The mixture was warmed slightly to partially dissolve the mercuric oxide. The flask was equipped with a mercury-sealed stirrer, a dropping funnel, and a reflux condenser. One-half mole (47.3 g.) of chloroacetic acid was added to the catalyst, the stirrer started, and 55 g. (excess) of butylacetylene added dropwise through the dropping funnel. The chloroacetic acid soon liquefied and an ice-bath was placed around the flask. The addition of butylacetylene required about one-half hour. Stirring was continued for another half hour at room temperature. After stirring, the flask was removed, 60 ml. of ether added and the mixture washed three times with 50-ml. portions of ice water and then with 50-ml. portions of cold 10% sodium carbonate solution until all unreacted acid had been removed. The ether extract was dried over calcium chloride, the ether removed by distillation, and the residue fractionated *in vacuo* at 20 mm. through a 30-cm. Vigreux style column. The yield of 2-(chloroacetoxy)-hexene-1 amounted to 60 g.

Action of Butylacetylene on Benzoic Acid.—The catalyst was prepared as described above, 61 g. (0.5 mole) of solid benzoic acid added, the stirrer started, and 82 g. (double the theoretical quantity) of butylacetylene added dropwise. The benzoic acid did not liquefy readily; consequently, after about one-fourth of the acetylene had been added, the flask was heated over a burner. The reaction then proceeded very vigorously. The remaining acetylene was added in a rapid stream of drops, heating at reflux temperature being maintained for one hour. Upon cooling the flask contents remained completely liquid. The ester was isolated as described above; yield, 45 g.

Proof of Structure of Alkenyl Esters.—The fact that the acyloxy attachments occur at the second carbon atom of the alkylacetylenes was shown by saponification[1] with alcoholic potash. The ketones formed, with the exception of acetone, were identified by their physical properties and by the melting points of their semicarbazones. Acetone, obtained from 2-acetoxypropene-1, was identified by the iodoform reaction and by the nitroprusside test.

Properties of Alkenyl Esters.—With the exception of 2-acetoxypropene-1, the esters described possess a characteristic, not unpleasant, odor. Acetoxypropene has a rather sharp odor. All of these esters were found to be quite stable. Some of these have been kept for over a year without any indication of polymerization. Apparently the alkyl group in the α position of the vinyl group exerts a marked stabilizing effect.

Summary

1. Monobasic organic acids react with monoalkyl acetylenes by direct addition, the main reaction being mole for mole addition. The acyloxy group attaches itself to the second (non-terminal) acetylenic carbon atom.

2. Five such addition compounds (alkenyl esters) are described, these being prepared from acetic, chloroacetic and benzoic acids with methyl-, butyl- and amylacetylenes.

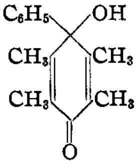
NOTRE DAME, INDIANA RECEIVED JUNE 4, 1934

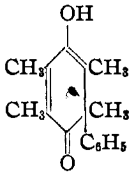
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, VASSAR COLLEGE]

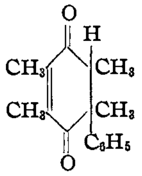
Isomeric Forms of 2,3,5,6-Tetramethyl-3-phenylcyclohexene-5-dione-1,4

BY H. MARJORIE CRAWFORD

In an earlier paper[1] on the reaction between duroquinone and phenylmagnesium bromide, three compounds ($C_{16}H_{18}O_2$) resulting from the addition of one mole of phenylmagnesium bromide to one mole of duroquinone were described. They were assigned the following structures


203°

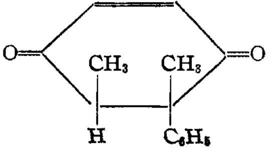

150°

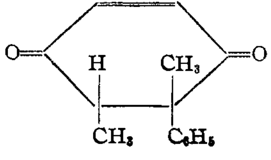

142°

Mention was also made of a pale yellow compound, melting at 62°, which was obtained when attempts were made to form the semicarbazone of the 142° compound. This low-melting substance was obtained in very small amounts, and aside from carbon and hydrogen analyses, very little was known about it.

In the present investigation, working with larger amounts of material, it is shown that the melting point is somewhat higher (72° instead of 62°), and that this low-melting compound and the one melting at 142° have the same molecular formula.

When this 72° compound was first encountered, we suggested that it is a geometric isomer of the 142° substance (2,3,5,6-tetramethyl-3-phenylcyclohexene-5-dione-1,4), which is the only one of the three monoaddition products capable of existing in two geometric forms





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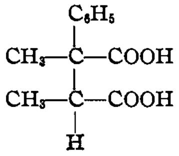
[1] Smith and Crawford, THIS JOURNAL, **50**, 869 (1928).

