396. *The Chemistry of Nitryl Chloride. Part III.*[1] *The Reaction with Naphthalene, Anisole, Phenol, and* p-*Diethoxybenzene.*

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The extent of the chlorination and nitration of naphthalene, anisole, phenol, and *p*-diethoxybenzene by nitryl chloride dissolved in an inert solvent has been measured. The principal reaction with anisole is chlorination and with phenol nitration. In the case of naphthalene and *p*-diethoxybenzene the two reactions proceed simultaneously.

It has been reported[1] that nitryl chloride chlorinates alkylbenzenes, the extent of nitration being almost negligible. On the other hand, Steinkopf and Kuhnel[2] found that only *o*-nitrophenol was formed when nitryl chloride interacted with phenol at low temperature, although at room temperature 2 : 4-dichloro-6-nitrophenol was obtained. Naphthalene was simultaneously chlorinated and nitrated, to give α-nitro- and α-chloronaphthalene. With anisole, they obtained a colourless easily decomposable product which appeared to be an addition compound: on decomposition, it evolved chlorine and nitrogen dioxide, leaving anisole. Price and Sears[3] studied the reactions of nitryl chloride with various aromatic compounds in the presence of Lewis acids such as aluminium

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[1] Part II, Gintz, Goddard, and Collis, *J.*, 1958, **445**.

[2] Steinkopf and Kuhnel, *Ber.*, 1942, **75**, 1323.

[3] Price and Sears, *J. Amer. Chem. Soc.*, 1953, **75**, 3276.

trichloride. They found that anisole, naphthalene, and phenol tended to undergo oxidative degradation; in the case of naphthalene they obtained a 31% yield of α-nitronaphthalene but with anisole and phenol they were only able to isolate traces of nitro-compounds. They found no evidence for chlorination.

The object of the present work was to study more closely the relative importance of chlorination and nitration, in the reaction of nitryl chloride with these more reactive aromatic nuclei. The results, which are tabulated, show that with anisole chlorination precedes nitration, and it is likely that nitration is due to nitrous acid formed in the chlorination. With naphthalene and *p*-diethoxybenzene the two reactions are simultaneous, and with phenol at low temperature nitration predominated. Lowering the temperature in the case of naphthalene reduced nitration and chlorination equally. A lower temperature could not be conveniently employed with *p*-diethoxybenzene since even at −80° both reactions were very rapid.

Compound	Temp.	NO_2Cl (mole/l.)	ArH : NO_2Cl	Solvent	Chlorination	Nitration
					(% based on initial NO_2Cl)	
Naphthalene ...	20°	0·22	3 : 1	CH_2Cl_2	62% in 2½ hr.	62% in 1½ hr.
Anisole	−20	1·9	1 : 1	,,	24% in 1 hr.	0% in 1 hr.
,, ...	,,	,,	,,	,,	46% in 1⅔ hr.	43% in 1⅔ hr.
,, ...	+5	1·7	1 : 1	C_6H_6	50% in 1¾ hr.	56% in 1¾ hr.
,, ...	+10	0·24	3 : 1	,,	35% in 1 hr.	0% in 1 hr.
Phenol	−60	0·13	3 : 1	CH_2Cl_2	14% in ½ hr.	62% in ½ hr.
p-$C_6H_4(OEt)_2$ ...	−80	0·13	1 : 1	,,	39% in ⅓ hr.	41% in ⅓ hr.
,, ...	+20	0·12	3 : 1	,,	58% in 1 hr.	69% in 1 hr.

Products of reaction with nitryl chloride.

Compound	Temp.	NO_2Cl (mole/l.)	ArH : NO_2Cl	Solvent	Reaction time	Products (and yields *)
Naphthalene	20°	1·2	2 : 1	CH_2Cl_2	1 hr.	1-Nitronaphthalene (45%)
Anisole	−20	1·9	1 : 1	,,	1⅔ hr.	Chloroanisoles (38%)
,, ...	+5	1·7	1 : 1	C_6H_6	1¾ hr.	,, (23%)
Phenol	−80	1·36	1 : 1	CH_2Cl_2	½ hr.	*p*-Nitrophenol (22%)
	−50° to +20°	0·52	1 : 2	,,	¼ hr.	2 : 4-Dichloro-6-nitrophenol (15%) 3 : 6-Dichloro-2-nitrophenol (5%)
p-$C_6H_4(OEt)_2$	−80	1·0	1 : 1	,,	½ hr.	1 : 4-Diethoxy-2-nitrobenzene (39%) 2-Chloro-1 : 4-diethoxybenzene (4%)

* Yields were based on the component in limited quantity, generally nitryl chloride.

