Chlorination of Some Aromatic Compounds with Tetrabutylammonium Trichloride[1)]

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Abstract

Tetrabutylammonium trichloride (TBA Cl_3) was prepared by bubbling chorine gas into a solution of tetrabutylammonium chloride in CH_2Cl_2. The reaction of such aromatic compounds as phenol, aniline, anisole, acetanilides, arenes, acetophenone, and styrene, with TBA Cl_3 in appropriate solvent at room temperature gave the corresponding chloro-substituted compounds, respectively.

For the chlorination of aromatic compounds, various reagents have been used in place of toxic gaseous chlorine. For example, t-butyl hypochlorite,[2)] sulfuryl chloride,[3)] N-chlorosuccinimide,[4)] copper(II) chloride,[5)] titanium(IV) chloride,[6)] trichloroisocyanuric acid,[7)] hexachlorocyclohexadienone derivatives,[8)] and N-Chlorotriethylammonium chloride,[9)] etc. have been used to chlorinate aromatic compounds.

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.[10)] In this paper, we wish to report on the electrophilic chlorination of aromatic compounds by use of tetrabutylammonium trichloride (TBA Cl_3).

Results and Discussion

TBA Cl_3, a hygroscopic solid (pale yellow), can be prepared by bubbling chlorine gas into a solution of tetrabutylammonium chloride (TBA Cl) in CH_2Cl_2. In this case, TBA Cl was prepared by passing aqueous solution of tetrabutylammonium bromide (TBA Br) through a column packed with anion exchange resin (Amberlite IRA-400[11)]) which was previously treated by 4 N-HCl.

The reaction of aromatic compounds such as phenol (**1a**), aniline (**1b**), anisole (**1c**), acetanilides (**1d**), arenes (**1e**), and acetophenone (**1f**) with TBA Cl_3 in CCl_4, CH_2Cl_2, or $CH_3COOH/ZnCl_2$ at room temperature gave the corresponding chloro-substituted compounds. The reaction of styrene (**1g**) with TBA Cl_3 in CH_2Cl_2 gave the addition products. These results are summarized in Table 1.

We can notice that TBA Cl_3 is a solidified matter of gaseous chlorine, and is an

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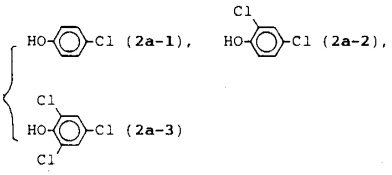
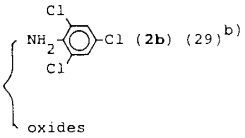
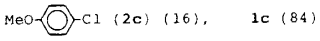
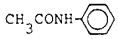
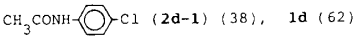
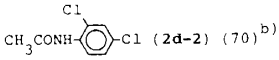
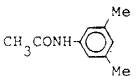
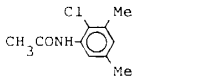
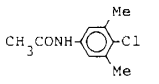
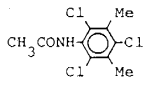
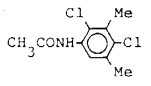
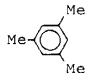
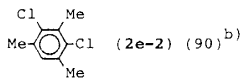
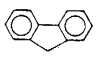
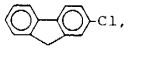
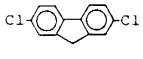
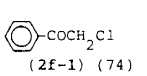
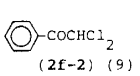
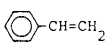
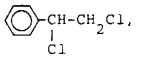
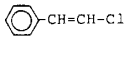
Table 1 Chlorination of Aromatic Compounds (1) with TBA Cl_3

Substrate (1)	Molar ratio TBA Cl_3/1	Solvent	Catalyst	Reaction time (h)	Product (2) (Yield %)[a]
 (1a)	3.1	CH_3COOH	-	3	 (2a-1), (2a-2), (2a-3)
 (1b)	3.0	CH_2Cl_2	$NaHCO_3$	5 min	 (2b) (29)[b], oxides
 (1c)	1.1	CH_3COOH	$ZnCl_2$	48	 (2c) (16), 1c (84)
 (1d)	1.0	CH_3COOH	-	3	 (2d-1) (38), 1d (62)
1d	3.1	CH_3COOH	-	3	 (2d-2) (70)[b]
 (1d')	1.1	CH_3COOH	$ZnCl_2$	20	 (2d'-1) (50)  (2d'-1') (50)
(1d')	3.1	CH_3COOH	$ZnCl_2$	20	 (2d'-3) (10)  (2d'-2) (90)
 (1e)	3.0	CH_3COOH	$ZnCl_2$	1	 (2e-2) (90)[b]
 (1e')	1.1	CH_2Cl_2	CH_3OH	12	 (2e'-1) (27)  (2e'-2) (23), (1e') (50)
 (1f)	1.1	CH_2Cl_2	-	12	 (2f-1) (74)  (2f-2) (9), (1f) (17)
 (1g)	1.1	CH_2Cl_2	-	3	 (2g-1) (66)  (2g-2) (34)

a) Yield was based on ^1H NMR. b) Yield of isolated product.

available and safe chlorinating agent for the aromatic compounds compared with toxic chlorine. However, unfortunately, its hygroscopic character brings about some difficulty to treat itself.

Experimental

Preparation of Tetrabutylammonium Trichloride (TBA Cl_3)

Hydrochloric acid (3-N, 500 ml) was added into a column (d ; 3.6 cm, l ; 28 cm) packed with power of Amberlite IRA-400, and the contents washed with water until effuent water showed pH= 5 . Then, a solution of tetrabutylammonium bromide (30 g, 93 mmol) in water (100 ml) was added into the column. The effuent solution was concentrated to afford tetrabutylammonium chloride (TBA Cl) as a white crystals ; yield 21.99 g (85%) ; mp 47-49℃ (lit.[12] 47-50℃).

Chlorine gas was bubbled enough into a solution of TBA Cl (22 g, 79 mmol) in CH_2Cl_2 (40 ml). The solvent was distilled off, and the obtained residue was dried under reduced pressure to give TBA Cl_3 as yellow crystals ; yield 20.3 g (74%). This crystals was an appreciably hygroscopic. Found : C, 54.93 ; H, 10.73 ; N, 4.07%. Calcd for $C_{16}H_{36}NCl_3$: C, 55.09 ; H, 10.40 ; N, 4.02%.

2,4-Dichloroacetanilide (2d-2) ; Typical Procedure : To a solution of acetanilide (1d-1) (0.50 g, 3.70 mmol) in acetic acid (20 ml) was added TBA Cl_3 (4.00 g, 11.47 mmol). The mixture was stirred for 3 h at room temperature, and then poured into a water (60ml). Obtained precipitate was filtered, washed with water, and was recrystallized from methanol-water (1 : 3) affording **2d-2** as colorless crystals ; yield 0.53 g (70%) ; mp 144-146℃ (lit. [13] mp 143-146℃).

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