213. *Chalkones: Reactivity of Phenyl* p-*Benzyloxystyryl Ketones.*

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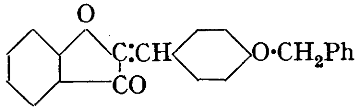
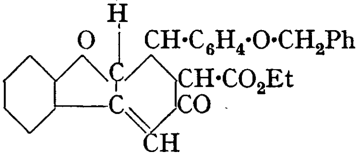
Phenyl *p*-benzyloxystyryl ketones react in the same manner as the corresponding *p*-alkoxystyryl derivatives; in particular one of the halogen atoms in the benzyloxychalkone dihalides reacts readily with alcohols. The keto-ethylene group in benzylidenecoumaranones reacts with ethyl acetoacetate similarly to the same group in chalkones.

Phenyl *p*-benzyloxystyryl ketones react in the same manner as the *p*-alkoxystyryl analogues; in particular the halogen atom in the dihalides adjacent to the nucleus containing the *p*-benzyloxy-group is rendered labile towards alcohols (cf. Nadkarni *et al.*, J., 1937, 1798) and towards aqueous acetone (cf. Werner, *Ber.*, 1906, **39**, 36). o-*Hydroxyphenyl α-bromo-β-methoxy-β-*p-*benzyloxyphenylethyl ketone*, obtained by the action of methyl alcohol on the corresponding *dibromide*, gives *4′-benzyloxyflavone* with alcoholic potassium cyanide (cf. Hutchins and Wheeler, this vol., p. 91) and 1-p-*benzyloxybenzylidenecoumaran-2-one* (I)

(I.)





(II.)

with alcoholic alkali (Nadkarni *et al.*, *loc. cit.*). The keto-ethylene group in (I) reacts with ethyl acetoacetate like the same group in a chalkone to give a *substance* which has probably formula (II) (cf. Panse and Wheeler, *Current Science*, 1938, **7**, 181). This formula is based on the course of the well-known Knoevenagel condensation of chalkones with ethyl acetoacetate (*Annalen*, 1894, **281**, 58).

Experimental.

Chalkones.—p-*Tolyl* p-*benzyloxystyryl ketone*, m. p. (alcohol) 111° (Found: C, 84·1; H, 6·1. $C_{23}H_{20}O_2$ requires C, 84·1; H, 6·1%), and o-*hydroxyphenyl* p-*benzyloxystyryl ketone* (1), m. p. (acetone–alcohol) 115° (Found: C, 80·3; H, 5·7. $C_{22}H_{18}O_3$ requires C, 80·0; H, 5·5%), were prepared by condensation of *p*-benzyloxybenzaldehyde with the corresponding acetophenones in presence of aqueous-alcoholic alkali (Sorge, *Ber.*, 1902, **35**, 1069). o-*Acetoxyphenyl* p-*benzyloxystyryl ketone*, m. p. (alcohol) 105—107° (Found: C, 77·3; H, 5·7. $C_{24}H_{20}O_4$ requires C, 77·4; H, 5·4%), was prepared from (1) by means of acetic anhydride and sodium acetate. These chalkones are yellow.

Halogenation of the Chalkones.—The following dihalides were obtained by treating the corresponding chalkones with the halides (1 mol.) in acetic acid or chloroform: p-*tolyl αβ-dichloro-β-*p-*benzyloxyphenylethyl ketone* (2), m. p. (benzene) 174° (Found: Cl, 17·6. $C_{23}H_{20}O_2Cl_2$ requires Cl, 17·8%); p-*tolyl αβ-dibromo-β-*p-*benzyloxyphenylethyl ketone* (3), m. p. (benzene) 160° (Found: C, 57·0; H, 4·4; Br, 33·5. $C_{23}H_{20}O_2Br_2$ requires C, 56·6; H, 4·1; Br, 32·8%); o-*hydroxyphenyl αβ-dibromo-β-*p-*benzyloxyphenylethyl ketone* (4), m. p. (chloroform) 153° (Found: Br, 32·6. $C_{22}H_{18}O_3Br_2$ requires Br, 32·7%); and o-*acetoxyphenyl αβ-dibromo-β-*p-*benzyloxyphenylethyl ketone* (5), m. p. (benzene–light petroleum) 114° (Found: Br, 30·5. $C_{24}H_{20}O_4Br_2$ requires Br, 30·1%).

