Mass spectrometry. The mass spectra at low ionizing voltage were determined with a modified Consolidated Electrodynamics Corporation model 21-620 mass spectrometer.

ATOMICS INTERNATIONAL
A DIVISION OF NORTH AMERICAN AVIATION, INC.,
CANOGA PARK, CALIF.

Allylic Rearrangements. XLVIII. The Absolute Configuration of (+)-α-Methylallyl Alcohol and (+)-α-Methylallyl Chloride[1]

WILLIAM G. YOUNG AND FREDERICK F. CASERIO, JR.[2]

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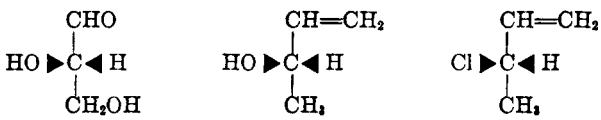
DISCUSSION

In connection with other studies[3,4] the determination of the relative configurations of optically active α-methylallyl chloride and α-methylallyl alcohol became necessary and this work is described below.

Catalytic hydrogenation of (+)-α-methylallyl alcohol yielded (+)-2-butanol which has the L-configuration[5] and therefore (+)-α-methylallyl alcohol is designated L- in agreement with the work of Wiberg.[6,7]

Reaction of thionyl chloride with D-(−)-α-methylallyl alcohol and tri-*n*-butylamine in ether yielded (+)-α-methyallyl chloride which was ozonized to (−)-α-chloropropionic acid known to possess the L-configuration.[8] It follows then that α-methylallyl alcohol and α-methylallyl chloride of like sign have like configurations about the asymmetric carbon. The absolute configurations are shown in Fig. 1.



L-(−)-Glyceraldehyde[9] L-(+)-α-Methylallyl alcohol L-(+)-α-Methylallyl chloride

Fig. 1 Absolute configuration of (+)-α-methylallyl alcohol and chloride

A lower limit for the rotation of optically pure L-(+)-α-methylallyl chloride of α_D^{25} +61° (for l = 1, neat) has been estimated from comparison of the rotation of the L-(−)-α-chloropropionic acid obtained in this work with that obtained by Lucas[10a,b] from the degradation of optically pure L-(+)-erythro-3-chloro-2-butanol. This comparison assumes that no racemization occurred during the present ozonization or Lucas' degradations, as the asymmetric centers under consideration were not directly involved in any reactions.

EXPERIMENTAL

dl-α-Methylallyl alcohol was prepared by the method of Delaby[11] as modified by Prevost,[12] b.p. 96–97°, n_D^{25} 1.4125.

Partial resolution of α-methylallyl alcohol was accomplished by the procedure of Kenyon and Snellgrove.[13] The purified alcohol had b.p. 97°, n_D^{25} 1.4121 and α_D^{27} +20.09 ± 0.02° (neat, l 1.0) which is 71.9% of optical purity based on α_D^{30} +13.8 (neat, l 0.5).[4] The mother liquors yielded a small amount of (−)-α-methylallyl alcohol of α_D^{25} −8.45° (neat, l 1.0).

Hydrogenation of (+)-α-methylallyl alcohol. A mixture having α_D^{25} +9.78 ± 0.02° (neat, l 1.0) of 2.21 g. of (+)-α-methylallyl alcohol and 2.36 g. of inactive 2-butanol was dissolved in 10 ml. of ether and hydrogenated at atmospheric pressure over 1.41 g. of 5% palladium on barium sulfate. Only about 30% of the theoretical hydrogen was absorbed. The solution was fractionated through a 30-cm. concentric tube column and yielded 1.8 g. of impure (+)-2-butanol in three fractions, the last of which had α_D^{24} +1.91 ± 0.02° (neat, l 1.0). The impurity was found to be methylethyl ketone which presumably arose from rearrangement of α-methylallyl alcohol caused by the catalyst. In another hydrogenation with Adam's catalyst, 80% of the theoretical hydrogen was absorbed.

(+)-α-Methylallyl chloride was prepared by dropwise addition of 16.5 g. (0.139 mole) of thionyl chloride over 50 min. to a stirred, ice cooled solution of 10.0 g. (0.139 mole) of (−)-α-methylallyl alcohol and 25.7 g. (0.139 mole) of tri-*n*-butylamine in 200 ml. of ether. Careful fractionation through a 30-cm. concentric tube column gave 3.3 g. of γ-methylallyl and 7.1 g. of (+)-α-methylallyl chlorides (83% yield).

