24. *Chalkones: Production of 2-Aryltetral-1-ones from Chalkone Dibromides* via *the Related β-Aroyl-α-arylpropionitriles.*

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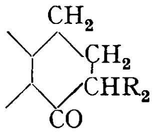
A number of β-aroyl-α-arylpropionitriles have been prepared from the corresponding chalkone dibromides (see J., 1937, 1798) and converted by hydrolysis and subsequent reduction into the related αγ-diarylbutyric acids, some of which have been cyclised into 2-aryltetral-1-ones.

Dodwadmath and Wheeler (*Proc. Indian Acad. Sci.*, 1935, **2**, 438; see also Nadkarni *et al.*, J., 1937, 1798) observed that the action of warm alcoholic potassium cyanide on chalkone dibromides (II) gave β-aroyl-α-arylpropionitriles (III); this method of synthesis is sometimes more satisfactory than that of Hann and Lapworth (J., 1904, **85**, 1359), which involves the direct addition of hydrogen cyanide to the parent chalkone (I). A number of the nitriles (III) have now been prepared by the new method and hydrolysed to the corresponding propionic acids (IV), which have been reduced to the αγ-diarylbutyric acids (V). Some of the last compounds have been cyclised to the 2-aryltetral-1-ones (VI),

$$\underset{\text{(I.)}}{R_1\cdot CO\cdot CH{:}CHR_2} \longrightarrow \underset{\text{(II.)}}{R_1\cdot CO\cdot CHBr\cdot CHBrR_2} \longrightarrow \underset{\text{(III.)}}{R_1\cdot CO\cdot CH_2\cdot CHR_2\cdot CN}$$

$$\longrightarrow \underset{\text{(IV.)}}{R_1\cdot CO\cdot CH_2\cdot CHR_2\cdot CO_2H} \longrightarrow \underset{\text{(V.)}}{R_1\cdot CH_2\cdot CH_2\cdot CHR_2\cdot CO_2H} \longrightarrow$$

$$(R_1 \text{ and } R_2 = \text{aryl})$$



(VI.)

of which few have hitherto been prepared (see Richardson, Robinson, and Seijo, J., 1937, 835; Newman, *J. Amer. Chem. Soc.*, 1938, **60**, 2947; Crawford, *ibid.*, 1939, **61**, 608). The conditions governing the cyclisation of a variety of γ-arylbutyric acids have been previously investigated (for references, see Attwood, Stevenson, and Thorpe, J., 1923, **123**, 1755; Fieser and Hershberg, *J. Amer. Chem. Soc.*, 1939, **61**, 1272).

Experimental.

The required β-aroyl-α-arylpropionic acids were prepared from the corresponding chalkones *via* the dibromides and nitriles by the methods described by Nadkarni *et al.* (J., 1937, 1798). The following are new: β-*naphthyl* αβ-*dibromo*-β-p-*anisylethyl ketone*, m. p. (glacial acetic acid) 156° (Found: Br, 36·0. $C_{20}H_{16}O_2Br_2$ requires Br, 35·7%); β-(β-*naphthoyl*)-α-*phenylpropionitrile*, m. p. (alcohol) 128° (Found: N, 4·9. $C_{20}H_{15}ON$ requires N, 4·9%); β-(β-*naphthoyl*)-α-p-*anisylpropionitrile*, m. p. (alcohol) 121° (Found: N, 4·5. $C_{21}H_{17}O_2N$ requires N, 4·4%); β-p-*toluoyl*-α-p-*anisylpropionic acid*, m. p. (benzene) 151° (Found: C, 72·9; H, 6·1. $C_{18}H_{18}O_4$ requires C, 72·5; H, 6·0%); β-(β-*naphthoyl*)-α-*phenylpropionic acid*, m. p. (alcohol) 187° (Found: C, 78·8; H, 5·3. $C_{20}H_{16}O_3$ requires C, 78·9; H, 5·3%), and β-(β-*naphthoyl*)-

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* The covalencies linking Au to the ethyl groups are known to be in the same plane as the other two valencies of the Au atom (J., 1937, 1690; *Proc. Roy. Soc.*, 1939, *A*, **173**, 147).