These results do not enable one to draw definite conclusions regarding the chlorinating and nitrating properties of nitryl chloride, but they indicate that nitryl chloride is less reactive as a nitrating than as a chlorinating agent. Thus, with the less reactive aromatic nuclei chlorination predominates, and with the more reactive compounds the inherent reactivity of the reagent is of less importance and nitration predominates. This principle is illustrated by the fact that toluene is brominated only 20 times faster than benzene by the more reactive agent Br^+ but 400 times faster by the less reactive agent Br_2.[4]

The orientation of one of the products (3 : 6-dichloro-2-nitrophenol) isolated when phenol was treated with an excess of nitryl chloride is very strange. We know of no explanation of this.

EXPERIMENTAL

Determination of the Extent of Chlorination and Nitration.—Portions of the reaction mixtures were withdrawn and hydrolysed, and the total acid and chloride were titrated. The amount of chlorination was obtained from the reduction in ionisable chlorine content and that of nitration by the reduction in the nitric or nitrous acid. When phenol was used, the total acid had to be determined potentiometrically owing to the colour of the nitrophenol.

Isolation of Products.—*Anisole.* 0·23 mole of anisole was added to 100 c.c. of a 2·3M-solution of nitryl chloride in methylene chloride cooled to −20°. After 1⅔ hr., the mixture was poured

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[4] Robertson, *Sci. Progr.*, 1955, **43**, 418.

into water and the organic layer separated and washed with sodium hydrogen carbonate solution. The washings were red, owing presumably to the presence of nitrophenols which have previously been noted as being formed in the nitration of anisole.[5] After being dried, the organic layer was evaporated at room temperature and 30 mm. The residue was fractionally distilled through a helix column at 10 mm. Excess of anisole distilled first, then the main fraction (10 c.c.), b. p. 74—75°/10 mm., a mixture of chloroanisoles. The small residue of yellow liquid did not distil at constant temperature and was assumed to be a mixture of nitroanisoles. The chloroanisole fraction was refractionated, to give 4·5 c.c., b. p. 75°/10 mm., 195°/740 mm. (lit., *p*-chloroanisole, b. p. 198°; *o*-chloroanisole, b. p. 195°) (Found: C, 59·0; H, 5·1; Cl, 24·8. Calc. for C_7H_7OCl: C, 59·0; H, 5·0; Cl, 24·9%).

Nitrated with fuming nitric acid, this product give pale yellow crystals, m. p. 96—98° (4-chloro-2-nitroanisole has m. p. 98°, 2-chloro-4-nitroanisole, m. p. 95°).

In a similar experiment with benzene as solvent, the mixture was kept at +5° for 1¾ hr. It developed an intense violet colour similar to that noted in the nitration of anisole.[5] The reaction was stopped by addition of methyl alcohol. The solvent and methyl alcohol were distilled off at 30 mm. The distillate separated into two layers, the lower of which contained 12% of chlorine, showing that it probably contained chloroanisole which had distilled as a constant-boiling mixture. On fractionation of the residue chloroanisole was isolated as before but in lower yield (23%).

Naphthalene. Naphthalene (0·22 mole) was added to a 1·22M-solution (90 c.c.) of nitryl chloride in methylene chloride at room temperature. In a short while an exothermic reaction set in which caused the mixture to boil with loss of some material. After 1 hr. the mixture was poured into sodium hydrogen carbonate solution and the organic layer washed with water and then dried. The solvent was distilled off, and the mixture chromatographed on alumina. Two products were separated, one being unchanged naphthalene and the other 1-nitronaphthalene (3·1 g.). Both were contaminated with a chloro-compound, presumably chloronaphthalene which could not be separated. The 1-nitronaphthalene, purified by recrystallisation from aqueous alcohol, had m. p. 58° (Found: C, 68·9; H, 4·1; N, 8·2. Calc. for $C_{10}H_7O_2N$: C, 69·4; H, 4·1; N, 8·1%).

