B. With Mineral Acid.—The dienone (0.200 g.) was dissolved in purified 1,2-dimethoxyethane (5 ml.) and treated with concentrated sulfuric acid (0.5 ml.). The reaction mixture was stored overnight at room temperature and then diluted with water and extracted with ether. The ether extracts were washed with sodium carbonate solution and with water and dried over magnesium sulfate. The ether was evaporated under reduced pressure to yield 0.129 g. of crude product. Vapor phase chromatography analysis showed the presence of at least seven compounds. The major product was 6-isopropyltetralin obtained in an absolute yield of 12%. Polymerization seemed to be a major side reaction under these conditions. The infrared spectrum of the crude product showed carbonyl absorption at 1695 cm.$^{-1}$. A variety of other acidic conditions were examined and in every case a complex mixture of products was obtained. The crude products were subsequently treated with hot ethanolic hydrochloric acid and examined for cyclopentanone absorption in the infrared region. In no case was there any indication of more than a trace of cyclopentanone formation.

C. 5-(2-Methylenecyclohexyl)-3-methylpent-1-en-3-ol in Formic Acid.—The alcohol (1.62 g., 0.0083 mole) was dissolved in benzene (15 ml.) and added during 15 min. to 95–97% formic acid (25 ml.) at 0–5°. The reaction mixture was stirred overnight at room temperature and then poured into 100 ml. of water. The resulting mixture was extracted with ether and the ether extracts were washed with saturated sodium hydrogen carbonate solution and water. The dried (magnesium sulfate) ether solution was concentrated under reduced pressure to give 1.40 g. of crude product which was chromatographed over 35 g. of Woelm neutral alumina, grade I. Elution with 150 ml. of petroleum ether (b.p. 30–60°) afforded 1.2 g. of hydrocarbon material which showed two peaks (retention times 4.0 and 7.1 min.) on vapor phase chromatography on a 5 ft. × 0.25 in. column of 20% Carbowax 20-M on firebrick at 190°. The predominant (15:1) 4.0-min. peak was collected and its infrared spectrum (chloroform solution) showed no carbonyl absorption, but had olefinic absorption at 1640 and a peak at 910 cm.$^{-1}$ ascribed to a terminal vinyl group. The infrared spectrum (carbon disulfide solution) did not show absorption at 890 cm.$^{-1}$ characteristic of an *exo*-methylene group and no peaks in the 830-cm.$^{-1}$ region which could be ascribed to a trisubstituted double bond. The n.m.r. spectrum exhibited a three-proton singlet at τ 9.03 (methyl protons), a broad singlet centered at τ 8.28 (eight protons) ascribed to the allylic protons, and 12 lines in the vinyl proton region (three protons). The following parameters gave the best agreement for the vinyl group: τ 4.36 (H_A), 5.15 (H_B), 5.15 (H_C), and J_{AB} = 10.0 c.p.s., J_{AC} = 18.0 c.p.s., J_{BC} = 1.5 c.p.s. It was not possible to get satisfactory analytical data for the compound and it appeared to take up oxygen because the sum of the carbon and hydrogen values was about 96% in two attempts.

A second run was carried out as just described except that the reaction mixture was hydrogenated at atmospheric pressure over 100 mg. of 5% palladium-on-carbon catalyst. The crude product was isolated as previously described and vapor phase chromatography under the conditions used previously showed two peaks in the ratio of 15:1. The analysis of the major product was satisfactory for a 2-methyl-2-ethyldecalin.

Anal. Calcd. for $C_{13}H_{24}$: C, 86.58; H, 13.42. Found: C, 86.77; H, 12.88.

The Conformation and Nuclear Magnetic Resonance Spectrum of Mesityl Oxide

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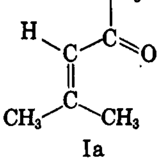
From comparisons of the n.m.r. spectra of mesityl oxide, 1,1,1-trideuterio-4-methyl-3-penten-2-one, and *cis*- and *trans*-3-penten-2-one, assignments for methyl n.m.r. absorptions in mesityl oxide are deduced. The evidence for stereospecific collision complexes between mesityl oxide and benzene is examined.

