

Friedel-Crafts Reaction of 1,3,5-Trialkylbenzenes with Sulfur Monochloride and *N*-Chlorodimethylamine

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Synopsis. The reaction of sulfur monochloride gave 2,4,6-tri-*t*-butylchlorobenzene (**3**) from 1,3,5-tri-*t*-butylbenzene (**1**), but gave the corresponding sulfide and disulfide from mesitylene (**2**). The reaction of *N*-chlorodimethylamine gave **3**, 2-chloro-3,5-di-*t*-butyltoluene and 2,4,6-trimethylchlorobenzene from **1**, 3,5-di-*t*-butyltoluene and **2**, respectively. The reaction of *N*-chlorodimethylamine with benzene gave chlorobenzene or *N,N*-dimethylaniline in 1-nitropropane or nitromethane.

The Friedel-Crafts reaction of sulfur monochloride gives diphenyl sulfide from benzene,¹⁾ and diaryl sulfide and disulfide from substituted benzene.²⁾ Similarly, *N*-chlorodimethylamine gives *N,N*-dimethylanilines in reactions with benzene and substituted benzenes.³⁾ We have found that the Friedel-Crafts reaction of 1,3,5-tri-*t*-butylbenzene (**1**) with phosphorus trichloride gave an abnormal product, *t*-butyl-3,5-di-*t*-butylphenylphosphinic chloride.⁴⁾

Therefore, the Friedel-Crafts reaction of 1,3,5-tri-alkylbenzenes with sulfur monochloride or *N*-chlorodimethylamine was investigated.

Reaction with Sulfur Monochloride in the Dark. In the case of **1**, 2,4,6-tri-*t*-butylchlorobenzene (**3**) was always obtained (Table 1). Use of aluminum chloride as a catalyst gave a yellow tarry material and the yield of **3** was lower than when iron powder was used. The reaction of mesitylene (**2**) in the presence of iron powder at 0 °C gave a mixture of dimesityl sulfide (**4**) and disulfide (**5**); their yields were 64 and 15%, respectively, by gas chromatography (glc).

Reaction with *N*-Chloromethylamine. Compounds **1,2**, and 3,5-di-*t*-butyltoluene (**6**) were allowed to react

in the presence of anhydrous aluminum chloride in nitromethane, nitrobenzene, or 1-nitropropane as solvents. Reaction with **1** gave always **3** (Table 2). The best result was obtained in 1-nitropropane by use of five molar amounts of *N*-chlorodimethylamine (Run 4). This method is applicable to the preparation of **3**, because **3** has been prepared from **1** through nitration, reduction, diazotization, and then Sandmeyer reaction.⁵⁾

The reaction of **2** with five molar amounts of *N*-chlorodimethylamine in nitropropane at room temperature gave 60%¹ of 2,4,6-trimethylchlorobenzene (**7**), a trace of 2,4-dichloromesitylene (**8**), and 3% of 3,3'-dichloro-2,4,6,2',4',6'-hexamethylbiphenyl (**9**). A similar reaction of **6** at 60 °C gave 65% of 2-chloro-3,5-di-*t*-butyltoluene (**10**).

The reaction of **2** in nitromethane gave **7** (38%), bimesityl (**11**, 4%), and 2,4,6-trimethylbenzonitrile (**12**, 2.6%). The nitrile (**12**) was also obtained from the Friedel-Crafts reaction of **2** with nitromethane.⁶⁾

Since **2** gave chloride (**7**), the reaction with benzene⁹⁾ was re-examined. The reaction in 1-nitropropane gave only chlorobenzene, but the reaction in nitromethane gave *N,N*-dimethylaniline. This difference is very interesting, but the reason for it is still obscure.

Experimental

All boiling and melting points are uncorrected. All reactions were carried out under nitrogen.

Materials. 1,3,5-Tri-*t*-butylbenzene (**1**)⁷⁾ (mp 73—74.5 °C), 3,5-di-*t*-butyltoluene (**6**)⁸⁾ (mp 29.5—31 °C), and *N*-chlorodimethylamine⁹⁾ (bp 43—44 °C) were prepared by the reported methods.

Reaction of **1 with Sulfur Monochloride (**13**).** A typical procedure is described below. To a stirred mixture of **1** (9.91 g, 40 mmol) and iron powder (13 mg, 0.23 mg-atom) in CS₂ (10 ml) was added dropwise **13** (5.9 g, 44 mmol) in CS₂ (5 ml) over 1.5 hr, and the mixture was stirred for an additional 4.5 hr. The reaction mixture was poured into water and extracted with ether and then CH₂Cl₂. The combined extracts were washed with water and dried with MgSO₄. After evaporation of solvent, ether was added to the residue to leave sulfur (1.65 g, 51.5 mg-atom). The filtrate was evaporated to leave 9.21 g as a residue, which was recrystallized three times from MeOH to give 1.31 g (12%)

TABLE 1. FRIEDEL-CRAFTS REACTION OF **1** WITH S₂Cl₂ IN CS₂

1 (mmol)	S ₂ Cl ₂ (mmol)	Cat. (mmol)	Temp.	Time (hr)	3 (%)
40	44	Fe 0.23	r.t.	6.0	57, ^{a)} 12 ^{b)}
17	25	Fe 0.42	0 °C	7.5	76, ^{c)} 16 ^{b)}
			then r.t.	24	
20	25	AlCl ₃ 3.2	0 °C	5.8	39, ^{a)} 10 ^{b)}

a) Determined by NMR. b) Isolated yields.

c) Contained a trace of sulfur.

