Photochemistry of Azocyclopropane

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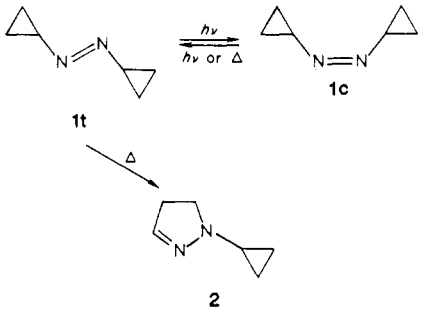
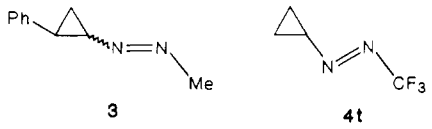
trans-Azocyclopropane (**1t**) has been irradiated in the gas phase at 254 nm and in hydrocarbon solution at several wavelengths. As with most acyclic azoalkanes, the dominant reaction is isomerization to the *cis*-azoalkane **1c**. In the gas phase or with short wavelength light, **1t** undergoes competitive C–N homolysis, giving cyclopropyl radicals, and ring fragmentation to ethylene. Triplet-sensitized isomerization of the azo linkage proceeds with unusually high efficiency ($\Phi_{t\rightarrow c} = 0.2$), but no experimental support could be found for the notion that cyclopropane ring cleavage leads to azo group isomerization. Since azocyclopropane behaves as a "reluctant azoalkane" that undergoes multiple photoreactions, it is not a particularly useful source of cyclopropyl radicals.

Seven years ago, we reported the synthesis and thermal chemistry of the simplest azocycloalkane, azocyclopropane **1**.[1] Unlike typical azoalkanes,[2,3] **1** does not lose nitrogen thermally or photochemically. Instead, UV irradiation interconverts the trans and cis isomers (**1t** and **1c**) while thermolysis affords pyrazoline **2**. Perusal of the literature



reveals only a few compounds with a cyclopropyl ring attached to the azo linkage.[4-8] We recently reinvestigated one of these (**3**) and found that cis–trans isomerization of the azo linkage is very much faster than any reported photoreaction.[9] The photochemistry of [(trifluoromethyl)azo]cyclopropane (**4**) has also been studied,[6] but as we shall see below, the reported products are severely inconsistent with those of related azoalkanes. Thus there



is a shortage of reliable data on photoreactions of azocyclopropanes. Our interest in forcing decomposition of reluctant azoalkanes,[10] in comparing laser irradiation with conventional light sources,[11,12] and in the chemistry of cyclopropyl radicals[13,14] prompted the present detailed study of **1**. Photolysis is examined under the following conditions: (1) in the gas phase at 254 nm with excess isobutane, (2) in hydrocarbon solution irradiating with an excimer laser and mercury lamps at several wavelengths, and (3) in solution under triplet sensitization. It is found that azocyclopropane is unusually photostable (a "reluctant azoalkane"), but when it does react, cleavage of a cyclopropane ring bond competes with the expected C–N homolysis.

Table I. Products of Gas-Phase Azocyclopropane Photolysis[a]

product	yield, %	product	yield, %
methane	0.5	hexamethylethane	4.6
ethane	2.1	isooctane	1.0
ethylene	11.0	4,4-dimethylpentene	0.91
cyclopropane	9.2	bicyclopropyl	0.22
propene	0.5	allylcyclopropane	0.02
isobutene	12.5	*tert*-butylcyclopropane	0.06

[a] Yields for 254-nm irradiation of ~20 mm **1t** and 700 mm isobutane; 70% of **1** disappeared.

Results and Discussion

Electronic Spectrum of 1. Figure 1 shows that in accord with the usual behavior of azoalkanes,[15-17] **1c** absorbs at longer wavelength and with a greater extinction coefficient than **1t**. However the wavelength maximum for **1t** (332 nm) is shorter than that of *trans*-azoisopropane (AIP, 358 nm), a reasonable model compound, while the ϵ of **1t** (51.5) is higher than that of AIP (14.8).[18] These differences suggest mixing of the weak azoalkane $n \rightarrow \pi^*$ transition with the more strongly allowed transitions of the cyclopropyl group.[19] The window in the 280-nm region of the azocyclopropane spectrum allows for selective irradiation of triplet photosensitizers while the strong absorption below 250 nm provides an opportunity to study the short wavelength photochemistry of **1**. Interestingly, the cyclopropyl group lowers the energy of the short wavelength transition, in contrast to its effect on the n,π^* transition. Thus the λ_{max} of gaseous **1t** (207 nm) is longer than that of gaseous AIP (195 nm).[20] Furthermore, the short wavelength band of **1c** is at higher energy than the corresponding band of **1t** (**1c**, 204 nm; **1t**, 213 nm, both in pentane). This difference is again in the opposite direction from the n,π^* band where the cis isomer absorbs

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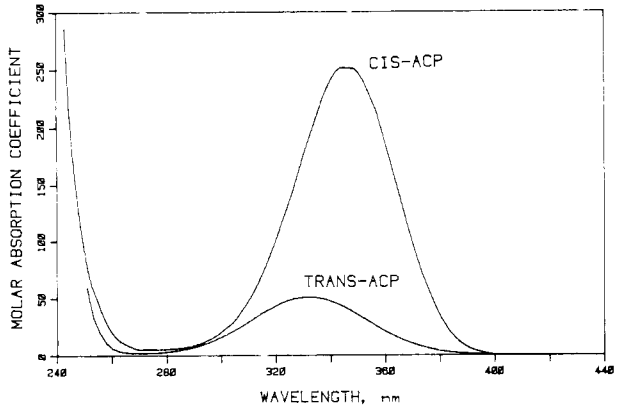


Figure 1. UV spectrum of *trans*- and *cis*-azocyclopropane.

