The elementary analysis indicated that the product might be 1,2-diacetylindazolone; however, the latter has been reported[7] to melt at 135° (this m.p. was not supported by analytical or other data) and the N-acetyl value (calcd. for two N-acetyl units, 39.49; found,[30] 46.25) of the present compound deviated unsatisfactorily from the theoretical value.

(b).—Nitroformaldehyde *o*-carbomethoxyphenylhydrazone (2.23 g., 0.01 mole) and 50 ml. of acetic anhydride were warmed, with stirring, to 50° and treated with 1 g. (0.01 mole) of fused potassium acetate. The solution, which warmed slightly, was heated at 80° for two hours. Most of the solvent was removed by distillation under reduced pressure, the residue was poured into 50 ml. of water and the mixture was warmed on the steam-bath until hydrolysis of the acetic anhydride was complete. As the solution cooled, a brown solid separated (0.8 g.). The crude product was recrystallized twice from ethanol–water (using charcoal), giving 0.6 g. of a pale tan solid, m.p. 83.5–85°. The product was not soluble in dilute sodium hydroxide.

Anal.[31] Calcd. for $C_{10}H_8N_4O_4$: C, 48.39; H, 3.25; N, 22.58. Found: C, 48.51; H, 3.00; N, 22.66.

The compound had a rather complicated spectrum (in nujol mull), the principal peaks above 1250 cm.$^{-1}$ being: 3158 (m), 1738 (s), 1607 (m), 1587 (w), 1540 (s), 1500 (w), 1485 (m), 1443 (s), 1359 (s), 1301 (s), 1271 (s). The spectrum in carbon tetrachloride solution differed little from that in the nujol mull.[31] The nature of this compound was not determined, but it was not likely that it was the sought after 3-nitro-4-hydroxycinnoline.

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[30] Analysis by Clark Microanalytical Laboratory, Urbana, Illinois.

[31] We are indebted to Prof. C. W. Rook for the determination of these spectra.

LINCOLN 8, NEBRASKA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

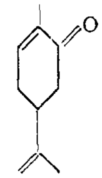
Terpenes. II. The Reactions of Carvone and Dihydrocarvone with Methanol in the Presence of Sulfuric Acid

BY G. BÜCHI AND ROBERT E. ERICKSON

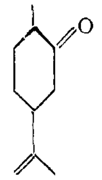
RECEIVED OCTOBER 17, 1953

The reactions of carvone and dihydrocarvone with methanol in the presence of sulfuric acid have been reported to yield compounds III and IV, respectively. In the present investigation carvone has been shown to give V and VI. Similarly dihydrocarvone gives VII and VIII. No abnormal additions to the isopropenyl system are involved in these reactions.

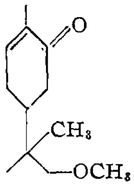
The reactions of carvone (I) and dihydrocarvone (II) with methanol and sulfuric acid have been reported[1] to yield compounds III and IV, respectively. The present investigation was undertaken to clarify this novel addition of the elements of dimethyl ether to the isopropenyl double bond and to determine whether the reaction might be generally applicable. A repetition of the reactions reported by Treibs[1] yielded in both cases a mixture of compounds, none of which had properties in agreement with structures III and IV.



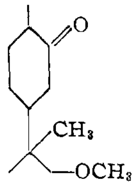
I



II

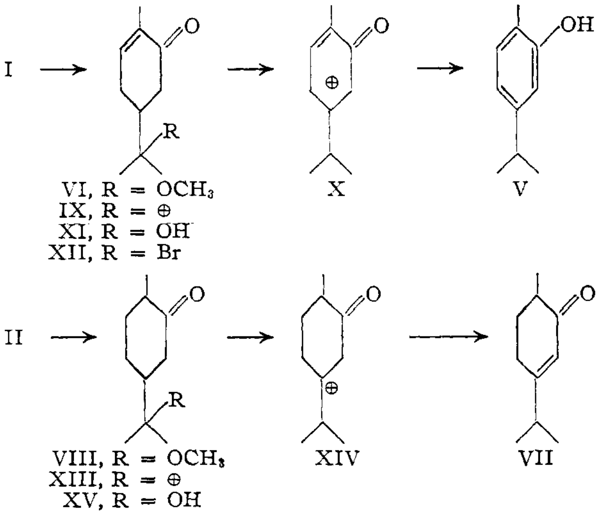


III



IV

The products from the reaction of carvone (I) with methanol were found to be carvacrol (V) and a methoxycarvotanacetone to which we have assigned structure VI. When dihydrocarvone (II) was allowed to react with methanol and sulfuric acid, carvenone (VII) and a methoxycarvomenthone (VIII) were formed. The following sequence of reactions appears to account satisfactorily for formation of the products found.



