

Studies in Light Absorption. Part XII. The Effects of Steric Conformation on the Ultraviolet and Infrared Spectra of Alicyclic Ethylenic Ketones.*

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The relations between the conformation of the conjugated enone system in alicyclic ethylenic ketones and their electronic and vibrational spectra are discussed. In the ultraviolet, *s-cis-trans*-isomerism affects mainly the intensity, and the interplanar angles θ deduced by the method of Part XI * for 1-acetyl-2-methylcyclohexene (II) and *tert.*-butyl 2-methylcyclohexenyl ketone (III), which has been synthesised, agree well with those derived for the benzenoid analogues. In the infrared spectra, *s-cis-trans*-isomerism affects the carbonyl as well as the ethylenic stretching frequencies, and the displacements can be correlated with θ .

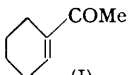
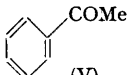
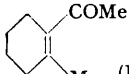
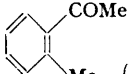
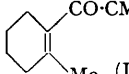
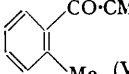
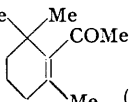
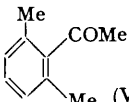
It was shown in Part XI * that steric effects (labelled type 1) resulting in a decrease in the intensity of a *K*-band characteristic of a conjugated system without accompanying hypsochromic shift may be ascribed to electronic transitions between non-planar ground states and uniplanar (or near-planar) excited states, and that the equilibrium interplanar angle θ_1 in the ground state may be estimated from the magnitude of the *ortho*-effect on ϵ . These principles were shown to be readily applicable to *ortho*-substituted acetophenones and related compounds, in which the absorption intensity (ϵ_0) which the system would have in the absence of steric hindrance to uniplanarity can be accurately assessed. Spectral effects of type (1) are also known to be exhibited by the corresponding tetrahydro-(acetylcyclohexene) derivatives and it was suggested in Part VI (*J.*, 1949, 1890) that the decrease in ϵ in 1-acetyl-2-methylcyclohexene (II) was due to the non-planarity caused by the methyl substituent. If it is assumed that ϵ_0 would be the same as for the parent compound, 1-acetylcyclohexene (I), the value of θ_1 calculated from the equation $\cos^2 \theta_1 = \epsilon/\epsilon_0$ is 44° , practically the same as that deduced for 2-methylacetophenone (see Table 1). Such a result is not unexpected since the geometries of the relevant parts of the two systems are almost identical.

* Part XI, preceding paper.

An alternative interpretation of the difference in the observed absorption intensities of acetylcyclohexene and 1-acetyl-2-methylcyclohexene was proposed by Turner and Voile (*J. Amer. Chem. Soc.*, 1951, **73**, 1403). They pointed out that ethylenic ketones in which the conjugated system has an enforced *s-cis*-configuration* exhibit considerably lower ϵ values than analogous compounds with an enforced *s-trans*-configuration, owing to the difference in effective chromophore length and transition moment (Mulliken, *J. Chem. Phys.*, 1939, **7**, 14 *et seq.*). On this basis Turner and Voile concluded that the chromophores in both 1-acetylcyclohexene (I) and 1-acetyl-2-methylcyclohexene (II) are essentially uniplanar, but that whereas the former exists in the *s-trans*-conformation, the latter has an *s-cis*-conformation (IIa). It seems to us that both interpretations of the spectral data *per se* are equally admissible, but that there are several considerations which favour a non-planar *s-trans*-conformation rather than the planar *s-cis*-conformation for 1-acetyl-2-methylcyclohexene. The question really is whether the system will be more stable with an interplanar angle θ_1 of about 45° or 180° , the angle being measured with respect to the planar *s-trans*-conformation (IIb) which, by general consent, has the lowest electronic potential energy (cf. Mulliken, *loc. cit.*).

Now, the absence of significant hypsochromic shifts generally implies (Part XI, *loc. cit.*) that steric hindrance to uniplanarity ($\theta \sim 0^\circ$ or 180°) is quite weak; in the present case, the methyl substituent actually produces the expected small bathochromic shift

TABLE I. Steric effects in the light absorption of alicyclic ethylenic ketones and their benzenoid analogues (for references, see text).

