tween 2 and 50 cu. mm. per gram of hydrogen, nitrogen, carbon monoxide and carbon dioxide, and no readily detectable quantities of methane or cyanogen.

A previous discrepancy between chemically and thermally determined hydrogen contents of terrestrial steels has been explained.

The essential similarity of the gases in terrestrial and meteoritic steels has been demonstrated.

CAMBRIDGE, MASS. RECEIVED MARCH 14, 1947

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE, AND THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Electric Moments and Ultraviolet Absorption Spectra of Some Derivatives of Cyclopropane and of Ethylene Oxide

BY MAX T. ROGERS

A number of studies have shown that derivatives of cyclopropane behave in many ways like the corresponding ethylene derivatives. Thus, the ultraviolet absorption spectra of a series of derivatives of benzoyl and anisoyl cyclopropane,[1] and of some steroids containing cyclopropane rings,[2] have been investigated and shown to resemble those of the corresponding compounds with conjugated double bonds.[3] Also the electric moments of the cyclopropyl halides lie between the values of the corresponding vinyl and isopropyl (or cyclopentyl) halides,[4] and the molecular refractions of cyclopropyl compounds[5] show an exaltation ($\cong$ 0.8 cc.) about half that of the carbon–carbon double bond (1.73 cc.). The chemical properties of cyclopropyl compounds have long been considered as evidence that the cyclopropane ring possesses a considerable degree of unsaturation.[6]

The electric moments and ultraviolet absorption spectra of some simple derivatives of cyclopropane are reported here and compared with the moments and spectra of the corresponding compounds in which the cyclopropane ring is replaced by a carbon–carbon double bond or by an aliphatic group. It should be possible to interpret the effect of the small ring on the spectrum with more confidence than in the previous studies on more complex derivatives. Two derivatives of ethylene oxide have been included since no data were available on compounds containing an ethylene oxide ring adjacent to a double bond.

Experimental Part

Materials

Benzene.—J. T. Baker C. P. benzene was dried over sodium and filtered before use, d^{25}_4 0.87340, n^{25}_D 1.49785.

Cyclopropyl Methyl Ketone.—Eastman Kodak Company White Label cyclopropyl methyl ketone was dried and fractionated through an efficient packed column; b. p. 110.5° (750 mm.), n^{25}_D 1.4222, d^{25}_4 0.8967.

3,4-Epoxybutene-1.—Eastman Kodak Company White Label material was dried and fractionated; b. p. 66.8° (750 mm.), n^{25}_D 1.4143, d^{25}_4 0.8697.

Propylene Oxide and Acrylonitrile.—Commercial samples were fractionated through an efficient packed column: propylene oxide b. p. 34° (750 mm.), n^{20}_D 1.3664, d^{20}_4 0.8311; acrylonitrile, b. p. 76.8° (748 mm.), n^{25}_D 1.3888, d^{25}_4 0.8003.

Vinyl Methyl Ketone.—A sample of the azeotrope was supplied by the Organic Chemicals Department of du Pont and Co. According to their directions, the pure ketone was prepared by cooling the azeotrope, treating with solid potassium carbonate, drying the non-aqueous layer over calcium chloride and fractionating; b. p. 80.8° (752 mm.), n^{25}_D 1.4086, d^{25}_4 0.8407.

2-Methylcyclopropanecarbonitrile.—A pure sample of this chemical was kindly supplied by Professor J. B. Cloke[7]; b. p. 144.5-145.5°, n^{25}_D 1.4258, d^{25}_4 0.8732.

Phenylcyclopropane.—This was prepared, according to the directions of Roberts and Byerly,[8] by a modification of the method of Kishner.[9] Cinnamaldehyde was converted to the pyrazoline using hydrazine hydrate and this was purified and decomposed with potassium hydroxide in the presence of platinized asbestos. The crude product was fractionated using a packed column, b. p. 77.5° (30 mm.), n^{25}_D 1.5302, d^{25}_4 0.9374.