Action of Alcohol on the Halides.—p-*Tolyl α-chloro-β-ethoxy-β-*p-*benzyloxyphenylethyl ketone*, m. p. (acetic acid) 140° (Found: Cl, 9·0. $C_{25}H_{25}O_3Cl$ requires Cl, 8·7%), separated on removal of the solvent from a solution of (2) in alcohol, to which benzene had been added to promote solution, and which had been heated under reflux for 2 hours. p-*Tolyl α-chloro-β-methoxy-β-*p-*benzyloxyphenylethyl ketone*, m. p. (acetic acid) 119° (Found: Cl, 9·1. $C_{24}H_{23}O_3Cl$ requires Cl, 9·0%), was similarly prepared. p-*Tolyl α-bromo-β-methoxy-β-*p-*benzyloxyphenylethyl ketone*, m. p. (methyl alcohol) 125° (Found: C, 65·4; H, 5·3; Br, 18·3. $C_{24}H_{23}O_3Br$ requires C, 65·6; H, 5·2; Br, 18·2%); p-*tolyl α-bromo-β-ethoxy-β-*p-*benzyloxyphenylethyl ketone*, m. p. (benzene–methyl alcohol) 145° (Found: C, 66·6; H, 5·7; Br, 17·0. $C_{25}H_{25}O_3Br$ requires C, 66·2; H, 5·5; Br, 17·6%); o-*hydroxyphenyl α-bromo-β-methoxy-β-*p-*benzyloxyphenylethyl ketone* (6), m. p.

(methyl alcohol) 103° (Found: Br, 18·3. $C_{23}H_{21}O_4Br$ requires Br, 18·1%); and o-*hydroxyphenyl* α-*bromo*-β-*ethoxy*-β-p-*benzyloxyphenylethyl ketone* (7), m. p. (alcohol) 102° (Found: Br, 17·6. $C_{24}H_{23}O_4Br$ requires Br, 17·6%), were similarly prepared from the corresponding alcohols and chalkone halides. (5) when heated under reflux with ethyl alcohol for 2 hours gave (7), hydrolysis of the acetoxy-group occurring during the reaction.

p-*Tolyl* α-*bromo*-β-*hydroxy*-β-p-*benzyloxyphenylethyl ketone*, m. p. (alcohol) 125° (Found: C, 65·5; H, 5·1; Br, 18·5. $C_{23}H_{21}O_3Br$ requires C, 64·9; H, 4·9; Br, 18·8%), formed a yellow residue on evaporation of the solvent from a solution of (3) in acetone which had been treated with water to turbidity, and heated under reflux for 1 hour.

Action of Pyridine on the Dihalides.—p-*Tolyl* α-*chloro*-p-*benzyloxystyryl ketone*, m. p. (alcohol) 116° (Found: C, 76·0; H, 5·4; Cl, 9·5. $C_{23}H_{19}O_2Cl$ requires C, 76·1; H, 5·2; Cl, 9·8%), and p-*tolyl* α-*bromo*-p-*benzyloxystyryl ketone*, m. p. (alcohol) 126° (Found: C, 67·7; H, 4·9; Br, 19·9. $C_{23}H_{19}O_2Br$ requires C, 67·8; H, 4·7; Br, 19·7%), separated from solutions of (2) and (3) respectively, in pyridine, which had been heated under reflux for 20 minutes, diluted with alcohol, and kept overnight. Both compounds are yellow.

Preparation of Flavones.—4′-*Benzyloxyflavone* (8), m. p. (75% acetic acid) 190° (Found: C, 80·2; H, 5·1. $C_{22}H_{16}O_3$ requires C, 80·5; H, 4·9%), separated from a solution of (4) or (6) in alcoholic potassium cyanide, which had been heated under reflux for 7 hours. 4′-Hydroxyflavone, m. p. 270° (acetyl derivative, m. p. 137°) (lit., 268° and 139° respectively), separated from a solution of (8) in glacial acetic acid containing hydrogen bromide, which had been kept overnight. 4′-*Benzyloxyflavonol*, m. p. (acetone–alcohol) 175—176° (Found: C, 77·0; H, 4·7. $C_{22}H_{16}O_4$ requires C, 76·7; H, 4·7%), separated in yellow needles from a solution of (1) (2 g.) in alcohol (40 c.c.), which had been treated with potassium hydroxide (1·2 g.) in alcohol (40 c.c.) and with hydrogen peroxide (perhydrol; 30 c.c.) and finally acidified with dilute sulphuric acid (cf. Algar and Flynn, *Proc. Roy. Irish Acad.*, 1934, **42** B, 1).

Preparation of Benzylidenecoumaranone Derivatives.—1-p-*Benzyloxybenzylidenecoumaran*-2-*one* (I), m. p. (acetic acid) 202° (Found: C, 79·8; H, 5·0. $C_{22}H_{16}O_3$ requires C, 80·5; H, 4·9%), separated as an orange solid from an alcoholic solution of (6) which had been treated with dilute aqueous potassium hydroxide under reflux for 15 minutes. The *dibromide*, m. p. (benzene) 156° (Found: Br, 32·5. $C_{22}H_{16}O_3Br_2$ requires Br, 32·8%), separated on evaporation of the solvent from a solution of (I) (1 g.) in chloroform (35 c.c.) which had been treated with bromine (0·6 g.) in chloroform (8 c.c.) and heated under reflux for 15 minutes.

The *substance* (II), m. p. (acetone–alcohol) 156° (Found: C, 76·3; H, 5·5. $C_{28}H_{24}O_5$ requires C, 76·3; H, 5·5%), separated as a white solid from a mixture of (I) (1 g.), ethyl acetoacetate (3 g.), and alcohol containing sodium ethoxide (0·1 g. of sodium), which had been heated under reflux for 4 hours.

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