1-(2,4-Dinitrophenyl)-3-oxidopyridinium: Rearrangement and Dipolar Additions

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Summary 1-(2,4-Dinitrophenyl)-3-oxidopyridinium rearranges spontaneously to the isomeric ether on attempted isolation, but can be trapped with olefins and behaves as a highly reactive 1,3-dipole.

3-Hydroxypyridine reacts[1] with 2,4-dinitrochlorobenzene to form the chloride (**1**), which is reported[1] to give the betaine (**2**) with $NaHCO_3$. Repeating this work demonstrates that the compound claimed to be (**2**) is actually (**3**), identical with authentic specimens prepared by two routes.[1,2] Structure (**1**) is confirmed by spectral measurements, and (**3**) forms a HCl salt distinct from (**1**).

The betaine (**2**) can be detected by n.m.r. and u.v. spectroscopy as an intermediate; rapid rearrangement to (**3**) precluded isolation,† but (**2**) was trapped by *in situ* formation from (**1**) and NEt_3 in the presence of olefins. Thus, (**2**) and methyl acrylate form the stereoisomeric adducts (**4**), m.p. 170—172°, and (**5**), m.p. 171°.

The considerable reactivity of (**2**) as a dipole is indicated by the reaction with acrylonitrile which produced the expected two stereoisomeric adducts (**6**), m.p. 221—223°, and (**7**), m.p. 193°, but in addition the positional isomer (**9**), m.p. 209—210°. The formation of (**9**) indicated that activation by the cyano-group was not needed [*cf.* (**10**)]. Indeed, reaction of (**2**) with the relatively unreactive dipolarophile,[3] styrene, produced only the *endo*-cycloadduct (**8**), m.p. 188—190°, in high yield (50%). These results indicate that 2,4-dinitrophenyl betaines of type (**2**) are valuable intermediates for the preparation of adducts and hence[4,5] of tropones.

We previously reported[6] that (**2**) reacts with benzyne[7] to yield (**11**): in reality this is a reaction of (**3**) with benzyne, which probably proceeds by phenylation at the pyridine nitrogen followed by elimination of the dinitrophenyl group to give (**12**), known[6] to react with benzyne to yield (**11**).

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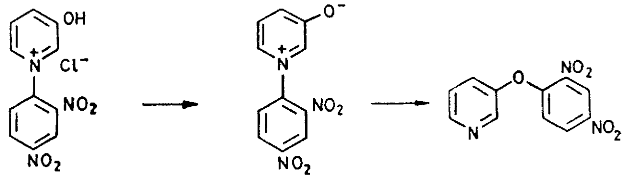
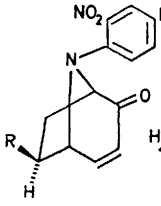
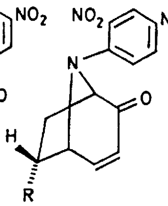


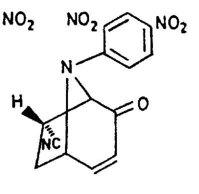
(1) (2) (3)



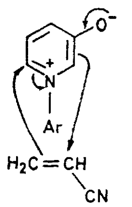
(4) $R = CO_2Me$
(6) $R = CN$



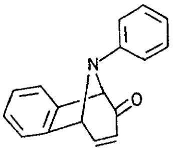
(5) $R = CO_2Me$
(7) $R = CN$
(8) $R = Ph$



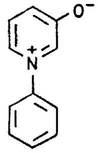
(9)



(10)



(11)



(12)

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† *Added in proof.* Treatment of the hydrochloride (**1**) in acetonitrile with NEt_3 has now given 1-(2,4-dinitrophenyl)-3-oxidopyridinium (**2**), m.p. 112° (85%), which reacts rapidly at room temperature with many olefins.

[1] A. F. Vompe and N. F. Turitsyna, *Zhur. obshchei Khim.*, 1957, **27**, 3282 (*Chem. Abs.*, 1958, **52**, 9112d).

[2] F. Yoneda, *Yakugaku Zasshi*, 1957, **77**, 944 (*Chem. Abs.*, 1958, **52**, 2855c).

[3] R. Huisgen, R. Grashey, and J. Sauer in 'The Chemistry of Alkenes,' in the series 'The Chemistry of Functional Groups,' ed. S. Patai, Interscience, London, 1964, p. 865.

[4] A. R. Katritzky and Y. Takeuchi, *J. Chem. Soc.* (*C*), 1971, 878.

[5] N. Dennis, A. R. Katritzky, and Y. Takeuchi, *J.C.S. Perkin I*, 1972, 2054.

[6] N. Dennis, A. R. Katritzky, S. K. Parton, and Y. Takeuchi, *J.C.S. Chem. Comm.*, 1972, 707.

[7] L. Friedman and F. M. Logullo, *J. Amer. Chem. Soc.*, 1963, **85**, 1549.