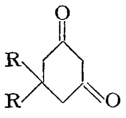
276. cyclo*Hexa*-1 : 3-*dione : A Reagent for the Characterisation of Aldehydes.*

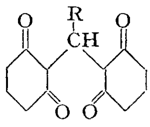
By F. E. King and D. G. I. Felton.

*cyclo*Hexa-1 : 3-dione, which can be readily obtained from resorcinol by catalytic reduction, has been used to prepare crystalline derivatives of a variety of aliphatic and aromatic aldehydes.

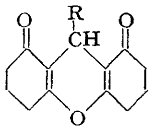
*cyclo*Hexa-1 : 3-dione (dihydroresorcinol) (I, R = H) was first described by Merling (*Annalen*, 1894, **278**, 28) who obtained it by the action of sodium amalgam on resorcinol in boiling aqueous solution. Merling noted the condensation of the ketone with formaldehyde (*loc. cit.*, footnote p. 30), but it was Vorländer and Kalkow (*ibid.*, 1899, **309**, 375) who formulated the resulting compound as (II, R = H), and a similar structure was assigned to the benzaldehyde derivative by Vorländer and Strauss (*ibid.*, 1899, **309**, 375). These primary condensation products were found to cyclise on being heated with acetic acid, etc., to so-called anhydrides (III) (Vorländer, *loc. cit.*).



(I.)



(II).



(III.)

Merling's preparation of *cyclo*hexa-1 : 3-dione is not very convenient, and no systematic attempt was made to exploit its possibilities as an aldehyde reagent, the need for which is usually met by the relatively expensive 5 : 5-dimethyl*cyclo*hexa-1 : 3-dione (dimedone) (I, R = Me) (*vide* " Organic Reagents for Organic Analysis ", Hopkin and Williams, London, 1944, p. 44). However, *cyclo*hexa-1 : 3-dione is very easily prepared by the catalytic hydrogenation of resorcinol in presence of strong bases (Hofmann-LaRoche, *Chem. Zentr.*, 1935, I, 632 : *Chem. Abs.*, 1935, **29**, 482), and details of the preparation, using Raney nickel and aqueous sodium hydroxide, are given below. The product readily condenses with aldehydes in warm alcoholic solution, and the reaction is catalysed by a small quantity of piperidine (cf. Horning and Horning, *J. Org. Chem.*, 1946, **11**, 95). The resulting *derivatives* (II) crystallise well, are conveniently high-melting, and can be purified by recrystallisation from aqueous ethanol, in which they are sparingly soluble in the cold. Dihydroresorcinol can also be caused to react with aldehydes under acid conditions; the products are of type (III), as denoted by the absence of colour on treatment with alcoholic ferric chloride.

Aldehyde.	M. p. of deriv.	Formula.	Analysis (*a*). Required, %. C.	H.	N.	Found, %. C.	H.	N.
Formaldehyde	134° (*b*)	—	—	—	—	—	—	—
Acetaldehyde	155	$C_{14}H_{18}O_4$	67·1	7·2	—	66·7	7·2	—
Propionaldehyde	118—119	$C_{15}H_{20}O_4$	68·2	7·5	—	68·2	7·5	—
n-Butaldehyde	97—98	$C_{16}H_{22}O_4$	69·1	7·9	—	69·0	8·0	—
Benzaldehyde	217—218 (*c*)	—	—	—	—	—	—	—
o-Nitrobenzaldehyde	212—213	$C_{19}H_{19}O_6N$	63·9	5·3	3·9	63·5	5·6	3·9
m-Nitrobenzaldehyde	209—210	$C_{19}H_{19}O_6N$	63·9	5·3	3·9	64·4	5·2	3·6
p-Nitrobenzaldehyde	218	$C_{19}H_{19}O_6N$	63·9	5·3	3·9	63·6	5·6	3·7
2 : 4-Dinitrobenzaldehyde	209—210	$C_{19}H_{18}O_8N_2$	56·8	4·5	7·0	56·6	4·6	7·3
o-Hydroxybenzaldehyde	233	$C_{19}H_{18}O_4$ (*d*)	73·6	5·8	—	73·6	6·0	—
m-Hydroxybenzaldehyde	257	$C_{19}H_{20}O_5$	69·5	6·0	—	69·4	5·7	—
p-Tolualdehyde	187	$C_{20}H_{22}O_4$	73·6	6·75	—	73·8	6·6	—
p-*iso*Propylbenzaldehyde	97	$C_{22}H_{26}O_4$	74·5	7·35	—	74·0	7·15	—
Cinnamaldehyde	216	$C_{21}H_{22}O_4$	74·6	6·5	—	74·8	6·4	—
Anisaldehyde	196	$C_{20}H_{22}O_5$	70·2	6·4	—	70·0	6·4	—
Vanillin	204–205	$C_{20}H_{22}O_6$	67·0	6·1	—	66·7	6·1	—
Veratraldehyde	164	$C_{21}H_{24}O_6$	67·8	6·4	—	67·9	6·5	—
Piperonal	212	$C_{20}H_{20}O_6$	67·4	5·6	—	67·2	5·7	—
p-Dimethylaminobenzaldehyde	150	$C_{21}H_{25}O_4N$	71·0	7·0	3·9	70·5	6·7	4·1
Furfuraldehyde	146	$C_{17}H_{18}O_5$	67·6	5·9	—	67·5	5·9	—

