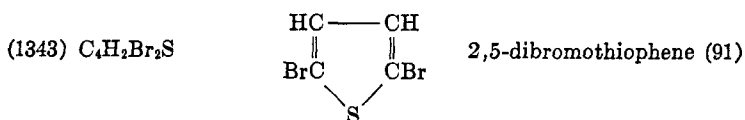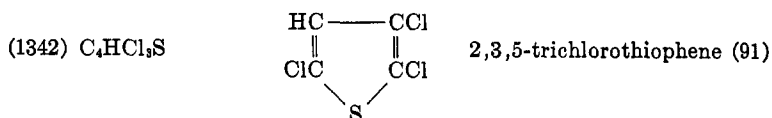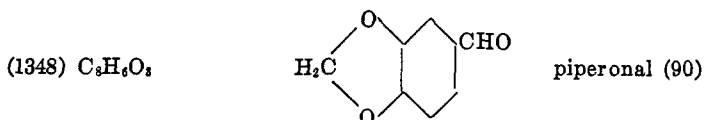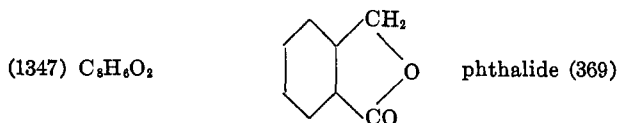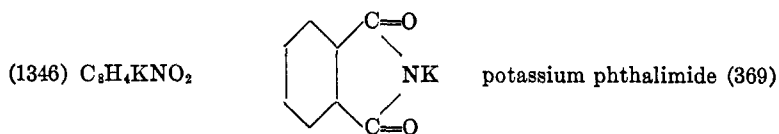
(1349) C_8H_6S thionaphthene (90)

(1350) C_8H_7N indole (90, 93)

(1351) C_9H_7N quinoline (83, 89, 242)

(1352) C_9H_7N isoquinoline (89)

(1353) $C_9H_7NO_2$ indole-2-carboxylic acid (90)

(1354) C_9H_9N 2-methylindole (90)

(1355) C_9H_9N 3-methylindole (90)

(1356) C_9H_9N 7-methylindole (90)

(1357) $C_9H_{11}N$ 2,3-dihydro-2-methylindole (90)

(1358) $C_9H_{11}N$ tetrahydroquinoline (89)

(1359) $C_9H_{11}N$ tetrahydroisoquinoline (89)

(1360) $C_{10}H_9N$ quinaldine (89)

(1361) $C_{10}H_9N$ 4-methylquinoline (89)

(1362) $C_{10}H_9N$ 6-methylquinoline (89)

(1363) $C_{10}H_9N$ 7-methylquinoline (89)

(1364) $C_{10}H_9N$ 8-methylquinoline (89)

(1365) $C_{10}H_{10}O_2$ safrole (456)

(1366) $C_{10}H_{10}O_2$ isosafrole (299, 301)

(1367) $C_{11}H_{11}N$ 2,4-dimethylquinoline (89)

(1368) $C_{11}H_{12}N_2O$ antipyrene (89)

(1369) $C_{13}H_{17}N$ 3,3-diethyl-2-methylindolenine (90)

(1370) $C_{13}H_{17}N_3O$ pyramidone (89)

INDEX OF COMPOUNDS[2]

[2] In naming these compounds the Geneva system was used generally for the higher members of the series. Whenever in the literature two names were used—the Geneva system name and one more commonly employed—the compound was indexed under the latter. The iso compounds were indexed under "iso". The prefixes "secondary" and "tertiary" were disregarded in placing names containing them in the index. When two or more radicals appeared in a name, they were listed in the order of increasing size.

[3] The numbers following the names of the compounds refer to the "formula numbers" used in the formula index.

SUPPLEMENT: INORGANIC COMPOUNDS

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Page 355.   In equation 5 the first ν should be $\bar{\nu}$.

The next to the last line should read "the mean restoring force is $1/2\bar{a}F$ and the necessary energy is $1/2\bar{a}^2F$, which may be equated to $h\nu c$,"

In the last equation substitute $2\pi^2$ for $4\pi^2$.

Page 393.   The figure attributed to Segré should be attributed to Bolla.

Page 453.   In line 19, R—C=N should read "R—C≡N."

Page 470.   Reference 172 should read "Mecke"; reference 173 should read "Mecke and Baumann"; reference 174 should read "Mecke and Freudenberg."

Page 477.   In section V, read "Carelli and Went" for "Carelli and West."

All references to the work of Kohlrausch and associates published in the *Sitzungsberichte*, as well as references 42, 56, and 57, should read "Abt. a" instead of "Abt. b."

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[5] These corrections are to be made in the previous article by Hibben (Chem. Rev. **13**, 345 (1933)).