The n.m.r. spectrum of mesityl oxide (I) has been reported[1] to show a doublet at τ 8.14 (3H), a singlet at 7.95 (6H), and a broad signal at 4.03 (1H). The doublet at τ 8.14 was assigned[1] to one of the two allylic methyl groups, since the CH_3CO– protons were considered incapable of significant coupling with the olefinic proton. From the results of n.m.r. investigations[2] of *cis* and *trans* α,β-unsaturated carboxylic esters, it seems reasonable to infer that the most deshielded of the two allylic methyl groups is *cis* to the carbonyl function and that this strong deshielding may be associated with a predominant (*S*)-*cis* (Ia) rather than an (*S*)-*trans* (Ib) conformation.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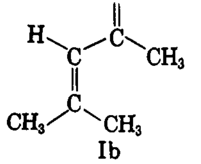
Ib

An inference from n.m.r. data that the (*S*)-*cis* conformation for mesityl oxide is favored at room temperature would agree with conclusions from stereochemical investigations of the molecule based on infrared,[3,4] Raman,[5] and ultraviolet[3] spectrophotometry, and on dipole moment determinations.[6,7]

More recent investigations[8] of the n.m.r. spectrum of mesityl oxide with equipment capable of higher resolution showed absorptions for the methyl groups at τ 7.893, 8.137, and 7.907. The signals at 7.893 and 8.137 are split into doublets by couplings of 1.2 and 1.4 c.p.s., respectively. A tentative assignment of the allylic methyl group *trans* to the carbonyl function for the doublet at 7.893 was made; the smaller coupling (1.2 rather than 1.4 c.p.s.) was assumed to be indicative of a *cis* relationship between methyl and the olefinic proton.[8] The other allylic methyl, *cis* to the carbonyl function, then corresponded to the signal at 8.137, and CH_3CO– protons to the singlet at 7.907.

Further, from a study[8] of the changes in chemical shifts experienced by the methyl groups of mesityl oxide in benzene, a stereospecific complex or collision complex between mesityl oxide and benzene was deduced (II).

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(1) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, pp. 84–85.

(2) L. M. Jackman and R. H. Wiley, *Proc. Chem. Soc.*, 196 (1958); *J. Chem. Soc.*, 2886 (1960).

(3) R. Mecke and K. Noack, *Chem. Ber.*, **93**, 210 (1960).

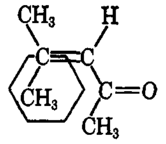
(4) R. L. Erskine and E. S. Waight, *J. Chem. Soc.*, 3425 (1960).

(5) K. Noack and R. N. Jones, *Can. J. Chem.*, **39**, 2201 (1961).

(6) J. B. Bentley, K. B. Everard, R. J. B. Marsden, and L. E. Sutton, *J. Chem. Soc.*, 2957 (1949).

(7) G. K. Estok and J. H. Sikes, *J. Am. Chem Soc.*, **75**, 2745 (1953).

(8) J. V. Hatton and R. E. Richards, *Mol. Phys.*, **5**, 153 (1962).



II

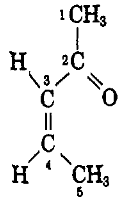
There is a clear conflict between the earlier assignments for the n.m.r. spectrum of mesityl oxide, with their implication of a dominant (*S*)-*cis* conformation for the molecule, and the more recent assignments and postulation of complex II in benzene solution. In an effort to resolve the difficulty, this paper compares the n.m.r. spectra of mesityl oxide, 1,1,1-trideuterio-4-methyl-3-penten-2-one, and *cis*- and *trans*-3-penten-2-one and notes their relevance to the n.m.r. spectral and conformational assignments. The available evidence for stereospecific complex or collision complex formation between mesityl oxide and benzene is discussed.

