Bromination of Cumene and Some 4-Hydroxycumenes with *N*-Bromosuccinimide

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Bromination of cumene with *N*-bromosuccinimide yielded 1,2-dibromo-2-phenylpropane, whereas 4-hydroxycumene gave either 3-bromo-4-hydroxycumene, 3,5-dibromo-4-hydroxycumene, or 1,3-dibromo-2-(3,5-dibromo-4-hydroxyphenyl)propene depending on the excess of reagent used. Similarly 4-hydroxy-3,5-di-t-butylcumene gave either 1,3-dibromo-2-(4-hydroxy-3,5-di-t-butylphenyl)propene or 1,3-dibromo-2-(2-bromo-4-oxo-3,5-di-t-butylcyclohexa-2,5-dienyl)propene.

In an attempt to prepare 2-bromo-2-(4-hydroxy-3,5-dit-butylphenyl)propane (Ia) which was required as an intermediate in the synthesis of certain 4-hydroxybenzyl dithiocarbamates,¹ 4-hydroxy-3,5-di-t-butylcumene (Ib) was brominated using N-bromosuccinimide (NBS). The reaction, which evolved considerable amounts of hydrogen bromide, gave however, only a small yield (ca. $2\cdot5\%$) of 1,3-dibromo-2-(4-hydroxy-3,5-di-t-butylphenyl)propene (IIa).

An increase in the ratio of N-bromosuccinimide to phenol from 1:1 to 3:1 had no effect on the yield of the

reaction yielded 3-bromo-4-hydroxycumene (Ic) and 3,5-dibromo-4-hydroxycumene (Id) respectively. An increase in the ratio to 3:1 led to an increased yield of the dibromo-compound, while four moles of N-bromosuccinimide to one of phenol gave side-chain halogenation with eventual formation of 1,3-dibromo-2-(3,5-dibromo-4-hydroxyphenyl)propene (IIc). With larger excesses of N-bromosuccinimide, an amorphous material with i.r. absorptions due to hydroxy and carbonyl was obtained suggesting that this was possibly a tautomeric mixture of the pentabromo-compounds (IId) and (IIIb).



dibromo-compound, but a ratio of four moles of *N*-bromosuccinimide to one of phenol led to 1,3-dibromo-2-(2-bromo-4-oxo-3,5-di-t-butylcyclohexa-2,5-dienyl)-

propene (IIIa). The structures of these compounds were established after examination of their ¹H n.m.r. and i.r. spectra. The ¹H n.m.r. spectrum of (IIa) showed singlets at $\tau 2.85$ (2H, aromatic), 3.55 (1H, vinyl), 4.85(OH), 5.65 (2CH₂) and 8.55 (18H, 2Bu^t). The i.r. spectrum of (IIa) showed absorption at 3650 cm.⁻¹ (OH) while that of (IIIa) showed absorption at 1640 cm.⁻¹ $\alpha\beta$ -unsaturated carbonyl).

The reason for the existence of the tribromo-compound in the keto and not in the tautomeric phenolic form (IIb) is clear from examination of molecular models of both structures. The introduction of the third bromine atom into the benzene ring causes very considerable steric crowding resulting in loss of planarity and formation of the relatively uncrowded keto-form.

The corresponding reactions using p-hydroxycumene in place of 4-hydroxy-3,5-di-t-butylcumene led to initial bromination of the nucleus. With one and two moles of N-bromosuccinimide to one of p-hydroxycumene, the Molecular models indicated that both structures are sterically feasible.

Treatment of cumene with N-bromosuccinimide yielded 1,2-dibromo-2-phenylpropane which was identified by comparison with an authentic specimen obtained by the photobromination of cumene.² The optimum yield (66%) obtained by using two moles of N-bromosuccinimide is superior to that (46.8%) obtained by the photobromination procedure.

The isolation of 1,2-dibromo-2-phenylpropane from bromination of cumene suggests that the corresponding phenolic compounds are possibly intermediates in the formation of 1,3-dibromo-2-(4-hydroxy-3,5-di-t-butylphenyl)propene and 1,3-dibromo-2-(3,5-dibromo-4-hydroxyphenyl)propene. The presence of the hydroxygroup would, however, facilitate loss of the tertiary bromine leading to a dehydrobrominated intermediate (IV) which could then suffer allylic bromination to yield the 1,3-dibromopropene product (II).