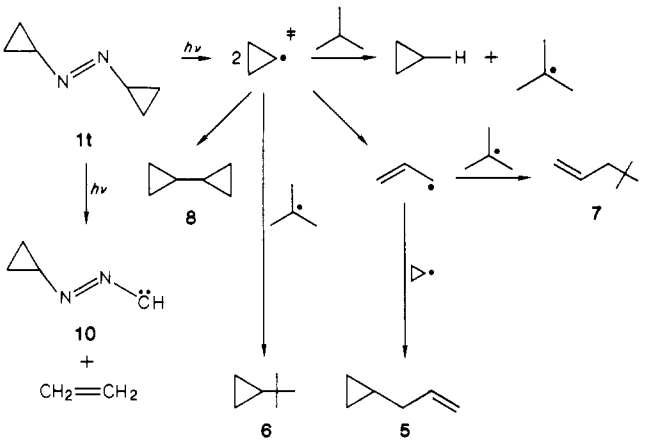
at lower energy. These effects are not readily explained, particularly since the spectral assignment of the azoalkane short-wavelength band is uncertain.[15,20,21]

Gas-Phase Photolysis. A sample of **1t** at approximately 20 mm of pressure and at 47 ± 3 °C was continuously mixed with 700 mm of isobutane while irradiating at 254 nm through vycor glass. GC analysis of the gaseous mixture showed the major products to be ethylene, cyclopropane, isobutane, and hexamethylethane (cf. Table I). Unlike most gas-phase azoalkane photolyses, irradiation of **1t** is far from quantitative. Not only does a polymeric material form on the vessel's walls, but the total yield of *tert*-butyl products is only 37.2%, while that of cyclopropyl products is even lower at 11.2%.

Authentic samples of the minor products allylcyclopropane (**5**)[22] and *tert*-butylcyclopropane (**6**)[23] were synthesized independently while 4,4-dimethyl-1-pentene (**7**) was identified by comparison with purchased material. Bicyclopropyl (**8**) was recognized by its characteristic mass spectrum.[24] At least four GC peaks accounting for 5–10% of the starting material remain unidentified, but a small amount of **1c** could be detected. Certain products expected on the basis of the work of Chakravorty, Pearson, and Szwarc (CPS)[6] were specifically shown to be absent. Thus the NMR spectrum of material washed down from the walls after the photolysis of **1t** did not exhibit any peaks in common with authentic unsubstituted 2-pyrazoline (**9**)[25] or with **2**.[1] The concentrated gaseous photolysate was then examined by GC and found not to contain either pyrazoline. Known samples of 1,5-hexadiene and isooctene were used to show that these compounds were not present in detectable amounts.

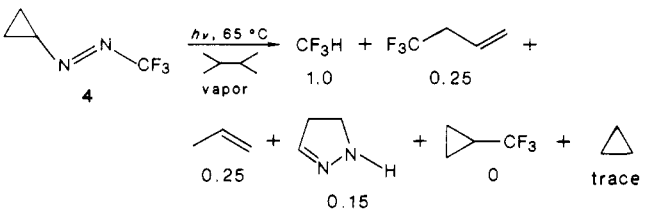
The nature of the gas-phase products immediately suggests two primary processes of **1t** (cf. Scheme I). Cleavage of the cyclopropyl ring affords ethylene in a reaction well-known in cyclopropanes[26] but discovered only recently in an azocyclopropane.[9] Interestingly, the high-resolution mass spectrum of **1t** shows more C_2H_4 than N_2. Although we were unable to detect products from **10**, this nitrile imine might have contributed to the polymeric

Scheme I. Photolysis of Gaseous Azocyclopropane in Isobutane



material on the vessel walls, especially since none of the components of the photolysis mixture are reactive enough to trap **10** cleanly.[27] The other primary photoreaction of **1t** is cleavage to cyclopropyl radicals that mainly abstract hydrogen from the bath gas. Very few of the cyclopropyl radicals afford radical recombination products, but some are sufficiently excited to rearrange to allyl radicals.[13] Although these allyl radicals show up in products **5** and **7**, they do not reach a high enough concentration to dimerize. The *tert*-butyl radicals undergo their usual recombination and disproportionation reactions, the isobutane from the latter process being undetectable in the presence of the large amount of this gas present initially. Apparently some *tert*-butyl radicals attack isobutene, affording *tert*-octyl radicals that appear as isooctane but not as isooctene.

Whereas all of the above reactions are reasonable in light of prior knowledge about azoalkanes and radicals, they contrast sharply with earlier results obtained by CPS[6] on [(trifluoromethyl)azo]cyclopropane (**4**). Their molar ratios of products relative to N_2 are reproduced below. CPS



found very little cyclopropane, our major cyclopropyl product, and they did not mention ethylene, the manifestation of a new primary process.[9] Moreover, they obtained a substantial quantity of a formal recombination product $CF_3CH_2CH{=}CH_2$ in the gas phase but not in solution. The cyclic mechanism written to rationalize this product has no analogy in azoalkane chemistry and if applied to **1t**, would give allylcyclopropane **5**. In accord with the usual ideas about cage effects,[28] we found very little of this recombination product or bicyclopropyl **8** in the gas phase. CPS reported a considerable amount of propene, but our study gave only 0.5% of this hydrocarbon, as expected from the poor hydrogen abstracting ability of the allyl radical. Finally, we proved the absence of 2-pyrazoline, another of CPS's reported products. It was proposed that cyclopropyldiazenyl radical **11** rearranges

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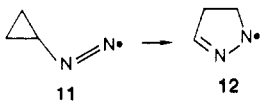
Table II. Quantum Yields of *trans*-Azocyclopropane Photolysis

wavelength, nm	solvent	$\Phi_{t\rightarrow c}$	$\Phi_{t\rightarrow N_2}$	% 1c at pss[a]
366	n-C_5H_{12}	0.6	<0.001[b]	9.5
313	C_6D_6	0.6	low	33
254	n-C_5H_{12}	0.2	0.005[b]	[c]
254	C_6D_6	0.6	<0.004[d]	44
193	n-C_5H_{12}	0.2	0.08[b]	[c]

[a] Percent 1c at the photostationary state. [b] Measured with a Toepler pump and gas buret. [c] No pss reached on account of photodecomposition. [d] NMR analysis of hydrocarbons assuming that 5% decomposition could have been seen.

to the pyrazolinyl radical **12** but **11** does not exhibit this behavior in solution[8] where rearrangement should be favored over fragmentation. Even if **12** formed, it would



11 **12**

be too unreactive to abstract hydrogen from the bath gas.[29] Although the structural difference between **1t** and **4** or our use of a shorter photolysis wavelength could account for these discrepancies, we tend to regard the results of CPS as highly suspect.[30]

Solution-Phase Direct Photolysis. Irradiation into the n,π^* band of azoalkanes normally leads to efficient trans → cis isomerization.[2] Since no quantum yields have been reported for isomerization of **1**, we determined the values at several wavelengths. Unfortunately, each of the three analytical methods employed to monitor the reaction suffered from some difficulty. UV analysis was complicated by the strongly overlapping absorption spectra of the isomers and it required knowing the extent of azoalkane decomposition. While both NMR and GC analyses require significant conversion to cis azoalkane, the high ϵ of **1c** relative to **1t** allowed undesired back reaction and necessitated low conversions. We employed the Lamola treatment[31] to correct for back reaction and compared the results to those from the initial slope of conversion versus time plots.

