yellow. Both bands migrate down the column and eventually into the receiver. The first 200–300 ml. of the solution coming through the bottom of the column is clear and contains very little of the carbohydrazide. The next 400 ml. is yellowish-orange having a *p*H of 4–7 and contains the sodium salt of 1,5-bis-(1-phenyl-4-sulfonic acid) carbohydrazide. Finally, a red solution which contains small amounts of the alkaline form of the carbohydrazide and excess sodium hydroxide comes through the column. This red solution may be discarded. The 400 ml. of yellowish-orange solution is concentrated under reduced pressure at 40–50° with nitrogen being slowly bubbled through to minimize oxidation. The product is precipitated with 95% ethanol, filtered, redissolved in a small volume of water, reprecipitated with alcohol, vacuum dried at room temperature and stored in a desiccator over a solution of calcium chloride at 30% relative humidity. A sample was dried to constant weight at 105–110° and analyzed for sodium by the uranyl zinc acetate method.

Anal. Calcd. for $(NaSO_3 \cdot C_6H_4 \cdot NH \cdot NH)_2C{=}O$: Na, 10.33. Found: Na, 10.13. Loss in weight at 105–110°, 10.86%; loss corresponding to 3 moles of water.

1,5-Bis-(phenyl-4-sulfonic acid) carbohydrazide was also isolated as the barium salt by using 0.13 *M* barium hydroxide for eluting the sulfonic acid from the column. Analysis of this product for barium by the gravimetric barium sulfate method and for water of hydration by drying to constant weight gave results as follows.

Anal. Calcd. for $Ba(SO_3 \cdot C_6H_4 \cdot NH \cdot NH)_2C{=}O$: Ba, 25.54. Found: Ba, 25.47, 25.43. The loss in weight at 105–110° was 8.73%, corresponding to 2.9 moles of water for the above formula.

Yields of the purified material were 10–20% but no attempt was made to establish the maximum yield.

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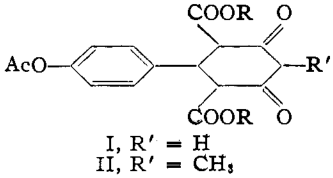
Synthesis of 1-(*p*-Acetoxyphenyl)-2,6-dicarbethoxy-4-methylcyclohexanedione-3,5. III

BY PHILIPPOS E. PAPADAKIS AND JOSEPH SCIGLIANO

In a previous communication[1] the synthesis of 1-(*p*-acetoxyphenyl)-2,6-dicarbethoxycyclohexanedione-3,5 (I) was reported. The object of the work presented here was the synthesis of a monomethyl derivative at carbon-4 of the cyclohexanedione ring (II). Since the direct methylation of I may result in isomeric monomethyl derivatives the following method was adopted which is assumed to give the desired product.

The sequence of the syntheses involved in this work is: *p*-acetoxybenzaldehyde → ethyl 4-acetoxybenzalmalonate → 1(*p*-acetoxyphenyl)-2,6-dicarbethoxy-4-methylcyclohexanedione-3,5 (II). The synthesis of II was accomplished by condensing and cyclizing the sodio derivative of ethyl β-oxopentanoate with ethyl 4-acetoxybenzalmalonate. Substance (II) will serve not only as reference compound in experiments involving direct methylation of (I) but also as an intermediate in the further synthesis of substances related to steroids and other physiologically important compounds.



I, R′ = H
II, R′ = CH_3

Experimental

Reagents.—Ethyl β-oxopentanoate[2] was prepared by Grignard reaction of ethylmagnesium iodide on ethyl cyanoacetate. Ethyl 4-acetoxy-benzalmalonate[3] was prepared from *p*-acetoxybenzaldehyde and diethyl malonate using diethylamine as condensing agent.

1-(*p*-Acetoxyphenyl)-2,6-dicarbethoxy-4-methylcyclohexanedione-3,5 (II).—Ethyl 4-acetoxybenzalmalonate (5.88 g.) was treated with a mixture of equivalent quantities of ethyl β-oxopentanoate (2.8 g.) and CH_3ONa in absolute methyl alcohol. The mixture was refluxed on a water-bath for five hours, the alcohol evaporated and the residue dried for two hours under vacuum (oil-bath temperature 130°).

Upon cooling the solution was acidified with cold 3 *N* HCl, and then 5 cc. in excess. The precipitate was filtered off, washed several times with distilled water and dried in a vacuum desiccator. The dry crystals were washed with ether several times, m.p. 157°. When the crystals are dissolved with absolute ethyl alcohol, the solution gives a yellow ferric chloride test. (The material which dissolved in ether gives a red purple color with $FeCl_3$.)

Anal. Calcd. for $C_{21}H_{24}O_8$: C, 62.37; H, 5.98. Found: C, 62.80; H, 6.19.

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[1] Papadakis, THIS JOURNAL, **67**, 1799 (1945).

[2] Blaise, *Compt. rend.*, **132**, 970 (1901).

[3] Knoevenagel and Albert, *Ber.*, **37**, 4481 (1904).

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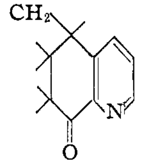
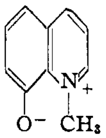
The Reaction of Diazomethane with 8-Quinolinols

BY J. P. PHILLIPS AND ROBERT W. KEOWN

The action of diazomethane on 8-quinolinol gives, in addition to 8-methoxyquinoline, a red, ether-insoluble solid originally thought to have structure I.[1] Apparently without further experimentation Schenkel-Rudin[2] pointed out that structure II, corresponding to nitrogen methylation of 8-quinolinol, was more in accord with the polar properties of the compound. (For convenience this compound will be called diazoxine hereafter.) The following new experimental facts support the Schenkel-Rudin structure.



I



II

5,7-Dibromo-8-quinolinol reacts with diazomethane to give a product showing a similar absorption spectrum (with a bathochromic shift due to the weighting effect of bromine) to that of diazoxine (Fig. 1). Diazoxine is quantitatively dibrominated to give a substance spectrophotometrically identical to the diazomethane-5,7-dibromo-8-quinolinol product.

Determination of the absorption spectrum of diazoxine in solutions of *p*H 1–13 shows only two different structures, a nearly colorless hydrochloride (which was isolated and analyzed) having absorption maxima at 313, 323 and 365 mμ, and an orange

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[1] Caronna and Sansone, *Gazz. chim. ital.*, **69**, 24 (1939).

[2] Schenkel-Rudin, *Helv. Chim. Acta*, **27**, 1456 (1944).