Results and Discussion

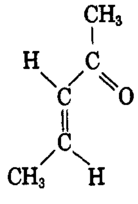
Two principal objections may be raised to the recent interpretation[8] of the n.m.r. spectrum of mesityl oxide. First, the generalization that coupling between methyl and hydrogen in systems $CH_3C(R){=}CHR'$ is larger for a *trans* isomer than for the *cis* which was applied[8] for the tentative assignment of n.m.r. absorptions in mesityl oxide is unreliable.[9] Second, both theoretical expectations[10] and experimental observations[2] argue for significant long-range deshielding by the carbonyl group in mesityl oxide of the *cis* β-methyl substituent, especially if the molecule adopts conformation Ia.

Additional evidence strengthening the earlier assignments of the unsplit methyl absorption at 7.91 to CH_3CO– was secured through synthesis of 1,1,1-trideuterio-4-methyl-3-penten-2-one and observation of a relative decrease in the strength of the n.m.r. absorption in this region.

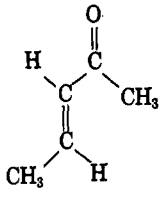
The n.m.r. chemical shift data for mesityl oxide and *cis*- and *trans*-3-penten-2-one (III and IV) summarized in Table I justify assignment of the deshielded methyl group in mesityl oxide at τ 7.89 to the *cis* β-methyl protons.



III



IVa



IVb

TABLE I

CHEMICAL SHIFTS[a] FOR PROTONS IN MESITYL OXIDE AND ANALOGS

Compd.	C-1 H	C-3 H	C-4 H	C-5,6 H
Mesityl oxide (I)	7.91[b]	4.03[c]		7.89,[b] 8.14[b]
cis-3-Penten-2-one (III)	7.88	3.95	3.91	7.88
trans-3-Penten-2-one (IV)	7.88	4.12	3.29	8.10

[a] Given in τ values. [b] See ref. 8. [c] See ref. 1.

From Raman spectrophotometric data it appears that *trans*-3-penten-2-one is a mixture of both (*S*)-*cis* and (*S*)-*trans* conformers at room temperature.[11] The observed n.m.r. spectrum showed no sign of a slowly equilibrating mixture of conformers.

Mesityl Oxide–Benzene Collision Complex.—Experimentally, substantial changes in chemical shifts for two of the three methyl groups in mesityl oxide have been observed[8] upon dilution with benzene. Extrapolation of the measured chemical shifts to infinite dilution gave τ 7.893 $\rightarrow$ 7.893, 8.137 $\rightarrow$ 8.540, and 7.907 $\rightarrow$ 8.143, for the three methyl groups. With the assignments for mesityl oxide given above, the two methyl groups experiencing large chemical shifts in benzene are CH_3CO– and the CH_3C *trans* to the carbonyl function. The CH_3C *cis* to the carbonyl group is not as sensitive to the magnetic anisotropic shielding effects of the solvent benzene. A similar correspondence between geometry and sensitivity to shielding by aromatic solvents holds for substituted amides; the *trans* N-methyl in N,N-dimethylformamide[12] and the *trans* isomer of N-methylformamide[13] are more sensitive to shielding by solvent benzene than are the corresponding *cis* N-methyl protons and *cis* isomer.

Theoretically, relationships[14] correlating the magnetic influence of the ring-current effect of benzene at a position ρ,z in a cylindrical coordinate system based on the benzene molecule and observed solvent-induced chemical shifts might permit calculation of spatial relationships in a postulated stereospecific one-to-one collision complex of solute and benzene. For such an approach to be useful, the gross approximations involved would have to introduce but small errors, and the equations used for calculations would have to be solvable.

Analytically, five parameters will fix the stereochemistry of a stereospecific one-to-one collision complex of mesityl oxide and benzene: two are needed to specify the center of mass of mesityl oxide relative to that of benzene, and three to fix the orientation of the molecule about that point.

In a present case,[8] since the number of observable quantities (three solvent-induced chemical shifts) is less than the analytically required unknown parameters (five coordinates), no solution is possible. An infinite number of stereochemistries for the mesityl oxide–benzene collision complex is consistent with the experimentally observed chemical shifts and the analytical requirements of the chosen model. Thus, no inference of stereochemistry for the postulated stereospecific complex may be justified through this approach alone.[15]

Even in those cases[15] where formal analytical requirements are met, fair agreement between chemical shifts calculated on the basis of some postulated stereospecific solvent–solute collision complex and experimentally determined chemical shifts by no means

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(9) R. R. Fraser and D. E. McGreer, *Can. J. Chem.*, **39**, 505 (1961).

