coal, the solution was evaporated to a volume of *ca.* 2 ml. and acidified with 6 *N* hydrochloric acid. On cooling, there was obtained 65 mg. of **18**, m.p. 88-92°, lit.[20] m.p. 94°. The infrared spectrum was identical with that of *p*-tolylacetic acid.[21]

Acknowledgment.—We wish to thank Professor G. A. Russell and Dr. Y. Kurita for supplying us with unpublished data relating to their e.s.r. experiments. We are indebted to a member of the analytical section of this laboratory for the microanalyses and physical determinations.

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[20] A. L. Wilds and A. L. Meader, Jr., *J. Org. Chem.*, **13**, 763 (1948).

[21] The Sadtler Standard Spectra, Vol. VIII, Midget Ed., Sadtler Research Laboratories, Philadelphia, Pa., 1962, Compound 6517.

Ultraviolet Irradiation of Carbonyl Compounds in Cyclohexene and 1-Hexene

JERALD S. BRADSHAW

Chevron Research Company, Richmond, California

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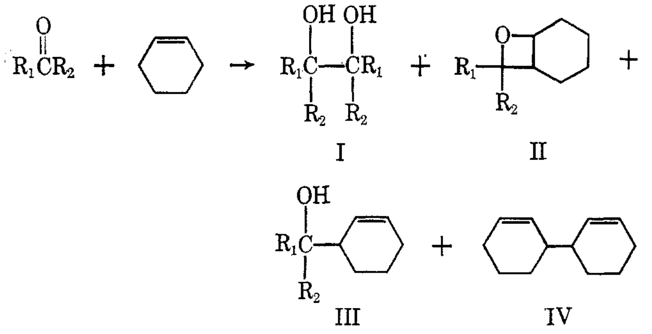
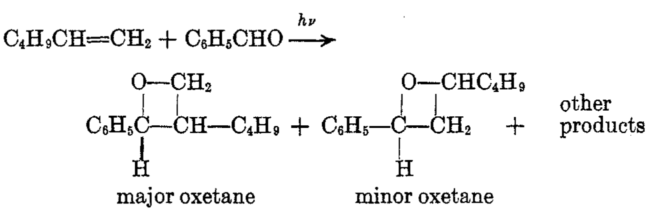
The photolysis of benzophenone and benzaldehyde in cyclohexene and 1-hexene gave four products—pinacol, oxetane, alcohol, and hydrocarbon dimer. Acetone and acetophenone yielded oxetane, alcohol, and bicyclohexenyl when irradiated in cyclohexene. The yields of oxetane from these reactions were smaller than those obtained with more highly substituted olefins. These differences in yields may be attributed to the greater stability of the more highly substituted diradical intermediate V.

Carbonyl compounds can undergo a variety of photolytic reactions in solution. Phenyl ketones are readily reduced to pinacols in the presence of hydrogen donors.[1-3] Alcohols and hydrocarbon dimers resulting from radical reactions are produced when aliphatic ketones react with cyclohexene[4] and are the byproducts of the benzophenone–alkylbenzene reaction.[2] When irradiated in di- and greater substituted acyclic and substituted cyclic olefins, carbonyl compounds react with the olefin to give oxetanes in high yields.[5-7] We have isolated from the photolysis of carbonyl compounds in α-olefins and cyclohexene, not a single product, but rather four products—pinacol, oxetane, alcohol, and hydrocarbon dimer. Others may have also been formed. Some of these products have obviously been overlooked in the past. For example, oxetane products were not reported for the irradiation of both acetone and benzophenone in cyclohexene.[4,6]


I II III IV

The carbonyl compounds were dissolved in the olefin and irradiated until most of the carbonyl had reacted. When benzophenone was used, benzopinacol separated during the reaction. The other products were isolated by chromatography on alumina. Table I records the results.

