

***N*-Oxides and Related Compounds. Part XLIII.¹ Formation of *N*-Nitroimides by Base-catalysed Nitration**

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4-Amino-1,2,4-triazole and 1- and 2-aminobenzotriazole are converted into *N*-nitroimides by nitration with ethyl nitrate in the presence of sodium ethoxide. 1-Aminobenzimidazole forms the *N*-nitroimide on nitration with NO₂BF₄. Some of the products are violent explosives; several of their reactions are described.

PUBLISHED methods¹⁻⁴ for the preparation of *N*-nitroimides all involve nitration under strongly acidic conditions. We reasoned that *N*-amino-azoles might be susceptible to nitration under base-catalysis conditions, by transformations of the type (1) → (4), in which anions such as (2) were reactive intermediates. The

present paper justifies this reasoning, and makes available a variety of azole *N*-nitroimides, a class of which previously only a single example⁴ was known.

Nitrate esters in strongly basic medium have been used previously to *C*-nitrate compounds with weakly acidic hydrogen atoms, *e.g.*, amides,⁵ ketones,^{6,7} and

¹ Part XII, A. R. Katritzky, E. Lunt, J. Epsztajn, J. W. Mitchell, and G. Roch, preceding paper.

² J. Epsztajn and A. R. Katritzky, *Tetrahedron Letters*, 1969, 4739.

³ J. Epsztajn, E. Lunt, and A. R. Katritzky, *Tetrahedron*, 1970, **26**, 1665.

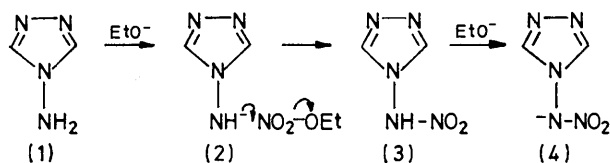
⁴ H.-J. Timpe, *Z. Chem.*, 1971, **11**, 340.

⁵ H. Feuer and B. F. Vincent, jun., *J. Org. Chem.*, 1964, **29**, 939.

⁶ H. Feuer, J. W. Shepherd, and C. Savides, *J. Amer. Chem. Soc.*, 1956, **78**, 4364.

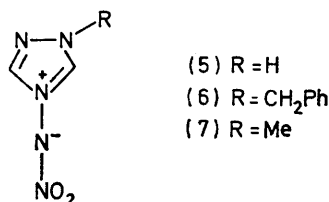
⁷ H. Feuer and C. Savides, *J. Amer. Chem. Soc.*, 1959, **81**, 5826.

nitriles.⁷ *N*-Nitration of primary and secondary amines⁸⁻¹⁰ has also succeeded at times, although concomitant cleavage of the C-O bond of the nitrate ester can occur, as in the known^{11,12} alkylation of tertiary



amines. Unsuccessful attempts have been made to nitrate hydrazine¹³ and 1,2,4-triazole¹⁴ and we ourselves found the method to fail for *as*-dimethylhydrazine, pyrazole, and 1-aminopyridinium salts.

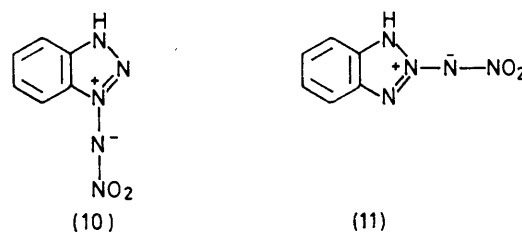
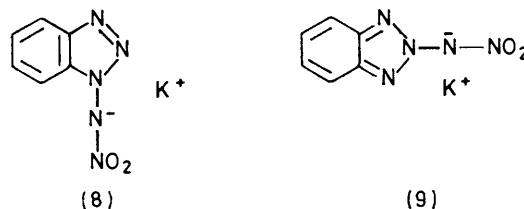
1,2,4-Triazole.—4-Amino-1,2,4-triazole (1) with nitric acid in acetic anhydride and acetic acid formed the nitrate salt of 1,2,4-triazole as the only isolable product (20%); however, treatment with ethyl nitrate and sodium ethoxide in ethanol gave the nitroimide sodium salt (4) in 90% yield. Treatment of this salt with hydrochloric acid gave 1,2,4-triazole 4-nitroimide (5).