α-p-*anisylpropionic acid*, m. p. (alcohol–acetone) 173° (Found, C, 75·5; H, 5·8. $C_{21}H_{18}O$ requires C, 75·4; H, 5·4).

Reduction of Aroylarylpropionic Acids to the Corresponding Diarylbutyric Acids.—β-Benzoyl-α-*p*-anisylpropionic acid (10 g.) was refluxed with a mixture of toluene (200 c.c.), hydrochloric acid (1 : 1; 150 c.c.), and amalgamated zinc (100 g.) for 24 hours. A second equal portion of hydrochloric acid was added to the boiling reaction mixture after 12 hours. The liquid was filtered hot, and the solid residue washed with toluene. The combined lots of toluene were extracted several times with sodium carbonate solution, which was then acidified to separate α-p-*anisyl*-γ-*phenylbutyric acid* (1) (7 g.), m. p. (aqueous acetic acid) 98° (Found: C, 75·2; H, 6·7. $C_{17}H_{18}O_3$ requires C, 75·6; H, 6·7%). The following were similarly prepared in similar yield: α-*phenyl*-γ-p-*tolylbutyric acid* (2), m. p. (hexane) 80° (Found: C, 79·8; H, 7·2. $C_{17}H_{18}O_2$ requires C, 80·3; H, 7·1%); α-p-*anisyl*-γ-p-*tolylbutyric acid* (3), m. p. (dilute alcohol) 115° (Found: C, 76·1; H, 7·2. $C_{18}H_{20}O_3$ requires C, 76·1; H, 7·0%); α-3 : 4-*methylenedioxyphenyl*-γ-*phenylbutyric acid* (4), m. p. (hexane) 98° (Found: C, 72·2; H, 5·5. $C_{17}H_{16}O_4$ requires C, 71·8; H, 5·6%); α-3 : 4-*methylenedioxyphenyl*-γ-p-*tolylbutyric acid* (5), m. p. (dilute alcohol) 96° (Found: C, 72·6; H, 5·9. $C_{18}H_{18}O_4$ requires C, 72·5; H, 6·0%); and α-p-*anisyl*-γ-β-*naphthylbutyric acid*, m. p. (dilute alcohol) 132° (Found: C, 78·9; H, 6·6. $C_{21}H_{20}O_3$ requires C, 78·8; H, 6·3%).

Cyclisation of Diarylbutyric Acids to 2-*Aryltetral*-1-*ones.*—2-p-*Anisyltetral*-1-*one*, m. p. (dilute alcohol) 107° (Found: C, 80·7; H, 6·7. $C_{17}H_{16}O_2$ requires C, 81·0; H, 6·3%), separated as an oil (0·5 g.) which afterwards solidified from a solution of (1) (1 g.) in phosphoryl chloride (3 c.c.) which had been refluxed (calcium chloride guard) for 10 mins., cooled, and poured on ice. The *oxime*, which was formed by heating the ketone for 5 hours with hydroxylamine hydrochloride in pyridine solution, had m. p. (dilute alcohol) 126° (Found: N, 4·9. $C_{17}H_{17}O_2N$ requires N, 5·2%). 2-*Phenyl*-7-*methyltetral*-1-*one*, m. p. (aqueous alcohol) 67° (Found: C, 86·2; H, 7·2. $C_{17}H_{16}O$ requires C, 86·4; H, 6·8%), and 2-p-*anisyl*-7-*methyltetral*-1-*one*, m. p. (aqueous alcohol) 108° (Found: C, 81·8; H, 6·7. $C_{18}H_{18}O_2$ requires C, 81·2; H, 6·8%), were similarly prepared in similar yield from (2) and (3), respectively. Solidification of the oils which first separated was accelerated by alkali extraction of the chloroform solution. Attempts to cyclise (4) and (5) were unsuccessful.

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[*Received, December 2nd,* 1940.]