Apparatus and Method

The absorption spectra were measured (in 95% ethanol unless otherwise stated) with a Beckman Quartz Ultraviolet Spectrophotometer using calibrated fused silica cells with widths (d) close to 1 cm. Molar extinction coefficients (ϵ) were calculated from the observed optical densities ($\log_{10} I_0/I$) and molar concentrations (c) using the equation $\epsilon = 1/cd \log_{10} I_0/I$. Measurements down to about λ = 2080 Å. were made (Table III).

Dielectric constants ϵ and densities d of dilute benzene solutions of solute mole fraction f_2 were measured at 25° using the apparatus and technique described previously.[3] The experimental data and the calculated molar polarizations P_2, at each concentration, are shown in Table I. The values of the molar polarization at infinite dilution, P_∞, obtained by graphical extrapolation are shown in Table II along with the measured values of the molecular refractions MR_D and the calculated dipole moments, μ.

Discussion of Results

The ultraviolet absorption bands of the compounds studied containing a three-membered ring adjacent to a double bond tend to occur at wave lengths about midway between those of analogous compounds with alkyl groups adjacent to the

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(1) E. P. Carr and C. P. Burt, THIS JOURNAL, **40**, 1590 (1918).

(2) I. Klotz, *ibid.*, **66**, 88 (1944).

(3) See also J. D. Roberts and C. Green, *ibid.*, **68**, 214 (1946).

(4) M. T. Rogers and J. D. Roberts, *ibid.*, **68**, 843 (1946).

(5) See, for example, N. Zelinsky and J. Zelikow, *Ber.*, **34**, 2856 (1901).

(6) E. P. Kohler and J. B. Conant, THIS JOURNAL, **39**, 1404 (1917).

(7) J. B. Cloke, E. Stehr, T. R. Steadman and L. C. Westcott, *ibid.*, **67**, 1587 (1945).

(8) J. D. Roberts and J. E. Byerly, private communication.

(9) N. Kishner, *J. Russ. Phys.-Chem. Soc.*, **45**, 950 (1913).

TABLE I

DIELECTRIC CONSTANTS, DENSITIES AND POLARIZATIONS IN BENZENE AT 25°

f_2	ϵ	d_4^{25}	P_2
	Methyl vinyl ketone		
0.000000	(2.2725)	(0.87340)	(P_1 = 26.636)
.001577	2.292	.87345	201.0
.003927	2.320	.87341	199.2
.004443	2.325	.87332	196.0
.007419	2.361	.87315	196.0
.010340	2.394	.87305	192.4
.012787	2.422	.87306	191.0
	3,4-Epoxybutene		
0.009882	2.317	0.87335	88.8
.013757	2.334	.87333	88.2
.019658	2.360	.87326	88.2
.020080	2.360	.87330	86.8
.026010	2.388	.87312	87.6
.041681	2.460	.87302	87.3
	2-Methylcyclopropanecarbonitrile		
0.003286	2.338	0.87351	313.0
.004304	2.357	.87329	310.5
.005986	2.393	.87357	314.3
.006568	2.402	.87345	309.0
.014603	2.565	.87353	302.8
.019716	2.668	.87353	297.4
	Cyclopropyl methyl ketone		
0.007152	2.351	0.87375	186.2
.012718	2.416	.87377	188.7
.017511	2.469	.87386	185.4
.024878	2.550	.87398	181.9
.031684	2.631	.87411	181.5
.047687	2.823	.87428	178.9
	Propylene oxide		
0.006111	2.302	0.87329	91.4
.010232	2.325	.87305	94.8
.015003	2.348	.87297	93.4
.021282	2.340	.87270	92.7
.026718	2.409	.87284	92.7
.039754	2.471	.87192	90.5
	Phenylcyclopropane		
0.006772	2.281	0.87482	45.4
.011120	2.283	.87526	45.3
	Acrylonitrile		
0.003978	2.340	0.87334	262.0
.007612	2.401	.87315	260.0
.012136	2.482	.87290	260.8
.021202	2.629	.87255	246.3
.026438	2.718	.87207	242.2
.067036	3.429	.87036	215.5