The oxetanes were characterized by their distinctive n.m.r. spectra (Figure 1). A mixture of *cis*- and *trans*-oxetane isomers was formed when benzaldehyde was irradiated in the presence of 1-hexene. The doublet at δ 5.85 has been tentatively assigned to the *cis* isomer, while that at δ 5.35 has been assigned to the *trans* isomer (Figure 1).[8] *trans*-Oxetane predominated by about 2 to 1. In addition to the major doublets between δ 5 and 6, the n.m.r. spectrum of the first oxetane fraction contained a small triplet at δ 5.5. This could correspond to a small amount of oxetane with the oxygen next to the $-CHC_4H_9$ group.[7]

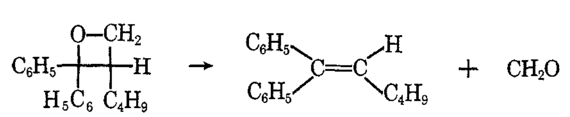

$$C_4H_9CH{=}CH_2 + C_6H_5CHO \xrightarrow{h\nu}$$

major oxetane

minor oxetane

other products

The oxetanes from cyclohexene gave molecular ions at the expected *m/e* in the mass spectrometer, while those prepared from 1-hexene gave large peaks at the expected mass less 30, corresponding to loss of formaldehyde. This latter is due to either a thermal decomposition in the 210° inlet system or occurs in the ionizing beam of the mass spectrometer. Such a cleavage was reported by Bardot in the pyrolysis of 2,2-diethyloxetane.[9]



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[1] For a review, see A. Schonberg and A. Mustafa, *Chem. Rev.*, **40**, 181 (1947).

[2] G. S. Hammond, W. P. Baker, and W. M. Moore, *J. Am. Chem. Soc.* **83**, 2795 (1961).

[3] (a) A. Becket and G. Porter, *Trans. Faraday Soc.*, **59**, 2038 (1963); (b) G. Porter and P. Suppon, *Proc. Chem. Soc.*, 191 (1964).

[4] P. de Mayo, J. B. Stothers, and W. Templeton, *Can. J. Chem.*, **39**, 488 (1961).

[5] G. Büchi, C. G. Inman, and E. S. Lipinsky, *J. Am. Chem. Soc.*, **76**, 4327 (1954).

[6] D. R. Arnold, R. L. Hinman, and A. H. Glick, *Tetrahedron Letters*, 1425 (1964).

[7] N. C. Yang, M. Nussim, M. J. Jorgenson, and S. Murov, *ibid.*, 3657 (1964).

[8] See N. S. Bhacca and D. H. Williams ("Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, p. 50) for dihedral angle dependence of *J*. The doublet at δ 5.85 has a *J* of about 9 c.p.s. which corresponds to either a 0 or 145° dihedral angle. Models show that the *cis* isomer has a dihedral angle of 0°. The *trans* isomer has a dihedral angle of 120°, corresponding to the *J* value of 6 c.p.s. observed for the δ 5.35 doublet.

[9] A. Bardot, *Ann. Chim.* (Paris), **11**, 519 (1939).

TABLE I

PRODUCTS OF THE PHOTOLYSIS OF CARBONYL COMPOUNDS AND OLEFINS

Carbonyl compd.	Olefin	Time, hr.	% conversion of carbonyl	Products, % Oxetane	Pinacol	Hydrocarbon dimer	Alcohol	Remarks
Benzophenone	Cyclohexene	68	95	13	47	>6	27	
Benzophenone	1-Hexene	67	85	20	49	>10	28	The hydrocarbon product contained three isomeric dimers
Acetophenone	Cyclohexene	154	90	15	Not obsd.	>10	17	Polymer also formed
Benzaldehyde	Cyclohexene	113	90	38	10	>4	18	
Benzaldehyde	1-Hexene	100	90	30	Not obsd.	>4	19	
Acetone	Cyclohexene	150	80	8	Not present	>26	45	

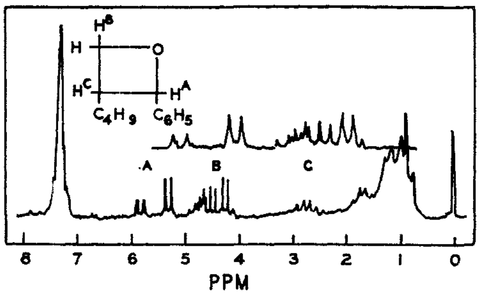


Figure 1.—N.m.r. spectra in carbon tetrachloride: sweep width 500 c.p.s., sweep time 250 sec.