	$\lambda_{\max.}$ (Å)	ϵ	ϵ/ϵ_0	θ		$\lambda_{\max.}$ (Å)	ϵ	ϵ/ϵ_0	θ
 (I)	2320	12500	1.0	0°	 (V)	2420	13000	1.0	0°
 (II)	2450	6500	0.52	44°	 (VI)	2420	8500	0.58	40°
 (III)	2390	1300	0.10	71°	 (VII)	(2360)*	1900	0.14	68°
 (IV)	2430	1400	0.11	71°	 (VIII)	2510	5500	0.34	55°

* Shoulder.

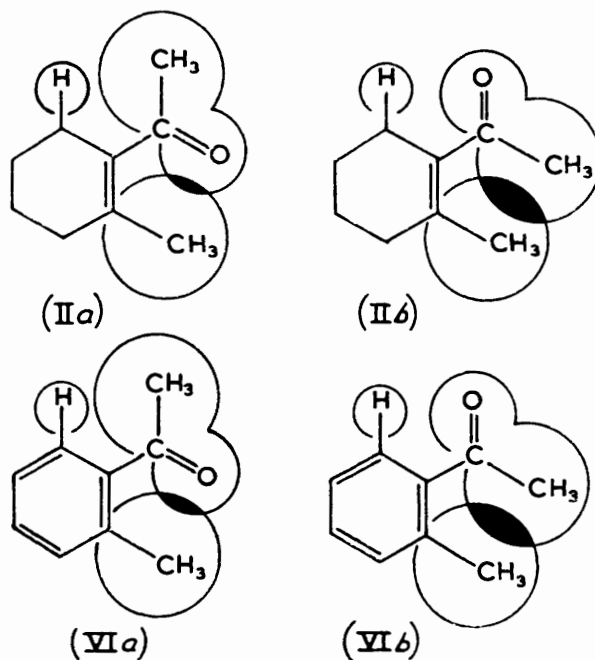
and any compensated hypsochromic displacement must amount to less than 20 Å, equivalent to about 1 kcal./mole. No data are available for the potential-energy difference between planar *s-cis*- and *s-trans*-conformations of the conjugated enone system $C=C-C=O$, but it seems reasonable to assume that it will be of the same order as for the diene system, $C=C-C=C$, *i.e.*, *ca.* 2.5 kcal./mole (Aston, Szasz, Woolley, and Brickwedde, *J. Chem. Phys.*, 1946, **14**, 67). Thus, it seems probable that the conformation with $\theta_1 = 45^\circ$ will have a lower potential energy ($E_0 + 1$ kcal./mole., where E_0 is the energy of the planar *s-trans*-system) than that ($E_0 + 2.5$ kcal./mole) of the conformation with $\theta_1 = 180^\circ$, and that the former will therefore be preferred. A more detailed schematic illustration of the suggested relations is given in Fig. 1. The solid and the broken curve represent the dependence of resonance energy and steric repulsion, respectively, on θ (it is assumed for simplicity that there is no steric hindrance to uniplanarity in the *s-cis*-conformation); since repulsion is a highly exponential function of non-bonded interatomic distances it will be much more sensitive to θ than will resonance, and decrease more rapidly as θ changes

* We use the terms "configuration" and "conformation" respectively in connection with stereoisomerism involving energy barriers greater and smaller, respectively, than *ca.* 20 kcal./mole.

from 0° to 90° . The difference between the curves for any value of θ represents the stabilisation energy for that particular conformation and the Figure depicts conditions under which this is greater for $\theta = 45^\circ$ (intercept *a*) than for $\theta = 180^\circ$ (intercept *b*).