TABLE II

MOLAR REFRACTIONS, MOLAR POLARIZATIONS AND DIPOLE MOMENTS

Substance	MR_D	P_∞ (25°)	μ (Debye)
Methyl vinyl ketone	20.59	202.5	2.98
3,4-Epoxybutene-1	20.15	89.4	1.84
2-Methylcyclopropanecarbonitrile	23.78	315.5	3.78
Cyclopropyl methyl ketone	23.87	189.0	2.84
Propylene oxide	15.67	95.5	1.98
Phenylcyclopropane	38.95	45.4	0.49
Acrylonitrile	15.67	266.0	3.51

TABLE III

THE ABSORPTION MAXIMA AND MOLECULAR EXTINCTION COEFFICIENTS OF COMPOUNDS CONTAINING THREE-MEMBERED RINGS

Substance	Short wave length absorption		Longer wave length absorption	
	$\lambda_{max.}$, Å.	$\epsilon_{max.}$	$\lambda_{max.}$, Å.	$\epsilon_{max.}$
Isopropyl methyl ketone[10,14]	1930	400	2800	21.5
Cyclopropyl methyl ketone	<2080	>422	2730	23.2
Methyl vinyl ketone[11]	<2190	>3600	3240	24
Ethylbenzene[10,14]	2060	32,000	2590	170
Phenylcyclopropane[13]	2200	8400	2740	280
Styrene[12]	2455	16,000	2904	550
Phenylethylene oxide[15]	2120	4700	2600	150
3,4-Epoxybutene	<2100	>250		
1,3-Butadiene[10,14]	2170	20,000		
Methyl cyanide[10]	1800			
2-Methylcyclopropanecarbontrile	2100	16		
Acrylonitrile	2140–2170	50		

double bond and those with conjugated double bonds; the intensities of the maxima are usually close to those observed in the conjugated systems. This is in agreement with previous observations[1,2,3] that the effect of a three-membered ring on the absorption spectrum of a compound is greater than expected for a comparable saturated substituent and resembles the effect of a double bond.

The absorption spectra in the region 2100–3000 Å. of isopropyl, cyclopropyl and vinyl methyl ketones are shown in Fig. 1 along with that of 3,4-epoxybutene. The short wave length band of high intensity in cyclopropyl methyl ketone lies between the corresponding bands of isopropyl methyl ketone and vinyl methyl ketone but more nearly resembles the latter. The long wave length continuous absorption band in the ketones is an exception to the above generalization in that it occurs at a shorter wave length in cyclopropyl methyl ketone than in the other ketones. The ab-

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(10) Tables in the following references were used: [a] J. R. Platt and H. B. Klevens, *Rev. Mod. Phys.*, **16**, 182 (1944); [b] H. Sponer and E. Teller, *ibid.*, **13**, 75 (1941).

(11) L. K. Evans and A. E. Gillam, *J. Chem. Soc.*, 815 (1941).

(12) M. Pestemer and L. Wiligut, *Monatsh.*, **66**, 119 (1935).

(13) Similar results were obtained in earlier work in this Laboratory by J. E. Byerly.[8]

(14) The value of the long wave length absorption of isopropyl methyl ketone used in Fig. 1 was measured in alcohol solution in this Laboratory. The values for ethylbenzene are in cyclohexane solution and those for butadiene are in hexane solution.

(15) Curve II of Fig. 1 for the oxide of 2-methylbutene-1, and curve III of Fig. 2 for the oxide of dimethylstilbene (both measured in alcohol solution) are taken from the paper of P. Ramart-Lucas, *Bull. soc. chim.*, **51**, 289 (1932). Phenylethylene oxide was measured in 95% ethanol solution in this Laboratory.

sorption band of 3,4-epoxybutene (curve III, Fig. 1) occurs at a considerably longer wave length than the analogous one in alkyl substituted ethylenes[10] or in the oxide of 2-methylbutene-1 (curve II, Fig. 1) and lies between those of pentene-1 ($\lambda_{\max.} <$ 1900 Å.) and butadiene ($\lambda_{\max.} =$ 2170 Å.).