The alcohols were isolated in an impure state and characterized by their infrared and proton magnetic resonance spectra. The infrared spectrum for the alcohol from acetone and cyclohexene was the same as that reported by de Mayo and co-workers.[4] The reaction mixtures were reduced and subjected to mass spectrometric analysis. Molecular ions were observed which could be due to alcohol dehydration products.

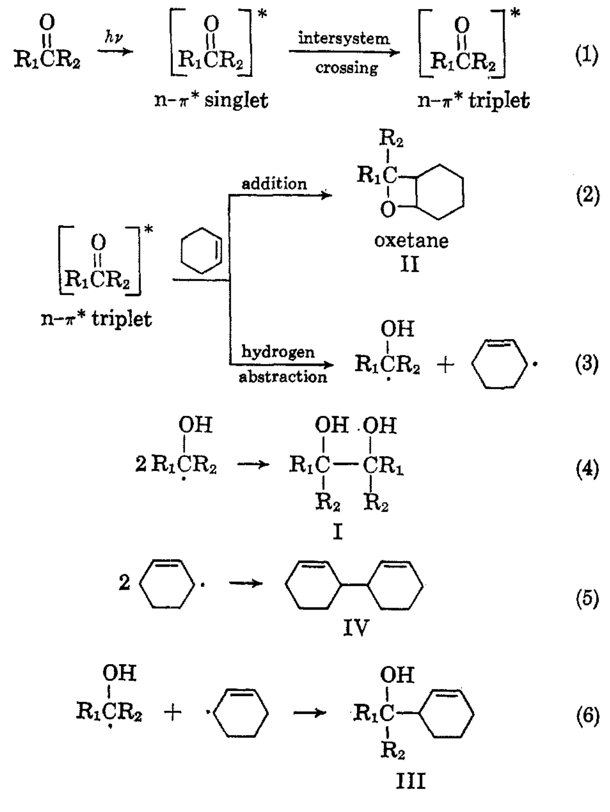
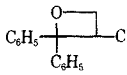
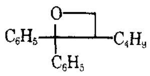
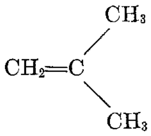
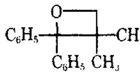
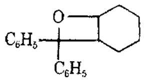
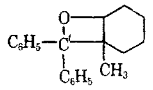


TABLE II

OXETANE YIELDS

Carbonyl	Olefin	Oxetane	Yield, %
$C_6H_5\overset{\overset{O}{\|}}{C}C_6H_5$	$CH_2{=}CHCH_3$		5[a]
$C_6H_5\overset{\overset{O}{\|}}{C}C_6H_5$	$CH_2{=}CHC_4H_9$		20[b]
$C_6H_5\overset{\overset{O}{\|}}{C}C_6H_5$			93[a]
$C_6H_5\overset{\overset{O}{\|}}{C}C_6H_5$	Cyclohexene		13[b]
$C_6H_5\overset{\overset{O}{\|}}{C}C_6H_5$	1-Methylcyclohexene		40[a]

[a] Reference 6. [b] This work.

The reaction probably proceeds through the carbonyl n-π* triplet state as demonstrated by Hammond and co-workers.[2,10] The excited triplet intermediate either adds to the olefin to form oxetane or abstracts a hydrogen atom. The radicals from the hydrogen abstraction probably react to form pinacols, alcohols, and hydrocarbon dimers.

The relative amounts of addition and hydrogen abstraction products are probably due to many factors. Some of these are the relative ease of hydrogen abstraction, stability of the diradical intermediate in the addition path, and steric hindrance.

It is possible either that the diradical intermediate is capable of closing to form oxetane or that the C–O bond breaks to form starting materials in the ground state. In the latter case, the excess energy in the system would be absorbed by changes in geometry during the bond-forming and -breaking steps. The diradical V with a greater number of substituents would be more stable. This greater stability would result in a greater yield of oxetane. This correlation between

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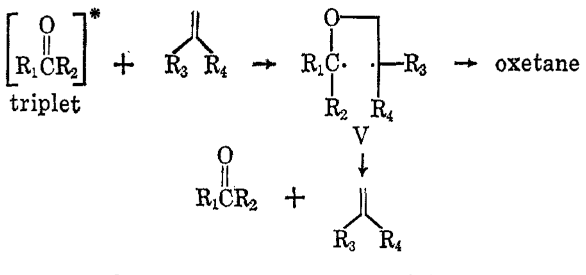
(10) M. W. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961), and related papers.

