Structures of the Photochemical Isomerization Products of Pyridinium Ylides. Diazepines and their Diels–Alder Adducts[1]

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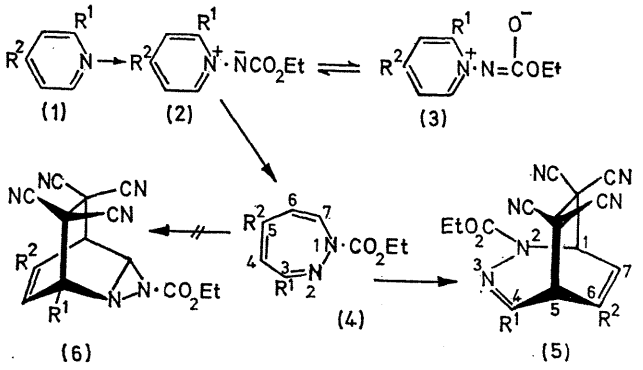
AZEPINE AND OXEPINE are isoelectronic with the cycloheptatrienide anion and, if planar, may be anti-aromatic.[2] The parent 1*H*-1,2-diazepine has not been synthesized, although the *N*-ethoxycarbonyl derivative was reported to



a; R^1 = Me, R^2 = H: b; R^1 = H, R^2 = Me: c; R^1 = R^2 = Me: d; R^1 = R^2 = H.

be obtained from 1-iminopyridinium betaine.[3] It has been suggested that the azepine may have been the 1*H*-1,3-isomer.[3]

We report now that the photomeric products of substituted 1-ethoxycarbonyliminopyridinium betaines are 1-ethoxycarbonyl-1*H*-1,2-diazepines on the basis of spectral evidence.[5] We have also studied the Diels–Alder reactions of the compounds.

The pyridinium betaines (2a—d) were prepared from α-, γ-picoline, 2,4-lutidine, and pyridine by a modified Gösl's method.[6] They showed absorption in the range 1620—1640 cm.$^{-1}$, (picrates 1735—1750 cm.$^{-1}$) which is assignable to the carbonyl stretching frequency.

Irradiation of a dioxan or benzene solution of (2a), (2b), (2c), and (2d) in a Pyrex vessel under nitrogen with a high-pressure mercury lamp (100 w), gave (4a), [λ_{max} (EtOH) 220 (ε 9830) and 325 nm. (426), ν (neat) 1715 cm.$^{-1}$ (CO), τ_{Me_4Si} ($CDCl_3$) 8·68 (t, 3H, CH_3, *J* 7·0 c./sec.), 5·70 (q, 2H, CH_2, *J* 7·0), 7·89 (s, H, CH_3), 3·61 (dd, 1H, 4-H, $J_{4,5}$ 5·0, $J_{4,6}$ 2·0) *ca.* 3·60 (m, 1H, 5-H), 4·31 (dq, 1H, 6-H, $J_{6,7}$ 7·5, $J_{6,5}$ 4·5, $J_{6,4}$ 2·0), 3·67 (dd, 1H, 7-H, $J_{7,6}$ 7·5, $J_{7,5}$ 1·5)] (4b) λ_{max} (n-hexane) 220 (ε 7400), 368 nm. (270), ν (neat) 1700 cm.$^{-1}$ (CO)], (4c) [ν (neat) 1707 cm.$^{-1}$ (CO)], or (4d)[3] [λ_{max} (n-hexane) 220 (ε 9163), 373 nm. (233), ν (neat) 1710 cm.$^{-1}$ (CO)], in 60—80% yields, respectively. The n.m.r. spectra of (4b), (4c), and (4d) were very similar to that of (4a) in the olefinic and aliphatic proton regions; these spectral properties clearly reveal that they are 1,2-diazepines. 1-Iminopyridinium betaines were not, however, converted into the expected diazepines.

The addition of dienophiles to medium-ring polyenes such as cycloheptatriene, oxepine and azepine frequently lead to abnormal products.[7] On the other hand, the diazepines, (4a), (4b), (4c), and (4d), proved surprisingly inert to

dienophiles such as maleic anhydride or dimethyl acetylenedicarboxylate, but did react readily with tetracyanoethylene in benzene at room temperature to give a crystalline 1 : 1 adduct, (5a) [(52·6%), ν (KBr) 2280w (CN), 1700 (CO), 1639 (C : C) cm.$^{-1}$, λ_{max} (EtOH) 248 nm. (ϵ 4450), τ_{Me_4Si} [$(CD_3)_2$SO] 8·73 (t, 3H, CH_3, J 7·0 c./sec.), 5·72 (q, 2H, CH_2, J 7·0), 7·88 (s, 3H, CH_3), 3·91 (dd, 1H, 1-H, $J_{1,7}$ 7·5, $J_{1,6}$ 1·5), 5·64 (dd, 1H,5-H, $J_{6,5}$ 7·0, $J_{5,7}$ *ca.* 1·0), 3·10 (br t, 1H, 6-H, $J_{6,7}$ 8·0, $J_{6,5}$ 7·0, $J_{6,1}$ 1·5), 3·41 (br t, 1H, 7-H, $J_{7,1}$ 7·5, $J_{7,6}$ 8·0, $J_{7,5}$ *ca.* 1·0), (5b) (63·8%), ν (KBr) 2280w (CN), 1710 (CO), 1620 (C : C) cm.$^{-1}$, λ_{max} (EtOH) 238 nm. (ϵ 4290)., (5c) (53·3%), ν(KBr) 2280w (CN), 1700 (C=O), 1638 (C=C) cm.$^{-1}$, and (5d) (56·5%), ν(KBr) 2280w (CN), 1715 (CO), 1625 (C : C) cm.$^{-1}$.

The n.m.r. spectra of (5b), (5c), and (5d) were similar to that of (5a) in these olefinic and aliphatic proton regions; the mass spectra of these adducts showed a molecular ion and a strong peak at $M^+ - 128$ indicating loss of $(NC)_2C : C(CN)_2$ which may be regarded as a retro-Diels–Alder type. From these data the adducts were in accordance with assignment as the 4,7-adduct [(4 + 2) adduct].

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[7] A. S. Kende, P. T. Isso and J. E. Lancasta, *J. Amer. Chem. Soc.*, 1965, **87**, 5044; J. H. vanden Hende and A. S. Kende, *Chem., Comm.*, 1965, 384; more recently, the unusual 1,6-cycloaddition reaction of *N*-ethoxycarbonylazepine with nitrosobenzene was reported; W. S. Murphy and J. P. McCarthy, *Chem. Comm.*, 1968, 1155.