Ozonization of (+)-α-methylallyl chloride. A solution of 8.39 g. (0.093 mole) of (+)-α-methylallyl chloride, α_D^{25} +5.87 ± 0.02° (neat, l 1.0) and 50 ml. of chloroform was ozonized at 0° with 2–3% ozone. After ozonization was completed, the solution was poured into 25 ml. of water. The mixture was stirred overnight at room temperature and then, after addition of 10 ml. of acetone, was heated cautiously to 50° for 4 hr. When cool, half of the mixture was saturated with magnesium sulfate then treated with 4.9 g. of potassium permanganate in about 100 ml. of water. The mixture was filtered, the filtrate saturated with sodium sulfate and acidified by addition of 2 ml. of concd. sulfuric acid. The colorless solution was extracted with ten portions

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(2) Standard Oil Company of California Predoctoral Fellow, 1952–1954.

(3) R. H. DeWolfe and W. G. Young, *Chem. Rev.*, **56**, 813 (1956).

(4) K. L. Olivier and W. G. Young, *J. Am. Chem. Soc.*, **81**, 5811 (1959).

(5) P. A. Levene, A. W. Walti, and H. Haller, *J. Biol. Chem.*, **71**, 465 (1927).

(6) K. B. Wiberg, *J. Am. Chem. Soc.*, **74**, 3981 (1952).

(7) Wiberg designates the (+) stereoisomer as D- and has the vinyl group correspond to the hydroxymethyl group of glyceraldehyde. In the present work the vinyl group corresponds to the carboxaldehyde group of glyceraldehyde and thus the L- designation given here is consistent with Wiberg's D- designation.

(8) W. A. Cowdry, E. D. Hughes, C. K. Ingold, S. Masterman, and A. D. Scott, *J. Chem. Soc.*, 1252 (1937).

(9) J. J. Bijvoet, A. F. Peerdeman, and A. J. Van Bommel, *Nature*, **168**, 272 (1951).

(10) (a) H. J. Lucas and H. K. Garner, *J. Am. Chem. Soc.*, **70**, 991 (1948); (b) W. F. Fickett, H. K. Garner, and H. J. Lucas, *J. Am. Chem. Soc.*, **73**, 5063 (1951).

(11) R. Delaby, *Compt. Rend.*, **175**, 967 (1922).

(12) C. Prevost, *Ann. Chim.*, **10**, 113, 147 (1928).

(13) J. Kenyon and D. Snellgrove, *J. Chem. Soc.*, **127**, 1174 (1925).

of ether. The combined ether extracts were dried over sodium sulfate and concentrated by distillation. The residue was distilled at reduced pressure to give three fractions of (−)-α-chloropropionic acid weighing a total of 1.1 g. (22%) and all with b.p. 69.5° (1.2 mm.). The third fraction had α_D^{25} −1.73 ± 0.02° (neat, l 1.0) and neutral equivalent 110.5 (calcd.: 108.5). The neutral equivalent solution after titration with standard base was dextrorotatory.

The other half of the ozonide hydrolysis solution was treated with 5 g. of 30% hydrogen peroxide. The α-chloropropionic acid obtained after extraction and distillation amounted to about 1 g. (20%) and had α_D^{25} −1.46 ± 0.02° (neat, l 1.0) but appeared to be quite impure.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
LOS ANGELES 24, CALIF.

The Structure of the Dimer of 1-Phenyl-4-methyl-2-penten-1-one

RAGINI ANET

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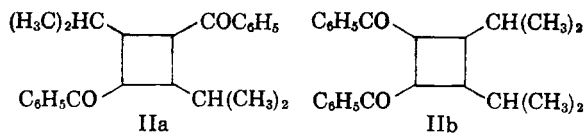
Kulka, *et al.* recently reported[1] that treatment of 1-phenyl-4-methyl-2-penten-1-one (I), (the condensation product of acetophenone with isobutyraldehyde), with aqueous methanolic alkali gave a dimer (II), m.p. 144.5–145°. Vacuum distillation of II in presence of catalytic amounts of sodium acetate gave back I. As attempts to detect an ethylenic linkage (catalytic hydrogenation, formation of a dibromide) failed, a 1,2,3,4-tetrasubstituted cyclobutane structure, IIa or IIb, was assigned to II. The formation of a dioxime and an infrared absorption band at 880 cm.$^{-1}$ were cited as evidence supporting such an assignment.