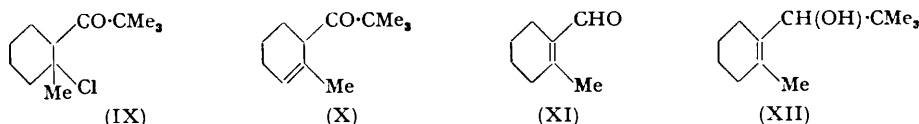
Some support for these views is provided by the close agreement between the interplanar angles calculated on this basis for 1-acetyl-2-methylcyclohexene and 2-methylacetophenone. There is no question that the *ortho*-effect in the latter is due to non-planarity and not to *s-cis-trans*-isomerism, since the chromophores of the two possible planar conformations (VIa) and (VIb) are identical (unless a high degree of asymmetry in the electron-distribution in the benzenoid ring is postulated). The possible ambiguity in the interpretation of the ultraviolet-light absorption of 1-acetyl-2-methylcyclohexene arises partly from the (as we believe, accidental) similarity between the ϵ value exhibited by this compound and by alicyclic ethylenic ketones with an enforced *s-cis*-configuration. Any further reduction in ϵ which might be observed in other cases would have to be entirely due to non-planarity. In order to provide a test case of this type and to demonstrate further the parallelism between the alicyclic and benzenoid series, we synthesised *tert.*-butyl 2-methylcyclohex-1-enyl ketone (III) for comparison with its analogue, *tert.*-butyl *o*-tolyl ketone (VII) which has been described by Ramart-Lucas, Hoch, and Vial (*Bull. Soc. chim. France*, 1952, 220), and exhibits a *K*-band of exceptionally low intensity (see Table 1).

Preparation of the ketone (III) was first attempted by the Friedel-Crafts reaction between 1-methylcyclohexene and pivalic anhydride in the presence of stannic chloride



by analogy with the methods previously employed for 1-acetyl-2-methylcyclohexene (cf. Part VI, *loc. cit.*; Royals and Hendry, *J. Org. Chem.*, 1950, 15, 1147). Dehydrochlorination did not occur during the working-up procedure—contrast the latter case—and the chloro-ketone (IX) was obtained in 60% yield. This was unaffected by refluxing diethylaniline, but on treatment with alcoholic potassium hydroxide afforded an ethylenic ketone which showed high-intensity absorption rising to a maximum below 2100 Å and was evidently the unconjugated isomer (X) of the desired ketone (III). It is interesting that in the case of the lower homologue, acetylmethylcyclohexene, where the desired product is less highly hindered, a mixture of the corresponding conjugated and unconjugated ketones is obtained (Part VI, *loc. cit.*).

However, 1-formyl-2-methylcyclohexene (XI) and *tert.*-butylmagnesium chloride gave the crystalline alcohol (XII) which was converted into the ketone (III) by oxidation with active manganese dioxide. This ketone was a liquid which, like its benzenoid analogue (Ramart-Lucas *et al.*, *loc. cit.*), did not form carbonyl derivatives under the usual conditions, but was shown to be substantially free from unchanged alcohol and unconjugated isomers



by its infrared spectrum. Its ultraviolet-light absorption shows a *K*-band at almost the normal wavelength, but of extremely low intensity, similar to that recorded for *tert.*-butyl *o*-tolyl ketone (see Table 1).

It may be noted that both ketones (III) and (VII) show small but definite hypsochromic shifts ($\Delta\lambda$ *ca.* -50 Å) with respect to the corresponding methyl ketones. These shifts

FIG. 1. Dependence of resonance energy and repulsion energy on interplanar angle (schematic).

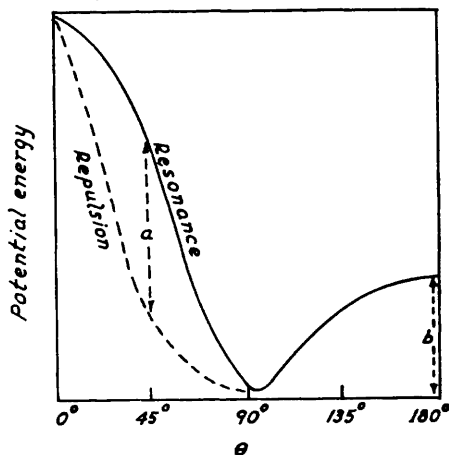
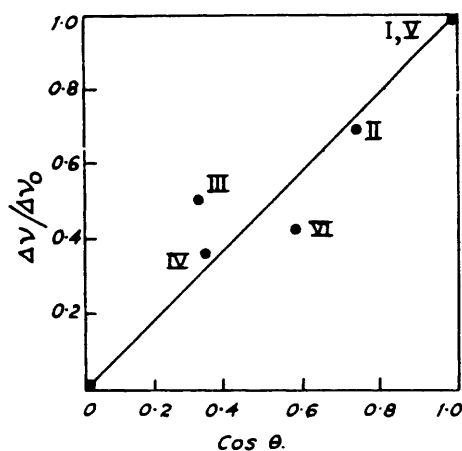


