

The Dimer of 1-(5-Nitro-2-pyridyl)-3-oxidopyridinium and its Reactions

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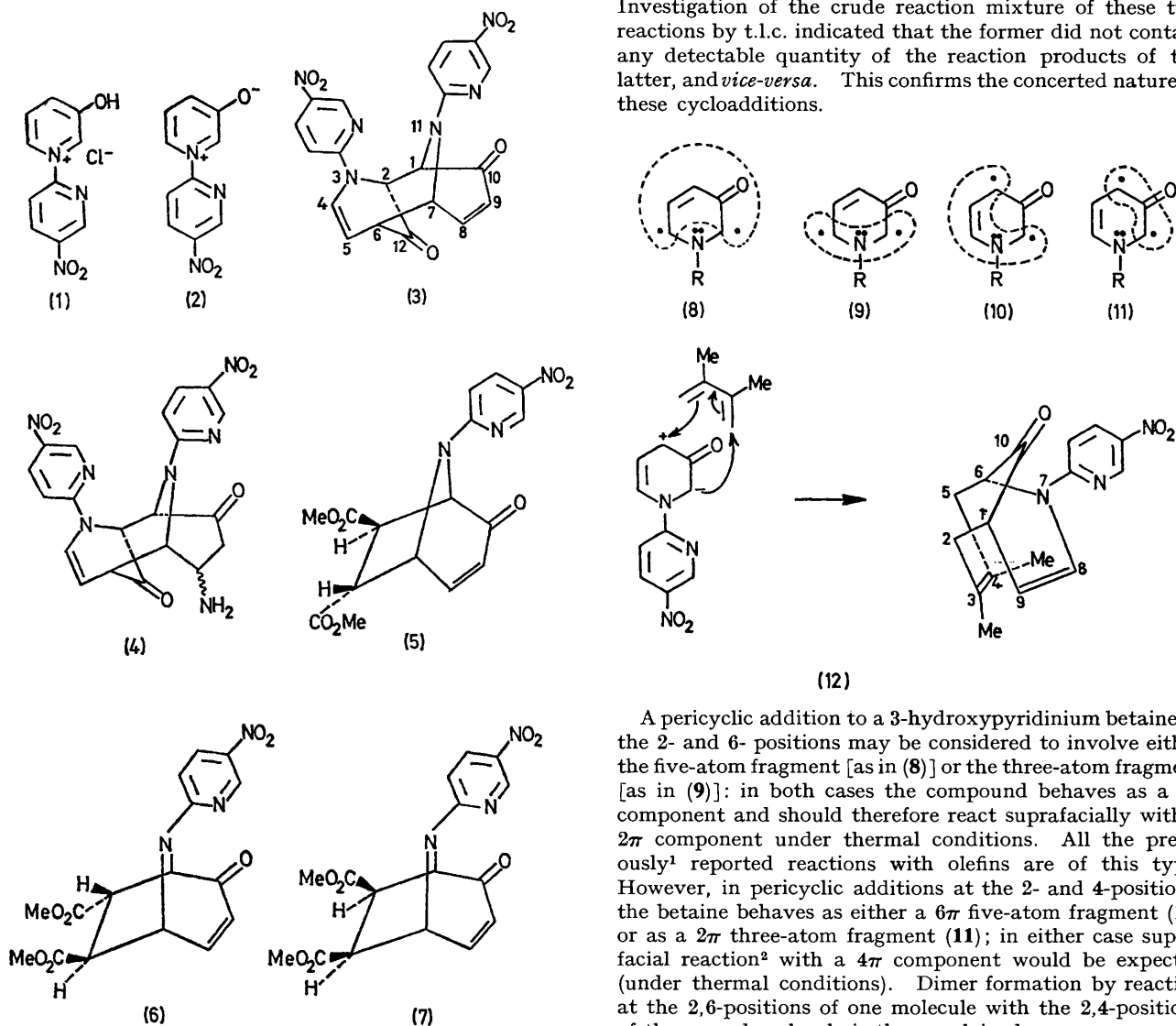
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Summary The betaine 1-(5-nitro-2-pyridyl)-3-oxidopyridinium reversibly forms a dimer which provides a convenient source of the reactive betaine monomer; olefinic dipolarophiles add readily at the 2,6-positions, 2,3-dimethylbutadiene reacts across the 2,4-positions and stereochemical integrity is preserved during the addition of maleic and fumaric esters.