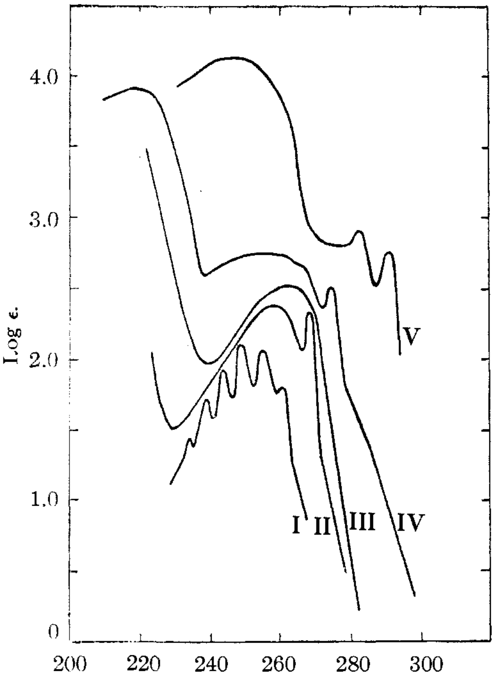

Fig. 1.—Absorption spectra of phenylcyclopropane and related compounds in 95% alcohol solution: I, benzene; II, *n*-propylbenzene; III, dimethylstilbene oxide; IV, phenylcyclopropane; V, styrene.

The absorption spectra of phenylcyclopropane, styrene, *n*-propylbenzene[16] and benzene are compared in Fig. 2. The phenylcyclopropane curve is remarkably similar in appearance to that of styrene but lies at wave lengths between the isopropylbenzene and styrene curves. The absorption curve of dimethylstilbene oxide (curve III, Fig. 2) is similar to that of phenylcyclopropane but shifted to somewhat shorter wave lengths, while that of phenylethylene oxide approaches ethylbenzene. It is also observed (curves not shown) that 2-methylcyclopropyl cyanide has a peak below (but near) 2120 Å. whereas the maximum for acrylonitrile in this region occurs at 2170 Å. and that of methyl cyanide[10] below 1800 Å.

The absorption maximum of shortest wave length occurs at about 1750 Å. in ethylene and at somewhat longer wave lengths in alkyl substituted ethylenes (but below 2000 Å.). Conjugation shifts this maximum to 2170 Å. in butadiene and to about the same position (<2190 Å.) in vinyl methyl ketone. This absorption band has been attributed[17] in each case to the $N \rightarrow V_1$ transition from the normal to the first excited state (a state largely ionic in character) of the molecule. It has further been shown[17] that a band of this type is shifted toward the red and increased intensity by changes in the molecule which lead to increased resonance particularly with ionic structures since these will, in general, stabilize the ionic relative to the normal state. The red shifts observed on alkylation may have the same origin,[18] the type of resonance involved then being termed hyperconjugation.[18,19] The maxima at 2455 Å. in styrene and at 2060 Å. in ethylbenzene also appear to arise from the $N \rightarrow V_1$ transitions in these molecules[20] and the peak at 2200 Å. in cyclopropane presumably also. The long wave length continuous absorption in cyclopropyl methyl ketone shows no red shift but is apparently not of the $N \rightarrow V$ type, but rather arises from an $N \rightarrow A$ transition[21]; the latter bands should also show the red shift on alkylation or conjugation,[21] however, so this result still seems anomalous.

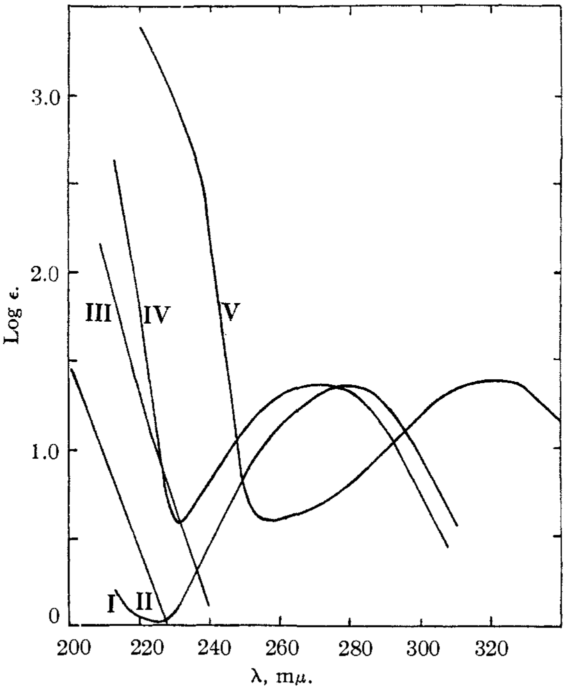

Fig. 2.—Absorption spectra of ketones and oxides in 95% alcohol solution: I, isopropyl methyl ketone; II, 2-methyl butene oxide; III, 3,4-epoxybutene-1; IV, cyclopropyl methyl ketone; V, vinyl methyl ketone.