IIa IIb

As the formation of such cyclobutane structures under alkaline conditions seemed surprising to us,[2] the structure of II was reinvestigated.

The NMR spectrum[3] of II, prepared according to Kulka, *et al.*, was determined in a deuterochloroform solution using tetramethylsilane as an internal standard,[4] and is shown in Fig. 1.

The spectrum rules out structures IIa and IIb and can only be interpreted on the basis of the structure given below.

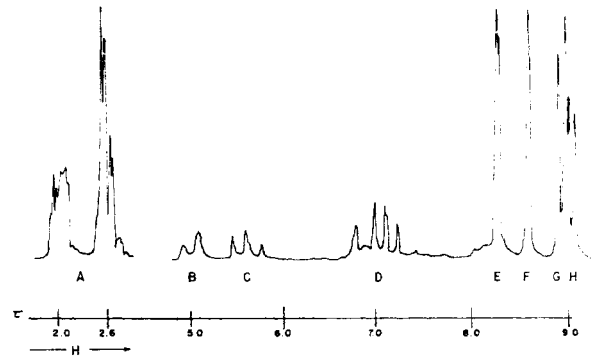
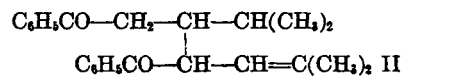


Fig. 1. The NMR spectrum of II in deuterochloroform (60 Mc/s)



This structure is compatible in every detail with the NMR spectrum and is in fact the Michael addition[5] product of the conjugate anion $C_6H_5—C(=O)—C^-H—CH=C(CH_3)_2$ of II to the α,β-unsaturated ketone I itself. The alkali-catalyzed dimerzation of the α,β-unsaturated ketones piperitone[6] and 3-methyl-cyclohex-2-en-1-one[7] has indeed been shown to occur *via* an initial Michael addition followed by further reactions.

The NMR spectrum clearly shows the presence of one isopropyl group. The bands G and H at highest field[8] (τ, 8.9, 9.0) are due to the two methyl groups split by a single hydrogen (J = 7.2 c.p.s.). The nonequivalence of the two methyl groups is due to the presence of an asymmetric center in the molecule, an observation made in the case of the alkaloid lunacrine.[9] The other two methyl groups (bands E and F) are not part of an isopropyl group, thus ruling out[10] structures IIa and IIb. Their position at low field (τ, 8.34, 8.60) corresponds to methyl groups attached to a doubly bonded carbon.[8] The magnitude of the splitting (1.3–1.5 c.p.s.) is too small for 1:2 coupling but is consistent with 1:3 coupling observed in olefinic compounds.[11]

(1) K. Kulka, R. J. Eiserle, J. A. Rogers, Jr., and F. W. Richter, *J. Org. Chem.*, **25**, 270 (1960).

(2) Cyclobutane compounds are well known in the photodimerization of ethylenic compounds, *cf.* A. Schönberg, *Präparative Organische Photochemie*, Springer-Verlag, Berlin, 1958.

(3) Varian V-4302 60 mc/s instrument.

(4) G. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

(5) E. D. Bergmann, D. Ginsburg, and R. Pappo, *Org. Reactions*, **10**, 179, (1959).

(6) W. I. Taylor, *Chem. and Ind.*, 252 (1954). W. A. Ayer and W. I. Taylor, *J. Chem. Soc.*, 2227 (1955).

(7) G. Buchi, J. H. Hansen, D. Knutson, and E. Koller, *J. Am. Chem. Soc.*, **80**, 5517 (1958).

(8) G. D. Tiers, *Tables of τ-values for a variety of Organic Compounds*, Part I, Minnesota Mining and Manufacturing Company, St. Paul, Minn., 1958.

(9) S. Goodwin, J. N. Shoolery, and L. F. Johnson, *J. Am. Chem. Soc.*, **81**, 3065 (1959).

(10) One or two isopropyl groups should be observed in the spectrum of IIa or IIb depending on the exact stereochemistry of the cyclobutane ring. In the analogous case of substituted truxillic and truxinic acids, the nonequivalence of substituents has been used to determine their stereochemistry. R. Anet, *Chem. and Ind.*, 897 (1960).

(11) L. M. Jackman, *Application of N.M.R. Spectroscopy in Organic Chemistry*, Pergamon Press, New York, 1959.