The 142° compound, on oxidation, gave an acid ($C_{12}H_{14}O_4$) which has since been synthesized[2] and proved to be α,α'-dimethyl-α-phenylsuccinic acid,



$$\begin{array}{l} \quad\ \ C_6H_5 \\ \quad\ \ | \\ CH_3—C—COOH \\ \quad\ \ | \\ CH_3—C—COOH \\ \quad\ \ | \\ \quad\ \ H \end{array}$$

This synthesis of a compound with two dissimilar asymmetric carbon atoms resulted in a low-melting (159–160°) and a high-melting (170–172°) racemic form of the acid. The high-melting form proved to be identical with the acid obtained by the oxidation of the 142° compound. If the 72° compound is a geometric isomer of the 142° compound, on oxidation it should yield the low-melting form of α,α'-dimethyl-α-phenylsuccinic acid. The 72° compound, which can be obtained in 60–70% yields by boiling an alcoholic solution of the 142° compound with sodium acetate, has been oxidized and gives an acid identical with the low-melting form of α,α'-dimethyl-α-phenylsuccinic acid.

Experimental

2,3,5,6-Tetramethyl-3-phenylcyclohexene-5-dione-1,4

High-Melting Form, 142°.—This compound is the main solid product resulting from the addition of phenylmagnesium bromide to duroquinone.[1] The yield was 16–20%, based on duroquinone reacting.

Low-Melting Form, 72°.—Ten grams of the 142° compound, 6 g. of fused sodium acetate and 150 cc. of 95% alcohol were heated for twenty hours under a reflux condenser. The alcohol was then allowed to evaporate, the sodium acetate dissolved in water, and the remaining solid recrystallized from alcohol. It is more soluble than the 142° compound; yield, 60–70%; m. p. 72–73°.

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.3; H, 7.5; mol. wt., 242.1. Found: C, 79.2, 79.9, 78.6; H, 7.5, 7.6, 7.3; mol. wt., 249, 246.

Oxidation.—To five grams of the 72° compound dissolved in 150 cc. of acetone, 7.5 g. of potassium permanganate was added slowly. The mixture was kept between 4–6°, and was shaken almost constantly. The dark brown solution was then allowed to warm up to 20°, when a heavy precipitate of manganese dioxide appeared. After filtering, the precipitate was decomposed with ice, sulfuric acid and sodium bisulfite. The ether extract of this solution was added to the acetone filtrate, and the organic acid extracted from the acetone–ether mixture by means of sodium carbonate solution. Acidifying the sodium carbonate solution and extracting with ether gave 0.7 g. of solid which, after several recrystallizations from 25% alcohol, melted at 158–160°. The synthetic acid[2] melted at 159–160° and a mixture of the two melted at 158–159.5°.

Anal. Calcd. for $C_{12}H_{14}O_4$ (222.1): C, 64.8; H, 6.35. Found: C, 64.2, 64.0; H, 6.4, 6.4. *Eq. wt.* Subs., 0.1115; NaOH (0.1030 *N*) 9.52 cc. = 0.0392 g. NaOH. Eq. wt., 113.7.

Summary

The low-melting form of α,α'-dimethyl-α-phenylsuccinic acid has been obtained by oxidizing the low-melting geometric isomer of 2,3,5,6-tetramethyl-3-phenylcyclohexene-5-dione-1,4.

POUGHKEEPSIE, N. Y. RECEIVED JUNE 8, 1934

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[2] H. M. Crawford, THIS JOURNAL, **56**, 139 (1934).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Structure of *d*-Glucoheptulose Hexaacetate

BY M. L. WOLFROM AND ALVA THOMPSON

A ketose of α-glucoheptose was synthesized by Bertrand and Nitzberg[1] through the action of the sorbose bacterium on α-glucoheptitol and was named α-glucoheptulose by these workers. Austin[2] prepared the enantiomorph of the above by the action of dilute alkali on *d*-α-glucoheptose and thus allocated his ketose to the *d*-series, a point which the Bertrand synthesis did not decide. This sugar is one of the ketoses that does not exhibit mutarotation.

Austin[3] obtained a strongly dextrorotatory hexaacetate ($[\alpha]_D + 87°$, $CHCl_3$) by the acetylation of this substance with sodium acetate and hot acetic anhydride and named the product α-*d*-glucoheptulose hexaacetate. To our knowledge, this is the only instance recorded in the sugar series where a dextrorotatory acetate was obtained by sodium acetate acetylation. The assignment of an α-ring structure to this acetate was based only upon the dextrorotation exhibited by the substance. The dextrorotatory pentaacetate of *d*-fructose has recently been shown to be an open chain or *keto*-fructose pentaacetate.[4] We have

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[1] G. Bertrand and G. Nitzberg, *Compt. rend.*, **186**, 925, 1172, 1774 (1928).

[2] W. C. Austin, THIS JOURNAL, **52**, 2106 (1930).

[3] W. C. Austin, *ibid.*, **54**, 1925 (1932).

[4] (a) E. Pacsu and F. V. Rich, *ibid.*, **54**, 1697 (1932); **55**, 3018 (1933); (b) M. L. Wolfrom and A. Thompson, *ibid.*, **56**, 880 (1934).