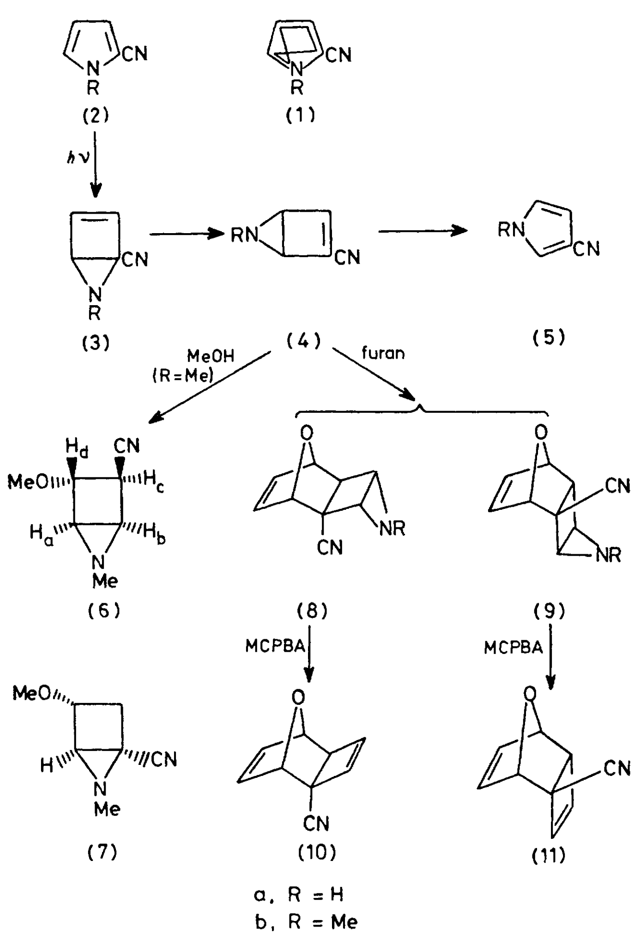
Phototransposition of 2-Cyanopyrroles: Evidence for the Intermediacy of 5-Azabicyclo[2.1.0]pent-2-enes

By JOHN A. BARLTROP, A. COLIN DAY,* and ROBERT W. WARD
(*The Dyson Perrins Laboratory, Oxford University, South Parks Road, Oxford* OX1 3QY)

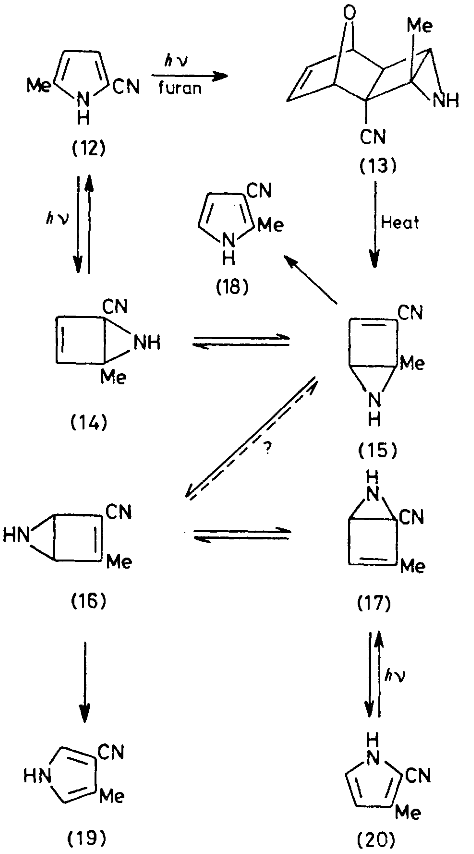
Summary Irradiation of 2-cyano-*N*-methylpyrrole in methanol and in furan and of 2-cyanopyrrole in furan gives, in addition to the corresponding 3-cyanopyrroles, adducts whose structures, together with other experiments, indicate a transposition mechanism involving 2,5-bonding followed by 'walk' of the aziridine nitrogen atom.

