313. *Studies of Trifluoroacetic Acid. Part V.* Trifluoroacetic Anhydride as a Condensing Agent in Reactions of Nitrous and Nitric Acids.*

By E. J. BOURNE, M. STACEY, J. C. TATLOW, and J. M. TEDDER.

IN earlier papers in this series (*J.*, 1949, 2976; *J.*, 1951, 718) it has been shown that mixtures of trifluoroacetic anhydride and carboxylic acids react with hydroxy-compounds and with activated aromatic compounds to give esters and ketones, respectively, and that trifluoroacetic anhydride–sulphonic acid mixtures behave in an analogous fashion to yield sulphonic esters and sulphones. A mechanism for these reactions was advanced recently by Bourne, Randles, Tatlow, and Tedder (*Nature*, 1951, **168**, 942). We have now shown that, as was expected, solutions of fuming nitric acid in trifluoroacetic anhydride can be used to synthesise nitrate esters from polyhydric alcohols and nitro-derivatives from aromatic compounds, including those possessing deactivating groups. For the nitration of cyanides, these solutions offer an advantage over the usual nitric–sulphuric acid nitrating mixture inasmuch as they cause negligible hydrolysis.

It was expected that solutions of alkyl nitrites in trifluoroacetic anhydride would introduce nitroso-groups into aromatic compounds; the direct introduction of such groups by accepted methods can be achieved usually only in the cases of phenols and tertiary amines. However, in place of the nitroso-derivatives, nitro-compounds, diazonium salts, and unidentified nitrogenous syrups were produced. With the less reactive aromatic compounds (*e.g.*, benzene and naphthalene), nitration was the predominant reaction, but diazonium salts (isolated as azo-dyes) were the main products from the more reactive aromatic compounds (*e.g.*, mesitylene, *ψ*-cumene, and anisole). Toluene and *o*-xylene gave only traces of diazonium salts. Improved yields of the diazonium salts resulted when nitroso-compounds were treated in the same way. Thus, it is probable that solutions of nitrites in trifluoroacetic anhydride do, in fact, function as nitrosating agents, but that the nitroso-compounds formed initially are subsequently converted into diazonium salts. A plausible explanation of the second stage is that dehydration of the nitrite gives dinitrogen trioxide, and thence, by disproportionation, nitric oxide and nitrogen dioxide, for it was demonstrated by Bamberger (*Ber.*, 1897, **30**, 512; 1918, **51**, 634) that nitroso-compounds and nitric oxide form diazonium nitrates:

$$R{\cdot}NO + 2NO \longrightarrow R{\cdot}N_2^+ NO_3^-$$

Whilst the results of the above nitrations and nitrosations accord with the hypothesis of Bourne, Randles, Tatlow, and Tedder (*loc. cit.*), developed for carboxylic acids, that the reactive entity present in mixtures of the oxy-acid XOH and trifluoroacetic anhydride is the ion X^+, it does not necessarily follow that the implied mechanism is correct for oxy-acids of nitrogen (cf. Hughes, Ingold, *et al.*, *J.*, 1950, 2400 *et seq.*).

Experimental.—Nitration of phenyl cyanide. A mixture of phenyl cyanide (0·50 c.c.), fuming nitric acid (0·80 c.c.), and trifluoroacetic anhydride (1·50 c.c.) was kept at 55° for 90 minutes, cooled, and poured into excess of aqueous sodium hydrogen carbonate. Extraction with chloroform, evaporation of the extracts, and recrystallisation of the residue from acetone–

---

* Part IV, *J.*, 1951, **826**.

light petroleum (b. p. 40—60°) gave *m*-nitrophenyl cyanide (85%), m. p. 117° (Found : C, 56·7; H, 2·8. Calc. for $C_7H_4O_2N_2$: C, 56·8; H, 2·7%). Bogert and Beans (*J. Amer. Chem. Soc.*, 1904, **26**, 464) recorded m. p. 117—117·5°. Ethereal extracts of the acidified aqueous layer afforded *m*-nitrobenzoic acid (1%).

A similar reaction, in which trifluoroacetic anhydride was replaced by concentrated sulphuric acid (0·50 c.c.), gave *m*-nitrophenyl cyanide and *m*-nitrobenzoic acid, the yields being 40 and 45%, respectively.

Other nitrations. In two similar experiments with trifluoroacetic anhydride, nitrobenzene gave *m*-dinitrobenzene (65%), and bromobenzene afforded the *o*-nitro- (1%), the *p*-nitro- (24%), and the 2 : 4-dinitro-derivative (60%). Mannitol and sorbitol, nitrated at 0°, gave the corresponding hexanitrates (45%).

