Mesoionic Oxadiazolium-olates and Oxatriazolium-olates from Aryl Isocyanides and Nitroform

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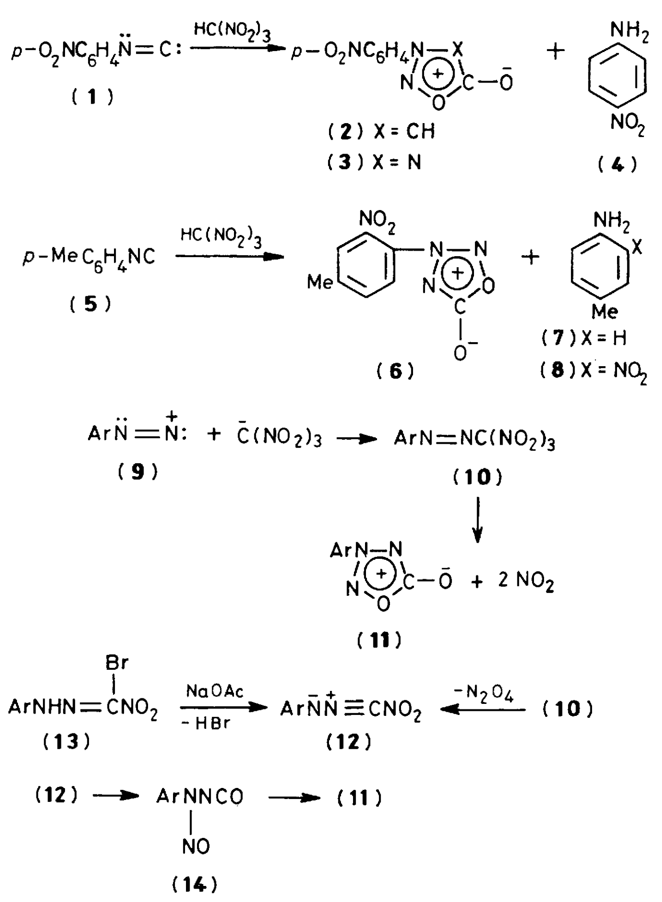
Nitroform converted *p*-nitrophenyl isocyanide into the mesoionic 3-*p*-nitrophenyl-1,2,3-oxadiazolium-5-olate (**2**) and 3-*p*-nitrophenyl-1,2,3,4-oxatriazolium-5-olate (**3**), together with *p*-nitroaniline; it converted *p*-tolyl isocyanide into the mesoionic 3-(2-nitro-4-methylphenyl)-1,2,3-oxatriazolium-5-olate together with 2-nitro-4-methylaniline and *p*-methylaniline.

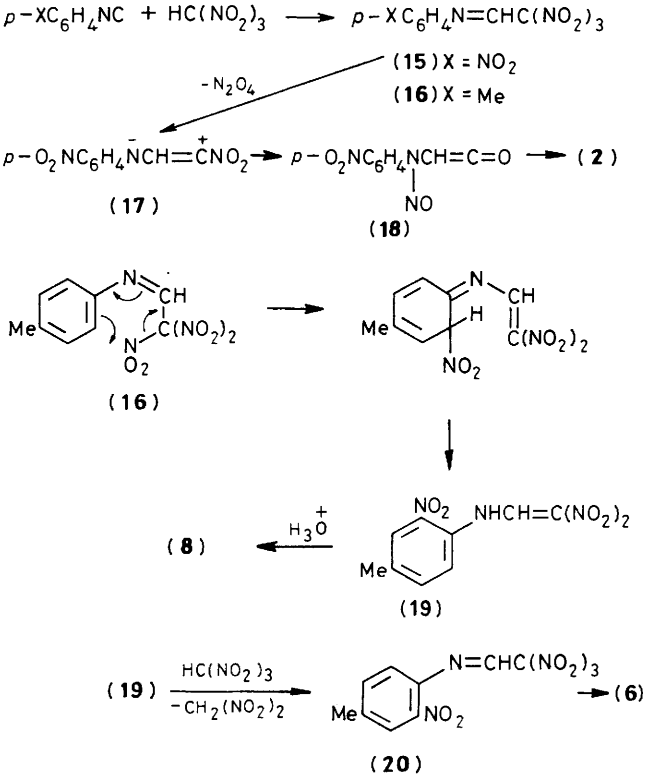
A new reaction between nitroform and *p*-nitrophenyl isocyanide (**1**) gave the mesoionic heterocycles, 3-*p*-nitrophenyl-1,2,3-oxadiazolium-5-olate (**2**) and 3-*p*-nitrophenyl-1,2,3,4-oxatriazolium-5-olate (**3**), and a trace of *p*-nitroaniline (**4**).