TABLE III

PHYSICAL PROPERTIES OF NEW REACTION PRODUCTS

					Mass spectrometric data		
						Mass	
Reaction	Product	Infrared, cm.$^{-1}$	N.m.r., δ	Other	Structure	Calcd.	Found
Benzophenone–cyclohexene	Oxetane	972, 947, 922[a]	m 7.4 (10), q 4.9 (1), q 3.3 (1), m 1.3–2.1 (8)	M.p. 86–90° (uncor.)	$C_{19}H_{20}O$	264.1514	264.1521
	Alcohol	3540	m 7.4 (10), q 5.7 (2), s 3.4 (1), m 1.3–2.1 (7)	Semisolid	$C_{19}H_{20}$[b]	248.1565	248.1566
Benzophenone–1-hexene	Oxetane	965[a]	m 7.4 (10), t 4.6 (1), t 4.2 (1), m 3.4 (1), m 1.2 (6), s 0.8 (3)	Semisolid	$C_{18}H_{20}$[c]	236.1565	236.1545
	Alcohol	3540	m 7.25 (10), m 4.8–5.5 (3), m 3.0 (1), s 2.3 (1), m 1.3 (~ 4), m 0.85 (~3)	Semisolid	$C_{19}H_{22}$[b]	250.1721	250.1712
	Hydrocarbon dimer	992, 962, 908[d]	m 4.2–5.9, s 2.0, s 1.3, d 0.9	V.p.c. showed three major dimer products			
Acetophenone–cyclohexene	Oxetane	985, 958, 928[a]	s 7.2 (5), m 4.85 (1), t 2.6 (1), s 1.65 (3), m 0.8–2.0 (~8)	Semisolid	$C_{14}H_{18}O$	202.1358	202.1357
	Alcohol	3470	m 7.2 (5), m 5.7 (2), s 2.1 (1), s 1.3 (3), m 0.9–2.0 (~8)	Semisolid	$C_{14}H_{18}$[b]	186.1408	186.1411
Benzaldehyde–cyclohexene	Oxetane	975, 948[a]	s 7.2 (5), d 5.85 (1), m 4.85 (1), t 2.8 (1), m 1.0–2.0 (8)	$n^{25}D$ 1.5276[e]	$C_{13}H_{16}O$	188.1201	188.1202
	Alcohol	3380	s 7.2 (5), m 5.8 (2), t 4.3 (1), s 2.6 (1), m 1.2–2.0 (~7)	Semisolid	$C_{13}H_{16}$[b]	172.1252	172.1248
Benzaldehyde–1-hexene	Oxetane	980[a]	Figure 1	$n^{24}D$ 1.5164[e]	$C_{12}H_{16}$[c]	160.1252	160.1251
	Alcohol	3410	s 7.2, m 4.2–5.5, m 2.8, m 0.8–1.8	Semisolid	$C_{13}H_{16}$[b]	172.1252	172.1253
	Hydrocarbon dimer	*f*	*f*				
Acetone–cyclohexene	Oxetane	945[a]	m 4.6 (1), m 2.3 (1), m 1.1–1.9 (~8), s 1.45 (3), s 1.2 (3)	Liquid	No mass spectral data could be obtained		
	Alcohol	3450	s 5.7 (2), s 3.1 (~1), m 0.9–2.1 (~7), d 1.1 (6)	Semisolid	C_9H_{16}[b]	124.1252	124.1249

[a] These values correspond to the infrared spectra for oxetanes (ref. 11). [b] These values correspond to the molecular weight of the dehydration product of the reduced alcohols. [c] These values correspond to molecular weight minus 30. (See ref. 9.) [d] The bands are attributable to $RCH{=}CH_2$ and *trans*-$RCH{=}CH{-}R$: L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 34. [e] Chromatographic fraction. [f] Same as those for the dimer from the benzophenone–1-hexene reaction.



degree of substitution and oxetane yield was observed in the case of both straight-chain and cyclic olefins (Table II). Benzaldehyde was an exception to this observation in that even though the diradical V was less substituted a good yield of oxetane was obtained (Table I). A smaller amount of steric hindrance may be an important factor in this case.

