ture of the *n*-propyl group remaining unaltered. 6-Isopropyl-7-methyltetralin gave 6-methyltetralin, the isopropyl group being eliminated. 6-Isopropyl-7-ethyltetralin and 6,7-di-*n*-propyltetralin were largely decomposed to products obtained in small yields only, and which could not be identified.

2. The theoretical aspects of these results have been discussed with reference to the theory of Arnold and Barnes on the mechanism of the Jacobsen rearrangement.

3. Satisfactory laboratory methods for preparation of the two 6-propyltetralins, *n*- and *iso*-, have been developed, and it has been shown that the structure of the *n*-propyl group remains unaltered when *n*-propylbenzene undergoes a Friedel–Crafts reaction with succinic anhydride.

4. Seven new 6,7-dialkyltetralins have been synthesized, in which one or both of the alkyl groups is methyl, ethyl, *n*-propyl or isopropyl.

5. The corresponding 2,3-dialkylnaphthalenes (and their picrates) have been prepared by dehydrogenation of the 6,7-dialkyltetralins. Syntheses of 1-isopropyl-2-methylnaphthalene and of 1-methylnaphthalene have been developed.

6. Several new intermediate ketones (acyl tetralins) and carbinols have been synthesized and characterized.

MINNEAPOLIS 14, MINNESOTA

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

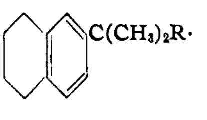
The Reaction between Tetralin and β,β-Dimethylacrylic Acid

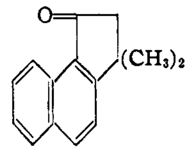
BY LEE IRVIN SMITH AND CHIEN-PEN LO[1]

The reaction between benzene or an alkylbenzene and β,β-dimethylacrylic acid in the presence of aluminum chloride leads to a β-aryl-isovaleric acid.[2] However, when a polyalkylbenzene is used in this reaction, one or more of the following abnormal transformations may occur: (a) the condensation may occur at a position other than the one involved when the acid chloride (ordinary Friedel–Crafts reaction) is used, as is the case with 1,2,3-trimethylbenzene[3]; (b) one of the alkyl groups may rearrange to another position on the benzene nucleus, as is the case with 1,2,4-trimethylbenzene[3]; (c) one of the alkyl groups may be eliminated during the reaction, as is the case with 1,3,5-trimethylbenzene.[4]

In order to explore the limits of this reaction, tetralin has been condensed with β,β-dimethylacrylic acid in the presence of aluminum chloride. Only one acid (70% yield) was isolated; this was identified as β-(6-tetralyl)-isovaleric acid, I, by comparison with a specimen synthesized by an independent method. Thus tetralin, unlike other polyalkylbenzenes, behaves normally in this condensation.

6-(Tetralyl)-dimethylcarbinol, II,[5] was converted by action of hydrochloric acid into the chloride III, which (without isolation) was used to alkylate diethyl malonate. The substituted malonic ester IV (also without isolation) was hydrolyzed to the malonic acid V, and V, on decarboxylation, gave the isovaleric acid I, identical with the product obtained from β,β-dimethylacrylic acid and tetralin.





VI

I, R = $-CH_2COOH$

II, R = OH

III, R = Cl

IV, R = $-CH(COOC_2H_5)_2$

V, R = $-CH(COOH)_2$

Cyclization of the acid I, by action of sulfuric acid, in view of the work of Cauquil and Barrera[6] on the closely related β-(6-tetralyl)-butyric acid, should lead to a mixture of two tetrahydrobenzhydrindones, linear and angular. However, cyclization of β-(2-naphthyl)-propionic acids generally leads to only one benzindanone, the angular.[7] The acid I was therefore converted into the methyl ester and the latter was smoothly dehydrogenated to methyl β-(2-naphthyl)-isovalerate by action of palladium–charcoal catalyst—a result substantiating the findings of Newman and Zahm[8] that a carbomethoxy group is not affected by the hydrogen evolved during dehydrogenation. The methyl ester was hydrolyzed to β-(2-naphthyl)-isovaleric acid, and the acid, subjected to the action of sulfuric acid was dehydrated to a single benzhydrindone assigned structure VI.