The photochemical rearrangement of 2-cyano- to 3-cyanopyrroles[1,2] scrambles the atoms of the ring as shown in the permutation pattern (**1**), with a minor contribution in one case (*viz.* **12**) from a different pattern.[2] We report here the results of trapping experiments with methanol and furan which afford strong evidence for the intermediacy of bicyclic species of the type (**4**) in the rearrangement and therefore for the previously proposed[2] mechanism in which 2,5-bonding is followed by 'walk' of the aziridine nitrogen as shown in Scheme 1. Other experiments are described which suggest that the rearrangement requires thermal activation.



Scheme 1

Irradiation† of 2-cyano-*N*-methylpyrrole (**2b**) in methanol gave, in addition to the 3-cyano-isomer, a methanol adduct (**6**), $C_7H_{10}N_2O$, which showed only end-absorption in the u.v. spectrum and had $\nu(CCl_4)$ 2250, 1212, 1161, 1135, 1118, and 1100 cm^{-1}; ^{1}H n.m.r. ($CDCl_3$)‡ τ 6·30 (H_d), 6·63 (MeO), 7·28 (H_a, H_b, H_c), and 7·70 (MeN); ^{1}H n.m.r. (C_6D_6)‡ τ 6·56 (H_d); 7·20 (MeO), 7·82 (H_c), 7·93 (H_a), 8·08 (H_b), and 8·25 (MeN), J_{ab} 3·6, J_{bc} 2·7, J_{bd} 2·9, and J_{cd} 2·0 Hz; ^{13}C n.m.r. ($CDCl_3$)‡ δ (p.p.m. from Me_4Si) 34·8 (d), 41·8 (overlapping d and q), 45·7 (d), 56·4 (q), 82·9 (d), and 117·5 (s). The i.r. (CCl_4) and ^{1}H n.m.r. (C_6D_6) data agree closely with those reported by Hiraoka[3] for an adduct obtained by irradiation of the pyrrole (**2b**) in methanol with a low-pressure mercury lamp. If, as seems reasonable, the identity of our adduct and Hiraoka's is accepted, then his formulation (**7**) must be ruled out in view of, *inter alia*, the ^{13}C n.m.r. multiplicities reported above. In confirmation of the structure (**6**), treatment of our adduct with *m*-chloroperoxybenzoic acid (MCPBA), a reagent known[4] to convert aziridines into alkenes, gave, in addition to nitrosomethane dimer, *trans,-trans*-1-cyano-4-methoxybuta-1,3-diene, which was probably formed by conrotatory electrocyclic ring-opening of initially formed *trans*-3-cyano-4-methoxycyclobutene. The genesis of the adduct (**6**) is most simply understood as involving nucleophilic attack of methanol upon the $\alpha\beta$-unsaturated nitrile function in the pyrrole valence tautomer (**4**).



Scheme 2

Irradiation† of 2-cyano-*N*-methylpyrrole (**2b**) in furan gave, in addition to (**5b**), the crystalline 1 : 1 adducts (**8b**) and (**9b**), the structures of which were established by ^{1}H n.m.r. spectroscopy‡§ of the adducts themselves, and of the

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† The pyrroles were irradiated as 0·001—0·01 M solutions with 254 nm light at *ca.* 31 °C in a Rayonet reactor.

‡ The n.m.r. spectra were temperature-dependent, owing to inversion of the aziridine nitrogen atom. The n.m.r. data reported in the text were recorded at 35 °C.

§ For example, the major adduct (**8b**) from (**2b**) had ^{1}H n.m.r. data ($CDCl_3$) τ 3·5 (2H, s), 4·92 (1H, s), 4·98 (1H, s), 7·34 (1H, dd, J 2·0 and 3·0 Hz), 7·5 (2H, overlapping doublets), and 7·7 (3H, s). in addition to weak temperature-dependent signals due to the epimer of opposite (*i.e.*, *endo*) configuration at aziridine nitrogen. The derived cyclobutene (**10**) had ^{1}H n.m.r. data ($CDCl_3$) τ 3·4 (2H, s), 3·6 (1H, d, J 2·8 Hz), 3·73 (1H, d, J 2·8 Hz), 5·27 (1H, s), 5·41 (1H, s), and 6·95 (1H, s). The n.m.r. spectra of the 2-cyanopyrrole adducts (**8a**) and (**9a**) showed similar features to those for the corresponding *N*-methyl adducts.

