Evidence for the Formation of Triplet 1,3-Biradicals on Photolysis of *cis*- and *trans*-3,4-Dimethyl-Δ^1-pyrazoline

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Summary The stereochemistry of the *cis*- and *trans*-1,2-dimethylcyclopropanes produced on photolysis of *cis*- and *trans*-3,4-dimethyl-Δ^1-pyrazoline indicates that triplet biradicals are intermediates; the results also indicate that triplet biradical production becomes more important on photolysis at shorter wavelengths.

Because they are thought to decompose to biradical intermediates, there has been considerable interest in the photochemical and thermal decomposition of cyclic azo-compounds.[1-3] Specifically, the thermolysis of Δ^1-pyrazolines has been interpreted to proceed through a trimethylene intermediate of defined stereochemistry,[2] whereas their photolysis is thought to produce an excited singlet trimethylene intermediate that has only a small barrier to internal rotation.[3] We present here evidence that the photolysis of Δ^1-pyrazolines also results in the production of a triplet trimethylene biradical intermediate. The relative importance of the triplet trimethylene pathway appears to increase on photolysis of these Δ^1-pyrazolines at shorter wavelengths in their first singlet band.

Table 1. *Decomposition products of* trans-3,4-*dimethyl*-Δ^1-*pyrazoline* (mol %)[a]

Excitation	Pressure (Torr)	(A)	(B)	(C)	(D)	(E)	(D)/(E)
Thermal[b]	100—200	0	16·3	15·8	21·8	46	0·47
334 nm	14	4·1	17·1	15·1	35·7	26·4	1·4
313 nm	311 (N_2)	7·1	13·9	13·0	42·4	23·6	1·8
313 nm	0·88	7·7	15·7	13·1	39·0	24.5	1·6
297 nm	286 (N_2)	8·7	11·2	10·7	48·2	21·2	2·3
Hg[c]	700 (Ar)	0	1·1	3·4	56	25	2·2
Ph_2CO[b]	Liquid	0	0·8	0·3	72	26	2·8

[a] (A) = *trans*-but-2-ene; (B) = 2-methylbut-2-ene; (C) = 2-methylbut-1-ene; (D) = *trans*-1,2-dimethylcyclopropane; (E) = *cis*-1,2-dimethylcyclopropane. [b] Ref. 3. [c] Ref. 6.

Tables 1 and 2 summarize the product compositions observed on decomposition of *trans*- and *cis*-3,4-dimethyl-Δ^1-pyrazoline. The gas-phase photolysis measurements were carried out with a 200 W high-pressure mercury lamp in conjunction with a grating monochromator. Because of the relatively small contribution of the pentene isomers to the total products[3] (*ca.* 7%), we did not characterize carefully the 1,2-hydrogen migration products produced on photolysis of *cis*-3,4-dimethyl-Δ^1-pyrazoline; consequently, we report only the ratio of the dimethylcyclopropanes produced on photolysis of this isomer. Under the conditions of our experiments no other C_5 compounds were observed in the products photolysis of either Δ^1-pyrazoline.

TABLE 2. *Product ratio of* trans-1,2-*dimethylcyclopropane* (D) *to* cis-1,2-*dimethylcyclopropane in the decomposition of* cis-3,4-*dimethyl*-Δ^1-*pyrazoline*

Excitation	Pressure (Torr)	(D)/(E)
Thermal[a]	100—200	0·8
334 nm	270—320 (N_2)	0·7
313 nm	160—380 (N_2)	1·4
297 nm	386 (N_2)	2·5
Hg[b]	700 (Ar)	2·2
Ph_2CO[a]	liquid	2·6

[a] Ref. 3. [b] Ref. 6.

For some systems there is considerable confidence that a triplet 1,2-dimethyltrimethylene biradical is formed as an intermediate: the addition of triplet methylene to but-2-enes,[4] the mercury- and triplet-benzene-sensitized decomposition of 2,3-dimethylcyclobutanones,[5] and the mercury,[6] and benzophenone-sensitized[3] decomposition of 3,4-dimethyl-Δ^1-pyrazoline. In all of these cases there appears to be a characteristic *trans*-dimethylcyclopropane/*cis*-dimethylcyclopropane product ratio of *ca.* 2·2—2·9, independent of the stereochemistry of the precursor, apparently indicative of an equilibrated triplet trimethylene biradical. The variation in the stereochemical ratio is due to the different vibrational energy content of the intermediate formed in these various systems.[5] Moreover, it appears that 1,2-hydrogen migration is relatively unimportant in the triplet biradical.

The results given in Tables 1 and 2 illustrate that on photolysis at shorter wavelengths of both Δ^1-pyrazoline isomers, the stereochemical ratio of the dimethylcyclopropane product, as well as the relative amount of 1,2-hydrogen migration product, become more characteristic of that observed on triplet sensitized decomposition of these Δ^1-pyrazolines. It appears likely that on photolysis, dissociation of the Δ^1-pyrazoline occurs in part from a triplet state that gives rise to triplet trimethylene biradicals, and that the relative contribution of the triplet state to decomposition becomes greater at shorter wavelengths.

This work has been supported by a National Science Federation grant.

(*Received*, 21*st December* 1971; *Com.* 2164.)

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