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THE BROMINATION OF METHYLARENES WITH NBS BY IRRADIATION USING A TUNGSTEN LAMP. PREPARATION OF BENZOTRIBROMIDES

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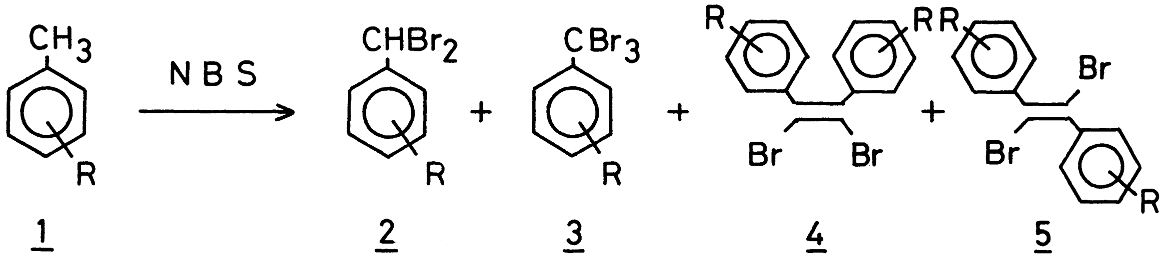
Bromination of toluene and its meta- and para-substituted derivatives with NBS by irradiation using a tungsten lamp gave benzotribromides and cis- and trans-1,2-dibromo-1,2-diarylethylenes, while ortho-substituted toluenes gave benzal bromides. o-Xylene gave tetra- and pentabromides and m-xylene afforded a mixture of dibromodiarylethylenes.

N-Bromosuccinimide (NBS) is a useful reagent for brominating in the allylic and benzylic positions.1) The bromination of toluene derivatives gave benzyl and benzal bromides respectively, depending upon the amount of NBS used.2) On the other hand, benzotribromide3,4) was prepared under harsh conditions from benzyl or benzal bromide by the bromination with Br_2 or CBr_4. No paper deals with the preparation of tribromomethylarenes by the reaction with NBS except the report by Kutney et al.;5) 4-methylpyridine exclusively afforded 4-tribromomethylpyridinium bromide.

Recently, dichlorine monoxide (Cl_2O)6) was shown as a powerful and selective chlorinating reagent which chlorinated toluene derivatives under mild conditions to give relatively inaccessible trichloromethylarenes.

Now, we report our finding that the NBS-bromination of meta- and para-substituted methylarenes by irradiation using a tungsten lamp gave the corresponding benzotribromides, while ortho-substituted derivatives afforded benzal bromides.

A mixture of toluene (1a) and NBS in CCl$_4$ was externally irradiated with a tungsten lamp[7] without cooling of the reaction vessel. The reaction was monitored with ^{1}H-NMR and VPC. As shown in Table 1, a mixture of di- and tribromo-



1a: R=H
1b: R=p-Br
1c: R=m-NO$_2$
1d: R=p-CH$_3$O
1e: R=o-Br
1f: R=o-CH$_3$O
1g: R=m-CH$_3$
2a: R=H
2e: R=o-Br
2f: R=o-CH$_3$O
3a: R=H
3b: R=p-Br
3c: R=m-NO$_2$
3d: R=p-CH$_3$O
4,5a: R=H
4,5b: R=p-Br
4,5c: R=m-NO$_2$
4,5g: R=m-CBr$_3$

Table 1. Bromination of methylarenes (1) with NBS by irradiation

1	Time/h	NBS/1[a]	Products,	Yield/%[b,c]						
a	0.5	3.1	2a,	(39)	3a,[d]	(53)	4a[e] +	5a,[e]	(8)	
a	1.5	3.1	2a,	(5)	3a,	(82)	4a +	5a,	(13)	
a	2.5	3.3			3a,	64	4a,	4	5a,	3
a	4	3.1			3a,	(78)	4a +	5a,	(22)	
a	8	3.1			3a,	(60)	4a +	5a,	(40)	
b	2.5	3.3			3b,[f]	56	4b,[g]	18	5b,[g]	5
c	4	3.1			3c,	46[h]	4c,[g]	25[i]	5c,	22[i]
d	0.5	3.1			3d,	92[h]				
e	1.5	2.2	2e,[j]	75						
f	1.5	2.2	2f,	68[k]						
g	9	6.1					4g,[g]	43[i]	5g,[g]	43[i]

