21. *The Preparation of Diaryl α-Diketones.*

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Oxidation of the nine aryl benzyl ketones now examined with selenium dioxide in acetic anhydride solution by Riley's method (compare Riley, Morley, and Friend, J., 1932, 1875; Simonsen, Evans, and Ridgion, J., 1934, 137) leads to almost quantitative formation of the corresponding α-diketones. The method thus appears to be a general one for the preparation of substituted benzils and, in view of the ready accessibility of aryl benzyl ketones (Jenkins, *J. Amer. Chem. Soc.*, 1933, **55**, 703; Jenkins and Richardson, *ibid.*, p. 1618), one of the most convenient. The yields of diaryl α-diketones previously prepared from aryl benzyl ketones by means of other oxidising agents have been much less satisfactory (Weiss, *Monatsh.*, 1919, **40**, 391; Ruggli and Reinert, *Helv. Chim. Acta*, 1926, **9**, 67; Ruggli and Jenny, *ibid.*, 1927, **10**, 228; Gomberg and van Natta, *J. Amer. Chem. Soc.*, 1929, **51**, 2238).

We have failed to confirm Weiss's (*loc. cit.*) description of 4-methylbenzil. We find that this substance melts at 31° and its structure has been established by conversion into the *r*-phenyl-*p*-tolylglycollic acid of McKenzie and Christie (J., 1934, 1074). Repeating Weiss's experiment, we have found his substance, m. p. 99—101°, obtained by hydrolysis of αα-dibromobenzyl *p*-tolyl ketone with alcohol, to be impure *p*-tolyl benzyl ketone, which is formed together with an oil containing much 4-methylbenzil. This hydrolysis therefore resembles that of αα-dibromodeoxybenzoin by water, in which benzil and deoxybenzoin are produced (Limpricht and Schwanert, *Annalen*, 1870, **155**, 68). The suspicion, at first entertained, that Weiss's substance might be *r*-*p*-toluoylphenylcarbinol arising from the monobromo-compound whose formation always accompanies that of the dibromo-compound, has revealed a more suitable method of preparation for this carbinol than those previously described (McKenzie, Martin, and Rule, J., 1914, **105**, 1583; Weissberger, Strasser, Mainz, and Schwarze, *Annalen*, 1930, **478**, 127). It is readily produced by hydrolysis of α-bromobenzyl *p*-tolyl ketone.

Experimental.

Oxidation of Phenyl Benzyl Ketone.—The following account indicates the general method employed. Phenyl benzyl ketone (4 g.; 0·02 mol.), selenium dioxide (3·4 g.; 0·03 mol.), and acetic anhydride (6 c.c.) were heated for 3—4 hours on an oil-bath at 140—150°. The liquid was filtered from precipitated selenium, the latter washed with acetic anhydride, the filtrates poured into water, and the mixture warmed to destroy the anhydride. The solid product (4·0 g.), which contained traces of selenium and organo-selenium compounds, was boiled with animal charcoal in alcohol containing a little dilute hydrochloric acid (yield, 3·7 g. of pure benzil).*

4-*Phenylbenzil.*—From 8·2 g. of 4-diphenylyl benzyl ketone (Pāpcke, *Ber.*, 1888, **21**, 1339) 4-phenylbenzil was obtained in similar manner. Yield, after crystallisation from methyl alcohol, 8·2 g.; m. p. 104—105° (compare Gomberg and van Natta, *loc. cit.*).

