Halogenation Using Quaternary Ammonium Polyhalides. XIX.[1] Aromatic Chlorination of Arenes with Benzyltrimethylammonium Tetrachloroiodate

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Synopsis. The reaction of arenes with a calculated amount of benzyltrimethylammonium tetrachloroiodate in acetic acid at room temperature or at 70 °C gave nuclear chloro-substituted arenes in fairly good yields.

Direct aromatic chlorination of arenes (**1**) with chlorine has usually been carried out in the presence of a catalyst such as iodine, iron(III) chloride, or an aluminium-mercury couple. As the chlorinating agents which are easier to handle than toxic gaseous chlorine, sulfuryl chloride,[2] iodine trichloride,[3] titanium(IV) chloride,[4] copper(II) chloride,[5] alumina-supported copper(II) chloride,[6] antimony(V) chloride,[7] tellurium(IV) chloride,[8] trichloroisocyanuric acid,[9] and poly(*N*-chloromaleimide),[10] etc. have been used to chlorinate **1**.

As one part of our investigation concerning the halogenation of aromatic compounds with quaternary ammonium polyhalides, we have recently found that a new reagent, benzyltrimethylammonium tetrachloroiodate (BTMA ICl_4), is an effective chlorinating agent.[1,11] In this paper we wish to report on the aromatic chlorination of **1** by the use of BTMA ICl_4.

Results and Discussion

A reaction of **1** with BTMA ICl_4 in acetic acid at room temperature or at 70 °C gave aromatic chloro-substituted arenes (**2**) together with benzyltrimethylammonium dichloroiodate (BTMA ICl_2).[12] Thus, the produced BTMA ICl_2 is easily separable from the reaction mixture, since BTMA ICl_2 is hardly

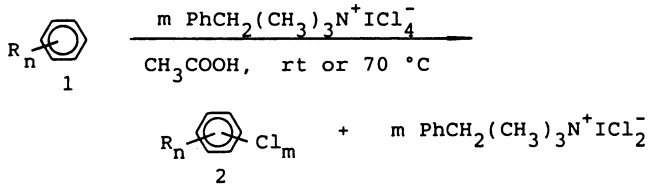


Table 1. Aromatic Chlorination of Arenes(**1**) with BTMA ICl_4 in AcOH

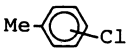
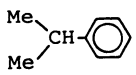
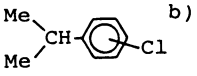
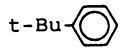
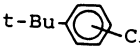
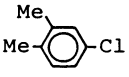
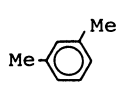
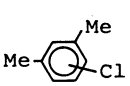
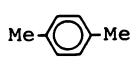
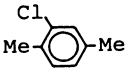
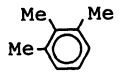
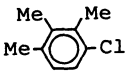
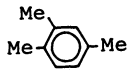
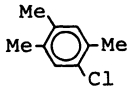
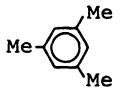
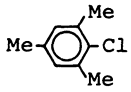
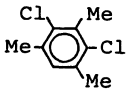
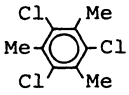
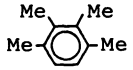
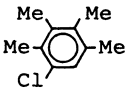
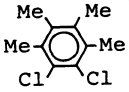
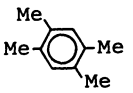
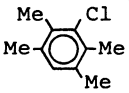
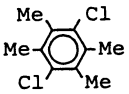
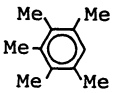
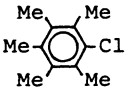
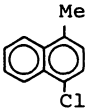
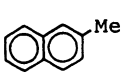
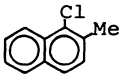
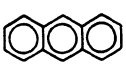
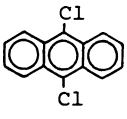
Substrate **1**	Molar ratio BTMA ICl_4/**1**	Reaction conditions Time/h	Temp/°C	Product **2**	Yield[a] %	Mp(°C) or Bp(°C/mmHg) Found	Reported
 (**1a**)	1.0	48	70	 (**2a**)	16	132—133/760	131.65—131.66/760[13]
 (**1b**)	1.0	24	70	 (**2b**)	88[c]	158—161/760	—
 (**1c**)	1.0	20	70	 (**2c**)	30[d]	187—189/760	—
 (**1d**)	1.0	20	70	 (**2d**)	66[e]	213—215/760	—
 (**1e**)	1.0	20	70	 (**2e**)	70	194—196/760	193—197/760[14]
 (**1f**)	1.0	20	rt	 (**2f**)	90[f]	185—187/760	—
 (**1g**)	1.0	20	70	 (**2g**)	66	185—187/760	186.8/760[15]

