ture. After standing for a few weeks, the colors had faded only slightly.

**Tri-$p$-alkylphenylmethyl Peroxides.**—The ethanes (or free radicals) were characterized by their corresponding peroxides. The peroxides were prepared by allowing the solutions of the ethanes to stand in the presence of the oxygen in the air. The color of the solutions was quickly discharged and after the silver-silver chloride mixture had been filtered off, the solvent was evaporated. The residue was taken up in as little benzene as possible, and five to ten times the volume of absolute alcohol was added. The white crystalline peroxides precipitated out on standing, and were recrystallized by the same process.

TABLE III

TRI-$p$-ALKYLPHENYLMETHYL PEROXIDES

| Alkyl group | M. p., °C. | Analysis, % Calculated C | | Found C | H |
|---|---|---|---|---|---|
| | | C | H | C | H |
| $C_2H_5$ | 159–160 | 87.42 | 7.93 | 87.03 | 7.99 |
| $n$-$C_3H_7$ | 140–141 | 87.22 | 8.63 | 87.08 | 8.63 |
| $i$-$C_3H_7$ | 162–163 | 87.22 | 8.63 | 86.79 | 8.71 |
| $n$-$C_4H_9$ | 127–128 | 87.02 | 9.20 | 86.75 | 9.30 |
| $i$-$C_4H_9$ | 135–136 | 87.02 | 9.20 | 87.08 | 9.23 |
| $s$-$C_4H_9$ | 147–148 | 87.02 | 9.20 | 86.95 | 9.28 |

The melting points and analyses of the peroxides are given in Table III.

## Summary

A series of hexa-$p$-alkylphenylethanes in which the alkyl group was ethyl, $n$-propyl, isopropyl, $n$-butyl, isobutyl and $s$-butyl has been prepared. The color of equimolar solutions of these ethanes becomes deeper as the weight of the alkyl group is increased.

URBANA, ILLINOIS RECEIVED MAY 6, 1935

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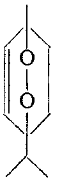
[CONTRIBUTION FROM THE LABORATORY OF DR. D. JAYNE AND SON, INC.]

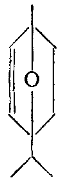
# Dehydrocineoles. I. The Preparation of 2-Isopropyl-5-methylfuran and its Condensation with Maleic Anhydride

BY LEWIS W. BUTZ

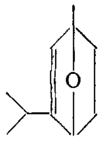
Compounds related to ascaridole (I) but lacking the peroxide group were desired. The dehydrocineoles (II-VII) are so related. Derivatives of these and of the related cineoles and menthadienes should be accessible through application of the reactions studied by Diels and Alder[1] to the isopropylmethylfurans.



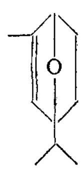
I



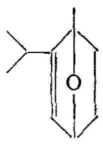
II



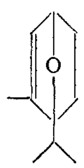
III



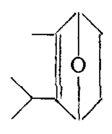
IV



V



VI



VII

None of the six possible isopropylmethylfurans has previously been prepared. 2-Isopropyl-5-methylfuran has now been obtained in 40% yield by the dehydration of 2-methylheptane-3,6-dione with sulfuric acid. This method seems not to have been employed previously with unsubstituted aliphatic 1,4-dicarbonyl compounds. Furan derivatives have been obtained by the action of concentrated sulfuric acid and other acid reagents on arylated, carbalkoxylated and other substituted 1,4-dicarbonyl compounds. Willstätter and Clarke[2] obtained a small quantity of tetramethylfuran from $\alpha,\beta$-diacetylbutyric ester by treatment with methyl iodide, sodium ethoxide and dilute sulfuric acid. Harries[3] obtained furan by heating succinaldehyde to 180°. Dietrich and Paal[4] made 2,5-dimethylfuran in 25% yield from acetonylacetone and zinc chloride.

The 2-isopropyl-5-methylfuran reported here is a colorless liquid with an odor somewhat similar to that of toluene. It has the following constants: b. p. (770 mm.) 135–137°; $d^{20}_4$ 0.8932; $n^{23}_D$ 1.4429. This furan gives a violet color in the pine shaving test as carried out by Reichstein,[5] and condenses with maleic anhydride to give a solid melting at 77°. Elementary analysis and titration with sodium hydroxide in water indicate the structure IX. The structure VIII is provisionally assigned to the furan although it cannot at present be stated with certainty that the product is free from isomers containing olefin linkages in

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[1] Diels and Alder, *Ber.*, **62**, 554 (1929); *Ann.*, **490**, 243 (1931).

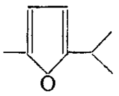
[2] Willstätter and Clarke, *Ber.*, **47**, 308 (1914).

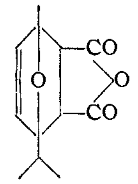
[3] Harries, *ibid.*, **34**, 1496 (1901).

[4] Dietrich and Paal, *ibid.*, **20**, 1085 (1887).

