# Photolyses and Pyrolyses of 3-Cyclopropyl-1-pyrazoline Derivatives

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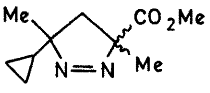
*Summary* Photolysis and pyrolysis of 3-cyclopropyl-1-pyrazoline derivatives does not involve the rearrangement of a cyclopropylcarbinyl radical intermediate.

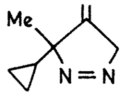
ALTHOUGH the rearrangements of cyclopropylcarbonium ions have been investigated,[1,2] relatively little is known about the behaviour of cyclopropylcarbinyl radicals.[2,3] We showed[4] that the nature of the biradicals, formed by decomposition of 4-alkylidene-1-pyrazoline derivatives, is strongly influenced by the decomposition conditions. We report here decomposition reactions of methyl 3-cyclopropyl-3-methyl-1-pyrazoline-5-carboxylate (I) and 3-cyclopropyl-3-methyl-4-methylene-1-pyrazoline (II). It was thought interesting to see if differences in the structure of the biradical would affect the fate of the cyclopropylcarbinyl radical portion of the biradical.

1-Cyclopropyl-1-diazoethane (III)[5] reacted rapidly with methyl methacrylate. However, the expected product (I) could not be isolated, as it decomposed slowly at room temperature (rapidly at 80°) to give a mixture of methyl 1,2-dimethyl-2-cyclopropylcyclopropanecarboxylates (IVa) and methyl 4-cyclopropyl-2-methyl-2-pentenoates (Va). The photolysis (Pyrex filter) of (I) also gave the same four products in similar proportions (see Table). The pyrolysis of (IVa) at 250° caused ring cleavage to give methyl 4-cyclopropyl-2-methyl-4-pentenoate (VI) whereas (IVb) was unchanged at this temperature.

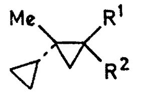
The reaction of (III) and allene afforded (II) as a distillable product, which, on pyrolysis (250°) or photolysis, gave 2-cyclopropyl-2-methyl-1-methylenecyclopropane (VII) and (1-cyclopropylethylidene)cyclopropane (VIII) identical with a sample of (VIII) prepared by another route. That the same products are formed in similar proportions both by



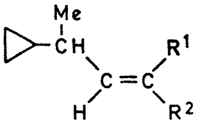
(I)



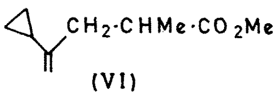
(II)



(IV) a; $R^1 = CO_2Me, R^2 = Me$
b; $R^1 = Me, R^2 = CO_2Me$

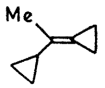


(V) a; $R^1 = CO_2Me, R^2 = Me$
b; $R^1 = Me, R^2 = CO_2Me$



(VI)

(VII)



(VIII)

*Product compositions (by g.l.c. peak area ratio)*

| | From (I) | | | | From (II) | |
|---|---|---|---|---|---|---|
| | (IVa) | (IVb) | (Va) | (Vb) | (VII) | (VIII) |
| Pyrolysis | 45·6 | 38·7 | 5·0 | 10·7 | 82 | 18 |
| *h*ν/Direct | 46·3 | 40·5 | 3·1 | 10·1 | 71 | 29 |
| *h*ν/Benzophenone | 50·7 | 46·5 | 0·9 | 3·3 | 70 | 30 |

photosensitised and unsensitised photolysis (see Table) is in strong contrast to our earlier observation. At 250°, (VII) and (VIII) reached an equilibrium consisting of (VII) (24%) and (VIII) (76%). Pyrolysis of (II) gave the thermodynamically less stable isomer (VII) in a greater proportion than that obtained by photolysis. In no case were products found which could have resulted from rearrangement of the cyclopropylcarbinyl radical. The effect of substituents on the mode of decomposition of (II) and related systems are being investigated.

All the compounds isolated had the expected spectral properties.

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[1] P. D. Bartlett, "Nonclassical Ions," Benjamin, New York, 1965.

[2] R. Breslow, "Molecular Rearrangements," ed. P. de Mayo, Interscience, New York, 1963, p. 233.

[3] L. K. Montgomery, J. W. Matt, and J. R. Webster, *J. Amer. Chem. Soc.*, 1967, **89**, 923; I. A. Halgren, M. E. H. Howden, M. E. Medof, and J. D. Roberts, *ibid.*, 3051; S. J. Cristol and R. V. Barbour, *ibid.*, 1968, **90**, 2832, and references therein.

[4] S. Sanjiki, H. Kato, and M. Ohta, *Chem. Comm.*, 1968, 496; *cf.* also S. D. Andrews and A. C. Day, *ibid.*, 1966, 667.

[5] A. C. Day, P. Raymond, R. M. Southam, and M. C. Whiting, *J. Chem. Soc.* (*C*), 1966, 467.