(10) J. A. Pople, *Proc. Roy. Soc.* (London), **A239**, 541, 550 (1957).

(11) K. Noack and R. N. Jones, *Can. J. Chem.*, **39**, 2225 (1961).

(12) J. V. Hatton and R. E. Richards, *J. Mol. Phys.*, **5**, 139 (1962).

(13) L. A. LaPlanche and M. T. Rogers, *J. Am. Chem. Soc.*, **86**, 337 (1964).

(14) Such as that developed by C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

(15) For other instances in which stereospecific collision complexes have been postulated. see N. A. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, Chapter 7.

demonstrates a stereospecific complex or verifies the postulated stereochemistry. That the observed solvent-dependent chemical shifts may reflect time-averaged environments for the groups involved or that the relative insensitivity of some calculated chemical shifts to variations in stereochemistry of the complex are possibilities which may not be ignored.

Experimental

1,1,1-Trideuterio-4-methyl-3-penten-2-one.—Methyl-d_3 bromide (Merck Sharp and Dohme of Canada, 909 mg., 9.27 mmoles) was transferred in a dry vacuum line to a magnetically stirred mixture of freshly cut lithium (158 mg., 22.8 mg.-atoms) in 40 ml. of ether. When the methyl-d_3 bromide had reacted, an atmosphere of dry, oxygen-free nitrogen was established. The ethereal methyllithium solution was frozen with a liquid nitrogen bath, 2.16 g. (1.82 mmoles) of β,β-dimethylacrylyl chloride was injected into the reaction mixture through a rubber serum-bottle stopper, and the reaction mixture was allowed to warm to room temperature with stirring in 15 min. The reaction mixture was filtered through glass wool into 10 ml. of aqueous ammonium chloride, and the ethereal layer was passed through a column of acid-washed alumina, wet-packed with ether. The fractions containing the labeled mesityl oxide were found by t.l.c. on alumina, concentrated, and analyzed by v.p.c. on a 20M Carbowax column. The product mixture contained approximately 33% of labeled 2,4-dimethyl-1,3-pentadiene and 37% of labeled mesityl oxide.

The n.m.r. spectrum of 1,1,1-trideuterio-4-methyl-3-penten-2-one isolated by preparative v.p.c. showed absorptions at τ 7.9 and 8.13 in a ratio of 1.46:1.0.

2,4-Dimethyl-1,3-pentadiene from trial preparations of mesityl oxide with unlabeled methyl bromide was collected by preparative v.p.c. and identified through its physical properties: b.p. 90° (Emich tube), $n^{22}\text{D}$ 1.4400 (lit.[16] b.p. 93°, $n^{20}\text{D}$ 1.4408), $\nu_{\max}^{\text{CCl}_4}$ 890 cm.$^{-1}$ (terminal methylene).

trans-**3-Penten-2-one (IV)** was isolated by v.p.c. on a 4-methyl-4-nitropimelonitrile column[17] from a commercial sample (Aceto Chemical Co., Inc.) of ethylideneacetone. Irradiation of the commercial ethylideneacetone as a solution in cyclohexane with ultraviolet light (Hanovia 450-w. high-pressure mercury lamp) for 22 hr. followed by repeated v.p.c. gave *cis*-**3-penten-2-one (III).**

Chemical shifts for the protons in these two isomers are reported in Table I. In addition to the reported absorptions, the *cis* isomer showed a weak signal at τ 7.97, presumably due to a trace impurity.

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[16] G. Egloff, "Physical Constants of Hydrocarbons," Vol. I, Reinhold Publishing Corp., New York, N. Y., 1939, p. 315.

[17] Compare H. O. House, D. D. Traficante, and R. A. Evans, *J. Org. Chem.*, **28**, 348 (1963).

