328. *The Chemistry of Reductone. Part III.* Alkenediols related to Reductone.*

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The anilino- and *N*-methylanilino-derivatives of phenylreductone (I*a*–*b*; R = Ph, R′ = H) have been prepared. The parent compound has been obtained only in solution. The ultra-violet light absorption spectra and the stabilities of these compounds are discussed.

Alkenediols of type (I*a*–*b*) may be difficult to isolate for three main reasons. In the first place, they can undergo rapid tautomeric change to the appropriate hydroxydicarbonyl compounds of type (II) (*e.g.*, ethyl αβ-dihydroxycrotonate yields ethyl α-hydroxy-β-ketobutyrate; Karrer, Kebrle, and Thakkar, *Helv. Chim. Acta*, 1950, **33**, 1711). Secondly, they may be transformed into esters of type (III), a change which is catalysed by hydroxyl ions; *e.g.*, (I; R = R′ = Ph) yields benzoyloxyacetophenone (III; R = R′ = Ph) (Karrer *et al.*, *loc. cit.*). And, thirdly, they may undergo oxidation in air.

$R{\cdot}C(OH){:}C(OH){\cdot}COR' \rightleftharpoons R{\cdot}CO{\cdot}C(OH){:}CR'{\cdot}OH$ (I*a*) (I*b*) $R{\cdot}CO{\cdot}CH(OH){\cdot}COR'$ (II) $R{\cdot}CO{\cdot}CH_2{\cdot}O{\cdot}COR'$ (III)

$RR'CH{\cdot}CO{\cdot}COR''$ (IV) $Ph{\cdot}CO{\cdot}C(OH){:}CH{\cdot}NRPh$ (V) $PhRN{\cdot}CH{:}C(OH){\cdot}CHO$ (VI)

Arndt, Loewe, and Ayça (*Chem. Ber.*, 1951, **84**, 333) have discussed some of the structural factors which can influence resistance to ketonisation and oxidation. In order to obtain information on these points we had previously set out to prepare αβ-dihydroxy-β-phenylacraldehyde (I*a*; R = Ph, R′ = H), hereafter called phenylreductone, and mesitylreductone (I; R = mesityl, R′ = H). Neither of these compounds was obtained as a stable solid; aqueous solutions of the former were, however, obtained.

Hydrolysis of 3-bromo-1-phenylpropane-1 : 2-dione (IV; R = H, R′ = Br, R″ = Ph) with barium hydroxide gave a barium salt with properties similar to those of an ene-diol, but phenylreductone could not be isolated from the salt; nor could phenylreductone be obtained by hydrolysis of the bromo-compound with sulphuric acid, although Hesse and Bucking (*Annalen*, 1949, **563**, 31) obtained a stable ene-diol from 3-chloro*cyclo*pentane-1 : 2-dione in this way.

3-Acetoxy-1-phenylpropane-1 : 2-dione (IV; R = H, R′ = OAc, R″ = Ph) was obtained in small yield by reaction of either the above bromo-diketone with acetic anhydride and sodium acetate, or lead tetra-acetate with 1-phenylpropane-1 : 2-dione (IV; R = R′ = H, R″ = Ph), benzoic acid being a by-product in the latter reaction. The acetoxy-compound fails to give a ferric reaction, whereas the related compound (IV; R = OAc, R′ = Ph, R″ = mesityl), enolises completely when its solution is kept (Barnes and Green, *J. Amer. Chem. Soc.*, 1938, **60**, 1549). Acid hydrolysis of the acetoxy-compound yielded a solution which gave colour and reducing reactions of an ene-diol, and iodine titrations indicated the production of an ene-diol, presumably phenylreductone, in theoretical quantity. It was not possible to isolate pure phenylreductone from the solution; kept under nitrogen, the solution was stable, although oxidation took place rapidly in air.

Anilino- and *N*-methylanilino-analogues of phenylreductone (V; R = H and Me, respectively) were readily obtained by reaction of 3-bromo-1-phenylpropane-1 : 2-dione with aniline and methylaniline, respectively. Both analogues gave a green ferric colour, exhibited complete enolisation towards iodine, and decolorised two equivalents of Tillmans's reagent in presence of mineral acid. Their ene-diol-like character steadily deteriorated when aqueous-alcoholic solutions were exposed to air. Whilst the anilino-compound gave Fearon and Kawerau's ene-diol (*o*-dinitrobenzene) reaction (*Biochem. J.*, 1943, **37**, 326), the methylanilino-compound gave no immediate colour, thus resembling the corre-

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* Part II, *J.*, 1950, 2052.

sponding analogues of reductone (VI; R = H and Me, respectively) (cf. Cocker, O'Meara, Schwarz, and Stuart, *J.*, 1950, 2052).

