

CONSECUTIVE 1,3-DIPOLAR CYCLOADDITIONS OF CYCLOIMMONIUM YLIDES TO BENZYNE: FORMATION OF NOVEL 18π BENZO[a]ISOINDOLO[1,2,3-cd]INDOLIZINESKiyoshi MATSUMOTO,* Takane UCHIDA,[†] Takazumi SUGI,[†] and Yoshiko YAGI[†]

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Benzo[a]isoindolo[1,2,3-cd]indolizines, a novel kind of 18π heterocycles, have been prepared by one pot successive 1,3-dipolar cycloadditions of pyridinium dicyanomethylides with benzyne.

Peripheral conjugate heterocyclic systems such as bridged heteroannulenes and cyclazines are desired in order to obtain experimental evidence regarding our recognition of the net energy changes associated with π -electron delocalizations.¹⁾ Since bicyclic nitrogen containing meso-ionic compounds, like indolizines and azapentalenes whose resonance hybrids involve an azomethine ylide structure could serve as a bicycloimmonium ylide,²⁾ we have investigated reactions of pyridinium dicyanomethylides with benzyne,³⁾ and now found that the title compounds were formed in one pot procedure.

Reaction of pyridinium dicyanomethylide (1a) with benzyne, generated from anthranilic acid and iso-amyl nitrite, gave benzo[a]isoindolo[1,2,3-cd]indolizines (4a),⁴⁾ 4 %; red needles; mp 129-130 °C, ¹³C-NMR(CDCl₃) δ 111.9(d, C-3), 116.7(d, C-2), 118.6, 120.6, 121.9 and 126.9(each d, C-4,5,6, 7), 120.7, 121.9(each s, C-3b, 7a), 124.6(s, C-7b), 125.5(s, C-3a) (these assignments are tentative) along with 6-cyanobenzo[a]indolizine(2a), 35 % mp 126-128 °C.

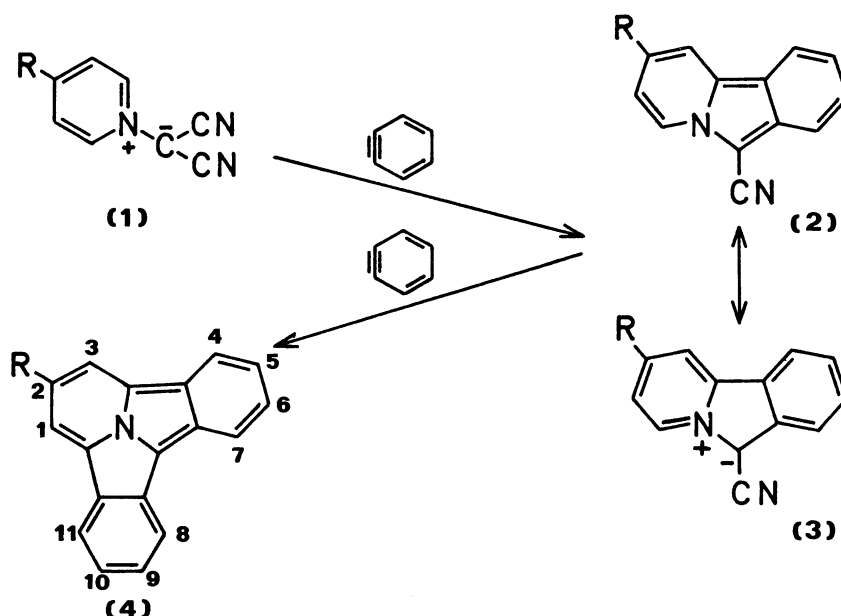
Similarly, 4-phenylpyridinium dicyanomethylide (1b) underwent cycloadditions with benzyne to produce a comparable yield of 2-phenylbenzo[a]isoindolo[1,2,3-cd]indolizine (4b), 2%; light brown needles, together with 6-cyano-2-phenylbenzo[a]indolizine (2b), 10 %; mp 154-155 °C. The presence of an electron withdrawing substituent in the pyridine ring would activate the azomethine ylide (3). In agreement with this, 4-benzoylpyridinium dicyanomethylide (1c) with benzyne afforded a 17 % yield of (4c) as orange fine needles, though the formation of (2c) was still predominant and in 24 % yield. In contrast, 4-methylpyridinium dicyanomethylide (1d) gave a 2 % yield of (4d), a 12 % of (2d) being isolated.

The intermediacy of (2) in the formation of (4) was established from the independent experiment in which (4d) was obtained from (2d) and benzyne in the same reaction condition.

The product (4) could be formed by a 1,3-dipolar cycloaddition of (1) with

benzyne, followed by loss of HCN giving the benzoindolizine (2) which undergoes a further 1,3-dipolar addition with a second molecule of benzyne and subsequent loss of HCN.

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(4)	R	Mp (°C)	M ⁺	v (cm ⁻¹)	pmr (CDCl ₃)
a	H	129-130	241	1610, 1597	7.47-7.97(m, 5H), 8.26-8.68(m, 6H)
b	Ph	175-176	317	1610, 1595	7.16-7.94(m, 9H), 8.27(d, J=9.6 Hz, 2H) 8.45(d, J=9.6 Hz, 2H), 8.56(s, 2H)
c	PhCO	243-244	345	1642, 1590	7.23-8.16(m, 9H), 8.42(d, J=7.8 Hz, 2H), 8.55(d, J=7.8 Hz, 2H), 8.99(s, 2H)
d	Me	181-182	255	1610, 1595	2.98(s, 3H), 7.10-7.82(m, 5H) 8.10-8.63(m, 5H)

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- 2) F. J. Swinbourne, J. H. Hunt, and G. Klinkert, *Adv. Heterocyclic Chem.*, **23**, 103 (1978); C. A. Ramsden, *Tetrahedron*, **33**, 3203 (1977); T. Uchida and K. Matsumoto, *Chem. Lett.*, **1980**, 149.
- 3) Two examples are known for the reactions of cycloimmonium ylides with benzyne: H. Igeta, H. Arai, H. Hasegawa, and T. Tsuchiya, *Chem. Pharm. Bull.*, **23**, 2791 (1975); Y. Yamashita, T. Hayashi, and M. Masumura, *Chem. Lett.*, **1980**, 1133.
- 4) According to the Boekelheide nomenclature,¹⁾ this is named 1,2,3,4-dibenzocycl-[3.2.2]azine. A typical reaction condition: To a refluxing solution of the dicyanomethylide (10.5 mmol) and *iso*-amyl nitrite (53 mmol) in dichloroethane (40 ml) was added dropwise for 6 h a solution of anthranilic acid (52.6 mmol) in dimethoxyethane (60 ml). Satisfactory elemental analyses were obtained for all new compounds.

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