When a three-membered ring is adjacent to a double bond large red shifts are observed in the

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[16] Curve II of Fig. 2 is for *n*-propylbenzene in methanol solution; M. Pestemer and O. Gubitz, *Monatsh.*, **64**, 426 (1934).

[17] R. S. Mulliken, *J. Chem. Phys.*, **7**, 35 (1939); H. L. McMurry, *ibid.*, **9**, 241 (1941).

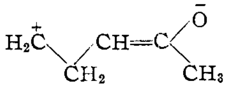
[18] R. S. Mulliken, *ibid.*, **7**, 121, 339 (1939).

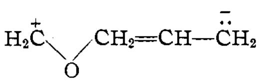
[19] R. S. Mulliken, C. A. Rieke and W. G. Brown, THIS JOURNAL, **63**, 41 (1941).

[20] R. S. Mulliken and A. C. Rieke, "Reports on Progress in Physics," Vol. 8, 1941, p. 231.

[21] H. L. McMurry and R. S. Mulliken, *Proc. Nat. Acad. Sci.*, **26**, 312 (1940).

absorption bands which, in the cases studied here at least, probably arise from the $N \rightarrow V_1$ transition. This is perhaps not surprising since the electrons of the ring bonds must be more loosely held than those of normal single bonds (the corresponding orbitals having also a larger extension in space[22]) and might qualitatively be expected to have properties resembling those of double bonds. A satisfactory theory of the apparent unsaturation of these compounds has not yet been formulated although there has been considerable recent theoretical work on cyclopropane itself[22,23,24] and the structures of some derivatives have been investigated by electron diffraction.[25] It is considered here that the apparent unsaturation of these molecules arises from a type of hyperconjugation and the observed properties are then attributed to small contributions to the normal and excited states of the molecule from the various structures of Type I in cyclopropyl methyl ketone, Types II, III, and IV in 3,4-epoxybutene, and Type V in phenylcyclopropane. These are unfavorable relative to the structures which are of importance in ordinary conjugation (VI, vinyl methyl ketone) because the bond broken has a slightly higher bond energy and because one of the conditions for favorable resonance, namely, coplanarity of the atoms of the conjugated system, is not met[25]; they therefore correspond more nearly to favorable hyperconjugation, although it is difficult to estimate their importance.


I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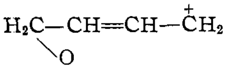
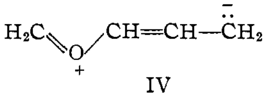
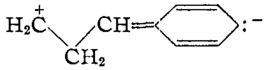
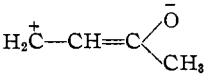

III

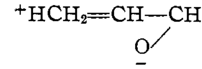

IV


V


VI

The electric moment of methyl *n*-propyl ketone in benzene solution[15] is 2.70 and that of acetophenone[26] is 2.85. The increase in moment of acetophenone and methyl vinyl ketone (2.98) over the saturated ketones is considered to be due to a small contribution of resonance forms such as VI to the ground state of the molecule. If the *s-trans*[27] configuration of the double bonds about the single bond is favored in methyl vinyl ketone, then such structures as I will give rise to a moment more nearly in the line of the original dipole than the corresponding structures in acetophenone. The moment of vinyl methyl ketone is observed to be 0.13 larger than that of acetophenone which suggests that the *s-trans* configuration in methyl vinyl ketone must predominate over the *s-cis*. The moment of cyclopropyl methyl ketone (2.84) lies between those of the isopropyl and vinyl compounds as would be expected if the contribution of structures of Type I to the ground state of the molecule were appreciable but relatively less important than structure VI is in vinyl methyl ketone.