For characterisation the benzils were transformed into 5 : 5-diarylhydantoins, which are readily produced, crystallise well, and have well-defined melting points. Together with the diarylhydantoin, amounts of diarylacetylenediureide,  $CO<\begin{smallmatrix}NH\cdot CAr-NH\\ NH\cdot CAr'\cdot NH\end{smallmatrix}>CO$, were produced which varied with the nature of the benzil. The last substances are therefore produced, not only in neutral media (see C. W. Porter, " Molecular Rearrangements," A.C.S. Monograph, No. 45, p. 96), but also in the presence of alkali. The preparation of 5-phenyl-5-(4′-diphenylyl)hydantoin indicates the general method employed. 4-Phenylbenzil (1·0 g.), potassium hydroxide (1·0 g.), urea (1·0 g.), and 96% alcohol (20 c.c.) were refluxed on a water-bath for 2 hours and then poured into water. The precipitated *phenyl*-4-*diphenylylacetylenediureide* (0·43 g.) crystallised from acetic acid in small white plates, m. p. 316—318° (Found : N, 14·9. $C_{22}H_{18}O_2N_4$ requires N, 15·1%). Saturation of the aqueous filtrate from the diureide with carbon dioxide precipitated almost pure 5-*phenyl*-5-(4′-*diphenylyl*)*hydantoin* (0·70 g.), which separated from alcohol in colourless needles, m. p. 242—242·5° (Found : N, 8·45. $C_{21}H_{16}O_2N_2$ requires N, 8·5%).

4-*Chlorobenzil.*—Obtained from 2·3 g. of 4-chlorophenyl benzyl ketone, this *benzil* (2·4 g.) crystallised from alcohol in light yellow needles, m. p. 73° (Found : Cl, 14·2. $C_{14}H_9O_2Cl$ requires Cl, 14·5%). Oxidation with hydrogen peroxide gave a mixture of 4-chlorobenzoic and benzoic acids.

Phenyl-4-*chlorophenylacetylenediureide* separated from acetic acid in white micro-crystals, m. p. 339° (Found : N, 16·65. $C_{16}H_{13}O_2N_4Cl$ requires N, 17·0%), and 5-*phenyl*-5-(4′-*chlorophenyl*)*hydantoin* from alcohol in white needles, m. p. 243° (Found : N, 9·6. $C_{15}H_{11}O_2N_2Cl$ requires N, 9·8%).

4-*Bromobenzil.*—Oxidation of 2·75 g. of 4-bromophenyl benzyl ketone (Kohler and Petersen, *J. Amer. Chem. Soc.*, 1933, **55**, 1073) gave 2·8 g. of 4-*bromobenzil*, which crystallised from alcohol in yellow needles, m. p. 86·5° (Found : Br, 27·8. $C_{14}H_9O_2Br$ requires Br, 27·65%).

5-*Phenyl*-5-(4′-*bromophenyl*)*hydantoin* crystallised from alcohol in small white needles, m. p. 239° (Found : N, 8·5. $C_{15}H_{11}O_2N_2Br$ requires N, 8·5%).

3 : 4-*Dimethylbenzil.*—Oxidation of 2·3 g. of *o*-4-xylyl benzyl ketone (Wege, *Ber.*, 1891, **24**, 3540) gave 2·4 g. of this *benzil*, which crystallised from methyl alcohol in pale yellow needles, m. p. 63·5° (Found : C, 80·1; H, 5·9. $C_{16}H_{14}O_2$ requires C, 80·6; H, 5·9%).

The orientation of the methyl groups in the preceding aryl benzyl ketone had not been definitely established. That they have the positions now assigned was shown by oxidation of the corresponding benzil to 3 : 4-dimethylbenzoic acid. The procedure of Schönberg and Malchow (*Ber.*, 1922, **55**, 3746) was found preferable to that of Weitz and Scheffer (*Ber.*, 1921, **54**, 2327). The following account indicates the method employed in all subsequent cases. 3 : 4-Dimethylbenzil (0·5 g.) in pyridine (1 c.c.) was treated with 30% hydrogen peroxide (2 c.c.) and then with *N*-sodium hydroxide (2·5 c.c.). After heating until the solution was clear (5 minutes), acidification with hydrochloric acid precipitated the mixed acids. The benzoic acid (m. p. 121°) was removed with hot water; the residual 3 : 4-dimethylbenzoic acid, after crystallisation from hot water, melted at 165°.