Experimental[9]

β-(6-Tetralyl)-isovaleric Acid (I).—To a stirred and cooled (−10°) solution of β,β-dimethylacrylic acid (7.5 g.) in tetralin (37.5 g.), powdered aluminum chloride (13.3 g.) was added (fifteen minutes) in small portions. The mixture was thereafter stirred at −10° for one hour, at room temperature for two hours, and poured into iced hydrochloric acid. The acid fraction of the product, a

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(1) Abstracted from a thesis by Chien-Pen Lo, presented to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the Ph.D. degree, September, 1947.

(2) (a) Eijkman, *Chem. Weekblad*, **5**, 655 (1908); (b) Hoffman, THIS JOURNAL, **51**, 2542 (1929).

(3) Smith and Prichard, THIS JOURNAL, **62**, 771 (1940).

(4) Smith and Spillane, *ibid.*, **65**, 202 (1943).

(5) Smith and Lo, *ibid.*, **70**, 2209 (1948).

(6) Cauquil and Barrera, *Compt. rend.*, **223**, 679 (1946).

(7) Johnson, "Org. Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 125.

(8) Newman and Zahm, THIS JOURNAL, **65**, 1097 (1943).

(9) Microanalyses by R. Amidon and S. Sundet.

yellow oil, was dissolved in dilute acetic acid and the solution was set aside in a refrigerator. The yellow solid, twice recrystallized from petroleum ether (b. p., 30–60°), weighed 9 g. (68%) and melted at 88°.

Anal. Calcd. for $C_{15}H_{20}O_2$: C, 77.81; H, 9.02. Found: C, 77.55; H, 8.68.

β-(6-Tetralyl)-β-methyl-α-carboxypropionic Acid (V).—A solution of 6-tetralyldimethylcarbinol[6] (II) (19 g.) in petroleum ether (20 cc., b. p., 40–75°) was saturated with dry hydrogen chloride at 0°, allowed to stand at room temperature for thirty minutes, then washed several times with water and dried over sodium sulfate. This solution of the crude chloro compound was added to an ethereal suspension of sodiomalonic ester (from ethyl malonate 16.5 g., sodium 2.3 g., ether 100 cc.) and the mixture was refluxed for several hours. Water was added carefully, and the organic layer was removed and washed successively with water, dilute hydrochloric acid, and water, and dried. The solvents were removed and the residual red oil was hydrolyzed by refluxing it for six hours with a solution of potassium hydroxide (22.5 g.) in methanol (70 cc.). The mixture was diluted with water and thoroughly extracted with ether. The aqueous layer was warmed to remove dissolved ether, and was acidified with dilute sulfuric acid. Some solid separated; the whole was extracted with ether and the ether solution was extracted with aqueous sodium carbonate (10%). Ether was removed from the aqueous extract, which was then acidified and set aside in a refrigerator. The product deposited as an oil which later solidified; after crystallization from ethanol, it weighed 4 g. and melted at 154–155° with effervescence.

Anal. Calcd. for $C_{16}H_{20}O_4$: C, 69.54; H, 7.30. Found: C, 69.66; H, 7.62.

β-(6-Tetralyl)-isovaleric Acid (I).—The above malonic acid (2 g.) was heated at 180° until effervescence ceased (about thirty minutes). The residue was recrystallized from petroleum ether (b. p. 30–60°), when it melted at 88–89°, alone or when mixed with I prepared from dimethylacrylic acid.

Methyl β-(6-Tetralyl)-isovalerate.—The acid I (7 g.) was refluxed in methanol (30 cc.) with sulfuric acid (1 cc.) for two hours. The methyl ester (5.2 g., 70%), isolated in the usual way, boiled at 161–164° (11 mm.) and had n^{20}_D 1.5250. *Anal.* Calcd. for $C_{16}H_{20}O_2$: C, 78.01; H, 9.00. Found: C, 78.02; H, 8.75.

