

Products of Nitration of Aromatic and Heteroaromatic Compounds by some Transition-metal Nitrate-compounds

By Robert G. Coombes* and Leslie W. Russell, Department of Chemistry, The City University, St. John Street, London EC1V 4PB

Compounds of a wide range of aromatic reactivity are nitrated by the nitrate-complexes of zirconium(IV) and iron(III) at room temperature. Product isomer ratios are reported. Studies of the nitration of pyridine with these reagents and with tetranitratotitanium(IV) have established conditions under which either 3- or mainly 4-nitropyridine may be formed. Either 7- or mainly 3-nitroquinoline may be obtained from the nitration of quinoline.

THE production of mixtures of aromatic nitro-compounds in different isomeric proportions from those usual in direct nitrations, and the nitration of compounds usually unreactive, would be of synthetic importance. Anhydrous transition-metal nitrate-compounds are of interest as reagents in this connection, and the special mechanism which we have proposed for the nitration of aromatic compounds by solutions of tetranitratotitanium(IV) in carbon tetrachloride¹ is also of relevance.

We report here the results of studies of products from the nitration of a wide range of aromatic compounds by tetranitratozirconium(IV) and tetranitratonitrosyliron(III). The reactions of the nitrate-complexes of titanium, zirconium, and iron with pyridine and quinoline have also been studied, and reactions with dinitratocopper(II) were attempted.

EXPERIMENTAL

Materials.—The nitrate-complexes were prepared by the procedures described by Field and Hardy,² although on occasions different starting materials were used. Tetranitratozirconium(IV) was prepared from zirconyl nitrate. Found: NO₃, 73.3. Calc. for Zr(NO₃)₄: NO₃, 73.1%. Tetranitratonitrosyliron(III) was prepared from iron wire (Found: Fe, 16.4; NO₃, 75.3. Calc. for [Fe(NO₃)₄]⁻NO⁺: † Fe, 16.7; NO₃, 74.2%). Dinitratocopper(II) was prepared from copper gauze [Found: Cu, 34.0; NO₃, 65.8. Calc. for Cu(NO₃)₂: Cu, 33.9; NO₃, 66.1%]. The preparation of tetranitratotitanium(IV) has been described previously.¹ All nitrate-complexes were purified by resublimation. They were extremely hygroscopic and were always handled in a dry box.

† It has been suggested³ that on prolonged heating and sublimation the complex becomes [Fe(NO₃)₄]⁻NO₂⁺. This structure would require NO₃, 88.7%.

¹ R. G. Coombes and L. W. Russell, *J.C.S. Perkin II*, 1974 830.

Substrates were suitably purified commercial reagents and were dried over type 4A molecular sieves. Comparison samples of 2-, 3-, and 4-nitropyridine were prepared by oxidation⁴ of the corresponding aminopyridines. We are grateful to Professor K. Schofield for samples of 3- and 7-nitroquinoline. Other nitro-compounds were commercial samples purified as necessary.

Nitration Conditions and Product Analysis.—The substrate (5—10 ml) was shaken with a weighed amount (0.1—0.5 g) of the nitrate-compound at room temperature (ca. 20°). In the case of tetranitratotitanium(IV), 25 ml of a ca. 0.1M-solution in carbon tetrachloride was used. Reactions seemed to occur within about 1 min, although the solutions were usually left for about 30 min before analysis. After addition of a known amount of nitro-compound as a standard the products were analysed quantitatively by g.l.c. Most conditions have been described previously.¹ For the nitropyridines a 5 ft × 1/4 in polyethylene glycol column at 150° was used, and for the nitroquinolines a 1½ ft × 1/4 in silicone SE30 column at 140°.

The nitro-products were identified by comparison of retention times with those of authentic samples, and in the cases of pyridine and quinoline the identity of products was confirmed by g.l.c.—mass spectrometry.

RESULTS

The product isomer distributions and the yields from the nitration of aromatic and heteroaromatic compounds by the nitrate-complexes studied are shown in Tables 1 and 2, respectively. No peaks which could be attributed to dinitration were observed in any case. Dinitratocopper(II) was found not to nitrate any of these substrates under similar conditions, although with

² B. O. Field and C. J. Hardy, *J. Chem. Soc.*, 1964, 4428.

³ C. C. Addison, P. M. Boorman, and N. Logan, *J. Chem. Soc.*, 1965, 4978.

⁴ A. Kirpal and W. Bohem, *Ber.*, 1937, 64, 767.

pyridine and quinoline a colour change due to complex formation⁵ was observed.