TABLE 2. REACTIONS OF **1** WITH *N*-CHLORODIMETHYLAMINE

Run	1 (mmol)	AlCl ₃ (mmol)	Me ₂ NCl (mmol)	Solvent (mmol)	Temp. (°C)	Time (hr)	3 (%)
1	20	19	15	MeNO ₂ 200	80	4	35, ^{a)} 7.4 ^{b)}
2	20	16	15	PhNO ₂ 161	80	4	24, ^{a)} 8 ^{b)}
3	20	16	15	PrNO ₂ 201	80	4	35, ^{a)} 27 ^{b)}
4	20	23	100	PrNO ₂ 201	65—70	1	79 ^{b)}

a) Determined by NMR. b) Isolated yield.

of **3**, mp 156.5–160 °C (lit.⁵) 162 °C).

Reaction of 2 with 13. To a stirred mixture of **2** (30.2 g, 252 mmol) and iron powder (20.5 mg, 0.37 mg-atom) was added dropwise **13** (3.38 g, 25 mmol) in CS₂ (3 ml) over 1.5 hr at 0 °C. The mixture was stirred at room temperature for one day. After a similar treatment, distillation gave 5.4 g of a yellowish brown substance, bp 174 °C/3 mmHg, which was fractionally recrystallized five times from EtOH to give 1.1 g (15%) of **5**, mp 123.5 °C (lit.⁹) 123–124 °C), and 1.0 g (15%) of **4**, mp 90–91 °C (lit.¹⁰) 91–92 °C). The yields of **4** and **5** were estimated to be 64 and 15% by glc.

Reaction of 1 with N-Chlorodimethylamine (14). To a stirred solution of **1** (5.01 g, 20 mmol) in 1-nitropropane (13.5 ml) was added AlCl₃ (3.0 g, 22.5 mmol) and then **14** (7.96 g, 100 mmol) in 1-nitropropane (4.5 ml) dropwise at 0 °C. The mixture was stirred at 65–70 °C for 1 hr and poured into ice-water. The reaction mixture was made alkaline with aq. NaOH and extracted with CH₂Cl₂. After drying, distillation *in vacuo* gave crude **3** (5.62 g, 98%), mp 153–156 °C, which was recrystallized from MeOH, mp 161–162 °C, yield 4.50 g (79%).

Reaction of 2 with 14. a) *In 1-Nitropropane:* To a stirred mixture of **2** (4.84 g, 40 mmol), 1-nitropropane (3.58 g), and AlCl₃ (5.5 g, 41 mmol) was added dropwise **14** (15.9 g, 200 mmol) at 0 °C. The mixture was stirred at room temperature for 3 hr. After a similar treatment, distillation under vacuum gave **7** (3.73 g, 60%), bp 39–40 °C/1 mmHg (lit.¹¹) 51–52 °C/1.5 mmHg). The residue was chromatographed on silica gel with *n*-hexane to give 35 mg (0.5%) of **8**, mp 58.3–59.8 °C (lit.¹²) 59 °C), and 180 mg (3%) of **9**, mp 131.1–131.9 °C (lit.¹³) 130–131.5 °C).

b) *In Nitromethane:* A mixture of **2** (9.62 g, 80 mmol), AlCl₃ (4.0 g, 30 mmol), **14** (1.59 g, 20 mmol), and nitromethane (4.88 g) was stirred for 5 hr at 80 °C. After a similar treatment, distillation under vacuum recovered **2** (3.53 g, 37%). The residue was chromatographed on silica gel. Elution with *n*-hexane gave 1.18 g (38%) of **7** and 207 mg (4%) of **11**, mp 101.5–102 °C (from EtOH) (lit.¹⁴) 101–102 °C). Elution with CCl₄ gave 308 mg (2.6% based on **2** used) of **12**, mp 48–48.5 °C (from EtOH) (lit.¹⁵) 50–52 °C); IR (KBr): 2200 cm⁻¹.

Reaction of 6 with 14. A mixture of **6** (3.39 g, 16.6 mmol), **14** (6.43 g, 81 mmol), AlCl₃ (2.2 g, 16.5 mmol), and 1-nitropropane (14.3 g) was stirred for 3 hr at 60 °C. After a similar treatment, the residue of the distillation was chromatographed on silica gel with *n*-hexane to give 2.57 g (65%)

of **10**, bp 113 °C/2.5 mmHg. NMR (CCl₄): δ 1.30 (s, 9H, *t*-Bu), 1.50 (s, 9H, *t*-Bu), 2.36 (s, 3H, Me), 6.99–7.05 (d, *J*_{HCCCH} 3 Hz, 1H, Ar-H), and 7.20–7.26 (d, *J*_{HCCCH} 3 Hz, 1H, Ar-H). Found: C, 75.39; H, 9.68; Cl, 15.09%. Calcd for C₁₅H₂₃Cl: C, 75.45; H, 9.71; Cl, 14.85%.

Reaction of Benzene with 14. A solution of benzene (6.26 g, 80 mmol) in 1-nitropropane (7.15 g), AlCl₃ (4.0 g, 30 mmol), and then **14** (1.58 g, 20 mmol) were mixed under stirring at –10 °C, and stirred at 80 °C for 5 hr. The reaction mixture was treated similarly. *N,N*-Dimethylaniline could not be detected by glc. After drying, the distillation gave 701 mg (31%) of chlorobenzene, bp 130–133 °C.

A mixture of benzene (5.27 g, 67.5 mmol), AlCl₃ (3.3 g, 24.7 mmol), nitromethane (4.08 g), and **14** (1.38 g, 17.4 mmol) was stirred for 5 hr at 80 °C; a similar treatment gave 625 mg (30%) of *N,N*-dimethylaniline, bp 40 °C/1.8 mmHg.

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