3-HYDROXYPYRIDINE and 2-chloro-5-nitropyridine readily give the quaternary salt (1) m.p. 205–206°, treatment of which with $\text{NEt}_3\text{-CH}_3\text{CN}$ yields, *via* the betaine (2), the

n.m.r. signals for two vinyl groups (four vinyl protons) $\delta[(\text{CD}_3)_2\text{SO}]$ 7.53 (dd, H-8), 7.21 (d, H-4), 6.25 (d, H-9), and 5.13 (dd, H-5)]. The dimer readily forms a mono-amino derivative (4), m.p. 252–253°, $\text{C}_{20}\text{H}_{17}\text{N}_7\text{O}_6$, M^+ 451.

The dimer (3) appears to be in dynamic equilibrium with the monomeric betaine (2), of which it forms a convenient source. Reaction of the dimer (3) with numerous olefins forms the expected adducts. Reaction with dimethyl fumarate gives the two adducts (5) m.p. 174° and (6) m.p. 141–142° in yields of 36% and 54%, whereas reaction with dimethyl maleate gives (7) m.p. 129–130° in 90% yield. Investigation of the crude reaction mixture of these two reactions by t.l.c. indicated that the former did not contain any detectable quantity of the reaction products of the latter, and *vice-versa*. This confirms the concerted nature of these cycloadditions.



dimer (3) (85%) m.p. 196°. The structure and stereochemistry of (3) were established largely by n.m.r., i.r., and mass spectrometry; especially significant were two distinct carbonyl stretching frequencies, at ν (Nujol) 1735 (saturated ketone) and 1680 cm^{-1} (α,β -unsaturated ketone), and the

A pericyclic addition to a 3-hydroxypyridinium betaine at the 2- and 6- positions may be considered to involve either the five-atom fragment [as in (8)] or the three-atom fragment [as in (9)]; in both cases the compound behaves as a 4π component and should therefore react suprafacially with a 2π component under thermal conditions. All the previously¹ reported reactions with olefins are of this type. However, in pericyclic additions at the 2- and 4-positions, the betaine behaves as either a 6π five-atom fragment (10) or as a 2π three-atom fragment (11); in either case suprafacial reaction² with a 4π component would be expected (under thermal conditions). Dimer formation by reaction at the 2,6-positions of one molecule with the 2,4-positions of the second molecule is thus explained.

The dimer (3) with 2,3-dimethylbuta-1,3-diene, gives the cycloadduct (12) (75%) m.p. 123–124°, $\text{C}_{18}\text{H}_{17}\text{N}_3\text{O}_3$. The single $\text{C}=\text{O}$ (Nujol) band at 1720 cm^{-1} (saturated ketone) precludes a structure derived from cycloaddition across the 2,6-positions of the betaine (2). The n.m.r. spectrum

(CDCl₃) shows two vinylic methyl groups (δ 1.50 and 1.70) and two vinyl protons [δ 7.19 (d, H-8), and 4.95 (dd, H-9)]. The conformation of the molecule was determined by extensive spin-spin decoupling experiments and lanthanide-induced shift experiments.

Under photochemical conditions, 2π components such as

olefins should add to the 2,4-positions and 4π components such as 1,3-dienes should add to the 2,6-positions.

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¹ N. Dennis, A. R. Katritzky, T. Matsuo, S. K. Parton, and Y. Takeuchi, *J.C.S. Perkin I*, 1974, 746 and refs. therein.

² R. B. Woodward and R. Hoffmann, *Angew. Chem. Internat. Edn.*, 1969, 8, 781.