The average results of many experiments are summarized in Table II, after making allowances for the probable errors. A summary of the individual runs can be found in Table V (cf. the Experimental Section). It should first be noted that irradiation at 313 or 366 nm into the n,π^* band of **1t** causes efficient isomerization to **1c**. The slightly higher quantum yield than the usual 0.5 suggests a small preference for decay of the ^{1}n,π^* state to **1c**. Photolysis to give nitrogen must be negligible at these wavelengths since the solutions reached a photostationary state (pss) with no evidence of decomposition. Moreover, direct measurement of the evolved gas in the 366-nm experiment showed only a miniscule amount of nitrogen. The extinction coefficient of **1t** is 14.9 at 366 nm and 33.0 at 313 nm while that of **1c** at these wavelengths is 142.1 and 80.7, respectively. If it is assumed that the excited azoalkane decays to cis and trans ground state, the fraction of cis (α) at the pss is formulated as $\alpha = 1/(1 + \epsilon_c\Phi_{c\rightarrow t}/\epsilon_t\Phi_{t\rightarrow c})$. The calculated percent cis for 366- and 313-nm irradiation come out 14 and 38, based on $\Phi_{t\rightarrow c} = 0.6$, in reasonable agreement with the experimental values in Table II.

We were able to isolate a sufficient quantity of **1c** to measure its isomerization quantum yield in benzene at 313 nm. The value obtained was 0.4, which, when added to the $\Phi = 0.6$ for **1t** → **1c** (Table II), gives unity. The pss contained 36% **1c**, in good accord with the 33% found with **1t** as the starting material (Table II). These results suggest that like other acyclic azoalkanes, the lowest singlet excited state of **1** partitions to both ground-state isomers.

Shorter wavelength irradiation decomposes **1t** more efficiently than near-UV light, though trans → cis isomerization remains the dominant reaction. This effect has been seen for other azoalkanes[10] but is not especially useful here for generating radicals because the photolyses are far from clean. It is interesting that 254-nm irradiation in benzene-d_6 causes more isomerization and less decomposition than in pentane. The isomerization quantum yield in benzene is the same as for long-wavelength irradiation; moreover, the fact that a photostationary state was attained shows that decomposition is negligible. This solvent effect undoubtedly arises because benzene is the major light absorber at 254 nm and it singlet sensitizes[32] the isomeric azoalkanes, leading to a pss composition containing nearly equal amounts of cis and trans. Not only does the fluorescence spectrum of benzene overlap the n,π^* band of **1t** and **1c**, but its singlet lifetime (30 ns)[33] is ample to sensitize ~0.1 M azoalkane. Thus the photochemistry seen on 254-nm irradiation in benzene is similar to that observed on direct n,π^* excitation of **1t**.

The most efficient loss of nitrogen from **1t** occurs on 193-nm laser irradiation. The observed homolysis cannot be attributed to thermolysis of photochemically formed cis because long-wavelength irradiation of **1t** produces **1c** but no nitrogen. Furthermore, this very stable cis azoalkane reverts to trans under forcing conditions rather than decomposing.[1] Thus 193-nm light must populate an upper excited state of trans (S_2^T) that sometimes loses nitrogen. Decay of S_2^T cannot occur exclusively to S_1, for $\Phi_{t\rightarrow c}$ should then be the same as if S_1 had been produced directly. Instead, the low value of $\Phi_{t\rightarrow c}$ seen both here and in related work[10,34,35] suggests that the major fates of S_2^T are decay to S_0 and decomposition to intractable materials. Trans–cis isomerization is still much more important here than in the gas phase where even S_1 is likely to decompose.[2]

Irradiation of Pentane. Before presenting the product studies of **1t** on short wavelength irradiation, it will be useful to relate our experience with photoreactions of pentane. Irradiation of spectral grade pentane alone at 254 nm and below gave considerable quantities of new hydrocarbons and hydrogen. The formation of hydrogen is insidious because it would be included in the nitrogen quantum yield when azoalkane is present. Because of this problem and the fact that some of the minor pentane photolysis products were also possible azocyclopropane products, extreme measures were taken to purify the solvent (cf. the Experimental Section). The resulting pentane had an absorbance below 0.2 at 200 nm and it showed but one miniscule impurity by GC. In a series of control experiments, irradiation of this purified pentane still caused photochemical reactions to occur, but at a much slower rate than before. Table III summarizes the

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Table III. Short-Wavelength Irradiation of Purified Pentane

	254 nm	248 nm	193 nm
dosage, mE[a]	1.2	8.9	0.8
UV[b]	a >2 at 200 nm	a >2 at 200 nm	λ_{max} = 223, a > 2
Φ (H_2)[c]	0.0008	0.003	0.007
ethane[d]	0.7	1.4	1.0 (s)
propane[d]	0.2	3.3	1.0 (s)
propene[d]	0.08	1.3	1.0 (m)
butane[d]	0	0.8	1.0 (s)
butenes[d]	0	0.7	1.0 (s)
pentenes[d,e]	0.05	19	1.0 (l)
decanes[d,f]	0.1	0.03	1.0 (l)

[a] Light dosage in milliEinsteins. [b] UV absorbance after irradiation. [c] Quantum yield of hydrogen based on incident, not absorbed, light intensity. [d] GC analysis on columns D and E. GC peak height relative to peak height in 193 nm solution after correction for differing light dosage. The absolute amounts of 193 nm products are designated as small (s), medium (m), or large (l). [e] Analysis on column A. [f] Major isomer was 4,5-dimethyloctane.

results for irradiation of degassed, neat, purified pentane in Suprasil tubes with a low-pressure mercury lamp (254 nm) and at two laser wavelengths (248, 193 nm). Because several GC columns were required to separate the complex hydrocarbon mixtures, not all of the products were identified, and only semiquantitative results were obtained for the 193-nm product distribution. Thus the product yields at 193 nm are designated only as small, medium, or large. The solutions from irradiation at three wavelengths were then compared on several GC columns, allowing measurement of the yield of each hydrocarbon class relative to that at 193 nm. The values in Table III have been divided by the light dosage, providing relative quantum yields based on incident light intensity. The apparent quantum yields of hydrogen are also based on the incident light intensity but the absorbance was initially so low that most of the light passed through the liquid. The 193-nm experiment led to a final solution with a UV maximum at 223 nm, in contrast to the structureless tail seen in other entries (cf. Table III). There are distinct differences between the product distribution of the three solutions, with the 254-nm experiment producing fewer hydrocarbons and less hydrogen than the laser irradiations. Moreover, irradiation at 248 nm, which is the most intense of the three sources, gave much more pentenes and less decanes than the other experiments. Several other minor GC peaks were not identified, but it was shown that acetylene and propyne were absent. Thus the laser seems to cause fragmentation of pentane, analogous to the effect of γ radiation.[36] This process may occur by C–H homolysis followed by photolysis of pentyl radicals at the high light fluxes.[37,38] In fact, alkyl radicals have substantial absorption in the 200–260-nm region.[39–41] Although the nature of the primary light absorber is unknown, it is interesting that aromatic hydrocarbons sensitize alkane homolysis in a frozen matrix.[42] This fact coupled with our observation that even 254-nm light causes photoreactions of pentane suggests that unsaturated impurities below the GC or UV detection limit are the initial light absorbers. With continued irradiation, more impurities form, raising the absorbance of the solution and accelerating its photolysis.