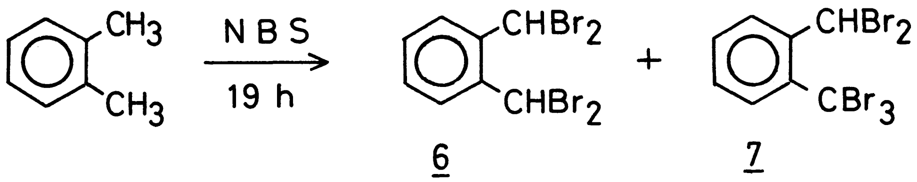
a) Molar ratio. b) Isolated yields are given unless otherwise stated. c) Yields in parentheses are relative yields determined by VPC. d) Ref. 4. e) H. Limpricht and H. Schwanert, Ber., 4, 379 (1871). f) M. Markarian, J. Am. Chem. Soc., 74, 1858 (1952). g) Satisfactory elemental analyses and spectral data were obtained. h) Determined as ethyl benzoates as stated in the text. i) Obtained as a mixture and determined by VPC. j) Ref. 10. k) An yield of the aldehyde as stated in the text.

methylbenzenes (2a and 3a), and cis- and trans-1,2-dibromo-1,2-diphenylethylenes (4a and 5a) were formed in an early stage of the reaction. Compound 2a disappeared in a short time and after 2.5 h, 3a, 4a, and 5a were obtained in 63, 4, and 3% yields, respectively. Further irradiation caused the conversion of 3a into 4a and 5a as shown in Table 1.

In the bromination of 1b and 1c bearing an electron-withdrawing group, 3b and 3c were formed, accompanied also by ethylenes 4b and 5b, and 4c and 5c, respectively. On the other hand, 1d having the electron-releasing methoxy group gave exclusively 3d in a high yield and even a prolonged irradiation did not yield the corresponding ethylenes. As 3c and 3d are unstable and could not be purified, their yields were determined as their ethyl benzoates.[8,9]

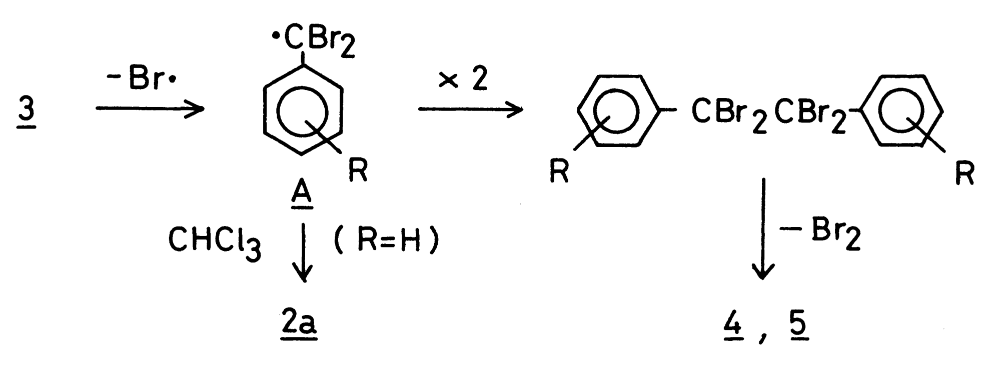
Substituent on the ortho-position obstructed the introduction of the third bromine atom. Thus, 1e gave the dibromide 2e[10] even when 3.3 equiv. of NBS was used and 1f gave the moisture-sensitive 2f which was easily hydrolyzed to afford o-methoxybenzaldehyde in 68% yield.

Next, the bromination of xylenes was investigated. o-Xylene gave the tetra- and pentabromides[11] (6 and 7) in 38 and 42% yields, but the hexabromide was



not formed. In the reaction of m-xylene (1g), a 1:1-mixture of cis- and trans-ethylenes (4g and 5g) was obtained in 86% yield, probably via the hexabrominated derivative.

Finally, the pathway leading to the formation of 4 and 5 is shown. Although



3a is stable in refluxing CCl_4, it gave 4a and 5a in 30 and 31% yields, respectively, when irradiated with a tungsten lamp in refluxing CCl_4 for 24 h. When irradiated in $CHCl_3$ at reflux for 4 h, 3a gave a mixture of 2a, 3a, 4a, and 5a in the ratio of 23:59:9:9. Thus, photo-induced reaction of 3 involves the cleavage of C-Br bond to yield the radical A which undergoes dimerization followed by elimination of a bromine molecule to give 4 and 5. Formation of 2a in the photolysis of 3a in $CHCl_3$ provides an evidence for the intermediacy of A.

Typical Procedure: A mixture of 1a (0.92 g) and NBS (5.87 g) in CCl_4 (50 ml) was externally irradiated with a tungsten lamp for 2.5 h and succinimide was filtered. The filtrate was evaporated in vacuo to leave a yellow solid which was chromatographed on silica gel using hexane as an eluent. Compound 3a (2.09 g) was first eluted, followed by 5a (0.05 g) and 4a (0.06 g).

Further investigation is in progress and will be reported in near future.

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