Table 1. (Continued)

Substrate 1	Molar ratio BTMA ICl_4/1	Reaction conditions Time/h	Temp/°C	Product 2	Yield[a] %	Mp(°C) or Bp(°C/mmHg) Found	Reported
 (1h)	1.0	20	rt	 (2h)	81	218—220/760	86—87/16[16]
 (1i)	1.0	20	rt	 (2i)	52	67—68	70.5—71[16]
 (1j)	1.0	22	rt	 (2j-1)	90	205—206/760	86—86.8/14[17]
1j	2.0	22	70	 (2j-2)	95	59—60	58—59[16]
1j	3.0	24	70	 (2j-3)	98	205.5—206	204—205[18]
 (1k)	1.0	20	rt	 (2k-1)	76	242—244/760	131—132/24[16]
1k	2.0	20	rt	 (2k-2)	96	189—191	193[19]
 (1l)	1.0	20	rt	 (2l-1)	73	43.5—44.5	47.5—48[16]
1l	2.0	20	rt	 (2l-2)	94	187—190	189—189.5[16]
 (1m)	1.0	20	rt	 (2m)	96	152—153	155[20]
 (1n)	1.0	24	70	 (2n)	65	256—258/760	106.5/5[21]
 (1o)	1.0	18	70	 (2o)	73	271—273/760	132.5—136/12[22]
 (1p)	1.0	15	70	 (2p)	95	273—275/760	120—122/4.5[2]
 (1q)	1.0	18	rt	 (2q-2)	40	212—213	214—215[23]
1q	2.0	24	rt	2q-2	99	212—213	214—215[23]

a) Yield of isolated product. b) Product was obtained as a mixture of 4- and 2-chloro derivatives, and its isomer ratio was determined by GC analysis and / or ^1H NMR spectrum. c) 4-Chloro deriv. / 2-chloro deriv. =3/7. d) 4-Chloro deriv. / 2-chloro deriv. =1/1. e) 4-Chloro deriv. / 2-chloro deriv. =7/3. f) 4-Chloro deriv. / 2-chloro deriv. =2/1.

soluble in acetic acid at room temperature. The results are summarized in Table 1.

The reaction of such polyalkylbenzenes as 1,3,5-trimethylbenzene (**1j**), 1,2,3,4-tetramethylbenzene (**1k**), and 1,2,4,5-tetramethylbenzene (**1l**), with equivalent weights of BTMA ICl_4 gave the desired mono-, di-, or trichloro-substituted arenes selectively. For example, the reactions of **1j** with 1.0, 2.0, and 3.0 equiv of BTMA ICl_4 gave 1-chloro- (**2j-1**), 1,3-dichloro- (**2j-2**), and 1,3,5-trichloro-2,4,6-trimethylbenzene (**2j-3**), in good yields, respectively.

We emphasize that the stable reagent BTMA ICl_4 is an excellent chlorinating agent for **1** since it can be treated safely and quantitatively in comparison with toxic gaseous chlorine. Readily separable by-product BTMA ICl_2 can be easily converted to BTMA ICl_4 by treatment with chlorine in dichloromethane.[24]

However, benzene and isopropylbenzene gave chloro-substituted products in poor yields, respectively, even with a Lewis acid-catalyst such as iron(III) chloride, titanium(IV) chloride, or zinc chloride.