FIG. 2. Relation between interplanar angle and relative carbonyl stretching frequency shifts in acetylcyclohexenes and acetophenones.






are almost certainly steric in origin rather than due to differences in hyperconjugation, and represent an energy change of *ca.* 3 kcal./mole; they indicate that the very marked increase in steric hindrance in going from the methyl to the *tert.*-butyl ketones very nearly causes a change-over from type (1) to type (2) steric effects (Part XI, *loc. cit.*).

Since the present work was commenced, another alicyclic ethylenic ketone showing a *K*-band of exceptionally low intensity, 1-acetyl-2:6:6-trimethylcyclohexene (IV), has been described (Henbest and Woods, *J.*, 1952, 1150). This can be compared with 2:6-dimethylacetophenone (VIII), but, unlike the other two cases, the calculated interplanar angle is rather larger than for the benzenoid analogue (see Table). The lower intensity of absorption and the greater non-planarity of the alicyclic ketone in this instance is, no doubt, due to the presence of two methyl groups in the 6-position; although only one of these is "quasi"-equatorial (cf. Barton, Cookson, Klyne, and Shoppee, *Chem. and Ind.*, 1954, 21) and is the main cause of interference, models show that the other "quasi"-axial methyl group also contributes to the steric effect.

It is of interest that the progressive increase in interplanar angle in the sequence (I) < (II) < (III), (IV) deduced from the differences in ultraviolet-light absorption is also reflected in the infrared spectra, particularly the carbonyl stretching frequencies (Table 2). The location of the carbonyl band of the methyl ketone (I) is normal for a

conjugated ethylenic ketone, whereas the location of the carbonyl bands of the hindered ketones (III) and (IV) approaches that of saturated ketones. This is clearly a consequence of the reduced extent of effective conjugation in the hindered, non-planar compounds, but it will be noted that while the main change in the electronic spectra is only in intensity, the vibrational spectra show a change in frequency (*i.e.*, wavelength). Analogous effects are shown in the acetophenone series by the Raman carbonyl stretching frequencies (Part XI, *loc. cit.*) and an approximately linear relation appears to exist between the interplanar angle θ_1 and $\Delta\nu/\Delta\nu_0$ where $\Delta\nu$ refers to the shift with respect to an unconjugated ketone (taken as 1707 cm^{-1}) and $\Delta\nu_0$ to the shift in the unsubstituted uniplanar compound (Fig. 2). Somewhat similar observations have also been recorded recently by Crombie (*J.*, 1955, 1007) with conjugated diene systems.* The phenomenon may well prove to be general and it may be qualitatively interpreted as follows. Electronic interaction, which controls resonance energy in the ground state and transition energy in electronic spectra, is a relatively insensitive function of interplanar angle, especially at low values of θ (cf. Guy, *J. Chim. phys.*, 1949, **46**, 469), and hence considerable non-planarity can be tolerated without significant changes in wavelength, although the intensity is decreased (type 1 steric effects, Part XI). By contrast, mechanical interaction, which controls force constants and transition energy in vibrational spectra, is a more highly