The ultra-violet light absorption characteristics of (V; R = H and Me) resemble each other (cf. the corresponding reductone derivatives; Cocker *et al.*, *loc. cit.*), and also those of 3-anilino-1-phenylprop-2-en-1-one (Bowden, Braude, Jones, and Weedon, *J.*, 1946, 45). The spectra of alcoholic solutions of (V; R = H and Me) change with time, but solutions in *cyclo*hexane are unaffected. The rate of change is very slow when a solution of (V; R = H), in alcohol saturated with nitrogen, is kept under nitrogen. In the reductone series, (VI; R = H) but not (VI; R = Me) undergoes a similar change. After long storage in alcoholic solution (V; R = H or Me) and (VI; R = H) show similar spectral characteristics. The change is probably due to oxidation (cf. Cocker *et al.*, *loc. cit.*).

Light absorption data.

	In *cyclo*hexane		In alcohol	
	$\lambda_{\text{max.}}$ (Å)	log ε	$\lambda_{\text{max.}}$ (Å)	log ε
(V; R = H)	2390	4·06	* 2420	4·06
	2650	3·93	3680	4·44
	3620	4·41	† 2350	4·23
(V; R = Me)	2410	4·04	* 2430	4·05
	2690	3·86	3670	4·36
	3660	4·37	‡ 2330	4·18
PhCO·CH:CH·NHPh	—	—	2420 2540	4·24
			3740	4·49

* Observation 20 min. after dissolution. † After 40 hr. ‡ After 48 hr.

Attempts to prepare mesitylreductone were unsuccessful. 1-Mesitylpropane-1 : 2-dione 2-oxime, prepared by the nitrosation of 1-mesitylpropan-1-one, was hydrolysed to 1-mesitylpropane-1 : 2-dione (cf. *Org. Synth.*, 1936, **16**, 44; 1943, **23**, 1). The latter could not be successfully brominated; nor was it acetoxylated with lead tetra-acetate. We were unable to prepare 2 : 3-diketo-3-phenyl- and -3-mesityl-propaldehyde (which could possibly be reduced to phenyl- and mesityl-reductone, respectively) by the oxidation of 1-phenyl- and 1-mesityl-propane-1 : 2-dione with selenium dioxide, although in the latter case the oily product yielded a compound, probably 2-mesitylquinoxaline, with *o*-phenylenediamine. 1-Mesitylpropane-1 : 2-dione did not give a quinoxaline (Fuson and Soper, *J. Org. Chem.*, 1944, **9**, 123).

The stability of the enol forms of phenylreductone and of its anilino-derivative under nitrogen indicates that, like reductone and its anilino-derivatives, these compounds do not ketonise spontaneously. However, the two series of compounds differ appreciably in their stability towards oxidation, phenylreductone and its derivatives being the more readily oxidised.

EXPERIMENTAL

Hydrolysis of 3-*Bromo*-1-*phenylpropane*-1 : 2-*dione* (IV; R = H, R′ = Br, R″ = Ph).—The bromo-compound (0·4 g.) was added to an ice-cold saturated solution of barium hydroxide (15 c.c.) under nitrogen. After 10 min., the golden-yellow precipitate (0·1 g.) of barium salt was collected and washed with ether. Dissolved in dilute acetic acid, this consumed 51·5% of the amount of N/10-iodine expected for the barium salt of phenylreductone.

3-*Acetoxy*-1-*phenylpropane*-1 : 2-*dione* (IV; R = H, R′ = OAc, R″ = Ph).—(a) *From* 3 *bromo*-1-*phenylpropane*-1 : 2-*dione*. A mixture of bromo-compound (1·3 g.), freshly fused and powdered sodium acetate (1·0 g.), and acetic anhydride (5 c.c.) was refluxed for 15 min. The dark brown product was poured into water and extracted with chloroform, and the extracts were washed repeatedly with water. After evaporation of the solvent, the main fraction distilled at 175—185°/12 mm. and partly solidified when rubbed and cooled. The *acetate* (0·07 g.) was separated and crystallised (charcoal) from light petroleum containing 1 drop of alcohol, giving plates, m. p. 88—89° (Found : C, 63·5; H, 5·4. $C_{11}H_{10}O_4$ requires C, 64·1; H, 4·9%). It was slowly soluble in 20% aqueous sodium hydroxide; after a few min., the solution gave a strong ene-diol colour reaction.

(b) *From* 1-*phenylpropane*-1 : 2-*dione*. A mixture of this compound (7·4 g.), freshly recrystallised lead tetra-acetate (22·5 g.), and glacial acetic acid (20 g.) was heated carefully to 100°. A vigorous reaction set in and the temperature was kept at 99—102° by cooling. After 10 min. the tetra-acetate had dissolved and after a further 5 min. the mixture had become brown. It was poured into water and extracted with ether, and the extract thoroughly shaken with 5% aqueous sodium hydrogen carbonate. The dried ethereal extract was distilled, leaving a brown oil (3·3 g.) which partly solidified (0·42 g.) at 0°. Crystallised from light petroleum–ethyl acetate, it did not depress the m. p. of a specimen of the acetate prepared by method (a).