VI, R = OCH_3
IX, R = ⊕
XI, R = OH
XII, R = Br

VIII, R = OCH_3
XIII, R = ⊕
XV, R = OH

The carbonium ion intermediate IX readily can rearrange to a new ion X as demonstrated by the ready isomerization of carvone (I) to carvacrol (V) under acidic conditions.[2,3] Either IX or X can react with methanol to yield the corresponding methyl ether. In view of the great tendency of X to lose a proton to form an aromatic ring the reaction of IX with methanol to give 8-methoxycarvotanacetone (VI) seems more probable. The optical activity of the product actually isolated provides further evidence for structure VI, because the corresponding compound derived from X should be optically inactive.

Analogous reactions of carvone with reagents other than methanol are known. The hydration of carvone (I) with dilute sulfuric acid has been

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[1] W. Treibs, *Ber.*, **70**, 384 (1937).

[2] H. Goldschmidt and E. Kisser, *ibid.*, **20**, 486 (1887).

[3] O. Wallach, *Ann.*, **305**, 237 (1899).

shown to give the hydroxyketone XI,[4] while addition of hydrogen bromide in acetic acid solution yielded the hydrobromide XII,[5] the negative substituent entering at position 8 in both cases.

Similarly the cation XIII can rearrange to XIV, a conversion demonstrated by the isomerization of dihydrocarvone (II) to carvenone (VII) in dilute sulfuric acid solution.[6]

The methyl ether formed in the reaction of dihydrocarvone (II) with methanol could originate from either one of the two cations XIII or XIV. The fact that carvenone (VII) does not react with methanol in the presence of sulfuric acid indicates that the methyl ether is derived from cation XIII and therefore must be 8-methoxycarvomenthone (VIII). This sequence of reactions is supported by the work of Rupe[7] who isolated 8-hydroxycarvomenthone (XV) when dihydrocarvone was allowed to react with dilute sulfuric acid.

The carbonium ions IX and XIII could theoretically rearrange with ring enlargement before reacting with methanol, but no support for such rearrangements to derivatives of cycloheptanone was obtained from infrared measurements which are in agreement with structures VI and VIII. Instead the ready conversion of VI to VIII by catalytic reduction[8] proves that the methoxyl group is in the same position in both compounds and that reaction occurs only with the isopropenyl group.

As shown in Table I, the analytical data, optical rotations and indices of refraction reported by Treibs[1] for III and IV are reasonably well approximated by the values calculated for definite mixtures of the compounds actually isolated in each case. The results obtained in this investigation show that no abnormal additions to the isopropenyl system are involved in the reactions of I and II with methanol in the presence of acid. The reactions simply represent other examples of the well-known acid-catalyzed additions of nucleophilic reagents to carbon–carbon double bonds.

TABLE I

COMPARISON OF CONSTANTS REPORTED FOR COMPOUNDS III AND IV WITH VALUES CALCULATED FOR MIXTURES OF COMPOUNDS ACTUALLY ISOLATED

Compound	Carbon, %	Hydrogen, %	$n^{20}D$	$[\alpha]^{25}D$
III	73.43	10.27	1.495[a]	+40.5
Mixture of VI (89%) and V (11%)	73.13	9.92	1.4914[b]	+36.1[b]
IV	72.68	11.18	1.470[c]	−20.8
Mixture of VIII (85%) and VII (15%)	72.44	10.89	1.4673[b]	−19.5[b]

[a] Estimated from $n^{15}D$ 1.4972. [b] Calculated on the assumption that these properties are linear functions of concentration. [c] Estimated from $n^{15}D$ 1.4720.