[5] Reichstein, *Helv. Chim. Acta*, **15**, 1112 (1932).

one or both side-chains. Kizhner[6] has been able to detect all of the three possible isomers of 2-methylfuran. With 2-isopropyl-5-methylfuran ten isomers are possible. In one or two runs a product was obtained with a higher boiling point and a higher refractive index than the furan described. The preparative procedure in those cases differed somewhat from that hereinafter described.


VIII


IX

## Experimental Part

**2-Methylheptane-2,3-diol-6-one.**—This glycol-ketone was prepared previously by Harries[7] by the oxidation of commercial methylheptenone with potassium permanganate. He did not, however, give working directions. A total of 550 g. of potassium permanganate was used to oxidize 330 g. of ketone. Fifty grams of the potassium permanganate in 2.5 liters of water was added to the ketone with constant stirring over a period of four hours, keeping the reaction mixture at 4° (not lower). After transferring to a crock cooled with ice–salt mixture, the remaining 500 g. of potassium permanganate in 12 liters was added during five hours. The temperature rose gradually from 3 to 11°, but stood at 6° most of the time. Thorough stirring during this second phase was very important since, without it, local over-oxidation occurred because of the relatively low density of the potassium permanganate solution. After standing for forty-eight hours the liquid portion was separated, the manganese dioxide mud washed with 10 liters of boiling water, and the water extract removed with suction. The combined filtrates were saturated with carbon dioxide and concentrated to about 2 liters at 30° under reduced pressure. Enough solid potassium carbonate was added with cooling and stirring (five minutes) to make a 50% solution, the crude glycol-ketone extracted with ether, and the ether removed after drying over anhydrous sodium sulfate. The yield of product of b. p. 132–142° at 11 mm. was 43% of the theoretical. The pure 2-methylheptane-2,3-diol-6-one boiled at 138.5° (11 mm.).

**2-Methylheptane-3,6-dione.**—The glycol-ketone (765 g.) was refluxed in two portions for six hours with 10 volumes of 5% sulfuric acid, the product washed with sodium bicarbonate solution, extracted with ether, dried over calcium chloride and distilled. Sixty grams of forerun and 200 g. of diketone, b. p. 90–92° at 11 mm., was obtained. The yield was 32%.

**2-Isopropyl-5-methylfuran.**—The diketone was heated at ordinary pressure for one-half hour in 0.2 mole portions (28.4 g.) with 0.6 cc. of concentrated sulfuric acid in a bath at 50°. The acid mixture was then heated with a small luminous free flame. Water distils first, after which the temperature of the vapor rises to 130–140°, within which range it is maintained throughout the distillation. Practically all the material taken distils if the temperature of the vapor is allowed to rise to 150° for the last 5 cc. One hour was required for the distillation. The product, which separates into two layers, was extracted with ether, dried over anhydrous sodium sulfate and distilled at 15–20 mm., the fraction boiling below 65° being taken. The average yield of 2-isopropyl-5-methylfuran b. p. 135–137° (770 mm.) for four such runs was 40%, and 14% of the diketone was recovered.

*Anal.* Calcd. for $C_8H_{12}O$: C, 77.4; H, 9.67. Found: C, 75.76, 76.08; H, 9.78, 9.86.

**2,3-Dehydro-1,4-cineole-5,6-dicarboxylic Acid (Anhydride).**—This adduct was prepared by the addition of 15.4 g. (0.125 mole) of 2-isopropyl-5-methylfuran to 9.8 g. (0.1 mole) of maleic anhydride partially dissolved in 60 cc. of dry ether. The materials were thoroughly cooled with ice–salt mixture before mixing. A brilliant yellow color appeared in the liquid when the reactants were mixed. This is also observed with 2,5-dimethylfuran but not with furan. The flask was set in the refrigerator (6–8°). All of the maleic anhydride had dissolved after one day. The solution remained one day more at 6–8° without any separation of crystalline adduct. The adduct from 2,5-dimethylfuran began to separate after six hours under precisely the same conditions. Removal of about one-third of the ether by suction, with the flask immersed in an ice–salt mixture, caused incipient separation of product after which the flask was replaced in the refrigerator for two days more. The solid which separated was washed with petroleum ether and then was recrystallized from a 1:1 mixture of ether and petroleum ether. It melted at 77°.

*Anal.* Calcd. for $C_{12}H_{14}O_4$: C, 64.8; H, 6.31. Found: C, 64.08, 64.32; H, 6.35, 6.43.

## Summary

1. The condensation of isopropylmethylfurans with compounds containing an activated multiple bond affords a general method for preparing derivatives of dehydrocineoles, cineoles and menthadienes. These comprise six series of isomers, one para, two meta and three ortho.

2. 2-Isopropyl-5-methylfuran has been prepared in 40% yield by heating 2-methylheptane-3,6-dione with sulfuric acid.

3. 2-Isopropyl-5-methylfuran and maleic anhydride formed an adduct which is probably *p*-2,3-dehydro-1,4-cineole-5,6-dicarboxylic anhydride.

PHILADELPHIA, PA.

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(6) Kizhner, *J. Gen. Chem.* (U. S. S. R.), **1**, 1212 (1931); *C. A.*, **26**, 5299 (1932).

(7) Harries, *Ber.*, **35**, 1181 (1902).