TABLE 2. *Infrared spectra of alicyclic ethylenic ketones.*

(a) With labile s-conformation.				
Ketone	$\nu_{\text{C=O}}$ (cm^{-1})	ν/ν_0	$\nu_{\text{C=C}}$ (cm^{-1})	$\nu_{\text{C=O}} - \nu_{\text{C=C}}$ (cm^{-1})
(I) ¹	1665	1.0	1637	28
(II) ¹	1678	0.69	1621	57
(III) ²	1684	0.55	—	—
(IV) ³	1693	0.33	1650	43
(b) With fixed s-trans-configuration.				
 ¹	1680	—	1626	54
 ¹	1665	—	1629	36
 ¹	1661	—	1626	35
Cholest-1-en-3-one ⁴	1680	—	1605	74
Cholest-4-en-3-one ⁴	1674	—	1615	59
Methyl 3-hydroxy-12-oxochol-9 : 11-enoate ⁴ ...	1680	—	1607	73
(c) With fixed s-cis-configuration.				
7-Oxoergosta-8(14) : 22-dien-3-yl acetate ² * ...	1680	—	1589	91
15-Oxocholest-8(14)-en-3 β -yl acetate ² *	1705	—	1625	80
15-Oxoergosta-8(14) : 22-dien-3-yl acetate ² *...	1697	—	1620	77

¹ This paper (liquid film). ² This paper (in CCl_4). ³ Henbest and Woods (*loc. cit.*) (in CCl_4).

⁴ Jones, Humphries, Packard, and Dobriner, *J. Amer. Chem. Soc.*, 1950, **72**, 86; Jones, Humphries, and Dobriner, *ibid.*, p. 956; Jones and Herling, *J. Org. Chem.*, 1954, **19**, 1252. (In CS_2 and CHCl_3 .)

* We are much indebted to Professor D. H. R. Barton, F.R.S., for kindly supplying samples of these compounds (Barton and Laws, *J.*, 1954, 52).

sensitive function of interplanar angle in a coupled system, and hence non-planarity has a more immediate effect on frequency. Further work is in progress to test the quantitative aspects of these matters.

Significant displacements are also observed in the ethylenic stretching frequencies. Like the carbonyl stretching frequencies, these are smaller by *ca.* 60 cm^{-1} than for isolated

• We are indebted to Dr. L. Crombie for kindly communicating his results in advance of publication.

double bonds, showing that the decrease in the force constants arising from conjugation is about equal for the C=O and C=C groups. Examination of a number of ethylenic ketones in which the configuration of the conjugated system is fixed reveals the interesting fact, however, that the location of the C=C stretching frequency depends markedly on whether the conformation is *transoid* or *cisoid* (Table 2). For three *transoid* examples, $\nu_{C=C}$ is 1627 ± 2 cm.⁻¹, whereas for the *cisoid* 7-oxergost-8(14)-ene derivative, $\nu_{C=C}$ is considerably smaller. This difference is not unexpected, since the stronger dipole interaction in the *cisoid*-system (A) than in the *transoid*-system (B) should result in an additional



decrease in the force constant of the stretching vibration. Higher ethylenic as well as carbonyl stretching frequencies are exhibited by the two 15-oxo-8(14)-steryl derivatives; these anomalies appear to be associated with ring-strain in these positions, similar, though opposite in sign, to the effects observed with isolated ethylenic bonds (Henbest, Meakins, and Wood, *J.*, 1955, 800). The differences between the ethylenic and carbonyl stretching frequencies are, however, consistently greater for *s-cisoid* (> 75 cm.⁻¹) than *s-transoid* (< 75 cm.⁻¹) derivatives. The close correspondence between the ethylenic stretching frequency of 1-acetyl-2-methylcyclohexene and those of enone systems with a fixed *s-trans*-configuration may be adduced as further support for the view that, at least under the conditions of the spectroscopic measurements, 1-acetyl-2-methylcyclohexene exists predominantly in a hindered *s-trans*- rather than in a *s-cis*-conformation.

EXPERIMENTAL

M. p.s were determined on a Kofler micro-m. p. block and arecorrected. Analytical data were determined by Mr. F. H. Oliver and the staff of the microanalytical laboratory of this Department.

Ultraviolet-light absorptions were determined by Mrs. A. I. Boston using Hilger-Spekker and Unicam instruments. Infrared data were determined by Dr. E. S. Waight and Mr. R. L. Erskine using Grubb-Parsons single-beam and double-beam instruments.