Table IV. Product Quantum Yields of 1t in Pentane

product	$10^3\Phi$ (193 nm)[a,b]	$10^3\Phi$ (248 nm)[b,c]	$10^3\Phi$ (254 nm)[c,d]
ethane	0.15[e]	0.15	0.07
ethylene	4–16	5.6	2.5
propane	0.02–2.2	0.06	0.01
propene	0.07–5.1	0.38	0.05
cyclopropane	11–22	1.8	1.4
n-butane	1–4	0.2	0.1
1-butene	0.04–2.3	0.2	0.1
1,5-hexadiene	0.2–1.3		
allylcyclopropane	1.7–6		
bicyclopropyl	12–20	1.6	0.4
pyrazoline **2**	11–25	0.6	0.5
azine **13**	1–5	0.8	1.3
1t disappearance	180–300	190	120–220[f]

[a] Range for four experiments. [b] Laser irradiation. Light intensity determined using laser power meter. [c] One experiment. [d] Mercury resonance lamp. Intensity determined by benzophenone–DBH actinometry. [e] Result of one experiment; three others gave no detectable ethane. [f] Range for three experiments.

Product Studies. Short-wavelength irradiation of **1t** led to an array of organic products that were identified by capillary GC comparison with authentic materials (cf. Table IV). Substantial variations in light dosage, initial concentration of **1t**, and time elapsed prior to analysis are responsible for the ranges in the 193 nm quantum yields; however, a systematic analysis of these variables was not undertaken.

Photolysis of the solvent is probably not a major contributor to the hydrocarbons in Table IV because the main products of pentane photolysis, pentenes and decanes, were absent when solutions of **1t** in highly purified pentane were irradiated. It is not surprising that photolysis of **1t** dominates over solvent photochemistry because the absorbance of the azoalkane was at least 1000 times greater than that of pentane. On the other hand, since irradiation of pentane alone did produce ethane, propane, propene, butane, and butenes, we cannot totally rule out solvent photolysis as a contributor to these hydrocarbons in Table IV, especially at the high light intensity of our laser where Beer's law may not apply.

The product distribution (Table IV) depends on both intensity and wavelength. Thus the 248-nm excimer laser, which is 7×10^9 brighter than the 254-nm mercury lamp, gives somewhat greater yields of C_2–C_3 hydrocarbons. This increase may mean that transient radicals such as cyclopropyl or pentyl undergo photofragmentation in the laser beam. The 193-nm laser is only half as intense as at 248 nm, yet it produces more azocyclopropane-derived compounds (ethylene, cyclopropane, bicyclopropyl, pyrazoline **2**, and azine **13**). Since both wavelengths fall into the second absorption band of **1t**, this wavelength effect[43] implies either that more vibrational excitation of S_2^T enhances the fragmentation yield or that the short-wavelength band of **1t** contains more than one electronic transition,[20] each having its own propensity to fragment.

Bicyclopropyl must be a cage recombination product of cyclopropyl radicals because any of these reactive species[44] that escaped the cage would surely have turned up as cyclopropane. The greater importance of the cage product bicyclopropyl in solution compared to the gas phase is entirely expected.[28] Some of the minor products in Table

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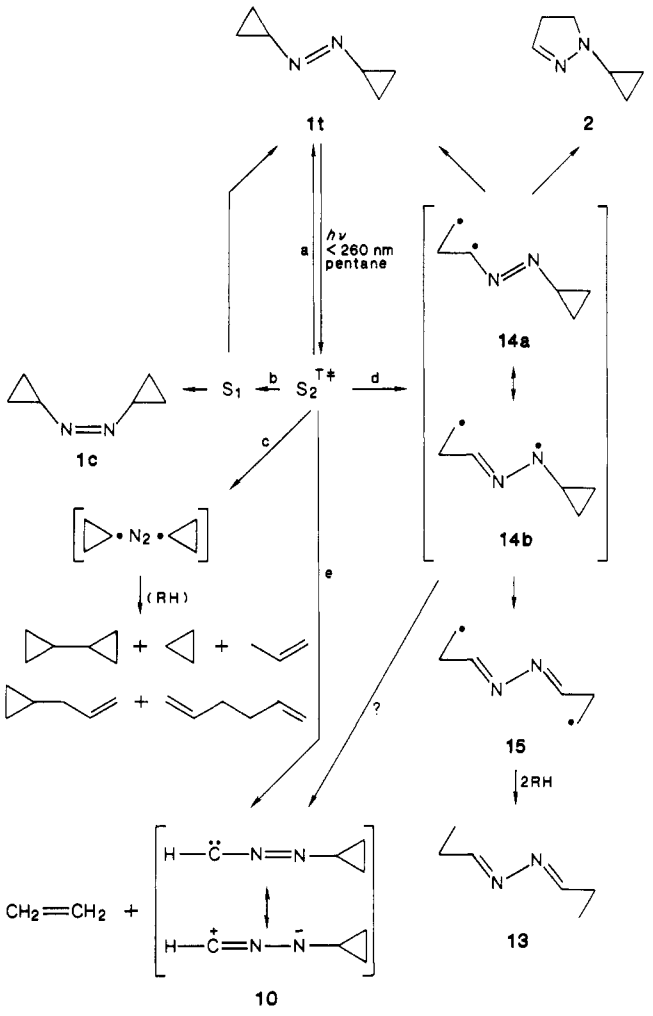
Scheme II. Major Reaction Pathways and Products for Short-Wavelength Irradiation of 1t in Pentane



IV (allylcyclopropane, 1,5-hexadiene) suggest ring opening[13] of vibrationally excited cyclopropyl radicals, since these hydrocarbons appear only at 193 nm.