5-*Phenyl*-5-o-4′-*xylylhydantoin* separated from alcohol as a white crystalline powder, m. p. 225° (Found : N, 10·0. $C_{17}H_{16}O_2N_2$ requires N, 10·0%). *Phenyl*-o-4-*xylylacetylenediureide* was obtained as a white powder from acetic acid, m. p. 333° (Found : N, 17·4. $C_{18}H_{18}O_2N_2$ requires N, 17·4%).

m-4-Xylyl benzyl ketone was obtained by Wege (*loc. cit.*) from *m*-xylene and phenylacetyl chloride by the Friedel–Crafts reaction and stated to undergo partial solidification on long stand-

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* For complete oxidation of the aryl benzyl ketones to the corresponding benzils an excess of selenium dioxide is necessary, since the acetic anhydride employed as solvent is simultaneously oxidised. Postovsky and Lugovkin (*Ber.*, 1935, **68**, 852) have shown that the acetic anhydride is thereby largely transformed into glyoxylic anhydride. Except that an excess of selenium dioxide is required, this oxidation of acetic anhydride appears not to interfere with these preparations of diaryl α-diketones.

ing. We have found this to occur only when the *m*-xylene is contaminated with *o*-xylene and to be due to the separation of *o*-4-xylyl benzyl ketone. Pure *m*-4-xylyl benzyl ketone is a colourless oil, b. p. 202—205°/13 mm. Wege's similar observation concerning *p*-xylyl benzyl ketone is likewise explained.

2 : 4-*Dimethylbenzil.*—*m*-4-Xylyl benzyl ketone (20 g.), selenium dioxide (15 g.), and acetic anhydride (15 c.c.), after being heated for 3 hours at 150° and worked up in the usual manner, gave an oil. This was taken up in benzene, the solvent removed, and the oil heated with animal charcoal in acidified alcohol. Filtration and distillation under reduced pressure gave a yellow oil, b. p. 228°/16 mm., which formed a glass at — 60° but did not solidify (Found : C, 80·2; H, 5·8. $C_{16}H_{14}O_2$ requires C, 80·6; H, 5·9%). Oxidation with hydrogen peroxide gave 2 : 4-dimethylbenzoic acid (m. p. 126°) and benzoic acid.

5-*Phenyl*-5-m-4′-*xylylhydantoin* crystallised from alcohol in small needles, m. p. 269° (Found : N, 9·9. $C_{17}H_{16}O_2N_2$ requires N, 10·0%).

2 : 5-*Dimethylbenzil.*—Oxidation of *p*-xylyl benzyl ketone (8 g.) yielded an oil (7·6 g.), which solidified at — 60°. Thereafter it crystallised from alcohol in pale yellow rosettes of needles, m. p. 41° (Found : C, 80·4; H, 5·9%). Oxidation with hydrogen peroxide produced 2 : 5-dimethylbenzoic acid (m. p. 132°) and benzoic acid. 5-*Phenyl*-5-p-*xylylhydantoin*, after crystallisation from alcohol, melted at 266° (Found : N, 10·1%).

2 : 4 : 6-*Trimethylbenzil.*—4·9 G. of this benzil were obtained by oxidation of mesityl benzyl ketone (4·8 g.). It crystallised from chloroform and alcohol in compact lemon-yellow crystals, m. p. 137° (Found : C, 80·8; H, 6·4. Calc. for $C_{17}H_{16}O_2$: C, 80·9; H, 6·4%). Gray and Fuson (*J. Amer. Chem. Soc.*, 1934, **56**, 2100) give m. p. 136—137°. Oxidation with hydrogen peroxide gave 2 : 4 : 6-trimethylbenzoic acid, m. p. 154°, and benzoic acid. Prolonged boiling with urea in alcoholic potash gave no diarylhydantoin.

4-*Methylbenzil.*—Oxidation of 12·6 g. of *p*-tolyl benzyl ketone gave 10 g. (theo., 13·4 g.) of a yellow oil, b. p. 219—221°/15 mm., which solidified in ether–solid carbon dioxide. It separated from alcohol at 0° in soft, pale yellow crystals, m. p. 31° (Found : C, 80·2; H, 5·4. Calc. for $C_{15}H_{12}O_2$: C, 80·3; H, 5·4%). Oxidation with hydrogen peroxide gave *p*-toluic acid, m. p. 176°, and benzoic acid.