Experimental

1-Chloro-2,4,6-trimethylbenzene (2j-1); General Procedure: To a solution of 1,3,5-trimethylbenzene (**1j**) (0.50 g, 4.16 mmol) in acetic acid (30 ml) was added BTMA ICl_4 (1.74 g, 4.16 mmol). The mixture was stirred for 22 h at room temperature. During the period of stirring BTMA ICl_4, which was only slightly soluble in acetic acid, gradually reacted with **1j** to give a product and a yellow precipitate. The precipitate (BTMA ICl_2, 1.02 g, 2.93 mmol) was filtered off. The filtrate was treated with 5% $NaHSO_3$ (20 ml) and then extracted with hexane (25 ml×4). The hexane solution was washed with 5% $NaHCO_3$ (30 ml) and was purified by column chromatography on alumina. The eluent was concentrated in vacuo to give an oily residue which was distilled, affording **2j-1** as a colorless liquid; yield 0.58 g (90%); bp 205—206 °C/760 mmHg (lit,[17] bp 86—86.8 °C/14 mmHg).

References

1) Part XVIII; S. Kajigaeshi, Y. Shinmasu, S. Fujisaki, and T. Kakinami, *Chem. Lett.*, **1989**, 415.

2) P. B. D. de la Mare and H. Suzuki, *J. Chem. Soc. C*, **1967**, 1586.

3) E. Campaigne and W. Thompson, *J. Am. Chem. Soc.*, **72**, 629 (1950).

4) G. K. Chip and J. S. Grossert, *Can. J. Chem.*, **50**, 1233 (1972).

5) D. C. Nonhebel, *Org. Synth.*, **43**, 15 (1963).

6) M. Kodomari, H. Satoh, and S. Yoshitomi, *J. Org. Chem.*, **53**, 2093 (1988).

7) P. Kovacic and A. K. Sparks, *J. Am. Chem. Soc.*, **82**, 5740 (1960).

8) M. Albeck and S. Shaik, *J. Chem. Soc., Perkin Trans. 1*, **1975**, 1223.

9) E. C. Juenge, D. A. Beal, and W. P. Duncan, *J. Org. Chem.*, **35**, 719 (1970).

10) C. Yaroslavsky and E. Katchalski, *Tetrahedron Lett.*, **1972**, 5173.

11) S. Kajigaeshi, T. Kakinami, H. Ikeda, and T. Okamoto, *Chem. Express*, **3**, 659 (1988).

12) S. Kajigaeshi, T. Kakinami, H. Yamasaki, S. Fujisaki, M. Kondo, and T. Okamoto, *Chem. Lett.*, **1987**, 2109.

13) R. H. Myers, M. E. Hobbs, and P. M. Gross, *J. Am. Chem. Soc.*, **76**, 4737 (1954).

14) D. R. Lyon, F. G. Mann, and G. H. Cookson, *J. Chem. Soc.*, **1947**, 662.

15) R. L. Datta and F. V. Fernandes, *J. Am. Chem. Soc.*, **38**, 1809 (1916).

16) L. I. Smith and C. L. Moyle, *J. Am. Chem. Soc.*, **58**, 1 (1936).

17) G. Illuminati and G. Marino, *J. Am. Chem. Soc.*, **78**, 4975 (1956).

18) C. P. Smith and G. L. Lewis, *J. Am. Chem. Soc.*, **62**, 949 (1940).

19) A. H. White, B. S. Biggs, and S. O. Morgan, *J. Am. Chem. Soc.*, **62**, 16 (1940).

20) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **79**, 5169 (1957).

21) A. I. Vogel, *J. Chem. Soc.*, **1948**, 654.

22) J. Sauer, R. Huisgen, and A. Hauser, *Chem. Ber.*, **91**, 1461 (1958).

23) Y. Nagai and M. Tanabe, *Kogyo Kagaku Zasshi*, **60**, 294 (1957).

24) S. Kajigaeshi, T. Kakinami, M. Moriwaki, T. Tanaka, and S. Fujisaki, *Tetrahedron Lett.*, **29**, 5783 (1988).