The formation of ethylene, **2**, and **13** demonstrate that cleavage of the cyclopropane ring competes successfully with the usual C–N bond homolysis. These processes are illustrated in Scheme II. Short-wavelength irradiation of **1t** produces vibrationally excited S_2 (S_2^T), which can then undergo five competing processes: (a) decay to **1t**, (b) internal conversion to S_1 followed by deactivation to **1c** and **1t**, (c) C–N bond homolysis to cyclopropyl radicals, which end up mainly as cyclopropane and bicyclopropyl, (d) ring homolysis leading to pyrazoline **2** and azine **13**, and (e) fragmentation to ethylene and nitrile imine, as discussed above for gas-phase photolysis. Biradical **14** could reclose to **1t**, a process that will be considered in detail below. A second ring opening[45,46] of **14** leads to **15**, which, on hydrogen abstraction from the solvent, accounts for the observed azine **13**. Irradiation of **1t** at 254 nm but not 193 nm gave an unidentified GC peak whose area was about 20% that of **13**. This peak was associated with a UV band at 305 nm, which interfered with UV analysis of the **1t**–**1c** mixtures (cf. Table V). The unknown was not propanal *N*-cyclopropylhydrazone (**21**) but the similarity of its retention time to that of **2** and **13** suggests a nitrogen containing compound, perhaps derived from **14** or **15**.[47]

(45) Danen, W. C.; West, C. T. *J. Am. Chem. Soc.* **1974**, *96*, 2447.
(46) Maeda, Y.; Ingold, K. U. *J. Am. Chem. Soc.* **1980**, *102*, 328.

Table V. Irradiation of *trans*-Azocyclopropane (1t) at Various Wavelengths

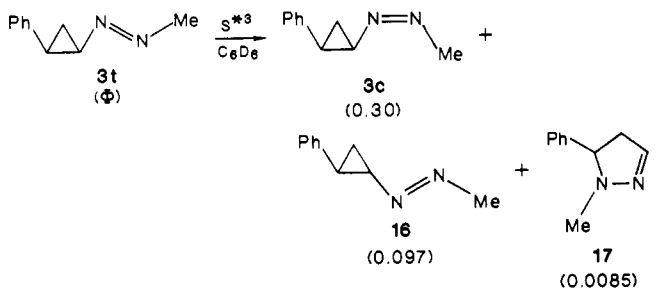
wavelength, experiment[a]	solvent[b]	analytical method	% conv[c]	$\Phi_{t\rightarrow c}$[d]	data treatment
366, A	P	UV[e]	9.9	0.62	initial slope[f]
366, B	P	UV[g]	9.5[h]	0.60	initial slope[f]
				0.53	Lamola
313, A	B	NMR[i]	33[h]	0.68	initial slope[f]
				0.73	Lamola
254, A	P	UV[g]	0	0.24	extrapolation[j]
254, B	P	UV[g]	0	0.23	extrapolation[j]
			31	0.10	final comp[k]
		GC	25	0.081	final comp[k]
254, C	P	UV[g]	0	0.55[l]	extrapolation[j]
			3	0.27	final comp[k]
		GC	2	0.12	final comp[k]
254, D	P	UV[g]	2.4	0.43[l]	extrapolation[j]
		GC	1.7	0.19	final comp[k]
254, E	B	NMR	58.5[h]	0.50	initial slope[f]
				0.52	Lamola
193, A	P	GC	40	0.062	final comp[k]
193, B	P	UV[g]	0	0.19	extrapolation[j]
			5	0.12	final comp[k]
		GC	5	0.10	final comp[k]
193, C	P	GC	28	0.093	final comp[k]
193, D[m]	P	GC	16	0.079	final comp[k]

[a] The first three digits are the irradiation wavelength in nanometers, and the letter designates a particular experiment. [b] P = purified pentane, B = benzene-d_6. [c] Percent conversion to **1c** determined by the analytical method shown. [d] Quantum yield of trans to cis isomerization. [e] Monitored only at 332 nm. [f] $\Phi_{t\rightarrow c}$ obtained from initial slope of conversion versus time plot. [g] Monitored at four to six wavelengths between 320 and 380 nm. [h] Photostationary state. [i] Data unusually scattered. [j] Extrapolation to zero conversion of plot of $\Phi_{t\rightarrow c}$ versus light dosage. [k] $\Phi_{t\rightarrow c}$ based on final composition of irradiated solution. Unless conversion is kept low, these Φ's are erroneously low due to back reaction c → t. [l] Inflated due to light-absorbing by product. [m] Laser intensity reduced by 4.4 times relative to experiment 193, C. GC analysis of the hydrocarbons revealed greater quantum yields by factors of 1.5–4.8 in 193, C than in 193, D. Φ_{N_2} was 2 times greater in 193, C.

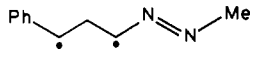
Although ethylene was formulated above as a primary photoproduct of S_2^T (process e, Scheme II), an alternate pathway is fragmentation of **14**. Alkylcyclopropanes seem to yield olefins via a biradical analogous to **14**,[51] but both stepwise and concerted pathways have been postulated for arylcyclopropanes.[52] The relative contribution of these two mechanisms to the fragmentation of **1t** is unknown.

Triplet Sensitization. Because triplet-sensitized isomerization of trans azoalkanes is never very efficient,[2] we were surprised to observe a moderately high quantum yield for this process in **1t**. Irradiation of xanthone at 313 nm in the presence of **1t** was monitored by NMR, giving $\Phi_{1t\rightarrow 1c} = 0.2$ and a pss of 80% **1t**, 20% **1c**. Since no cyclopropane was detected by GC of the irradiated solution, C–N bond homolysis must be negligible. The high efficiency of the triplet process **1t** → **1c** calls for a comparison with the previously studied **3t**. We have reported that direct irradiation of **3t** leads to azo group isomerization (**3c**), cyclopropane ring isomerization (**16**) and expansion (**17**), and ring fragmentation (styrene).[9]

(47) The 305-nm wavelength maximum for this unknown rules out a simple alkyl pyrazole,[48] a simple hydrazone, and an α,β-unsaturated azoalkane (cf. Gillis, B. T.; Hagarty, J. D. *J. Am. Chem. Soc.* **1965**, *87*, 4576). Photochemical dehydrogenation of pyrazolines can take place in the absence of oxygen[49] but the 305-nm band built up too fast to be a secondary product from **2**. Contrary to our published comment,[9] Grimshaw and de Silva[50] correctly cited the work of Yamamoto.[49]
(48) *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C. W., Eds.: Pergamon: Oxford, 1980; Vol. 5, Part 4A, p 198.
(49) Yamamoto, H.; Sano, Y.; Shirota, Y.; Seki, H.; Mikawa, H. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1533.
(50) Grimshaw, J.; Prasanna de Silva, A. *J. Chem. Soc., Perkin Trans. 2*, **1983**, 1679.
(51) Leigh, W. J.; Srinivasan, R. *Acc. Chem. Res.* **1987**, *20*, 107.
(52) Hixson, S. S. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1979; Vol. 4, pp 191–260.