The dipole moment of propylene oxide in benzene solution is 0.10 higher than the value 1.88 observed in an earlier investigation[28] and 0.10 higher than the value 1.88 observed[29] for ethylene oxide in the vapor state. The values for ethylene oxide and propylene oxide are scarcely comparable, but are in the direction expected if hyperconjugation, with such structures as



$$^{+}\mathrm{HCH_2{=}CH{-}CH_2}\quad \bar{\mathrm{O}}$$

contributing, is significant. 3,4-Epoxybutene has a lower moment than either of the above indicating that structures II and IV are together more important in the ground state than III.

The observed moment of cyclopropyl cyanide[4] is 3.76 and that of 2-methylcyclopropyl cyanide is 3.78 showing that the added methyl group has a negligible effect on the dipole moment; this does not indicate whether or not hyperconjugation is important since structures which might contribute have moments distributed in such directions that the net effect would be small, assuming the *cis* configuration of the molecule.[7] The value 3.51 found for acrylonitrile in benzene solution is lower than propionitrile by about the same amount that the vapor values differ[30] and this anomaly has been discussed.[30]

The value 0.5 found for phenylcyclopropane is slightly larger than the moment of toluene (0.4) and may result from hyperconjugation (V); the magnitude and direction should, however, be further studied by measuring the moment of a *para* substituted phenylcyclopropane.

It should be pointed out that many factors whose importance is difficult to assess may affect the electric moments of the small-ring compounds. Among these will be the effect on bond moments of changed hybridization of the orbitals of the ring carbon atoms,[22] the effect of the incomplete overlapping of the orbitals used for the ring bonds,[22] and the possible electronegativity difference (perhaps as a result of the above factors) between a ring carbon atom and a carbon atom of a substituent.

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[22] C. A. Coulson and W. E. Moffitt, *J. Chem. Phys.*, **15**, 151 (1947).

[23] J. E. Kilpatrick and R. W. Spitzer, *J. Chem. Phys.*, **14**, 463 (1946).

[24] A. D. Walsh, *Nature*, **159**, 164 (1947); M. S. Dewar, *J. Chem. Soc.*, 406 (1946).

[25] J. M. O'Gorman and V. Schomaker, THIS JOURNAL, **68**, 1138 (1946).

[26] Table of dipole moments, *Trans. Faraday Soc.*, Appendix (1934).

[27] R. S. Mulliken, *Rev. Mod. Phys.*, **14**, 265 (1943), has suggested the term *s-trans* to indicate a *trans* configuration of conjugated double bonds about the intervening single bond such as is apparently favored in butadiene.

[28] J. S. Allen and H. Hibbert, THIS JOURNAL, **56**, 1398 (1934).

[29] H. A. Stuart, *Physik. Z.*, **51**, 49 (1928).

[30] E. C. Hurdis and C. P. Smyth, THIS JOURNAL, **65**, 83 (1943).

Acknowledgment.—The author wishes to acknowledge his indebtedness to Dr. J. D. Roberts for helpful suggestions in the course of this work.

Summary

The electric moments and ultraviolet absorption spectra of phenylcyclopropane, cyclopropyl methyl ketone, 2-methylcyclopropyl cyanide and 3,4-epoxybutene have been measured along with the moments and spectra of some related compounds containing an alkyl group or ethylenic double bond in place of the three-membered ring.

The ultraviolet absorption bands of the compounds containing a three-membered ring adjacent to a multiple bond are found at wave lengths intermediate between those of the corresponding compounds in which the small ring is replaced in turn by an alkyl group and by a double bond, at least when the bands correspond to an $N \rightarrow V_1$ transition. The behavior of the spectra and electric moments of small-ring compounds has been shown to be qualitatively that which would be expected if the small ring were "conjugated" with the double bond; this is in agreement with previous knowledge of the properties of these substances.

EAST LANSING, MICHIGAN RECEIVED APRIL 14, 1947

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, THE UNIVERSITY OF CHICAGO]

Reduction of Organic Compounds by Lithium Aluminum Hydride. II. Carboxylic Acids

BY ROBERT F. NYSTROM AND WELDON G. BROWN

The reduction of various derivatives of carboxylic acids, *i. e.*, esters, anhydrides, and acid chlorides, to the primary alcohols by lithium aluminum hydride has been described in a previous paper.[1] It was not expected that the reduction of the free acids, or rather the lithium and aluminum salts which must be the primary product in the reaction of acids with lithium aluminum hydride, would proceed as readily. However, it has been found that in many cases the reduction does in fact occur readily and it has been possible thereby to prepare a number of alcohols which are not otherwise easily accessible.