Experimental

Materials.—The carvone was obtained from Fritzsche Bros., Inc., New York, and purified by distillation. The fraction used had b.p. 108.6–110° at 15–16 mm. and $n^{25}D$ 1.4970. The dihydrocarvone was prepared from carvone by the procedure of Wallach[9] and purified by preparation of the semicarbazone.[10] Regeneration of the ketone with oxalic acid followed by distillation gave a fraction which had b.p. 89–90° at 8 mm. and $n^{20}D$ 1.4719.

Reaction of Carvone and Methanol.—A solution of carvone (15 g., 0.1 mole) and concentrated sulfuric acid (3.0 g.) in absolute methanol (30 ml.) was heated under reflux in an atmosphere of nitrogen for 17 hours. The mixture was poured into 250 ml. of water, the organic layer extracted into ether, the ether solution washed with water, 5% sodium hydroxide solution, again with water and finally dried over anhydrous magnesium sulfate. The ether was removed by distillation through a short column to yield 18.2 g. of a yellow liquid. Distillation of the crude product through a semi-micro column gave two fractions plus a small amount of highly colored, high-boiling residue. The sodium hydroxide wash solution was acidified with concentrated hydrochloric acid, the organic layer extracted into ether, washed with water and dried over anhydrous magnesium sulfate. Removal of the ether yielded 1.4 g. of a colorless oil.

Carvacrol (V).—The acidic material obtained above (1.4 g., 8%) had a strong phenolic odor and gave a slight green color with 1% ferric chloride in ethanol. Treatment with phenyl isocyanate yielded a phenylurethan, m.p. 139–140.5° (cor.), recrystallized from petroleum ether. Admixture with an authentic sample of carvacrol phenylurethan did not depress this value.

Carvone (I).—The lower-boiling fraction (5.17 g., 28%) was redistilled through the semimicro column to yield a colorless liquid, b.p. 87–88° (7 mm.). Treatment with 2,4-dinitrophenylhydrazine in ethanol and sulfuric acid yielded a 2,4-dinitrophenylhydrazone, m.p. 190.5–191.5° (cor.), recrystallized from a mixture of ethanol and ethyl acetate. Admixture with an authentic sample of carvone 2,4-dinitrophenylhydrazone did not depress this value.

8-Methoxycarvotanacetone (VI).—The higher-boiling fraction (9.55 g., 52%) was redistilled through the semimicro column to yield a colorless liquid. The infrared spectrum and analytical values for this product indicated contamination with carvacrol. A solution of the product in petroleum ether was passed over 75 g. of neutral alumina. Removal of the solvent from the first 250 ml. of eluate yielded 90% of a product which after distillation through a Hickman column[11] had b.p. 124–125° (6 mm.), $n^{20}D$ 1.4876, $\alpha]^{25}D$ +40.6° (c 9.30 in chloroform).

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found: C, 72.35; H, 9.80.

Treatment with semicarbazide acetate in methanol gave a semicarbazone, m.p. 166.5–168° (cor.) recrystallized from aqueous ethanol.

Anal. Calcd. for $C_{12}H_{21}N_3O_2$: C, 60.22; H, 8.85. Found: C, 60.28; H, 8.78.

Reaction of Dihydrocarvone and Methanol.—A solution of dihydrocarvone (II) (14.14 g., 0.093 mole) and concentrated sulfuric acid (3.0 g.) in absolute methanol (30 ml.) was heated under reflux in an atmosphere of nitrogen for 17 hours and worked up as above to yield 15.83 g. of a pale-yellow liquid which was separated into two fractions plus a small amount of high-boiling residue by distillation through a semi-micro column.

Carvenone (VII).—Redistillation through a semi-micro column of the lower-boiling fractions (8.59 g., 54%) yielded a colorless liquid, b.p. 95–96° (8 mm.). Treatment with semicarbazide acetate in methanol yielded a semicarbazone, m.p. 199–201° (cor.), recrystallized from aqueous ethanol. Admixture with an authentic sample of carvenone semicarbazone did not depress this value.

