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$2\pi + 8\pi$ CYCLOADDITION REACTIONS OF 3-OXIDOPYRIDINIUM BETAINES[1]

Nicholas Dennis, Alan R. Katritzky* and Gebran J. Sabounji

School of Chemical Sciences, University of East Anglia, Norwich, NR4 7TJ

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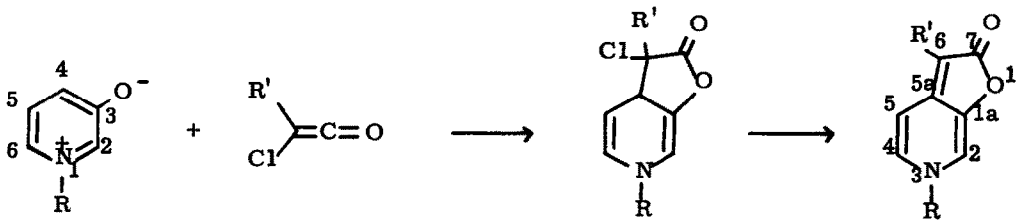
We have reported cycloadditions of 3-oxidopyridinium betaines 1 in which they act as 4π-components (adding 2π[2] or 6π[3] addends across the 2,6-positions) or as $2\pi/6\pi$-components (adding thermally 4π[4] or photochemically $2\pi/6\pi$[5] addends across the 2,4-positions). We now describe cycloadditions in which they act as 8π components, adding 2π addends across the oxygen and the carbon 4.

Dichloroketene (2, R' = Cl) generated in situ from dichloroacetyl chloride[6] or from chloral,[7] in the presence of betaines 1a-d[8] gave, we believe via intermediates 3 which spontaneously lost HCl, the new bicyclic compounds 4a-d (Table).[9] Monochloroketene (2, R' = H) generated from monochloroacetyl chloride[10] yielded compound 4e (R' = H) (Table). For example, treatment of 3-hydroxy-1-phenylpyridinium chloride[11], the precursor of betaine 1b[12] and dichloroacetyl chloride in CH_2Cl_2 with NEt_3 at 0°C gave the adduct 3H-7-oxo-3-phenylfuro[3,2-d] pyridine, 4b. The structures 4 are supported by UV, NMR and mass spectra; the IR spectra (Table) are characteristic for $\alpha\beta$-unsaturated γ-lactones.[13] The NMR spectrum had a 1H doublet at δ 6.90 (J = 8 Hz), a 5H multiplet at δ 7.50, a 1H doublet of doublets at δ 8.10 (J = 8 and 2 Hz) and a 1H fine doublet at δ 8.30 (J = 2 Hz) assigned to the olefinic H-5, the phenyl, the olefinic H-4 and H-2 protons of 4c respectively.



1 2 3 4

R = a, CH_2Ph; b, Ph; c, 3,5-dimethoxy-2,4,6-triazin-1-yl; d, 3,5-dimethyl-2,6-pyrimidin-1-yl; e, Ph. R' = Cl for a-d; R' = H for e.

Ketenes generally undergo concerted $\pi 2s + \pi 2a$ cycloadditions,[14] although formal $2\pi + 4\pi$ additions of ketenes have been reported.[15] Recently, dichloroketene (2, R' = Cl) was reacted[16] with tropone in a $2\pi + 8\pi$ sense to yield a bicyclic lactone by elimination of HCl from an intermediate dichlorolactone.

TABLE. PHYSICAL PROPERTIES OF 3-SUBSTITUTED-7-OXO-3H-FURO[3,2-d]PYRIDINES

Cpd.	IR(ν_{max})($CHBr_3$)(film)				λ_{max} (log ε)(CH_3CN)	Crystal form, m.p. (°C)
	C=O	C=C	C=N	N-C=C		solvent, yield (%)
4a	1740	1545			408 (4.47), 396s (4.37), 265 (3.80)	gold flakes, 279-280° (EtOH)(25%)
4b	1730	1660			366 (4.70), 235 (3.00)	yellow needles, 222-223° (EtOH) (57%)
4c	1734		1600	1670	398 (4.34), 378 (4.36), 217 (3.56)	red needles 245-246°, (DMSO) (30%)
4d	1740	1610		1660	396 (4.46), 374 (4.06), 237 (3.08)	orange-red needles, 275-276° (EtOH) (85%)
4e	1740	1660 1640			367 (4.60), 245 (3.00)	needles 220-222° (dec) (MeOH/EtOEt) (25%)

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