Attempted Isolation of Phenylreductone (I; R = Ph, R′ = H).—Powdered 3-acetoxy-1-phenylpropane-1 : 2-dione (0·35 g.) was stirred with concentrated sulphuric acid (11 g.) for 15 min. at –5°. The acetate slowly dissolved, giving a pale orange solution which was poured on ice under nitrogen (total volume after melting, 33·0 c.c.; 1 c.c. of this solution decolorised 10·2 c.c. of N/100-iodine. Calc. for complete hydrolysis to phenylreductone = 10·3 c.c.). After being kept overnight under nitrogen, the aqueous solution showed no change in iodine titre, but when air was admitted the titre decreased rapidly. The product was extracted under nitrogen with chloroform, which was evaporated under reduced pressure at 0°, leaving a colourless oil which slowly crystallised. However, on admission of air the crystals gave an intractable oil.

3-*Anilino*-2-*hydroxy*-1-*phenylprop*-2-*en*-1-*one* (V; R = H).—3-Bromo-1-phenylpropane-1 : 2-dione (1·65 g.) and aniline (0·64 g.) were mixed, with cooling, and the resulting red gum was rubbed with light petroleum, giving a pale yellow hygroscopic hydrobromide (1·25 g.) which could not be purified. This was shaken with a mixture of chloroform and 5% sodium hydrogen carbonate solution, and the chloroform layer was washed with water, dried, and treated with charcoal. Addition of light petroleum yielded the required *anilino*-compound, which crystallised from chloroform–light petroleum as golden-yellow prisms, m. p. 135° (open tube), decomp. 173° (sealed tube) (Found: C, 75·0; H, 5·5. $C_{15}H_{13}O_2N$ requires C, 75·3; H, 5·4%).

2-*Hydroxy*-3-N-*methylanilino*-1-*phenylprop*-2-*en*-1-*one* (V; R = Me).—3-Bromo-1-phenylpropane-1 : 2-dione (3·3 g.) in ether (5 c.c.) was added to methylaniline (1·56 g.) in ether (10 c.c.). A pale yellow hydrobromide (3·4 g.) separated overnight. It was shaken with 5% sodium hydrogen carbonate solution and ether, and the ethereal solution was washed with water, dried, and evaporated. The remaining oil was dissolved in benzene (10 c.c.) and purified on an alumina column. Development with benzene gave three bands, the second of which was eluted with benzene containing 10% of alcohol, giving the *methylanilino*-compound (1·7 g.) as a yellow oil which solidified when rubbed. This crystallised from chloroform–light petroleum as yellow needles, m. p. 118·5° (sealed tube) (Found: C, 70·6; H, 5·6. $C_{16}H_{15}O_2N,H_2O$ requires C, 70·8; H, 6·3%). On recrystallisation from benzene–light petroleum, the water of crystallisation was lost (Found: C, 75·6; H, 6·7. $C_{16}H_{15}O_2N$ requires C, 75·9; H, 5·9%).

1-*Mesitylpropane*-1 : 2-*dione* 2-*Oxime*.—This (57·0 g.) was prepared from 1-mesitylpropan-1-one (62 g.) by the method described for oximinopropiophenone (*Org. Synth.*, 1936, **16**, 44). It crystallised from benzene–light petroleum as colourless plates, m. p. 123° (Found: C, 70·4; H, 7·6. $C_{12}H_{15}O_2N$ requires C, 70·3; H, 7·3%). Hydrolysis with sulphuric acid (*Org. Synth.*, 1943, **23**, 1) gave 1-mesitylpropane-1 : 2-dione (cf. Fuson and Soper, *loc. cit.*), b. p. 133—134°/14 mm. (Found: C, 75·6; H, 7·5. Calc. for $C_{12}H_{14}O_2$: C, 75·8; H, 7·4%).

Attempted Preparation of 2 : 3-*Diketo*-3-*mesitylpropaldehyde*.—The above diketone (1·9 g.) was refluxed for 2 hr. with selenium dioxide (1·0 g.) in dioxan (25 c.c.) and water (0·25 c.c.). The filtered solution was evaporated under reduced pressure, leaving an intractable gel (2·1 g.), which (0·42 g.) was refluxed with *o*-phenylenediamine (0·22 g.) in glacial acetic acid (6·0 c.c.). The cooled mixture was poured into 5% sodium hydrogen carbonate solution and extracted with ether, from which a brown oil (0·06 g.) was obtained. It slowly solidified, and was then crystallised from alcohol (charcoal) as colourless needles, m. p. 297·5° (Found: C, 77·1; H, 5·9. Calc. for $C_{18}H_{16}ON_2$: C, 78·3; H, 5·8%). It gave a blood-red colour with concentrated sulphuric acid.

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