topic enrichment of the alcohol (30% excess C^{13}) suggests that detection of C^{13} in carbon-4 would have been achieved, had mechanism (1) occurred to the extent of 20% or more.

The above arguments lead to the conclusion that under strong acid conditions carbonium ion rearrangements of the neopentyl system do not occur mainly *via* protonated cyclopropanes.[5]

(5) Since our interests when we started this work were not centered around the intermediacy of protonated cyclopropanes in carbonium ion rearrangements, no attempt was made to identify any product of cyclopropane skeleton. We wish to emphasize that our arguments do not necessarily apply to reactions done under basic conditions,[1a] nor do they exclude protonated cyclopropanes as intermediates in the formation of cyclopropane compounds.[1b] In addition we wish to point out that the work of J. D. Roberts and J. A. Yancy, THIS JOURNAL, **77**, 5558 (1955), on the reaction of 2,3,3-trimethyl-2-butanol-1-C^{14} with concentrated hydrochloric acid also excludes any protonated cyclopropane intermediates prior to formation of classical carbonium ions, or before reaction of classical carbonium ions with chloride ions.

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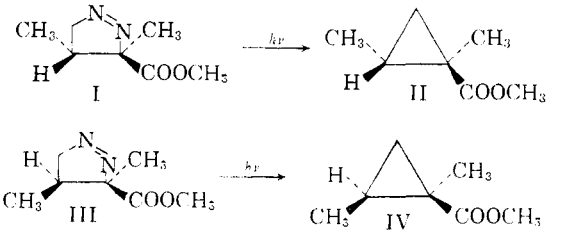
LIGHT-INDUCED DECOMPOSITION OF PYRAZOLINES. AN IMPROVED ENTRY INTO THE CYCLOPROPANE SERIES

Sir:

Thermal decomposition of pyrazolines is a well-known route to cyclopropanes.[1,2,3,4] The synthetic value of the reaction is reduced considerably, however, by the extensive formation of olefinic products,[2,3,4,5,6] by a lack of stereospecificity,[5] and often by extensive tar formation.[2] We now wish to report that light-induced decomposition of stereoisomeric pyrazolines has led to the formation of cyclopropanes stereospecifically, and without olefin formation.

When 3-carbomethoxy-*cis*-3,4-dimethyl-1-pyrazoline (I), prepared by treatment of methyl tiglate with diazomethane,[5,7] was irradiated with a sunlamp at *ca.* 15°, the sole product (by gas-liquid chromatographic analysis) was methyl *cis*-1,2-dimethylcyclopropane - 1 - carboxylate (II), $n^{25}D$ 1.4289 [*Anal.* Found: C, 65.26; H, 9.44].



Irradiation at *ca.* 30–35° of 3-carbomethoxy-*trans*-3,4-dimethyl-1-pyrazoline (III),[5] prepared from methyl angelate and diazomethane, gave a mixture of esters which gas chromatographic analysis showed to consist of 87% methyl *trans*-1,2-dimethylcyclopropane - 1 - carboxylate (IV), $n^{25}D$ 1.4218 [*Anal.* Found: C, 65.86; H, 9.50], 2% II, 7% methyl 2,3-dimethyl-2-butenoate (V) (identified by infrared spectrum and gas chromatographic retention time identical with those of an authentic sample), and 4% methyl angelate (identified in the same manner as V). At 33–35° irradiation of I gave a mixture of esters found by gas chromatography to consist of 73% II, 3% V, and 20% methyl tiglate (identified in the same manner as V). The methyl angelate and methyl tiglate formed in these irradiations resulted from the apparent reversal of pyrazoline formation, a reaction which has not been previously observed.

The structures of the products were established as cyclopropanes by their infrared, ultraviolet, and n.m.r. spectra. The infrared spectra of II and IV (in carbon tetrachloride) contain no olefinic bands in the 1700–1600 or 950–880 cm.$^{-1}$ regions,[8] while their ultraviolet spectra show only weak end absorption (ϵ *ca.* 200). Olefinic hydrogen peaks are absent from their n.m.r. spectra, while cyclopropane hydrogens appear in the region τ[9] = 8.6–9.8.[10]

Steric assignments of II and IV were made on the basis of (a) competitive saponification of a mixture of II and IV in which the less hindered ester moiety of II was hydrolyzed more rapidly than that of IV, and (b) their formation from pyrazolines, in which stereospecific inversion is considered to be unlikely.

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THE METABOLISM OF ALDOSTERONE: ISOLATION AND CHARACTERIZATION OF TWO NEW METABOLITES[1]

Sir:

In this report we describe the isolation of two new metabolites of *d*-aldosterone, 5α-(4,5)-dihydroaldosterone (Ia) and 3βOH,5α-(4,5)-tetrahydroaldosterone (IIa), from the incubate of *d*-aldosterone with rat liver homogenates. In addition, the synthetic preparation of 5α-(4,5)-dihydroaldosterone 21-acetate (IIIb), 3βOH,5α-(4,5)-tetrahydroaldosterone (IIb), the 3-keto etiolactone (IVb), and the 3-hydroxy etiolactone (VIb) are recorded. Romani, *et al.*,[2] have suggested the formation of

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(2) J. D. Romani, C. Bessard, J. Sosa-Castellanos and A. Keller, *Ann. Endocrinol.*, **20**, 209 (1959).