Phenol. Phenol (0·11 mole) was added to a 1·36M-solution (80 c.c.) of nitryl chloride in methylene chloride at −80°. The mixture was shaken but did not become completely homogeneous. After ½ hr. it was poured into 2M-sodium carbonate (100 c.c.) and the organic layer washed several times with a solution M in sodium carbonate and M in sodium hydrogen carbonate. The aqueous portions which were assumed to contain the nitrophenol were acidified, nitrite destroyed by the addition of sulphamic acid, and the whole steam-distilled. The initial distillate was yellow but only a small amount of what was assumed to be *o*-nitrophenol separated as a semi-solid. The residue was extracted with ether, and the ether layers were re-extracted with 2N-sodium hydroxide. On evaporation yellow crystals of sodium *p*-nitrophenoxide (4 g.) separated from the alkaline solution. The sodium salt was recrystallised several times from dilute sodium hydroxide and then converted into *p*-nitrophenol, m. p. 111—113° (Found: C, 52·6; H, 3·9; N, 10·2. Calc. for $C_6H_5O_3N$: C, 51·8; H, 3·6; N, 10·1%) (benzoate, m. p. 143°) [yield (based on impure sodium salt), 22%].

In another experiment, a 3M-solution (20 ml.) of phenol in methylene chloride was added to a 1·13M-solution (94 ml.) of nitryl chloride in the same solvent at −50°. The heat generated caused the temperature to rise rapidly despite cooling. In the working up, which was similar to that above, the nitrophenols were extracted with sodium hydrogen carbonate. On steam-distillation of the acidified extracts 3·3 g. of yellow solid were obtained. By fractional crystallisation from alcohol the solid was separated into 2 : 4-dichloro-6-nitrophenol (1·8 g. impure), m. p. 123—124° (lit., 122—123°) (Found: C, 34·8; H, 1·3; N, 6·5; Cl, 34·4. Calc. for $C_6H_3O_3NCl_2$: C, 34·6; H, 1·45; N, 6·7; Cl, 34·1%), and 3 : 6-dichloro-2-nitrophenol (0·6 g. impure), m. p. 70—72° (lit., 70°) (Found: C, 36·7; H, 1·6; N, 7·8; Cl, 32·2%).

p-*Diethoxybenzene.* *p*-Diethoxybenzene (0·11 mole) was added to a M-solution (100 c.c.) of nitryl chloride in methylene chloride at −80°. The mixture was well shaken but a large amount of solid remained undissolved. After ½ hr. it was poured into sodium carbonate solution. The organic layer was separated, dried, and evaporated. The residue, chromatographed on alumina, gave 1 : 4-diethoxy-2-nitrobenzene (7·7 g.), m. p. 49° (Found: C, 57·3; H, 6·0; N, 6·6. Calc for $C_{10}H_{13}O_4N$: C, 56·9; H, 6·2; N, 6·6%), and a white pasty solid which contained

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[5] Bunton, Hughes, Ingold, Jacobs, Jones, Minkoff, and Reed, *J.*, 1950, 2628.

chlorine. The latter, assumed to be a mixture of chloro-*p*-diethoxybenzene with unchanged *p*-diethoxybenzene, was chromatographed again but the components were not completely separated.

In another experiment, with a slight excess of nitryl chloride (ratio NO_2Cl : ArH 1 : 0·8), diethoxynitrobenzene was isolated as before (yield 43%) but the chlorodiethoxybenzene fraction was still not pure. However, on distillation of the latter a small quantity (0·8 g.) of pure 2-chloro-1 : 4-diethoxybenzene, b. p. 264—266°, was obtained (Found: C, 60·1; H, 6·6; Cl, 17·9. Calc. for $C_{10}H_{13}O_2Cl$: C, 59·8; H; 6·5; Cl, 17·7%).

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