(*a*) All samples for analysis were dried at 100° in a vacuum except those from *n*-butaldehyde and *p*-*iso*propylbenzaldehyde, which were dried at 80°.

(*b*) Vorländer and Kalkow (*loc. cit.*) record m. p. 132—133°.

(*c*) Vorländer and Strauss (*loc. cit.*) record m. p. *ca.* 208°.

(*d*) The derivative obtained from *o*-hydroxybenzaldehyde using piperidine, was probably an anhydride.

EXPERIMENTAL.

cyclo*Hexa*-1 : 3-*dione* (I, R = H).—Resorcinol (110 g.), dissolved in sodium hydroxide solution (40 g., 1 mol., in 400 c.c. of water) was hydrogenated over Raney nickel at 60—70°/100 atmospheres until absorption of hydrogen ceased. After removal of the catalyst, the solution was brought to pH 7 (either by careful addition of acid or by a stream of carbon dioxide) and extracted with ether (4 × 50 c.c.) to remove unchanged resorcinol. The solution was then strongly acidified and extracted with chloroform; after being dried (Na_2SO_4), the extract on evaporation yielded *cyclo*hexa-1 : 3-dione (*ca.* 110 g.) as pale yellow crystals, m. p. 105—106°.

As an alternative, the dihydroresorcinol can be isolated with ether, which is removed after rapid drying. This method yields a nearly colourless product, but difficulties may arise owing to the relative insolubility of the product in dry ether. Dihydroresorcinol may, if desired, be recrystallised from ethyl acetate–ether, but the product from hydrogenation is pure enough for condensation with aldehydes.

Veratraldehyde Derivative.—Details of this preparation are given as an example of the general method. Veratraldehyde (1·1 g.) was added to a solution of *cyclo*hexa-1 : 3-dione (1·5 g., 2 mols.) in ethanol (10 c.c.) and water (10 c.c.). Piperidine (0·5 c.c.) was added and the mixture warmed on a steam-bath for 5 minutes. After cooling for 1 hour, the crystalline *product* (2·0 g.) was collected, washed with ice-cold ethanol, and dried. It then had m. p. 163—164°, and when recrystallised from aqueous ethanol afforded colourless prisms, m. p. 164° (efferv.) (Found : C, 67·9; H, 6·5. $C_{21}H_{24}O_6$ requires C, 67·8; H, 6·4%).

Anhydride of the Veratraldehyde Derivative.—Veratraldehyde (0·4 g.) was added to a solution of *cyclo*hexa-1 : 3-dione (0·5 g.) in ethanol (10 c.c.), a few drops of concentrated hydrochloric acid were added, and the mixture was warmed on a steam-bath for 5 minutes. After standing at room temperature for 3 hours, the *product* (0·4 g.) was collected and washed with ethanol and ether. Recrystallisation from benzene gave colourless rhombs, m. p. 182—183° (Found : C, 71·4; H, 6·4. $C_{21}H_{22}O_5$ requires C, 71·2; H, 6·2%).

The benzaldehyde anhydro-derivative, similarly prepared, separated in colourless prisms from benzene; m. p. 264° (Found : C, 77·2; H, 6·28. Calc. for $C_{19}H_{18}O_3$: C, 77·5; H, 6·12%). Vorländer and Strauss (*loc. cit.*) record m. p. 255°.

The authors thank the Medical Research Council for a maintenance grant to one of them (D.G.I.F.), during the tenure of which this work was carried out.

DYSON PERRINS LABORATORY, OXFORD. [*Received, September* 11*th*, 1947.