

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

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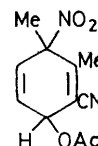
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Summary Reaction of 2,3- and 3,4-dimethylbenzonitriles with nitric acid in acetic anhydride gives 1,4- (nitro-acetoxy-) adducts in which the nitro-group is attached to that nuclear carbon atom bearing a methyl group which is *meta* to the cyano-group;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

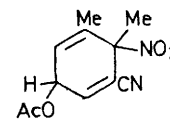
A RECENT report¹ of a 1,2-nitro-migration in the decomposition of the acetyl nitrate adduct of *o*-xylene indicates that there is continuing interest in unusual nitration products.² Nitration of 2,3-dimethylbenzonitrile in acetic anhydride gave the adduct (1) as well as the 4-, 5-, and 6-nitro-derivatives of 2,3-dimethylbenzonitrile. 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-nitrobenzonitrile 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-nitrobenzonitrile and the original 2,3-dimethylbenzonitrile. When (1) was decomposed by heating with more than 1 mol. proportion of mesitylene, the 2,3-dimethyl-5-nitrobenzonitrile and the 2,3-dimethylbenzonitrile were obtained in the same ratio and no 2-nitromesitylene was detected. Thus the nitrobenzonitrile 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.

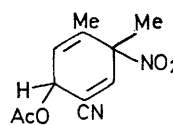
Nitration of 3,4-dimethylbenzonitrile gave the adduct (3) in addition to 3-, 5-, and 6-nitro-derivatives. This adduct did not exhibit the 10 Hz vinyl coupling which would be expected for structure (4). Formation of (3) again exhibits the *meta* directing effect of the cyano-group for nitration at



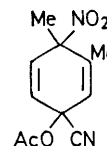
(1)



(2)



(3)



(4)

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-dimethylbenzonitrile and 3,4-dimethyl-5-nitrobenzonitrile as well as a small amount of 2-acetoxy-4,5-dimethylbenzonitrile. When the decomposition was carried out in mesitylene the 3,4-dimethylbenzonitrile and 3,4-dimethyl-5-nitrobenzonitrile were obtained, but no nitromesitylene was formed, consistent with an intramolecular 1,3-migration of the nitro-group.

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