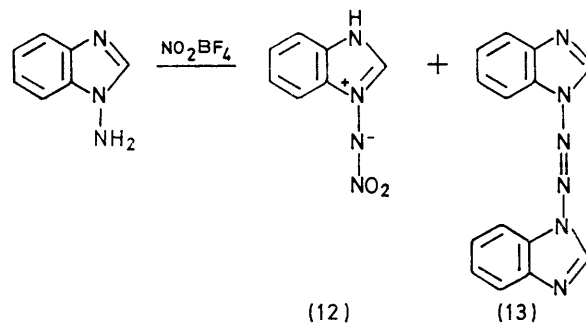
Reaction of the salt (4) with benzyl chloride gave 1-benzyl-1,2,4-triazole 4-nitroimide (6), previously prepared⁴ by nitration of the sulphonyl ylide, and reaction of (4) with methyl toluene-*p*-sulphonate gave 1-methyl-1,2,4-triazole 4-nitroimide (7). The nitroimide (5) was also obtained directly from 4-amino-1,2,4-triazole by reaction with nitronium tetrafluoroborate in acetonitrile (65% yield).

Benzotriazole.—Benzotriazole reacts with hydroxylamine-*O*-sulphonic acid to produce 1- and 2-aminobenzotriazole.¹⁵ Reaction of each of these compounds with ethyl nitrate and potassium ethoxide in ethanol produced the corresponding nitroimides as potassium salts (8) and (9), which were acidified to give the nitroimides (10) and (11). These were exceptionally dangerous compounds, exploding at their respective m.p. (74.5 and 81°), very sensitive to impact, and liable to undergo spontaneous violent decomposition, even in solution. Attempts to methylate (8) with methyl fluorosulphonate (either neat or with acetonitrile as solvent) were unsuccessful, the only product isolated being 1-methylbenzotriazole.

Benzimidazole.—T.l.c. showed that the reaction of 1-aminobenzimidazole with ethyl nitrate and potassium ethoxide was not fast enough to be significant in comparison with decomposition of the ethyl nitrate to yield



diethyl ether and potassium nitrate. 1-Aminobenzimidazole reacted readily with NO₂BF₄ in acetonitrile to give benzimidazole 1-nitroimide (12) in 65% yield. 1,1'-Azobisbenzimidazole (13) (5%) was a by-product,



precipitating out as its tetrafluoroborate salt. Its structure was confirmed by analytical, n.m.r., and mass spectral data.

EXPERIMENTAL

1,2,4-Triazole 4-Nitroimide, Sodium Salt.—Ethanol sodium ethoxide [from sodium (6 g) and EtOH (250 ml)], ethyl nitrate (14 g), and 4-amino-1,2,4-triazole¹⁶ (12 g) were heated under reflux for 1.5 h; the mixture was filtered hot, and allowed to cool. Dilution with ether (700 ml) precipitated the *sodium salt monohydrate* (21.6 g, 90%) which crystallised as plates from EtOH, m.p. 223–224° (decomp.) (Found: C, 14.3; H, 2.5; N, 41.4. C₂H₄N₅NaO₃·H₂O requires C, 14.2; H, 2.4; N, 41.4%).

¹² E. S. Lane, *J. Chem. Soc.*, 1953, 1172.

¹³ R. T. Merrow and R. W. van Dolah, *J. Amer. Chem. Soc.*, 1954, **76**, 4522.

¹⁴ C.-F. Kröger and R. Miethchen, *Z. Chem.*, 1969, **9**, 378.

¹⁵ C. D. Campbell and C. W. Rees, *J. Chem. Soc. (C)*, 1969, 742.

¹⁶ C. F. H. Allen and A. Bell, *Org. Synth.*, Coll. Vol. III, 1955, 96.

⁸ A. Angeli and G. Maragliano, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1905, **14**, ii, 127 (*J. Chem. Soc.*, 1905, **88**, I, 873).

⁹ E. Bamberger, *Ber.*, 1920, **53**, 2321.

¹⁰ L. J. Winters, D. B. Learn, and S. C. Desai, *J. Org. Chem.*, 1965, **30**, 2471.

¹¹ D. T. Gibson and A. K. Macbeth, *J. Chem. Soc.*, 1921, 438.

1,2,4-Triazole 4-Nitroimide.—(a) To concentrated HCl (1 ml) was added the sodium salt (0.20 g) in MeOH (10 ml). EtOH (30 ml) was then added and the solution cooled for 1 h. The precipitate was filtered off and recrystallised from EtOH–H₂O to give the *nitroimide* as plates (0.11 g, 70%), m.p. 172° (explodes) (Found: C, 18.9; H, 2.5; N, 54.1. C₂H₃N₅O₂ requires C, 18.6; H, 2.3; N, 54.3%).

(b) 4-Amino-1,2,4-triazole (0.10 g) in dry MeCN (4 ml) and NO₂BF₄¹⁷ (0.16 g) in dry MeCN (5 ml) were mixed. Concentration of the mixture to 2 ml and dilution with ether (10 ml) gave a precipitate of the *nitroimide* (0.10 g, 65%), identical in properties with the material prepared previously.

1-Benzyl-1,2,4-triazole 4-Nitroimide.—The sodium salt (0.15 g) of 1,2,4-triazole 4-nitroimide was heated under reflux for 24 h with benzyl chloride (0.5 g) in EtOH (15 ml). The solution was filtered to remove NaCl and allowed to cool for 24 h to give the *nitroimide* as plates (0.02 g, 10%), m.p. 159–161° (lit.,⁴ 164°).