From the reaction of 4-methylbenzil (2 g.) with urea in alkaline alcoholic solution there were isolated 0·47 g. of *phenyl*-p-*tolylacetylenediureide*, m. p. 335° after crystallisation from acetic acid (Found : N, 17·9. $C_{17}H_{16}O_2N_4$ requires N, 18·2%), and 1·82 g. of 5-*phenyl*-5-p-*tolylhydantoin*, obtained as a white micro-crystalline solid from alcohol (Found : N, 10·4. $C_{16}H_{14}O_2N_2$ requires N, 10·5%).

Contrary to Weiss's statement (*loc. cit.*), 4-methylbenzil has been found to yield the corresponding benzilic acid readily on treatment with alcoholic potash. 4-Methylbenzil (2 g.), potassium hydroxide (1 g.), and 96% ethyl alcohol (10 c.c.) were refluxed together for 2 hours, the mixture was poured into water, and the filtered solution neutralised. One drop of very dilute hydrochloric acid was added, and the slight precipitate collected. After three repetitions of this process acidification precipitated *r*-phenyl-*p*-tolylglycollic acid, m. p. 127—129°, and 132° after crystallisation from chloroform–light petroleum.

Hydrolysis of αα-Dibromobenzyl p-*Tolyl Ketone.*—The dibromo-ketone (2·9 g.) was prepared by gradually adding 3·6 g. of bromine in 18 c.c. of chloroform to a boiling solution of 2 g. of *p*-tolyl benzyl ketone in 10 c.c. of chloroform and, after 1 hour, removing the chloroform and washing the crystalline residue with light petroleum. (The petroleum extracts contain a mixture of mono- and di-bromo-derivatives.) It separated from benzene–light petroleum in colourless hexagonal prisms, m. p. 128—129° (Found : Br, 43·2. Calc. for $C_{15}H_{12}OBr_2$: Br, 43·4%). When 2 g. of this material were heated for 6 hours at 160° with 12 c.c. of alcohol, the latter was entirely converted into ether and water. From the ethereal layer a semi-solid material was obtained, separable into a white crystalline solid (0·2 g.), m. p. 90—100°, and a yellow oil. Crystallised from methyl alcohol, the solid formed white needles, m. p. 110—111°, identified as *p*-tolyl benzyl ketone by mixed m. p. and by conversion into the dibromo-derivative. The yellow oil was shown to be crude 4-methylbenzil by rearrangement to *r*-phenyl-*p*-tolylglycollic acid.

α-Bromobenzyl p-*Tolyl Ketone.*—To a boiling solution of *p*-tolyl benzyl ketone (2 g.) in chloroform (10 c.c.), bromine (1·7 g.) in chloroform (10 c.c.) was added during 15 minutes. After 1 hour's refluxing, the chloroform was removed, and the residue crystallised from benzene–light petroleum. α-Bromobenzyl *p*-tolyl ketone separated in long needles, m. p. 87·5—88° (Found : Br, 27·5. Calc. for $C_{15}H_{13}OBr$: Br, 27·6%).

r-p-*Toluoylphenylcarbinol.*—1 G. of the above bromide was added, with shaking, to 0·2 g.

of sodium methoxide in 10 c.c. of methyl alcohol cooled in ice. After ¾ hour the mixture was poured into water and the oil separating was extracted with ether. Evaporation of the ether and addition of light petroleum gave a white solid. By crystallisation from aqueous methyl alcohol 0·44 g. (theo., 0·78 g.) of *r*-*p*-toluoylphenylcarbinol was obtained, m. p. 110—111° (Found : C, 79·8; H, 6·2. Calc. for $C_{15}H_{14}O_2$: C, 79·6; H, 6·2%).

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