

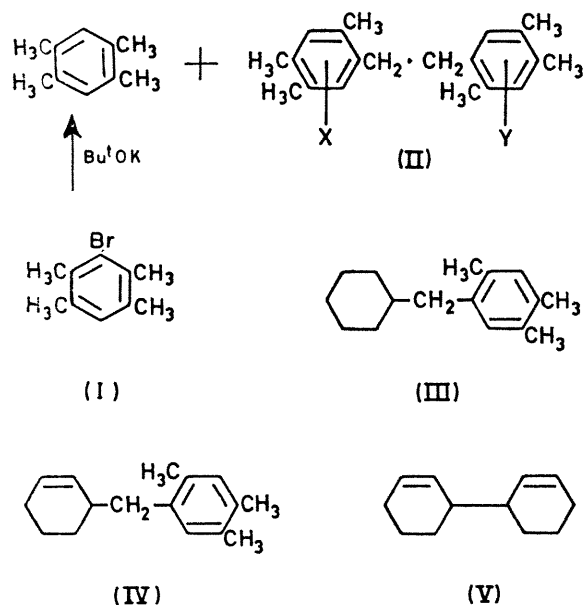
Reactions of Bromodurene and Related Compounds with Strong Bases: a Novel 1,3-Dehydrobromination

By J. I. G. CADOGAN,*† MISS JULIA K. A. HALL, J. T. SHARP, and A. K. ROBERTSON

(Departments of Chemistry, †University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ,
and University of St. Andrews, St. Andrews, Fife)

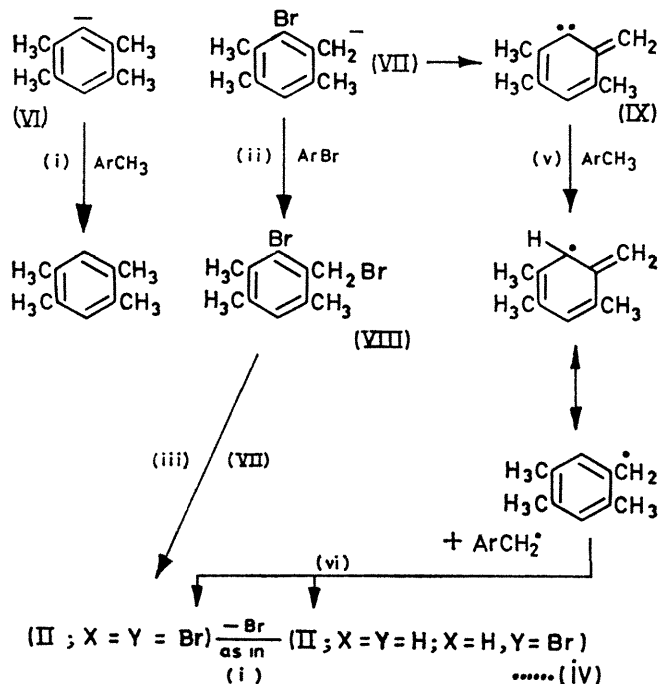
Summary Reaction of bromodurene (I) with potassium t-butoxide at 225° led to almost quantitative dehydrobromination to give durene (34%), t-butyl alcohol (74%), 2,4,5,2',4',5'-hexamethylbibenzyl and its mono- and di-bromo-derivatives, similar reactions being observed with sodamide and with other related polymethylhalogenobenzenes.

ALTHOUGH 1,2-dehydrohalogenation of aryl bromides to give arynes is well known, dehydrohalogenations of aryl bromides which do not contain protons *ortho*- to the halogen, *e.g.* bromodurene (I), have not been reported. In theory this could occur *via* 1,3- or 1,4-(aryl-H or alkyl-H) eliminations only, and, if it occurred at all, might give reactive intermediates capable of novel reactions.



We now report that reaction of anhydrous, solvent-free, potassium t-butoxide¹ with bromodurene (excess), at 225°, proceeds *via* dehydrobromination to give potassium bromide (>90%) t-butyl alcohol (74%), durene (34%), 2,4,5,2',4',5'-

hexamethylbibenzyl (II; X = Y = H; 1%) and mono- and di-bromohexamethylbibenzyls (II; X = H; Y = Br; X = Y = Br; total 19%), by mass spec./g.l.c. and by comparison with authentic specimens. Bromopentamethylbenzene, bromomesitylene, and 1-bromo-2,6-dimethylbenzene similarly gave the respective polymethylbenzenes (33—37%); the yields of the corresponding mixtures of bibenzyls decreased as the degree of methylation increased (38, 20, 4, and 0% respectively). In analogous reactions using sodamide as the base the same products were formed but in different amounts; no reaction occurred at low temperatures.



SCHEME

Reaction of bromodurene with potassium t-butoxide in cyclohexene gave durene (66%) and solvent derived products (III, 19%; IV, 4%; and V, 43%). Bromopentamethylbenzene and chlorodurene reacted similarly.

In the case of undiluted bromodurene, these experiments suggest initial nucleophilic attack on bromine to give (VI) and on a side-chain proton to give (VII), and so on *via* (VIII) as in steps (i)—(iv) of the Scheme. Alternatively bibenzyls could be formed by a radical route, possibly *via* (IX) and its subsequent reaction as a triplet [steps (v) →

(vi) → II], or *via* the formation and homolysis of t-butyl hypobromite. No products delivered from the latter could be detected (g.l.c.), however.

Similar considerations apply to the reaction in cyclohexene.

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¹ J. I. G. Cadogan, J. K. A. Hall, and J. T. Sharp, *J. Chem. Soc. (C)*, 1967, 1860.