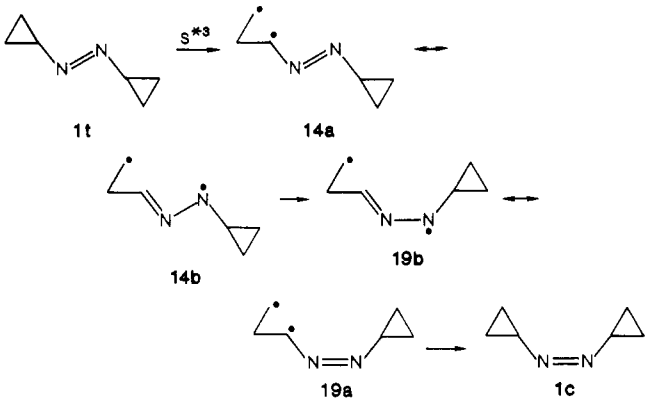


Further experiments reveal that xanthone sensitization of **3t** induces most of the same reactions, including efficient azo group isomerization (cf. quantum yields shown above). Since triplet sensitization of arylcyclopropanes causes trans–cis ring isomerization,[52] and since ring cleavage is important in the singlet photochemistry of **1t**, it is appealing to postulate triplet 1,3-biradical **18** as the precursor of **16** and **17**. In fact such a biradical could also lie on the



18

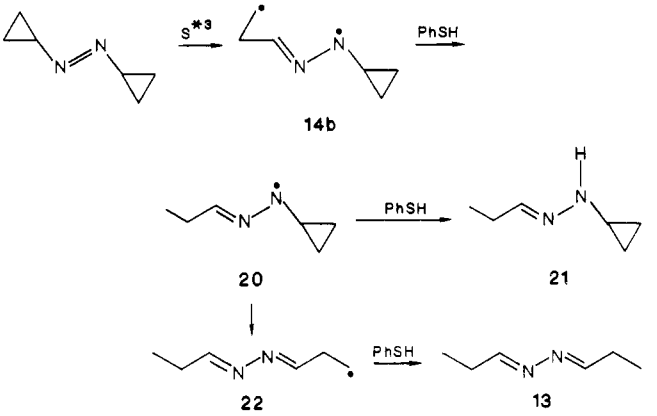
pathway to **3c** and an analogue might be involved in the isomerization of **1t** to **1c**. The intervention of these biradicals constitutes a new mechanism of azo group isomerization that is unique to azocyclopropanes. As illustrated below, scission of the cyclopropane ring could give biradical **14a–14b**, which will have a low barrier to rotation about



the N–N bond, as shown by theoretical calculations[29] and ESR experiments[53] on hydrazonyl radicals. Reclosure of the rotated biradical **19a** to **1c** completes the isomerization. In the case of **3t**, it is reasonable that **18**, which is delocalized on both ends, might survive long enough to reclose to **16** and **17**.[54] The absence of pyrazoline **2** in the triplet-sensitized isomerization of **1t** does not rule out the biradical mechanism since the sequence **14** → **19** → **1c** might be much faster than the allylic coupling needed to form **2**. Ring isomerization, analogous to the process **3** → **16**, is of course a degenerate reaction in **1t**.

Thus the high quantum yield of triplet-sensitized azo group isomerization of both **1t** and **3t**, coupled with known properties of cyclopropanes and hydrazonyl radicals, led us to consider a new mechanism of azocyclopropane isomerization proceeding via biradicals **14** and **19**. In order to test this mechanism, we attempted to intercept the proposed biradical. As will be described below, the initial encouraging results were soon found to have a different cause, and a more stringent mechanistic test failed to support the new mechanism.

Attempted Interception of Biradical 14. A benzene solution of 0.072 M **1t**, xanthone, and 0.12 M thiophenol was irradiated at 366 nm (experiment A) in hopes that triplet biradical **14b** might be trapped.



This hope was based on the known ability of thiols to intercept 1,4-biradicals[55] and on the report that another 1,3-biradical survived for 15 ns,[56] which is long enough to be trapped with 20% efficiency by thiophenol ($k_t = 1.5 \times 10^8$ M^{-1} s^{-1}).[57] Since **20** could rearrange to **22**[45,46] before abstracting hydrogen from thiophenol, the formation of either **13** or **21** would be evidence for our proposed mechanism.

In fact, the only products detected by NMR and GC in experiment A were **13**, **21**, and diphenyl disulfide. While a control irradiation of **1t** and xanthone at 366 nm gave exclusively **1c**, none of this isomer was present in the thiophenol tube. These pleasing results were at first rationalized as complete diversion of **14b** from its usual role as the azo cis–trans isomerization intermediate. However, a potential defect in the trapping experiment (experiment A) soon came to mind; namely, thiophenol could quench xanthone triplets, producing radicals that attack **1t** and eventually lead to **13** and **21**. Indeed, thiophenol turned out to be a faster quencher of triplet xanthone[58] ($k_q = 3.6 \times 10^9$ M^{-1} s^{-1}) than mesitylene-2-thiol is of triplet benzophenone ($k_q = 7 \times 10^8$ M^{-1} s^{-1}).[59] Although we did not determine k_q for **1t** and triplet xanthone, our quenching studies of lower energy sensitizers[60,61] place the triplet energy (E_T) of **1t** at about 54 kcal/mol, similar to that of other azoalkanes. Even with a diffusion controlled k_q, **1t** intercepts less than half of the xanthone triplets at the concentrations employed. Since irradiation of ketones with thiols produces ketyl and thiyl radicals,[62] both of these species must be considered in possible reactions with **1t**.

