379. *The Reactivity of Unsymmetrical Distyryl Ketones.*

By W. P. Jennings and A. McGookin.

The work of Heilbron and his collaborators (J., 1924, **125**, 2067; 1925, **127**, 2163; 1927, 921; 1928, 2868) has been extended to the condensation of ethyl acetoacetate with *4′-hydroxy-3-chloro-*, *4′-hydroxy-4-chloro-*, *3-chloro-4′-methoxy-*, and *4-chloro-4′-methoxy-distyryl ketones*. The addition occurs in each case at the double bond adjacent to the first substituent mentioned.

The results of addition in this series are so inconsistent that the use of ethyl acetoacetate had to be abandoned. The anomalies are probably due to the highly active nature of the reactants. Moreover the yields of addition products are not quantitative, so that the whole course of the reaction cannot be ascertained. It is hoped that the use of some more simple addition reagent, *e.g.*, hydrogen, may be more successful.

Although certain methoxydistyryl ketones were prepared normally by condensation, it was not possible to produce 2- and 3-methoxy-, 2 : 3′- and 2 : 4′-dimethoxy-distyryl ketones by this means. Methylation of the corresponding hydroxy-compounds was not employed, since the results of the investigation did not justify further experiments.

Ethyl 3-p-*methoxyphenyl*-5-m-*chlorostyryl*-Δ^5-cyclo*hexen*-1-*one*-2-*carboxylate*, formed by the methylation of the corresponding hydroxy-compound, was shown to be isomeric with *ethyl* 3-m-*chlorophenyl*-5-p-*methoxystyryl*-Δ^5-cyclo*hexen*-1-*one*-2-*carboxylate*, formed by condensing 3-chloro-4′-methoxydistyryl ketone with ethyl acetoacetate, both by a depression in the mixed melting point and by the production of *m*-chloro- and *p*-methoxy-benzoic acids respectively on oxidation.

EXPERIMENTAL.

4-*Methoxydistyryl Ketone.*—The following modification of Baeyer and Villiger's method (*Ber.*, 1902, **35**, 3022) was used. A solution of styryl methyl ketone (11 g.) and anisaldehyde (10·25 g.) in alcohol (200 c.c. of 50%) was treated with sodium hydroxide (20 c.c. of 8%). The yellow oil crystallised in a few hours. Pale yellow needles (15 g.) from acetone, m. p. 96°.

4′-*Hydroxy*-2-*methoxydistyryl Ketone.*—4-Hydroxystyryl methyl ketone (2 g.) was condensed with 2-methoxybenzaldehyde in alkaline solution. After standing, the precipitate formed on acidification was crystallised from ethyl acetate, giving yellow prisms (1·5 g.), m. p. 137° (Found : C, 76·8; H, 5·7. $C_{18}H_{16}O_3$ requires C, 77·1; H, 5·7%).

3 : 4′-*Dimethoxydistyryl Ketone.*—4-Methoxystyryl methyl ketone (16·1 g.) was condensed by means of hydrogen chloride with 3-methoxybenzaldehyde. After 3 days the red crystals were treated with alkali and the resulting solid was purified from acetone, forming pale yellow needles (10·5 g.), m. p. 77—78° (Found : C, 77·6; H, 6·3. $C_{19}H_{18}O_3$ requires C, 77·6; H, 6·1%). The condensation product of this compound and ethyl acetoacetate was an oil.

3-*Chloro*-4′-*hydroxydistyryl Ketone.*—4-Hydroxystyryl methyl ketone (10 g.) and 3-chlorobenzaldehyde were condensed by means of alkali. After 1 day the diluted and acidified solution gave an oil, which finally solidified and separated from acetic acid in yellow prisms (9·3 g.), m. p. 167° (Found : C, 71·55; H, 4·55. $C_{17}H_{13}O_2Cl$ requires C, 71·7; H, 4·6%).

4-*Chloro*-4′-*hydroxydistyryl Ketone.*—4-Hydroxystyryl methyl ketone (10 g.) and 4-chlorobenzaldehyde were condensed in alkaline solution. After 16 hours the diluted solution was acidified; the precipitate crystallised from acetic acid as yellow prisms (10·5 g.), m. p. 200—201° (Found : C, 71·8; H, 4·5%). During this reaction a small quantity of a yellow solid, m. p. 235°, was obtained which was identified as 4 : 4′-dihydroxydistyryl ketone formed from the products of alkali fission of 4-hydroxystyryl methyl ketone (compare McGookin and Heilbron, J., 1924, **125**, 2101).