Decomposition of the Anion of the Tosylhydrazones of Several Cycloalkene Aldehydes[1]

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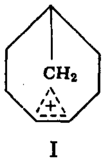
The products of the thermal decomposition of the title compounds were investigated. In the case of the cycloheptenecarboxaldehyde and the cyclopentenylacetaldehyde derivatives intramolecular carbene addition to the double bond took place to a minor extent, with formation of tricyclo[5.1.0.0^{4,8}]octane (II) and nortricyclene (VII), respectively. No intramolecular carbene-addition product could be detected in the decomposition product of the cyclohexenylacetaldehyde tosylhydrazone anion. The major product of the decomposition reaction of the cycloheptenecarboxaldehyde derivative was found to be 2,3-diazatricyclo[3.3.2.0^{2,6}]dec-2-ene (III) formed by intramolecular 1,3-addition. The decomposition of the cycloheptenecarboxaldehyde and the cyclohexenylacetaldehyde derivatives took place at low temperatures indicating double-bond participation.

The chemistry of carbenes and their reactions with olefins has attracted considerable attention during the past 15 years.[3] There are, however, very few reports in the literature of intramolecular addition of methylenes to double bonds. The majority of the cases reported deal with the intramolecular reaction of unsaturated α-ketocarbenes, obtained from the corresponding α-diazo ketone either by copper powder catalyzed thermal decomposition or by photolysis.[4] One other instance was reported by Skattebøl,[5] who obtained tricyclo[4.1.0.0^{4,6}]heptane from 1,1-dibromo-2-(but-3-enyl)-cyclopropane and methyllithium *via* the cyclopropylidene intermediate. It occurred to us that unsaturated carbenes amenable to intramolecular addition might be derived from systems analogous to those which have been reported to undergo facile ring closure, yielding bridged compounds by the so-called "π-route." The first such system was disclosed by Le Ny,[6] and involved the acetolysis of 4-cycloheptenylmethyl *p*-bromobenzenesulfonate, which led to *cis*-2-bicyclo[3.2.1]octyl acetate *via* the nonclassical carbonium ion I. Subsequently, Lawton,[7a] Bartlett and Bank,[7b] and Winstein and Carter[7c] reported other model compounds, such as 3-cyclopentenylethyl and 3-cyclohexenylethyl arenesulfonates, from which bicyclo[2.2.1]heptane, bicyclo-[2.2.2]octane, and bicyclo[3.2.1]octane derivatives may be obtained by the "π-route." Most recently Hanack and Kaiser[8] showed that the solvolysis of 4-



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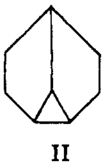

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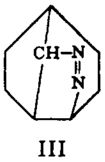

III

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[1] Presented in part at the 146th National Meeting of the American Chemical Society, Denver, Colo., Jan. 1964; Abstracts, p. 34C.

[2] To whom inquiries should be sent: Entomology Research Division, Agricultural Research Service, U. S. Department of Agriculture, Beltsville, Md. 20705.

[3] J. Hine, "Divalent Carbon," The Ronald Press Co., New York, N. Y., 1964.

[4] G. Stork and J. Ficini, *J. Am. Chem. Soc.*, **83**, 4678 (1961); W. von E. Doering and B. Ferrier, cited by W. von E. Doering and W. R. Roth, *Angew. Chem., Intern. Ed. Engl.*, **2**, 115 (1963); W. von E. Doering and M. Pomerantz, *Tetrahedron Letters*, **No. 17**, 961 (1964); S. Masamune, *J. Am. Chem. Soc.*, **86**, 735 (1964).

[5] L. Skattebøl, *Chem. Ind.* (London), 2146 (1962).

[6] G. Le Ny, *Compt. rend.*, **251**, 1526 (1960).

[7] (a) R. G. Lawton, *J. Am. Chem. Soc.*, **83**, 2399 (1961); (b) P. D. Bartlett and S. Bank, *ibid.*, **83**, 2591 (1961); (c) S. Winstein and P. Carter, *ibid.*, **83**, 4485 (1961).

[8] M. Hanack and W. Kaiser, *Angew. Chem., Intern. Ed. Engl.*, **3**, 583 (1964).