8-Methoxycarvomenthone (VIII).—Redistillation through a semi-micro column of the higher-boiling fraction (5.44 g., 34%) yielded a colorless liquid, b.p. 114–115° (8 mm.), $n^{20}D$ 1.4642, $[\alpha]^{25.5}D$ −22.9 (c 10.65 in chloroform).

Anal. Calcd. for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 71.65; H, 10.94.

Treatment with 2,4-dinitrophenylhydrazine in ethanol and

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(4) H. Rupe and P. Schlochoff, *Ber.*, **38**, 1719 (1905).

(5) A. Baeyer, *ibid.*, **27**, 810 (1894).

(6) O. Wallach, *Ann.*, **286**, 119 (1895).

(7) H. Rupe and K. Liechtenhan, *Ber.*, **39**, 1119 (1906).

(8) The catalytic reduction formed a mixture of *cis*- and *trans*-8-methoxycarvomenthones which was converted to the pure *trans* isomer (both substituents in equatorial position) by equilibration with base.

(9) O. Wallach, *Ann.*, **275**, 110 (1893).

(10) The authors would like to thank Mr. Dhiam Hok Liem for preparing this compound.

(11) K. C. D. Hickman, *Chem. Revs.*, **34**, 51 (1944).

sulfuric acid yielded a 2,4-dinitrophenylhydrazone, m.p. 152–153° (cor.) after recrystallization from aqueous ethanol.

Anal. Calcd. for $C_{17}H_{24}N_4O_5$: C, 56.03; H, 6.64. Found: C, 56.21; H, 6.56.

Reaction of Carvenone and Methanol.—In two attempts to carry out this reaction under the conditions described above for carvone, quantitative recovery of starting material (identified by boiling point, refractive index and semicarbazone) was obtained.

Reduction of VI to VIII.—A solution of VI (0.65 g.) in absolute methanol (10 ml.) was stirred with palladium-on-carbon catalyst (0.5 g.) under hydrogen at room temperature and pressure. The calculated volume for one mole of hydrogen was taken up in 1 hour. After removal of the catalyst by filtration, the solution was concentrated under reduced pressure. A portion of the colorless product yielded a 2,4-dinitrophenylhydrazone which did not show a constant m.p. on repeated recrystallization. The infrared spectrum of a second portion, after distillation through a small Hickman column, appeared to be identical with that of VIII. A third portion (100 mg.) of the product was heated under reflux with a 10% solution of sodium methoxide in methanol for 1 hour. The mixture was poured into water, the organic material extracted into ether, washed with water, dried over magnesium sulfate and concentrated under reduced pressure to a liquid which yielded a 2,4-dinitrophenylhydrazone, m.p. 149–151° (cor.), recrystallized from aqueous ethanol. Admixture with the 2,4-dinitrophenylhydrazone prepared from VIII did not depress this value.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

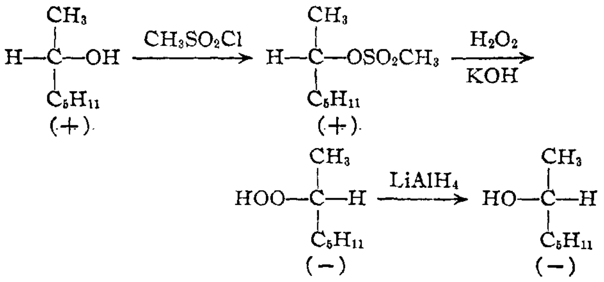
Organic Peroxides. III. The Mechanism of the Reaction of Alkyl Methanesulfonates with Hydrogen Peroxide

BY HOMER R. WILLIAMS AND HARRY S. MOSHER

RECEIVED JANUARY 18, 1954

The sequence of reactions: 2-heptanol → 2-heptyl methanesulfonate → 2-heptyl hydroperoxide → 2-heptanol, has been studied using optically active 2-heptanol. *Dextrorotatory* 2-heptanol was converted by these steps to *levorotatory* 2-heptanol with 90% of the rotation of the starting alcohol. These results clearly establish the reaction of alkyl methanesulfonates with hydrogen peroxide in the presence of base as a typical S_N2 displacement which proceeds by inversion.

