

## 1,4-Dienes from the Nitration of 2,3- and 3,4- Dimethylbenzonnitriles and a 1,3-Rearrangement of a Nitro-group

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**Summary** Reaction of 2,3- and 3,4-dimethylbenzonnitriles with nitric acid in acetic anhydride gives 1,4- (nitro-acetoxy-) adducts in which the nitro-group is attached to that nuclear carbon atom bearing a methyl group which is *meta* to the cyano-group; thermolysis of these adducts gives the original dimethylbenzonnitrile, together with 2,3-dimethyl-5-nitrobenzonnitrile and 3,4-dimethyl-5-nitrobenzonnitrile, respectively.

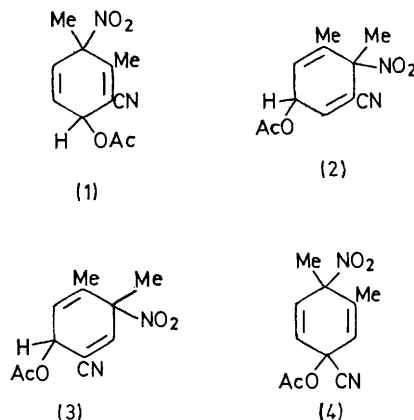
A RECENT report<sup>1</sup> of a 1,2-nitro-migration in the decomposition of the acetyl nitrate adduct of *o*-xylene indicates that there is continuing interest in unusual nitration products.<sup>2</sup> Nitration of 2,3-dimethylbenzonnitrile in acetic anhydride gave the adduct (1) as well as the 4-, 5-, and 6-nitro-derivatives of 2,3-dimethylbenzonnitrile. The n.m.r. spectrum, which showed two adjacent vinyl protons ( $J$  10 Hz) is consistent with structure (1) and not with the alternative (2) in which the nitro-group has attacked the other methyl-substituted nuclear position, *ortho* to the nitrile function. Of the normal nitro-substitution products, 2,3-dimethyl-5-nitrobenzonnitrile was formed in greater amount than its 4-nitro-isomer which likewise exceeded the 6-nitro-compound in quantity.

Decomposition of (1) by heating under reflux in acetic acid, or by heating under sand at 200°, gave a *ca.* 1:1 mixture of 2,3-dimethyl-5-nitrobenzonnitrile and the original 2,3-dimethylbenzonnitrile. When (1) was decomposed by heating with more than 1 mol. proportion of mesitylene, the 2,3-dimethyl-5-nitrobenzonnitrile and the 2,3-dimethylbenzonnitrile were obtained in the same ratio and no 2-nitromesitylene was detected. Thus the nitrobenzonnitrile obtained as a decomposition product is not formed by an electrophilic nitration process and in particular not by dissociation of (1) into acetyl nitrate and the original nitrile followed by normal nitration at the 5-position.

<sup>1</sup> P. C. Myhre, *J. Amer. Chem. Soc.*, 1972, **94**, 7921.

<sup>2</sup> B. A. Collins, K. E. Richards, and G. J. Wright, *J.C.S. Chem. Comm.*, 1972, 1216; A. J. M. Reuvers, F. F. van Leeuwen, and A. Sinnemar, *ibid.*, p. 828; H. Suzuki and K. Nakamura, *ibid.*, p. 340; G. Illuminati, L. Mandolini, E. M. Arnett, and R. Smoyer, *J. Chem. Soc. (B)*, 1971, 2206; D. J. Blackstock, A. Fischer, K. E. Richards, G. J. Wright, and J. Vaughan, *Chem. Comm.*, 1970, 641.

Nitration of 3,4-dimethylbenzonnitrile gave the adduct (3) in addition to 3-, 5-, and 6-nitro-derivatives. This adduct did not exhibit the 10 Hz vinyl coupling which would be expected for structure (4). Formation of (3) again exhibits the *meta* directing effect of the cyano-group for nitration at



a substituted position. Decomposition of (3) by heating under sand or by injection into the inlet of a g.l.c. instrument gave the original 3,4-dimethylbenzonnitrile and 3,4-dimethyl-5-nitrobenzonnitrile as well as a small amount of 2-acetoxy-4,5-dimethylbenzonnitrile. When the decomposition was carried out in mesitylene the 3,4-dimethylbenzonnitrile and 3,4-dimethyl-5-nitrobenzonnitrile were obtained, but no nitromesitylene was formed, consistent with an intramolecular 1,3-migration of the nitro-group.

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