In order to determine whether thiophenyl radicals were the culprits, an equimolar solution of **1t** and diphenyl disulfide in C_6D_6 was irradiated at 313 nm (experiment B).[61] The extinction coefficients at this wavelength for the two components are 33 and 930, respectively, so that the

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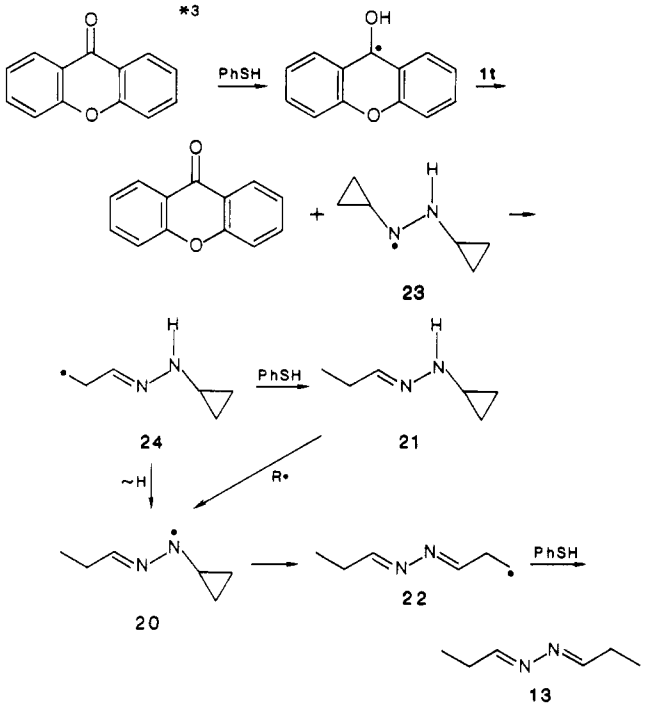
(54) Adam, W.; Grabowski, S.; Wilson, R. M.; Hannemann, K.; Wirz, J. *J. Am. Chem. Soc.* **1987**, *109*, 7572.
(55) Wilson, R. M. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1985; Vol. 7, pp 339–466.
(56) Mizuno, K.; Ichinose, N.; Otsuji, Y.; Caldwell, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 5797.
(57) Glenn, A. G.; Horner, J. H.; Newcomb, M. Abstract of Papers, Southwest Regional ACS Meeting, Houston, Texas, Nov 19–21, 1986; Paper 407.
(58) Pownall, H. J.; Huber, R. *J. Am. Chem. Soc.* **1971**, *93*, 6429.
(59) Inbar, S.; Linschitz, H.; Cohen, S. G. *J. Am. Chem. Soc.* **1982**, *104*, 1679.
(60) Quenching rate constants of triplet sensitizers by **1t** were found to be: triplet energy (kcal/mol), $10^6 k_q$ (M^{-1} s^{-1}); chrysene, 56.6, 105; benzil, 53.7, 7.3; 9-fluorenone, 53.3, 4.7.
(61) We thank Dr. Akihide Kitamura for carrying out these experiments.
(62) Cohen, S. G.; Rose, A. W.; Stone, P. G.; Ehret, A. *J. Am. Chem. Soc.* **1979**, *101*, 1827.

Scheme III. Chemical Sensitization of Azocyclopropane



disulfide absorbs >96% of the light. A small amount of **1c** and thiophenol were the only products seen by NMR after 10-min irradiation. However, 30-s irradiation of only **1t** in C_6D_6 under identical conditions gave nearly as much **1c**, demonstrating that the isomerization seen in experiment B was due to trivial light absorption by **1t**. A control irradiation of diphenyl disulfide in C_6D_6 for 10 min produced an amount of thiophenol[63] comparable to that found in experiment B. Since diphenyl disulfide certainly gave thiophenyl radicals,[64,65] the absence of **13** and **21** in experiment B shows that these radicals are not responsible for the supposed biradical trapping products. We further conclude that thiophenyl radicals do not induce isomerization of **1t** to **1c** and that **1c** survives long enough (though eventually isomerizing to **1t**) in the presence of thiophenol that it would have been detected in experiment A. The absence of **1c** in the latter case then implies such a long lifetime for triplet biradical **14** that thiophenol trapped all of it, or more likely, that some other radical in the xanthone system converted **1t** to **13** and **21**.

The key to this puzzle was the discovery that **1t** quenched benzhydryl radicals ($k_q = 4 \times 10^6$ M^{-1} s^{-1}) generated by flash photolysis of benzophenone and triethylamine.[66,67] Furthermore, irradiation of this three component mixture at 313 nm where **1t** absorbed only 6% of the light caused rapid destruction of **1t**.[61] It is therefore likely that formation of **13** and **21** proceeds via chemical sensitization,[68] as illustrated in Scheme III. In support of this mechanism, azobenzenes are known to be reduced by ketyl radicals.[69,70] It is not clear whether **21** lies on the pathway from **24** to **20** since intramolecular hydrogen transfer can occur via a six-center transition state. On the other hand, the amount of **21** decreased on extended irradiation, suggesting attack by external radicals.

Scheme IV. Synthesis of Stereospecifically Deuteriated Azocyclopropane

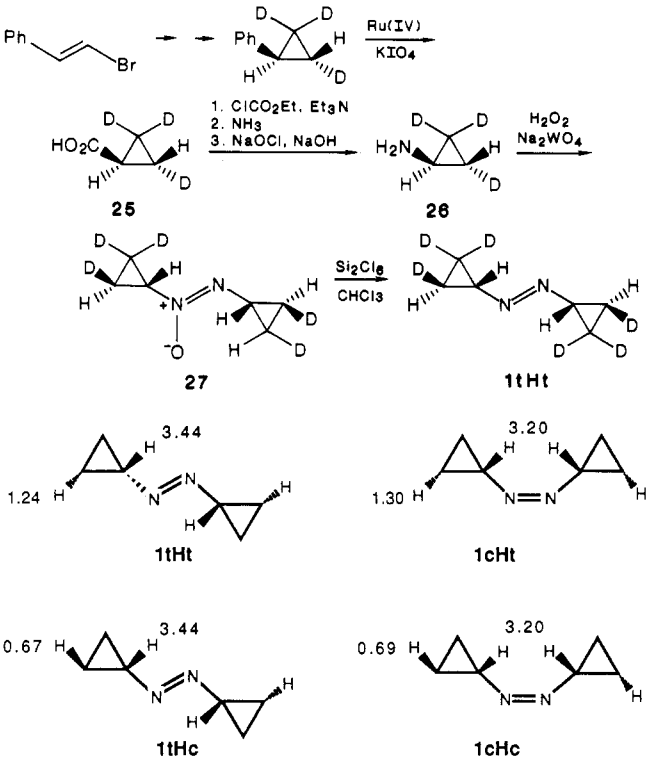


Figure 2. NMR assignments (δ, ppm), structure, and abbreviated name for each isomer of 1-d_6. Deuterium occupies all unmarked positions.