1-Methyl-1,2,4-triazole 4-Nitroimide.—The sodium salt (2 g) and methyl toluene-*p*-sulphonate (5.5 g) in tetrahydrofuran dioxide (35 ml) were stirred at 100° for 1 h. Me₂CO (50 ml) was added to the cooled solution and the precipitate filtered off. After addition of ether (600 ml), the solution was set aside for 2 h at 0° to give the *nitroimide* (1.10 g, 65%) as needles from EtOH–H₂O, m.p. 154–155° (decomp.) (Found: C, 25.5; H, 3.6; N, 48.2. C₃H₅N₅O₂ requires C, 25.2; H, 3.5; N, 48.9%).

Benzotriazole 1-Nitroimide.—Potassium (3.5 g) was dissolved in EtOH (250 ml) under N₂. 1-Aminobenzotriazole (10 g) and ethyl nitrate (8 g) were added and the mixture was heated under reflux for 1.5 h. It was filtered hot and cooled, and ether (100 ml) was slowly added, giving a precipitate of the *potassium salt of benzotriazole 1-nitroimide* (13.3 g, 82%) as needles from ethanol–ether, m.p. 181–182° (decomp.) (Found: C, 33.0; H, 2.0; N, 31.8. C₆H₄KN₅O₂ requires C, 33.2; H, 1.9; N, 32.2%).

Concentrated HCl (1 ml) was added to the potassium salt (0.5 g). Dilution with EtOH (20 ml) and, after 10 min, filtration to remove KCl, gave a solution which was evaporated down (water-bath temp. not above 35°). Two successive portions of EtOH (10 ml) were added and evaporated off, followed by one of CHCl₃. The residual

oil was taken up in a little CHCl₃; careful addition of light petroleum (b.p. 60–80°) caused crystallisation of the *nitroimide* as needles (0.35 g, 85%), m.p. 74.5° (explodes). Because of its very dangerous nature, analytical data were not obtained for this compound; assumption of its identity was based on similarity in properties, especially i.r. spectrum, to benzotriazole 2-nitroimide, which was slightly more stable.

Benzotriazole 2-nitroimide was prepared in a similar manner. Its *potassium salt* (55%) crystallised from EtOH–H₂O as the *dihydrate* (needles), m.p. 258° (decomp.) (Found: C, 28.3; H, 2.5; N, 27.6. C₆H₄KN₅O₂·2H₂O requires C, 28.5; H, 3.2; N, 27.7%). Acidification as before gave the *nitroimide* as needles (75%), m.p. 81° (explodes) (Found: C, 40.5; H, 3.0; N, 38.1. C₆H₅N₅O₂ requires C, 40.2; H, 2.8; N, 39.1%).

Benzimidazole 1-Nitroimide.—NO₂BF₄ (0.2 g) in MeCN (15 ml) was slowly added, with stirring, to 1-aminobenzimidazole¹⁸ (0.15 g) in MeCN (5 ml). After 10 min the precipitate (0.02 g) was filtered off; the filtrate was mixed with ether (100 ml) to give the *nitroimide* (0.125 g, 62%), prisms (from EtOH), m.p. 169° (explodes) (Found: C, 47.4; H, 3.7; N, 31.9. C₇H₆N₄O₂ requires C, 47.2; H, 3.4; N, 31.4%).

The precipitate from the original reaction mixture was considered to be 1,1'-azobisbenzimidazole *dihydrotetrafluoroborate*, needles, m.p. 272° (decomp.) (Found: C, 37.7; H, 3.0; N, 19.2. C₁₄H₁₂B₂F₈N₆ requires C, 38.4; H, 2.8; N, 19.2%); ν_{\max} (Nujol) 3260 (NH), 1150–1000s, br (BF₄⁻), and 775 cm⁻¹. Recrystallisation of this fluoroborate from EtOH produced 1,1'-azobisbenzimidazole as needles (0.007 g, 5%), m.p. 270° (decomp.) (Found: C, 64.3; H, 4.2; N, 31.8. C₁₄H₁₀N₆ requires C, 64.1; H, 3.8; N, 32.1%); ν_{\max} (Nujol) 1500s, 1450s, 1365, 1350, 1275s, 1230vs, 785, and 745s cm⁻¹; τ [(CD₃)₂SO; 60 MHz] 7.08–7.43 (3H, m), 7.48–7.86 (1H, m), and 8.03 (1H, s); *m/e* 262vs.

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¹⁷ S. J. Kuhn, *Canad. J. Chem.*, 1962, **40**, 1660.

¹⁸ M. N. Sheng and A. R. Day, *J. Org. Chem.*, 1963, **28**, 736.