3-*Chloro*-4′-*methoxydistyryl Ketone.*—3-Chloro-4′-hydroxydistyryl ketone (5 g.) was methylated with methyl sulphate. The product crystallised from acetone in yellow needles (5 g.), m. p. 115·5° (Found : C, 72·5; H, 5·1. $C_{18}H_{15}O_2Cl$ requires C, 72·4; H, 5·0%).

4-*Chloro*-4′-*methoxydistyryl ketone*, prepared as above, formed faintly yellow needles from acetone, m. p. 157—157·5° (Found : C, 72·5; H, 5·1%).

Ethyl 3-p-*Hydroxyphenyl*-5-m-*chlorostyryl*-Δ⁵-cyclo*hexen*-1-*one*-2-*carboxylate.*—3-Chloro-4′-hydroxydistyryl ketone (5 g.) was condensed with ethyl acetoacetate. After 2 days, water (1 l.) was added, the solution acidified with dilute hydrochloric acid, and the precipitate crystallised from acetic acid, forming yellow prisms (4·1 g.), m. p. 202° (Found : C, 69·3; H, 5·4. $C_{23}H_{21}O_4Cl$ requires C, 69·6; H, 5·3%). Oxidation of this product with permanganate in acetone solution yielded *m*-chlorobenzoic acid, mixed m. p. 154°.

Ethyl 3-p-*Methoxyphenyl*-5-m-*chlorostyryl*-Δ⁵-cyclo*hexen*-1-*one*-2-*carboxylate.*—The above *cyclo*hexenone was methylated with methyl sulphate. The *methyl* ether crystallised from ether in yellow prisms, m. p. 121° (Found : C, 69·9; H, 5·5. $C_{24}H_{23}O_4Cl$ requires C, 70·2; H, 5·6%). Oxidation gave *m*-chlorobenzoic acid, mixed m. p. 153°.

Ethyl 3-p-*Hydroxyphenyl*-5-p-*chlorostyryl*-Δ⁵-cyclo*hexen*-1-*one*-2-*carboxylate.*—4-Chloro-4′-hydroxydistyryl ketone (5 g.) was condensed with ethyl acetoacetate. The product consisted of yellow needles (4·5 g.), m. p. 200° (Found : C, 69·55; H, 5·3. $C_{23}H_{21}O_4Cl$ requires C, 69·6; H, 5·3%). Oxidation yielded *p*-chlorobenzoic acid, mixed m. p. 236°.

Ethyl 3-m-*Chlorophenyl*-5-p-*methoxystyryl*-Δ⁵-cyclo*hexen*-1-*one*-2-*carboxylate.*—3-Chloro-4′-methoxydistyryl ketone (5 g.) was condensed with ethyl acetoacetate. The diluted solution was ether-extracted. After drying, the ethereal solution deposited yellow crystals (3·6 g.), m. p. 123° (Found : C, 70·3; H, 5·6. $C_{24}H_{23}O_4Cl$ requires C, 70·2; H, 5·6%). Oxidation produced anisic acid, mixed m. p. 187°. This *cyclo*hexenone and its isomeride, ethyl 3-*p*-methoxyphenyl-5-*m*-chlorostyryl-Δ⁵-*cyclo*hexen-1-one-2-carboxylate, gave a mixed m. p. of 108—115°.

Ethyl 3-p-*chlorophenyl*-5-p-*methoxystyryl*-Δ⁵-cyclo*hexen*-1-*one*-2-*carboxylate* was prepared as above. The ethereal extract was washed with dilute sulphuric acid, then with water, dried, and evaporated; yellow crystals (3 g.) separated, m. p. 128° (Found : C, 70·0; H, 5·8. $C_{24}H_{23}O_4Cl$ requires C, 70·2; H, 5·6%). Oxidation yielded anisic acid, mixed m. p. 186·5°.

THE UNIVERSITY, LIVERPOOL.

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