1-Formyl-2-methylcyclohexene (XI).—5-Formyl-4-methylcyclohexene was prepared in 200-g. batches by heating a stirred mixture of butadiene (310 g.), freshly distilled crotonaldehyde (278 g.), and quinol (4 g.) in an autoclave at 150° for 5 hr. (cf. Diels, Alder, Lübbert, Navjoks, Querberitz, Röhl, and Segeberg, *Annalen*, 1929, 470, 62; Shortridge, Craig, Greenlee, Derfer, and Boord, *J. Amer. Chem. Soc.*, 1948, 70, 946). Fractionation of the product through a 14' Fenske column gave the aldehyde, b. p. 67°/16 mm., in 39–46% yields (3 experiments).

This product, even after being kept overnight with Raney nickel in methanol, could not be hydrogenated appreciably at atmospheric pressure with palladium black or 5% palladium-calcium carbonate in methanol with or without acetic acid (cf. Diels *et al.*, *loc. cit.*), but reduction proceeded readily in the presence of platinum oxide. The reaction was interrupted after 0.9 mol. of hydrogen had been absorbed. Isolation of the products and fractionation afforded (i) 1-formyl-2-methylcyclohexane (25%), b. p. 65–73°/15 mm., n_D^{21} 1.4574 (semicarbazone, m. p. 152–155°) (Diels *et al.*, *loc. cit.*, give b. p. 61–62°/11 mm., semicarbazone, m. p. 155°; Skita, *Annalen*, 1923, 431, 1, gives b. p. 72°/24 mm., n_D^{20} 1.4498, semicarbazone, m. p. 152° for the *trans*-compound) and (ii) 2-methylcyclohexylmethanol (52%), b. p. 73–100°/15 mm., n_D^{21} 1.4644–1.4748 (Skita, *loc. cit.*, gives b. p. 192–192.5°, n_D^{20} 1.4665, for the *trans*-compound). The colourless 3 : 5-dinitrobenzoate, crystallised from aqueous methanol, had m. p. 69–71° (Found : C, 56.2; H, 5.5; N, 8.7. C₁₅H₁₈O₆N₂ requires C, 55.9; H, 5.6; N, 8.7%). The alcohol was oxidised to the aldehyde in 24% yield by chromic oxide in acetic acid (Skita, *loc. cit.*), but not by selenium dioxide in refluxing dioxan (15 hr.).

1-Formyl-2-methylcyclohexane was converted into 1-formyl-2-methylcyclohexene by the method of Heilbron, Jones, Richardson, and Sondheimer (*J.*, 1949, 737) and after regeneration from the semicarbazone, m. p. 239–241° (Heilbron *et al.*, *loc. cit.*, give m. p. 232–233°), had b. p.

96—99°/17 mm., n_D^{21} 1.5082, λ_{\max} . 2420 Å (ϵ 11,000 in EtOH) (Heilbron *et al.*, *loc. cit.*, give b. p. 103°/27 mm., n_D^{18} 1.5091; Dreiding and Nickel, *J. Amer. Chem. Soc.*, 1954, **76**, 3965, give n_D^{25} 1.5088).

2 : 2-Dimethyl-1-(2-methylcyclohex-1-enyl)propan-1-ol (XII).—A solution of the above aldehyde (5.6 g.) in anhydrous ether (10 ml.) was added to a stirred ethereal solution of *tert.*-butylmagnesium chloride (from Mg, 2.2 g., and *tert.*-butyl chloride, 17 g.) at room temperature. Stirring was continued overnight and saturated aqueous ammonium chloride (30 g.) was then added. Extraction with ether and distillation gave the alcohol (5.6 g., 74%), b. p. 67°/0.5 mm., n_D^{25} 1.4868, which solidified and crystallised from aqueous methanol in prisms, m. p. 59—60° (Found : C, 79.0; H, 12.2. $C_{12}H_{22}O$ requires C, 79.0; H, 12.2%). Light absorption in EtOH : ϵ 4000 at 2100 Å, and ϵ 1400 at 2200 Å.