Methyl β-(2-Naphthyl)-isovalerate.—The above ester (4 g.) was heated in a stream of carbon dioxide with palladium–charcoal catalyst (0.1 g.) at 220–260° for three hours and then at 300° for thirty minutes. The product was dissolved in ethanol, the solution was filtered from the catalyst, and solvent was removed, and the residue was distilled. The distillate (2.8 g., 71%) boiled at 174–177° (10 mm.), and had n^{20}_D 1.5700. *Anal.* Calcd. for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.03; H, 7.20.

β-(2-Naphthyl)-isovaleric Acid.—The above methyl ester (2.6 g.) was hydrolyzed by refluxing it with aqueous sodium hydroxide (20 cc., 20%) for one hour. The acid was obtained as a colorless solid (2.4 g., 98%) which, after crystallization from petroleum ether (b. p. 30–60°) melted at 86–87°. The mixed m. p. with I (m. p. 88°) was 79–81°. *Anal.* Calcd. for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.93; H, 7.36.

3,3-Dimethylbenz(e)indanone-1 (VI).—A solution of the above acid (1 g.) in sulfuric acid (8 cc.) was allowed to stand at room temperature for five hours. It was then poured over ice, the semi-solid precipitate was removed by ether extraction and crystallized twice from aqueous ethanol, when it melted at 65.5–67°.

Anal. Calcd. for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.04; H, 6.81.

Summary

1. The reaction between tetralin and β,β-dimethylacrylic acid in the presence of aluminum chloride has been shown to yield predominantly (70%) a single acid, identified as β-(6-tetralyl)-isovaleric acid by an independent synthesis. No other product was isolated.

2. This acid has been converted (3 steps) into β-(2-naphthyl)-isovaleric acid, and the latter has been cyclized to a benzhydrindone.

3. Tetralin, unlike other polyalkylbenzenes, behaves normally in this condensation.

MINNEAPOLIS 14, MINNESOTA

RECEIVED FEBRUARY 21, 1948

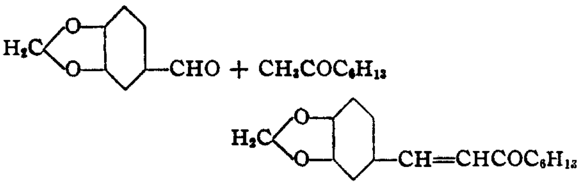
[A JOINT CONTRIBUTION FROM THE INSECTICIDE FELLOWSHIP, MELLON INSTITUTE, AND THE RESEARCH LABORATORY, DODGE & OLCOTT, INC.]

Methylenedioxyphenyl Cyclohexenones

BY OSCAR F. HEDENBURG AND HERMAN WACHS

In the search for new synthetic insecticidal materials which were to take the place of pyrethrins, 3-alkyl-5-(3,4-methylenedioxyphenyl)-2-cyclohexene-1-ones were prepared. These compounds are of very definite value where they are used as such, but they are of particular interest because of their ability to synergize the action of pyrethrins to an extraordinary degree.[1,2] They also share with pyrethrins the property of being practically nontoxic to warm-blooded animals.

The alkyl 3,4-methylenedioxystyryl ketones, precursors of the cyclohexenones, were prepared by the condensation of piperonal with methyl ketones in the presence of alkali. For example, methyl hexyl ketone gives hexyl 3,4-methylenedioxystyryl ketone I. This crystalline product is effective as an insecticide against flies, but is of little practical use because of its limited solubility in the usual vehicles, kerosene and Freon. Reduction of the ethylenic bond of I gave a liquid, soluble in kerosene and Freon but with little insecticidal activity.



I

The condensation of hexyl 3,4-methylenedioxy-

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[1] Hedenburg, pending patent applications.

[2] Wachs, *Science*, **105**, 530 (1947).