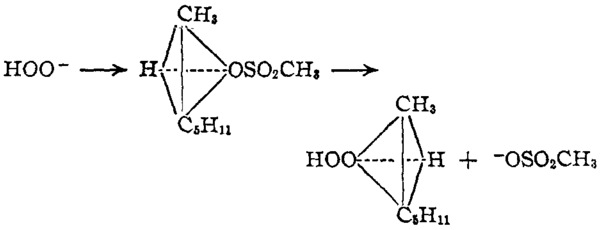
A study has been made of the stereochemical course of the reactions involved in the preparation of 2-heptyl hydroperoxide by the action of 2-heptyl methanesulfonate on hydrogen peroxide in the presence of a base. This example was chosen because of the ease of resolution of 2-heptanol[1] and the satisfactory yield obtained in the preparation of 2-heptyl hydroperoxide. Dextrorotatory 2-heptanol (97.5% optical purity) was converted to dextrorotatory 2-heptyl methanesulfonate by the method of Sekera and Marvel[2] in 70% yield. This 2-heptyl methanesulfonate was then converted to levorotatory 2-heptyl hydroperoxide by the method employed for the preparation of the normal and secondary alkyl hydroperoxides,[3] and described in detail in the experimental section. The levorotatory 2-heptyl hydroperoxide was then reduced with lithium aluminum hydride to give levorotatory 2-heptanol.



$$\underset{(+)}{\mathrm{H{-}\underset{C_5H_{11}}{\overset{CH_3}{C}}{-}OH}} \xrightarrow{\mathrm{CH_3SO_2Cl}} \underset{(+)}{\mathrm{H{-}\underset{C_5H_{11}}{\overset{CH_3}{C}}{-}OSO_2CH_3}} \xrightarrow[\mathrm{KOH}]{\mathrm{H_2O_2}}$$

$$\underset{(-)}{\mathrm{HOO{-}\underset{C_5H_{11}}{\overset{CH_3}{C}}{-}H}} \xrightarrow{\mathrm{LiAlH_4}} \underset{(-)}{\mathrm{HO{-}\underset{C_5H_{11}}{\overset{CH_3}{C}}{-}H}}$$

The optical rotation of the final alcohol was opposite in sign and 90% of the starting alcohol. Since there appears to be no reasonable mechanism whereby inversion can occur during the first or last step it follows that the inversion resulted from a backside attack of the hydroperoxy ion on the alkyl methanesulfonate by an S_N2 mechanism.



The data show that 95% of the reaction goes by such a mechanism. This reaction is then completely analogous to the established inversion of tosylates by reagents such as the carboxylate and alkoxide ions.[4] It can safely be assumed that the same mechanism operates in the case of the reaction of hydrogen peroxide in basic solution on the *n*-alkyl sulfonates[4] and very probably in the method of Baeyer and Villiger[5] as well. This mechanism is in contrast to the carbonium ion mechanism[6] which undoubtedly operates in the preparation of tertiary hydroperoxides by the action of hydrogen peroxide on tertiary alcohols in the presence of strong acid catalysts.[6,7] The application of both S_N1 and S_N2 reactions to the alkylation of hydrogen peroxide now makes potentially available all types of aliphatic primary, secondary and tertiary hydroperoxides.

Acknowledgment.—We wish to thank the California Research Corporation for a grant which made these studies possible.

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(1) R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **99**, 45 (1911).

(2) V. Sekera and C. S. Marvel, THIS JOURNAL, **55**, 345 (1933).

(3) H. R. Williams and H. S. Mosher, *ibid.*, **76**, 2987 (1954).

(4) R. H. Phillips, *J. Chem. Soc.*, **127**, 2552 (1925).

(5) A. Baeyer and V. Villiger, *Ber.*, **33**, 3387 (1900); **34**, 738 (1901).

(6) D. G. Davies, R. V. Foster and A. M. White, *J. Chem. Soc.*, 1541 (1953).

(7) N. A. Milas, U. S. Patent 2,273,807 (Dec. 3, 1940); N. A. Milas and D. M. Surgenor, THIS JOURNAL, **68**, 205, 643 (1946).