¹ A. O. Fitton, A. Rigby, and R. J. Hurlock, preceding paper. ² G. A. Russell and H. C. Brown, J. Amer. Chem. Soc., 1955, 77, 4025.

N-Bromosuccinimide was purified by the method of Dauben and McCoy.³ I.r. spectra were determined for Nujol mulls or for liquid films and n.m.r. spectra were peroxide (50 mg.). After cooling to moderate the initial exothermic reaction, the mixture was heated under reflux for 0.5-2 hr., then cooled, and the precipitate of succinimide was filtered off. Evaporation of the carbon tetra-

	Ratio of NBS:	Dura- tion of			М.р.					Relevant
	com-	reflux		Yield	or	Found		Reqd.	N.m.r. data	i.r. data
Compound	pound	(hr.)	Product	(%)	b.p.	(%)	Formula	(%)	$(\tau \text{ values})$	(cm1)
(Ib)	1:1	1	(IIa)	$2 \cdot 5$	86° a	C, 50·5 H. 6·0	$\mathrm{C_{17}H_{24}Br_{2}O}$	C, 50·5 H. 6·0	8.55, 5.65, 5.85, 3.55, 2.85	3650 (OH hindered)
(Ib)	4:1	2	(IIIa)	27	136— 137 ^b	C, 42·5 H, 4·8	$\mathrm{C_{17}H_{23}Br_{3}O}$	C, 42·3 H, 4·8	8.7, 5.5, 3.0, 2.9 (d, J 3 c./sec.), 2.7 (d, J 3 c./sec.)	1640 ($\alpha\beta$ - unsat.
4-Hydroxy- cumene	1:1	0.2	(Ic) °	12	85/4·5 mm.	C, 50·7 H, 5·4	C ₉ H ₁₁ BrO	C, 50·3 H, 5·2	8-85d, 7·25 (m, J 7 c./sec.) 4·75, 3·1 (d, J 20 c./sec.), 2·95 (d, J 18 c./ sec.), 2·9 d, J 18 c./sec.)	3550 (OH, br) 1380 (gem- di-Me)
4-Hydroxy- cumene	2:1	0.5	(Id) •	41 ^d	104/0·7 mm.	C, 36·8 H. 3·3	$\mathrm{C_9H_{10}Br_2O}$	C, 36·8 H. 3·4	8.85d, 7.25 (m, J 7 c./sec.), 4.3, 2.75	3550 (OH hindered)
4-Hydroxy- cumene	4:1	1	(IIc)	10	96—98	C, 24·3 H 1·3	$C_9H_6Br_4O$	C, 24.0 H. 1.3	5.65, 4.1, 3.4, 2.5	3650 (OH) hindered)
Cumene	2 : 1 (optimum)	1	1,2-Dibromo- 2-phenyl- propane	66		· ,		_, _ •		·/

Table of results

^a Distillate solidified and was crystallised from light petroleum (b.p. 40-60°). ^b Distillate solidified and was crystallised from ethanol. ^c No hydrogen bromide evolution observed. ^d Yield increased to 70% by increase in ratio to 3:1. ^e Product purified chromatographically on silica gel by elution with benzene-light petroleum (b.p. 40-60°); (Id) (3%) was also obtained from this reaction. I Reaction mixture separated by g.l.c. and main product identified by comparison with an authentic specimen.²

determined at 60 Mc./sec. for carbon tetrachloride solutions (tetramethylsilane as internal reference).

distilled.

The experimental procedure was similar in all cases and is outlined below. Any minor modifications to the general method are listed after the Table.

Bromination with N-Bromosuccinimide.-To the cumene derivative (0·1m) in carbon tetrachloride (100 ml.) was added N-bromosuccinimide (0.1-0.4M) and dibenzoyl chloride from the filtrate gave an oil which was fractionally

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³ H. J. Dauben and L. L. McCoy, J. Amer. Chem. Soc., 1959, 81, 4863, 5404.