Equimolar portions of *p*-nitrophenyl isocyanide (**1**)[1] and nitroform[2] in a mixture of hexane and ether at 25 °C became light yellow then brown during 20 min and evolved brown fumes (nitrogen dioxide) after about 2 h. The mixture was stirred for 14 h at 25 °C. Removal of solvent left a paste which was applied to an alumina column. A mixture (1:9) of ethyl acetate and benzene eluted *p*-nitroaniline (**4**) (4%), m.p. and mixed m.p. 148—149 °C[3] and the same solvent mixtures with ratios 1:5 and 5:1 eluted the oxatriazolium-olate (**3**) (42%), m.p. 167—168 °C,[4] i.r. (KBr): 1825s, 1785s (CO), 1540s (NO_2), and 1340s cm^{-1} (NO_2); *m/z* (70 eV): 178(10%) ($M-30$) and 122(100) ($O_2NC_6H_4$); n.m.r. ($CDCl_3$): δ 8.41 (d, 2H, J 9 Hz) and 8.65 (d, 2H, J 9 Hz); and the oxadiazolium-olate (**2**) (6%), m.p. 197—198 °C (decomp.),[5] i.r.(KBr): 1700m (CO), 1590s, 1520s (NO_2), and 1340s (NO_2) cm^{-1}; *m/z* (70 eV): 209(3%) ($M + 2$), 191(8), 174(12), 164(90), 122(15) ($O_2NC_6H_4$), and 90(100) (C_6H_4N).

Under comparable conditions nitroform converted *p*-tolyl isocyanide (**5**)[1] into the mesoionic compound (**6**) (48%), m.p. 140—141 °C; satisfactory analyses for C, H, and N; i.r. (KBr): 1790s (oxatriazolium-olate), 1535s (NO_2), and 1350s (NO_2) cm^{-1}; n.m.r. ($CDCl_3$ and CD_3SOCD_3): δ 2.65 (s, 3H, CH_3), 7.90 (d, 1H, J 8 Hz), 8.06 (d, 1H, J 8 Hz), and 8.16 (s, 1H); *m/z* (70 eV): 192(15%) ($M-30$) and 164(100) ($C_7H_6N_3O_2$); 2-nitro-4-methylaniline (**8**) (21%) m.p. 115—117 °C;[6] and a small amount of *p*-toluidine (**7**) (3%) m.p. and mixed m.p. 45—46 °C.[7] A trace of the isocyanide (**5**) was recovered; an oxadiazole was not detected.

Quilico obtained the mesoionic oxatriazolium-5-olates (**11**) and nitrogen dioxide in 1932 by warming arylazotrinitromethanes (**10**), the unstable adducts from aryldiazonium cations (**9**) and the anion of nitroform.[4] Initial α,α-elimination of dinitrogen tetroxide from the methane (**10**) is proposed to enable the conversion (**10**) $\rightarrow$ (**11**) and the dehydrobromi-





nation of the arylhydrazones (**13**) of bromonitroformaldehyde to produce the oxatriazolium-olates (**11**)[8] to share a nitro-nitrilimine intermediate (**12**) and its isomerization to a nitrosaminoisocyanate (**14**), an open-chain tautomer of the heterocycle (**11**).†

The anils (**15**) and (**16**) were the expected α,α-adducts from nitroform and the isocyanides (**1**) and (**5**).[9] Their intermediacy was supported by the isolation of the aniline derivatives (**4**) and (**7**).‡ A zwitterion (**17**) and the isomeric nitrosaminoketene (**18**) are proposed intermediates to correlate the conversion (**15**) → (**2**) with (**10**) → (**11**).†[10]

Insofar as it would have initiated a similar conversion into an oxadiazolium-5-olate which was not detected, an α,α-elimination of dinitrogen tetroxide from the anil (**16**) did not occur. To account for the *ortho*-nitro groups in the products (**6**) and (**8**) a rearrangement of the anil to the anilinoethene (**19**) followed by conversion into the anil (**20**) by a Michael addition of nitroform and an elimination of dinitromethane is proposed.[11] Hydrolysis of the enamine (**19**) and/or the anil (**20**) could account for the formation of the aniline derivative for the amine (**8**). The conversions (**20**) → (**6**) and (**15**) → (**3**) were apparently related.

The formation of the oxatriazolium-olates (**3**) and (**6**) from the isocyanides (**1**) and (**5**) requires a replacement of ArNC– by ArNN–. Although this conceivably could occur by interaction between dinitrogen tetroxide and anils or other intermediates, a more detailed statement awaits further investigation.

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† The complete identification of pathways for the conversions (**13**) → (**11**) and (**15**) → (**2**) awaits further investigation. A minimum of two rearrangements are required for the creation of new NN and CO bonds in each conversion.

‡ The anilines (**4**), (**7**), and (**8**) are formed during chromatographic separation of the product mixture. Under the conditions employed the isocyanides (**1**) and (**5**) and the heterocycles (**2**), (**3**), and (**6**) were not hydrolysed.

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