TABLE 1
Nitration of aromatic compounds

Substrate	Position of substitution	Reagent Zr(NO ₃) ₄		Reagent Fe(NO ₃) ₄ NO	
		% ^{a,b}	Yield ^c	% ^{a,b}	Yield ^c
Toluene	2	46	1.5	43	2.0
	3	2		2	
	4	52		55	
Ethylbenzene	2	31	1.1	30	1.6
	3	2		2	
	4	67		67	
t-Butylbenzene	2	8	1.4	7	1.8
	3	4		4	
	4	88		89	
o-Xylene	3	35	1.2	33	1.5
	4	65		67	
m-Xylene	2	8	1.2	10	1.9
	4	92		90	
Chlorobenzene	2	27	1.0	23	1.7
	3	<0.1		<0.1	
	4	73		77	
Bromobenzene	2	30	1.0	25	1.4
	3	<0.1		0.2	
	4	70		75	
Nitrobenzene	2	7	0.9	7	0.8
	3	92		92	
	4	1		1	

^a % of total nitro-product. ^b Determined from two or three experiments, which always showed excellent agreement. ^c Moles of nitro-product per mole of reagent.

TABLE 2
Nitration of pyridine and quinoline

Position of substitution	Reagent Zr(NO ₃) ₄		Reagent Fe(NO ₃) ₄ NO		Reagent Ti(NO ₃) ₄ in CCl ₄	
	% ^{a,b}	Yield ^c	% ^{a,b}	Yield ^c	% ^{a,b}	Yield ^c
Pyridine						
2	<0.01	0.09	<0.01	0.10	<0.01	0.06
3	36		20-30		100	
4	64		80-70		<0.1	
Quinoline						
3	4	0.9	18	0.4	85	0.2-0.4
5	<0.1		<0.1		<0.1	
6	<0.1		<0.1		<0.1	
7	96		82		5	
8	<0.1		<0.1		10	

^a % of total nitro-product. ^b Determined from at least two experiments, which always showed excellent agreement. ^c Moles of nitro-product per mole of reagent.

DISCUSSION

The isomer ratios presented in Table 1 are similar for both reagents and resemble those previously reported

• Yields quoted are based on the possibility of release of one nitro-group from each molecule of reagent, the substrate being in excess.

⁵ N. Logan and W. B. Simpson, *Spectrochim. Acta*, 1965, **21**, 857; R. V. Biagetti, W. G. Bottjer, and H. M. Haendler, *Inorg. Chem.*, 1966, **5**, 379.

for tetranitratotitanium(IV) alone⁶ and in carbon tetrachloride solution.¹ In the case of toluene there is a considerable difference between the values from all these reagents and those encountered in conventional nitrations. This is not so for the other substrates. It is also only in the case of toluene that any significant difference between these reagents is apparent. The proportion of *m*-nitrotoluene from the reaction with tetranitratotitanium(IV) in carbon tetrachloride solution ($0.8 \pm 0.1\%$) is less than that observed with any of the nitrate-compounds in the absence of solvent (2-5%).

The reactions with pyridine and quinoline, however, may be of synthetic importance. Normally very vigorous conditions (KNO₃-H₂SO₄ at 300-370°) have to be used even to obtain low (*ca.* 4%) yields of 3-nitropyridine, accompanied by 0.5-2% of 2-nitropyridine,⁷ and under non-acidic conditions the *N*-nitropyridinium ion is formed.⁸ The present procedure (Table 2) leads at room temperature to 6-10% yields* of 3-nitropyridine with tetranitratotitanium(IV), and similar yields of mainly 4-nitropyridine with tetranitratotitanium(IV) or tetranitratotitanium(IV) and similar yields of mainly 4-nitropyridine with tetranitratotitanium(IV) or tetranitratotitanium(IV).

In the case of quinoline, better yields are obtained. Reaction with tetranitratotitanium(IV) gives mainly 3-nitroquinoline, and with tetranitratotitanium(IV) or tetranitratotitanium(IV) gives mainly 7-nitroquinoline. A 90% yield of almost pure 7-nitroquinoline from the tetranitratotitanium(IV) reaction is especially noteworthy.

We have previously suggested that, in the nitration of aromatic compounds by tetranitratotitanium(IV), the product-determining stage may involve an intramolecular rearrangement within a co-ordination complex of the aromatic and some titanium-containing species. In the case of the heterocyclic molecules the position of co-ordination would be the heteroatom, and hence if this mechanism were generally applicable a major factor influencing the position of substitution would be the size and stereochemistry of the complex. It is therefore possible to account for the complete change in isomer ratios on changing the reagent in the cases of pyridine and quinoline.

We thank J. G. Golding for some preliminary experiments with pyridine and the preparation of the nitropyridines. We also thank the S.R.C. for a studentship (to L. W. R.) and the P.C.M.U., Harwell, for mass spectroscopic measurements.

[4/586 Received, 25th March, 1974]

⁶ D. W. Amos, D. A. Baines, and G. W. Flewett, *Tetrahedron Letters*, 1973, 3191.

⁷ H. J. den Hertog and J. Overhoff, *Rec. Trav. chim.*, 1930, **49**, 552.

⁸ J. Jones and J. Jones, *Tetrahedron Letters*, 1964, 2117; G. A. Olah, J. A. Olah, and N. A. Overchuk, *J. Org. Chem.*, 1965, **30**, 3373.