Mesitylazo-β-naphthol. Amyl nitrite (2·20 c.c.) was added slowly, at 0°, to a mixture of mesitylene (0·40 c.c.) and trifluoroacetic anhydride (4·30 c.c.); a deep brown colour developed rapidly. After being kept at 0° for 2 hours, the whole was poured into crushed ice and excess of sodium hydrogen carbonate, and extracted with ether. The aqueous layer was treated with excess of β-naphthol in sodium hydroxide. The azo-dye was extracted with chloroform. Recrystallised from aqueous acetone, the product gave bright red needles of *mesitylazo-β-naphthol* (0·39 g., 47%), m. p. 131—133° (Found : C, 78·3; H, 6·2. $C_{19}H_{18}ON_2$ requires C, 78·6; H, 6·2%).

In a second experiment, mesitylene (0·40 c.c.) was treated with ethyl nitrite (1·50 c.c.) and trifluoroacetic anhydride (2·00 c.c.) at 0° for 20 minutes, and the azo-dye was obtained in 47% yield, having m. p. 130—131°.

2 : 4 : 5-*Trimethylphenylazo-β-naphthol.* A mixture of trifluoroacetic anhydride (2·10 c.c.), *ψ*-cumene (0·50 c.c.), and amyl nitrite (1·60 c.c.) was treated as above. Recrystallised from aqueous acetone, the azo-dye (0·15 g., 13%) had m. p. 159° (Found : C, 78·9; H, 6·2. Calc. for $C_{19}H_{18}ON_2$: C, 78·6; H, 6·2%). Charrier and Ferreri (*Gazzetta*, 1914, **44**, 120) reported m. p. 160—161°.

p-*Methoxyphenylazo-β-naphthol.* A mixture of trifluoroacetic anhydride (1·90 c.c.), anisole (0·36 c.c.), and ethyl nitrite (1·40 c.c.) was kept at 0° for 20 minutes, mixed with ice and excess of sodium hydrogen carbonate solution, and treated with β-naphthol as reported above. Recrystallised from aqueous acetone, the product gave *p*-methoxyphenylazo-β-naphthol (0·19 g., 21%), m. p. 139—140° (Found: C, 73·4; H, 4·8. Calc. for $C_{17}H_{14}O_2N_2$: C, 73·4; H, 5·1%). Koch, Milligan, and Zuckerman (*Ind. Eng. Chem., Anal.*, 1944, **16**, 755) gave m. p. 140—141°.

Phenylazo-β-naphthol from nitrosobenzene. Nitrosobenzene (0·15 g.) was added, at 0°, to a mixture of amyl nitrite (0·40 c.c.) and trifluoroacetic anhydride (0·80 c.c.), which had been kept previously at 40° for 5 minutes. After 1 hour at 0°, the reaction mixture was treated with ice and excess of sodium hydrogen carbonate solution, and the azo-dye was prepared in the usual fashion. The product, recrystallised from acetic acid, gave dark red needles (0·16 g., 48%), m. p. 131°. Koch, Milligan, and Zuckerman (*loc. cit.*) reported m. p. 131—132°.

Mesitylazo-β-naphthol from nitrosomesitylene. A mixture of nitrosomesitylene (0·074 g.), amyl nitrite (0·30 c.c.), and trifluoroacetic anhydride (0·50 c.c.) was kept at 0° for 1 hour, and treated with β-naphthol as before. The product (0·087 g., 60%) had m. p. 130°, alone or on admixture with mesitylazo-β-naphthol.

1-*Nitronaphthalene.* A mixture of trifluoroacetic anhydride (0·70 c.c.), amyl nitrite (0·40 c.c.), and naphthalene (0·15 g.) was kept at 0° for 3 hours, poured into excess of sodium hydrogen carbonate solution, and extracted with chloroform; the extracts were dried ($MgSO_4$), filtered, and evaporated, leaving a solid residue, which, when recrystallised from aqueous alcohol, gave 1-nitronaphthalene (0·16 g., 79%), m. p. 61° alone or on admixture with an authentic specimen. When the aqueous layer resulting from the chloroform extraction was treated with β-naphthol no azo-dye was formed.

One of us (J. M. T.) is indebted to the British Empire Cancer Campaign for the award of a scholarship.

CHEMISTRY DEPARTMENT, THE UNIVERSITY,
EDGBASTON, BIRMINGHAM, 15.

[*Received, January 22nd,* 1952.]