tert.-Butyl 2-Methylcyclohex-1-enyl Ketone (III).—The foregoing alcohol (4 g.) was shaken with a suspension of manganese dioxide (40 g.) in pentane (400 ml.) under nitrogen for 4 days (cf. Braude and Forbes, *J.*, 1951, 1755; 1953, 2208; Attenburrow, Cameron, Chapman, Evans, Hems, Jansen, and Walker, *J.*, 1952, 1094; Bharucha and Weedon, *J.*, 1953, 1571). Filtration, evaporation of the pentane, and distillation afforded the ketone as a colourless oil (1.2 g., 30%), b. p. 115—116°/20 mm., n_D^{29} 1.4760 (Found : C, 79.7; H, 11.5. $C_{12}H_{20}O$ requires C, 80.0; H, 11.2%). Ultraviolet absorption in EtOH : λ_{\max} . 2390 (ϵ 1300) and $\lambda_{\text{infl.}}$ ~2900 Å (ϵ 8.8). Infrared absorption in CCl_4 : ν_{\max} . 1684 cm^{-1} . The ketone did not form an oxime or a 2 : 4-dinitrophenylhydrazone under the usual conditions.

tert.-Butyl 2-Methylcyclohex-2-enyl Ketone (X).—Pivalic anhydride was prepared by adding pyridine (28 g.) followed by pivalic acid (28 g.) in benzene (28 ml.) to a solution of pivaloyl chloride (36 g.) in benzene (200 ml.) at 5—10° with shaking (cf. Adkins and Thompson, *J. Amer. Chem. Soc.*, 1949, **71**, 2242). The reaction was allowed to proceed at room temperature for 1 hr., after which the precipitated pyridine hydrochloride was filtered off and washed with benzene. The combined benzene filtrates were washed with water and aqueous sodium hydrogen carbonate, dried (Na_2SO_4), and distilled, giving the anhydride (42 g., 75%), b. p. 112—114°/63 mm., n_D^{21} 1.4080 (Greenwood, Whitmore, and Crooks, *J. Amer. Chem. Soc.*, 1938, **60**, 2028, give b. p. 124°/93 mm., n_D^{20} 1.4093; Conn, Kistiakowsky, Roberts, and Smith, *ibid.*, 1942, **64**, 1747, give b. p. 95.0°/28 mm.).

The anhydride (45 g.) was added in drops to a stirred mixture of methylcyclohexene (31 g.) and stannic chloride (52 g.), the temperature being kept at 25—35°. After a further $\frac{1}{4}$ hour's stirring, the mixture was poured on ice (70 g.) and extracted with ether. The ethereal extract was washed with water and with aqueous sodium hydrogen carbonate, dried (Na_2SO_4), and distilled, giving crude *tert.*-butyl 2-chloro-2-methylcyclohexyl ketone (32 g., 62%), b. p. 133—160°, n_D^{25} 1.4753—1.4800. This product was recovered almost unchanged after 3.5 hours' refluxing with diethylaniline, but dehydrochlorination was effected by refluxing the chloro-ketone (22 g.) with potassium hydroxide (9 g.) in 80% aqueous ethanol (25 ml.) for 1.5 hr. After dilution with water, the product was isolated with ether and distilled, giving the ethylenic ketone (9 g.), b. p. 111—113°/13 mm., n_D^{20} 1.4711 (Found : C, 80.3; H, 11.3. $C_{12}H_{20}O$ requires C, 79.9; H, 11.2%). Ultraviolet light absorption in EtOH : infl. at 2900 Å ($\epsilon = 45$); ϵ at 2100 and 2200 Å, 2100 and 1100 respectively, corresponding to an isolated, trialkylated ethylenic bond (Bladon, Henbest, and Woods, *J.*, 1952, 2737). Infrared absorption (liquid film) : ν_{\max} . 1701 (unconjugated C=O stretching). The 2 : 4-dinitrophenylhydrazone, which was formed slowly during 24 hr., after chromatography on alumina and elution with benzene, crystallised from ethanol as light orange needles, m. p. 136—138°, λ_{\max} . 3710 Å (ϵ 23,500 in $CHCl_3$) (Found : C, 59.7; H, 6.8; N, 15.6. $C_{18}H_{24}O_4N_4$ requires C, 60.0; H, 6.7; N, 15.6%).

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