The sole exception encountered in studying the behavior of a variety of carboxylic acids was triphenylacetic acid which was recovered unchanged upon acidification of the reaction mixture. This acid could be converted indirectly to the carbinol without difficulty by conversion to the acid chloride which is readily reduced by lithium aluminum hydride.

It is found that hydroxyl and amino groups do not interfere in the reduction of hydroxy- and amino-acids, other than by the decomposition of an amount of hydride equivalent to the active hydrogens. This process has been applied to the preparation of a number of substituted benzyl alcohols by the direct reduction of the corresponding hydroxy- and amino-benzoic acids. Numerous further applications of this kind will be obvious.

The possibility of selectively reducing one of the carboxyl groups of dibasic acids was explored with sebacic acid as a model. This acid was found to be reduced to the corresponding diol in excellent yield by an excess of lithium aluminum hydride. But when the calculated amount of lithium aluminum hydride for the reduction of one carboxyl group was added to an ether solution of the acid (reversing the usual order of addition) the product consisted of a mixture of diol and unchanged acid. The same products were obtained by reduction of the half ethyl ester of sebacic acid under similar conditions. Further experimentation at lowered temperatures is indicated.

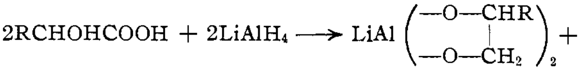
In conformity with previous observations on carboxylic acid derivatives, the double bonds of aliphatic unsaturated acids, *e. g.*, sorbic acid, are not affected by lithium aluminum hydride. However, cinnamic acid undergoes concurrent reduction at the double bond yielding hydrocinnamyl alcohol. It appears to be characteristic of the reagent that ethylenic nuclei, substituted on one side by a phenyl group and on the other by a reducible group (carboxyl, carbonyl, nitro, etc.) are hydrogenated. Further examples will be seen in forthcoming papers.

The equations given below are not intended to be literally accurate with respect to the constitution of the products but will serve to show the stoichiometry for the reduction of various classes of acids.

SIMPLE MONOCARBOXYLIC ACIDS

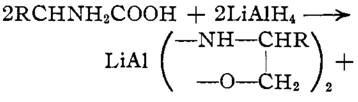
$$4\text{RCOOH} + 3\text{LiAlH}_4 \longrightarrow \text{LiAl(OCH}_2\text{R)}_4 + 2\text{LiAlO}_2 + 4\text{H}_2 \quad (1)$$

HYDROXY ACIDS



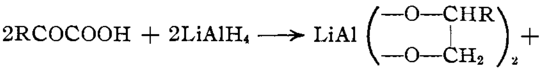
$$2\text{RCHOHCOOH} + 2\text{LiAlH}_4 \longrightarrow \text{LiAl}\left(\begin{array}{l}\text{—O—CHR}\\ \qquad\ \ |\\ \text{—O—CH}_2\end{array}\right)_2 + \text{LiAlO}_2 + 4\text{H}_2 \quad (2)$$

AMINO ACIDS



$$2\text{RCHNH}_2\text{COOH} + 2\text{LiAlH}_4 \longrightarrow \text{LiAl}\left(\begin{array}{l}\text{—NH—CHR}\\ \qquad\quad\ |\\ \quad\text{—O—CH}_2\end{array}\right)_2 + \text{LiAlO}_2 + 4\text{H}_2 \quad (3)$$

KETO ACIDS



$$2\text{RCOCOOH} + 2\text{LiAlH}_4 \longrightarrow \text{LiAl}\left(\begin{array}{l}\text{—O—CHR}\\ \qquad\ \ |\\ \text{—O—CH}_2\end{array}\right)_2 + \text{LiAlO}_2 + 2\text{H}_2 \quad (4)$$

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[1] Nystrom and Brown, THIS JOURNAL, **69**, 1197 (1947).