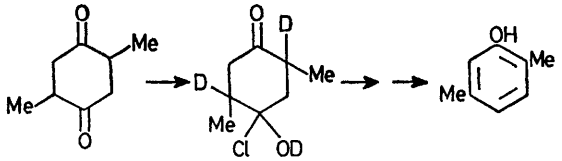
Acid-induced Conversion of Cyclohexane-1,4-diones into Monohydric Phenols

By C. GUNDU RAO, S. RENGARAJU, and M. VIVEKANANDA BHATT*

(*Department of Organic Chemistry, Indian Institute of Science, Bangalore-560012, India*)

Summary Treatment of cyclohexane-1,4-diones with concentrated hydrochloric acid under refluxing conditions, produces monohydric phenols in good yields.

IN connection with another study, we observed that heating of 2,6-diethoxycarbonyl-2,6-dimethylcyclohexane-1,4-dione (I) with conc. aqueous HCl produced 2,5-dimethylphenol (II). Heating of 2,6-dimethylcyclohexane-1,4-dione with conc. HCl also produced (II) in 70—75% yield.



(III) (IV) (II)

This reaction to produce monohydric phenols from cyclohexane diones in fair yield is general, and can also be brought about by constant boiling HBr in slightly better yield, but not by 15N-H_2SO_4. Cyclohexane-1,4-dione itself gave mainly a polymer and 15% of phenol.

TABLE. Conversion of cyclohexanediones into phenols by conc. HCl (reflux; 15 h)

Dione	Product[a]	Yield (%)
2,5-Dimethylcyclohexane-1,4-dione	2,5-Dimethylphenol	70—75[b]
2,5-Diethylcyclohexane-1,4-dione	2,5-Diethylphenol	70—80
Perhydronaphthalene-1,4-dione	5,6,7,8-Tetrahydronapthalen-1-ol	70

[a] Satisfactory analytical, mass spectral, i.r., and n.m.r. data were obtained for all compounds. [b] 80—85% with constant boiling HBr.

Spectroscopic data for compound (III) in $CDCl_3$ in the presence of DCl suggest that the halohydrin (IV) may be an intermediate {i.r. 3450 (OH stretch) and 2700 cm^{-1} (OD stretch), with a decrease in intensity of the CO stretch; δ 1·05 (d, J 6 Hz, Me) [compound (III)] and 0·93 and 1·23 (s, Me) [compound (IV)]}. Under basic conditions aromatic ring formation by enolization and dehydration of ketones has been reported with α-tetralones,[1] but no such reactions are known in acidic media.

(*Received, 11th March* 1974; *Com.* 280.)

[1] A. J. Birch and D. A. White, *J. Chem. Soc.*, 1964, 4086; J. M. Springer, C. W. Hinman, E. J. Eisenbraun, P. W. K. Flanagan, and M. C. Hamming, *J. Org. Chem.*, 1970, **35**, 1260.