tricyclic 3-cyanocyclobutenes (**10**) and (**11**) obtained by treatment with MCPBA. Analogously, 2-cyanopyrrole gave adducts (**8a**) and (**9a**), degradable to (**10**) and (**11**) with MCPBA. With both (**2a**) and (**2b**), the major furan adduct was that (**8**) conforming to the *endo*-addition rule for Diels-Alder addition of furan to the dienophilic acrylonitrile grouping in (**4**).

The formation of azabicyclopentenes (**4**), for which the structures of the various adducts described afford compelling evidence, must involve a thermally activated step, since irradiation of 2-cyano-*N*-methylpyrrole at −68 °C yielded no detectable transposition product. If, as seems probable, the 2,5-bonded species (**3**) is the precursor of (**4**), then this temperature effect suggests that the thermal reversion of (**3**) to (**2**) has a lower activation energy than the isomerisation to (**4**).

Clearer evidence of the thermal interconversion of intermediates in 2-cyanopyrrole photochemistry was obtained by pyrolysis of the furan photoadducts. For example, the major adduct (**13**) from 2-cyano-5-methylpyrrole (**12**) [presumably formed *via* (**14**) and (**15**)], when heated at 174—180 °C for 3 h, gave, in addition to furan, the four cyanopyrroles (**12**), (**18**), (**19**), and (**20**) in the ratio 4 : 6 : 2 : 1, respectively (Scheme 2). The simplest interpretation of this result is that Diels-Alder retrogression of (**13**) yields (**15**), thereby giving access to the three isomeric azabicyclopentenes (**14**), (**16**), and (**17**) that are derivable from (**15**) by one or more nitrogen 'walk' steps. Evidently, all three isomers (**14**), (**16**), and (**17**) must be formed from (**15**) at rates competitive with aromatisation rates at 174—180 °C. In these terms 'walking' of the aziridine ring becomes progressively less favourable relative to aromatisation as the temperature is lowered. The −68 °C irradiation experiment is the extreme case. At our normal irradiation temperature (*ca.* 31 °C), the formation of products requiring more than a single 'walk' step is rare [*e.g.*, (**20**) gave solely (**19**) upon irradiation[2]], and even when such further scrambling is observed it is a relatively minor pathway. Thus, the previously reported[2] irradiation of (**12**), which presumably effects entry at (**14**) into the same set of azabicyclopentenes [(**14**)—(**17**)] as that formed pyrolytically from (**13**), gave (**18**) and only minor amounts of (**19**) by, respectively, single- and double-'walk' processes (**14** → **15** → **18** and **14** → **15** → **16** → **19**).[¶] Moreover, in contrast to the pyrolysis of (**13**), the photoisomerisation of (**12**) gave none of the 2-cyanopyrrole (**20**).

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[¶] By irradiation of [4-^{2}H]-(**12**) in methanol, we have now established unique permutation patterns for the photoproducts consistent with the mechanism shown, *i.e.*, the single-'walk' route to (**18**) and the double-'walk' route to (**19** (J. A. Barltrop, A. C. Day, J. N. Hepburn, and R. W. Ward, unpublished results). This reaction also gave a methanol adduct, 2-cyano-4-deuterio-3-methoxy-1-methyl-5-azabicyclopentane, the analogue of the adduct (**6**) obtained from (**2b**).

[1] H. Hiraoka, *Chem. Comm.*, 1970, 1306.
[2] J. A. Barltrop, A. C. Day, P. D. Moxon, and R. W. Ward, *J.C.S. Chem. Comm.*, 1975, 786.
[3] H. Hiraoka, *Chem. Comm.*, 1971, 1610.
[4] H. W. Heine, J. D. Myers, and E. T. Peltzer III, *Angew. Chem. Internat. Edn.*, 1970, **9**, 374.