Photolysis of 4-Alkylidene-Δ^1-pyrazoline-3-carboxylates

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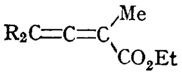
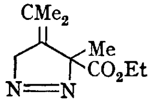
The thermal rearrangement of methyl-substituted methylenecyclopropanecarboxylates was found to give the alkylidenecyclopropanecarboxylates rather than the expected methylcyclopropylideneacetates.[1] To better understand the mechanism of this rearrangement, particularly with respect to the structure of the intermediate and the kinetically controlled process, we studied the decomposition of 4-alkylidene-Δ^1-pyrazoline-3-carboxylates (II and III), and report our preliminary findings which are complementary to the results reported by Andrews and Day.[2,3]

The reaction of allenecarboxylates (I; R = Me and R = H) and diazoalkanes proceeded normally[‡] to give the 4-alkylidene-Δ^1-pyrazolines (II and III[§]). Pyrazolines (II) and (III) were irradiated in pentane solution, using a high pressure mercury lamp with Pyrex filter, to give four products; the two main products were identified as alkylidenecyclopropanecarboxylates (IV) and (V) and the minor ones were tentatively considered as ethyl *cis*- and *trans*-α-2,2-dimethylcyclopropylidenepropionates (VIa and VIb) from spectroscopic data.[¶] The results given in the Table show that the carbon skeletons of the pyrazolines are mostly conserved during the reaction. The same four components were formed by benzophenone-sensitized photolysis of both (II) and (III), in this case in a similar product ratio, as shown in the Table; this result suggests that (II) and (III) decompose through an identical (presumably a 2-methylenetrimethylene bi-radical)[4] intermediate. Although both (IV) and (V) were photo-stable in the presence or absence of benzophenone, (V) was found to rearrange completely at 135° to (IV) and not to (VI). Thus, it may be concluded that (IV), rather than (V), is the favoured product of both the kinetically and thermodynamically controlled process.

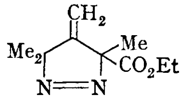


$R_2C{=}C{=}C(Me)CO_2Et$

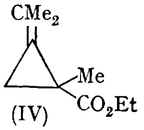
(I)



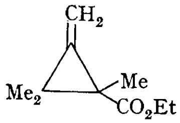
(II)



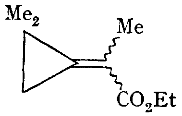
(III)



(IV)



(V)



(VIa) and (VIb)

TABLE

Photolysis conditions	*Relative yields of products* (%)			
	(IV)	(V)	(VIa)	(VIb)
(II) direct	78·6	6·8	7·8	6·8
(III) direct	6·1	84·6	9·0	0·3
(II) sensitized ..	84·0	9·2	4·9	1·9
(III) sensitized ..	82·8	11·2	5·0	1·0

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[‡] An example of an abnormal addition is reported in ref. 3.

[§] All the new compounds described have been characterized by combustion analyses, i.r. and n.m.r. spectra.

[¶] These two components show similar spectra: i.r. absorptions at 3040, 1710, and 1140 cm.$^{-1}$ and n.m.r. peaks at τ 8·07t (3*H*), 8·80s (6*H*) besides those for the ethyl groups. The signals of ring methylene protons are superimposed with the above signals. The geometry of these two products has not yet been elucidated.

[1] A. Nishimura, H. Kato, and M. Ohta, unpublished results.
[2] S. D. Andrews and A. C. Day, *Chem. Comm.*, 1966, 667.
[3] S. D. Andrews and A. C. Day, *Chem. Comm.*, 1967, 902.
[4] P. Dowd, *J. Amer. Chem. Soc.*, 1966, **88**, 2587; R. J. Crawford and D. M. Cameron, *ibid.*, p. 2589; P. Dowd and K. Sachdev, *ibid.*, 1967, **89**, 715; R. G. Doerr and P. S. Skell, *ibid.*, p. 3062; P. S. Skell and R. G. Doerr, *ibid.*, p. 4689.