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

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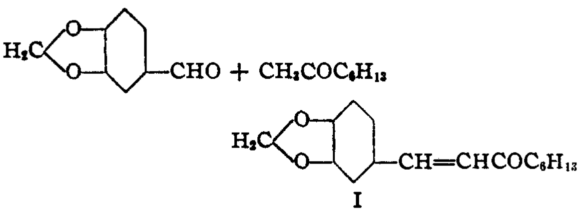
Methylenedioxyphenyl Cyclohexenones

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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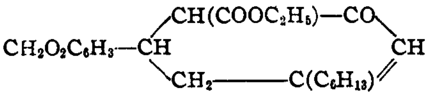
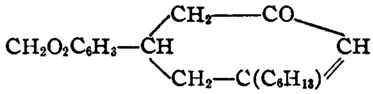
(1) Hedenburg, pending patent applications.

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

styryl ketone with ethyl acetoacetate[3,4] gave a 50% yield of crystalline 3-hexyl-5-(3,4-methylenedioxyphenyl)-2-cyclohexen-1-one (III). Saponification of the mother liquor gave more of the cyclohexenone, presumably formed from the initial cyclized addition product II. Saponification equivalents of the crude reaction product indicated approximately 30% of II. The crude reaction mixture is being used for insecticidal purposes, under the name of "Piperonyl Cyclonene."



II



III

The condensation of ethyl acetoacetate with the isobutyl styryl ketone gave approximately the same proportion of ketone and ester but only 15% of the ketone could be obtained in crystalline form. The amyl compound failed to give any solid product.

Catalytic hydrogenation of III gave the cyclohexanone, which was ineffective as an insecticide. It is therefore apparent, at least in this series of substances, that the conjugated system, =CH—CO—, is essential for insecticidal activity.

Experimental

Hexyl 3,4-Methylenedioxystyryl Ketone, I.—To a stirred mixture of 38.4 g. (0.3 mole) of methyl hexyl ketone, 48 g. of methanol and 7.5 g. of 20% sodium hydroxide was added 45 g. (0.3 mole) of piperonal over a period of thirty minutes, keeping the temperature between 20 and 25°. Stirring was continued until crystallization began and the mixture was then allowed to stand overnight. The usual manipulations gave 68 g. of solid product which can be either recrystallized from methanol or distilled *in vacuo*. The ketone boils from 175–185° at 1 mm. and gives light yellow crystals melting at 61°.

Anal. Calcd. for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74; CO, 10.73. Found: C, 73.61; H, 7.63; CO, 10.84.

Amyl 3,4-Methylenedioxystyryl Ketone.—The amyl ketone, prepared by the above method, boils from 171–181° at 1.3 mm. and melts at 73°.

Anal. Calcd. for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37; CO, 11.37. Found: C, 73.41; H, 7.48; CO, 11.34.

Isobutyl 3,4-Methylenedioxystyryl Ketone.—The isobutyl ketone boils from 166–173° at 2 mm. and melts at 66.5°.

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94; CO, 12.05. Found: C, 72.51; H, 7.14; CO, 11.88.

Piperonylmethyl Hexyl Ketone.—An alcohol solution of I was hydrogenated at room temperature and under 20 lb. pressure, using palladium-charcoal catalyst, until one mole of hydrogen was absorbed. The liquid product boils at 204° at 4.5 mm., has a specific gravity of 1.0539 at 25° and a refractive index of 1.5109 at 20°.

Anal. Calcd. for $C_{16}H_{22}O_3$: C, 73.25; H, 8.46; CO, 10.69. Found: C, 73.39; H, 8.23; CO, 10.31.

3-Hexyl-5-(3,4-Methylenedioxyphenyl)-2-cyclohexen-1-one, III.—To a stirred solution of 24.1 g. of sodium in 600 cc. of absolute alcohol was added 260 g. of I and then, over a period of fifteen minutes, 143 g. of ethyl acetoacetate. During the addition the bath temperature was 21.5° while the temperature of the solution rose to 24°. Stirring was continued for one hour while the bath temperature was raised to 33°. One hundred cc. of benzene was then added to dissolve the remaining solid, after which the solution was allowed to stand in the bath overnight.

The solution was poured into 100 g. of concentrated hydrochloric acid in 1200 cc. of water, 350 cc. of benzene was added, the mixture was thoroughly agitated, the bottom layer separated and extracted with 50 cc. of benzene. The combined benzene solution was washed with salt water, neutralized with sodium bicarbonate, shaken with Celite, filtered, and the benzene was finally removed *in vacuo*. The product, weighing 320 g., was a thick, reddish oil of specific gravity 1.136 at 25° and with a saponification value of 60. After standing for five weeks, the solid which had crystallized from the oil was isolated by centrifugation. About 160 g. of white crystals was obtained melting at 59° after recrystallization from alcohol.

Anal. Calcd. for $C_{19}H_{24}O_3$: C, 75.8; H, 8.0. Found: C, 75.9; H, 8.1.

Saponification of the above mother liquor with 0.5 *N* potassium hydroxide gave more of the cyclohexenone, identified by mixed melting point.

3-Hexyl-5-(3,4-methylenedioxyphenyl)-cyclohexanone.—An alcohol solution of the cyclohexenone readily absorbed one mole of hydrogen at room temperature and atmospheric pressure, using palladium-charcoal catalyst. The cyclohexanone is a liquid which could not be crystallized at −20°. It has a specific gravity of 1.0754 at 25° and a refractive index of 1.528 at 20°.

Anal. Calcd. for $C_{19}H_{26}O_3$: C, 75.46; H, 8.66; CO, 9.26. Found: C, 75.21; H, 8.69; CO, 9.15.

3-Isobutyl-5-(3,4-methylenedioxyphenyl)-2-cyclohexen-1-one.—Prepared by the procedure used for the hexyl compound, there was obtained a pale orange product, which melted at 70.5° after recrystallization from alcohol.

Anal. Calcd. for $C_{17}H_{20}O_3$: C, 74.9; H, 7.4; CO, 10.28. Found: C, 74.9; H, 7.2; CO, 10.35.

The oxime of the isobutyl cyclohexenone melts at 106.5°.

Anal. Calcd. for $C_{17}H_{21}O_3N$: C, 71.08; H, 7.37; N, 4.87. Found: C, 69.84; H, 7.29; N, 4.80.

Summary

Alkyl 3,4-methylenedioxystyryl ketones, as well as their condensation products with ethyl acetoacetate, were prepared and found to be useful as non-toxic insecticides and as synergists for pyrethrins.

Hydrogenation of the methylenedioxystyryl ketones and of the cyclohexenones destroys the insecticidal activity.

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(3) Michael, *J. prakt. Chem.*, **35**, 351 (1887).

(4) Knoevenagel, *Ber.*, **37**, 4464 (1904).