Experimental Section

Materials.—Benzophenone and acetophenone were used as received from Eastman Kodak. Benzaldehyde (Braun-Knecht-Heimann Co.), acetone (Allied), and 1-hexene (Phillips) were used as received. Cyclohexene (Eastman Kodak) was purified prior to use by passing it through alumina. Catalyst grade alumina was obtained from Harshaw.

Photolysis of Benzophenone in Cyclohexene.—A solution of 25 g. (0.137 mole) of benzophenone in 175 ml. of cyclohexene was placed in a 250-ml. reaction vessel. A quartz immersion well was fitted into the reaction vessel. A Pyrex sleeve (filters out all light below 2900 Å. wave length) and a Hanovia 450-w. lamp were placed into the immersion well. The solution was then irradiated until about 5% of the benzophenone remained in solution (68 hr.). Solid white crystals (6.1 g.) were collected. The filtrate was concentrated in a nitrogen stream and diluted with 100 ml. of pentane. The cooled solution yielded an additional 3.5 g. of solid (total yield 9.6 g. or 38%). This solid proved to be benzopinacol: m.p. 185–186° (lit.[2] m.p. 187°); n.m.r. δ 7.1–7.3 (10 protons) and 2.95 (1 proton). This latter band disappeared when the sample was shaken with deuterium oxide; the infrared spectrum showed a strong OH band.

The filtrate was concentrated, and 4.40 g. was absorbed on 150 g. of alumina. The column was eluted with 250 ml. of pentane and then 250-ml. portions of increasing amounts of ether in pentane, ether, methanol in ether, and methanol. Fractions (50 ml.) were collected in weighed 50-ml. flasks. The solvent was removed carefully in a nitrogen stream on the steam bath.

Fractions 1–5 contained material, 0.45 g., the infrared and n.m.r. spectra of which were consistent with bicyclohexenyl. A small amount of this material was reduced and found to have the same infrared spectrum as bicyclohexyl (Eastman Kodak).

Fractions 10–15 contained solid white material, 0.95 g., m.p. 86–90°. The infrared spectrum was consistent with oxetane, with bands in the 930–980-cm.$^{-1}$ region.[11] The n.m.r. spectrum showed strong aromatic (10 protons) and aliphatic (9 protons) bands, as well as bands at δ 4.9 (1 proton) and 3.35 (1 proton). The latter two peaks can be attributed to protons α and β to oxygen in the oxetane ring.[6] The mass spectrum of this material showed a large parent peak at mass 264, which is the calculated molecular weight.

Fractions 21–33 contained material, 1.90 g., whose infrared spectrum was consistent with cyclohexenyldiphenylcarbinol. The n.m.r. spectrum contained bands at δ 7.05 and 7.55 (10 protons), 5.75 (2 protons), 3.4 (1 proton), and 1.3 to 2.1 (7 protons).

The remaining material on the column, 0.65 g., was found to be benzopinacol. The total calculated yields of the reaction were benzopinacol (47%), oxetane (13%), bicyclohexenyl (6% or more), and cyclohexenyldiphenylcarbinol (27%).

Other Photolysis Reactions.—These reactions were carried out as illustrated above for benzophenone and cyclohexene. The total yields of products are given in Table I. Table III gives the physical properties for all new products from these reactions.

Mass Spectrometric Analysis.—The reaction mixtures were reduced by hydrogen over platinum in dioxane. This gave mixtures with the alcohol two mass units higher than the oxetane. The resulting material was introduced into the high-resolution mass spectrometer AEI MS-9 by means of a 210° inlet system. The oxetanes from cyclohexene gave molecular ions at the expected *m/e*, whose exact mass corresponded to calculated values. (See Table III.) The oxetanes from 1-hexene gave large peaks at the expected mass less 30, corresponding to a loss of formaldehyde.[9] The exact mass of these compounds corresponded to calculated values (Table III). Other hydrocarbon ions were observed which could be due to the dehydration products of the reduced alcohols (Table III).

Acknowledgment.—The author wishes to thank Dr. L. P. Lindeman, who recorded and analyzed the n.m.r. spectra, and Dr. R. H. Teeter for the mass spectrometric analysis.

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[11] G. M. Barrow and S. Searles, *J. Am. Chem. Soc.*, **75**, 1175 (1953).

Correlation of Configuration and Rotatory Direction for Several 4-Substituted Cyclohexenes

STANLEY I. GOLDBERG AND FUK-LUEN LAM

Department of Chemistry, University of South Carolina, Columbia, South Carolina

Received June 24, 1965

In addition to providing corroboration of the absolute configuration of 4-methylcyclohexene, relative configurations for 4-carboxycyclohexene, 4-hydroxymethylcyclohexene, cyclohexen-4-ylmethyl hydrogen phthalate, and 4-tosyloxymethylcyclohexene were determined and placed on an absolute basis through correlation with 3-methylhexadienoic acid of known absolute configuration.

In order to provide a basis for formulation of a consistent model to account for the details of asymmetric selection during elimination of the original optically active group (AH) from the 4-methylcyclohexyl systems represented by I, reliable information regarding stereochemical arrangements, including absolute correlation between rotational signs[1] and configurations, is required for both the starting systems (Ia–d) and the optically active product, 4-methylcyclohexene (II).

II

Ia, A = –OOCCR′R″R‴
b, A = –NOR′R″
c, A = –SOR′
d, A = –POR′R″

In the carbalkoxy systems, represented by Ia, observation of an asymmetric process (production of optically active II) carries very important implications regarding the mechanistic details of ester pyrolysis.[2] Since we have already completed syntheses and pyrolyses of each of the four stereomers [(+)- and (−)-*cis* and (+)- and (−)-*trans*] of one such system (Ia, A = α-phenylpropionoxy)[3] with definitive assignments of stereochemical details to each, and have observed formation of optically active II during careful pyrolysis of each stereomer,[4] we only required absolute correlation of rotational sign with configuration of the predominant enantiomeric 4-methylcyclohexene obtained in each case.

Despite the fact that it was possible to deduce this information from work already reported,[5] there also appeared to be sufficient justification for additional corroborative experimental work since a question possibly concerning the correctness of the resultant configurational assignment to (+)-4-methylcyclohexene (IIa) was raised recently by Wiberg and Nielsen.[6]

In the course of substantiating the configurational assignments to the enantiomeric 4-methylcyclohexenes during the present work, correlations between rotational signs and configurations were also obtained for several other 4-substituted cyclohexenes.

Partial resolution of 4-carboxycyclohexene (III) was obtained *via* formation and fractional crystallization of the diastereomeric quinine salts, and each enantio-

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[1] All rotatory signs (directions) reported and referred to in this paper are based upon measurements made at the so-called sodium D line (roughly 589 mμ).

[2] J. C. Scheer, E. C. Kooyman, and F. L. J. Sixma, *Rec. trav. chim.*, **82**, 1123 (1963), and references therein.

[3] For preliminary accounts of this work, see S. I. Goldberg and F-L. Lam, *Tetrahedron Letters*, 1893 (1964); Abstracts, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964, p. 48S.

[4] The manuscript containing a full report of these experiments is in preparation.

[5] M. Mousseron, R. Richaud, and R. Granger [*Bull. soc. chim. France*, **13**, 222 (1946)] converted (+)-3-methylcyclohexanone into IIa. The former was subsequently produced from (−)-3-carboxyl-1-cyclohexanol by D. S. Noyce, *et al.* [*J. Am. Chem. Soc.*, **74**, 5912 (1952); **76**, 768, 3630 (1954)], who also, through a series of steps, showed the configurational relationship of (+)-3-methylcyclohexanone and (−)-3-carboxy-1-cyclohexanol to that of (−)-2-methoxyhexane whose relationship to (+)-glyceraldehyde was established earlier by P. A. Levene and co-workers [*J. Biol. Chem.*, **65**, 49 (1925); **67**, 329 (1926); **71**, 465 (1927)]. It should also be noted that Wallach [*Ann.*, **289**, 340 (1896)] obtained (+)-3-methylcyclohexanone from (+)-pulegone, and that the latter was oxidized to (+)-3-methylhexandioic acid by J. v. Braun and F. Jostes [*Chem. Ber.*, **59**, 1091 (1926)]. The relationship of this acid to glyceraldehyde is discussed above.

[6] K. B. Wiberg and S. D. Nielsen, *J. Org. Chem.*, **29**, 3353 (1964).