With the demise of the trapping experiment, a better method was sought to detect azo group isomerization via cyclopropyl ring opening. The structure of the cyclopropyl radical has been studied by stereospecific deuterium labeling and we quickly recognized that isomerization of the cyclopropyl ring of **1t** could be probed by using the same approach. Moreover, the cyclopropanecarboxylic acid-d_3 (**25**) employed earlier[71,72] was a likely precursor for stereospecifically labeled azocyclopropane. We improved the elegant synthesis of **25**[72] by replacing ozonolysis of phenylcyclopropane with ruthenium(IV) oxidation.[73,74] Scheme IV summarizes the synthesis of labeled **1t**.

Since ring isomerization of **1tHt** (trans azo linkage and trans ring hydrogens) was to be investigated by NMR, a complete spectral assignment was undertaken. The chemical shifts deduced are shown in Figure 2 for the four possible isomers of 1-d_6, assuming that only one cyclopropane ring isomerizes. The isotope shifts of deuterium on geminal hydrogen was less than 0.03 ppm. Xanthone-sensitized irradiation of **1tHt** was carried to 11% conversion but the only new NMR peaks were at 1.30 and 3.20 ppm, corresponding to pure azo group isomerization. No change was seen in the region of 0.67 ppm as would be expected if **1tHc** or **1cHc** were formed. The results of direct irradiation at 313 nm or of benzene singlet sensitization at 254 nm were the same: only the azo group isomerized. We may conclude that biradical **14a** either

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(67) Inbar, S.; Linschitz, H.; Cohen, S. G. *J. Am. Chem. Soc.* **1980**, *102*, 1419.
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(71) Johnston, L. J.; Ingold, K. U. *J. Am. Chem. Soc.* **1986**, *108*, 2343.
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(74) Baldwin, J. E.; Barden, T. C. *J. Am. Chem. Soc.* **1984**, *106*, 5312.

Table VI. GC Columns Used in This Work

desig-nation	dimensions	column material[a]	mesh size
A	30 ft × $^1/_8$ in.	10% $AgNO_3$–benzyl cyanide (P)	60/80
B	8 ft × $^1/_4$ in.	15% OV-17 (W)	60/80
C	15 ft × $^1/_8$ in.	20% UCON 550X LB (P)	60/80
D	20 ft × $^1/_4$ in.	20% TCEP (P)	45/60
E	6 ft × $^1/_8$ in.	Alltech *n*-octane/porosil C[b]	80/100
F	5 ft × $^1/_8$ in.	OPN/porosil C[b]	80/100
G	28 ft × $^3/_{16}$ in.	poropak Q	
H		HP quartz capillary SE-54	
I		HP quartz capillary SE-30	
J	32 ft × $^1/_8$ in.	20% TCEP (P)	60/80
K	6 ft × $^1/_8$ in.	10% FFAP (W)	60/80
L	6 ft × $^1/_8$ in.	10% $AgNO_3$–benzyl cyanide (P)	60/80
M	7 ft × $^1/_8$ in.	5% OV-17 (W)	60/80

[a] Percent liquid phase; chromosorb solid supports are indicated in parentheses. [b] Chemically bonded liquid phases.

does not form or that it forms and recloses to **1t** before rotation about the C–CHD bond. In the latter case, the lifetime of the singlet and triplet biradical must be very short indeed.[75,76] If the biradical is too short lived to allow rotation of the CHD group, it is surely too short for rotation about the N–N bond. Thus biradical **14a** is not a viable intermediate for azo group isomerization. The experimental result that prompted this study, namely the high quantum yield for triplet-sensitized azo isomerization, remains unexplained. However, there is evidence for mixing of cyclopropane ring electronic transitions with those of the azo group, as noted above. This mixing could alter the shape of the triplet surface so that the excited state decays more often than usual to the cis isomer.

In summary, we have delineated at least three primary processes in the photochemistry of azocyclopropane: cis–trans isomerization of the azo group, C–N bond homolysis, cyclopropyl ring cleavage, and possibly extrusion of ethylene. The latter could also be a secondary reaction of the ring opened biradical **14**. Triplet-sensitized isomerization of the azo group proceeded with unusually high efficiency, raising the possibility that azo isomerization occurred following ring opening. However, a series of trapping experiments and stereochemical studies failed to support this new mechanism. Although **1t** was inert to thiophenyl radicals, it is attacked by ketyl radicals to afford products **13** and **21**. Azocyclopropane cannot be recommended as a source of cyclopropyl radicals because photolysis is inefficient even at short wavelengths and it leads to polymers and nitrogen-containing products.

Experimental Section

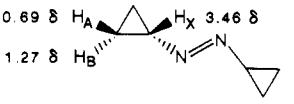
General Methods. NMR spectra were obtained on a JEOL FX90 or an IBM AF300 spectrometer; chemical shifts (δ) are in ppm. UV spectra were obtained on a Cary 17 spectrophotometer. GC analyses were performed on either an Antec 300 (FID and TC detectors) or a Hewlett-Packard (HP) 5890 (FID) gas chromatograph set up for capillary GC. The HP was interfaced to an IBM XT compatible computer to allow storage, manipulation, and integration of chromatograms. The GC columns used throughout this work will be referred to by letter as indicated in Table VI. GC/MS analyses were done on a Finnigan 3300 low-resolution mass spectrometer, while high-resolution mass spectra were obtained on a CEC Du Pont 21-110B spectrometer.

Commercially available reagent grade solvents were used in synthesis except as noted. Solvents used in irradiation experiments were spectrophotometric grade or, in the case of C_6D_6, Aldrich gold label or Cambridge Isotope Laboratories (96%). Pentane and hexane were filtered through alumina immediately prior to use, while benzene was used without further purification, except as noted.

For irradiation experiments with $\lambda < 300$ nm, pentane was rigorously purified by the following procedure. Approximately 400 mL of pentane (Omnisolv or Baker, spectrophotometric grade) was washed with two 50-mL portions of concentrated H_2SO_4 and then stirred overnight with an equal volume of 0.5 N $KMnO_4$ in 3 M H_2SO_4. The pentane was separated and washed twice with water and three times with saturated $NaHCO_3$. Next the pentane was dried over $MgSO_4$, distilled from P_2O_5, and spinning band distilled. The acceptable fractions (GC on column C) were then combined and filtered through a $AgNO_3/Al_2O_3$ column prepared according to the method of Murray and Keller.[77] This sequence reduced the pentane UV absorption at 200 nm from 0.7 to ≤0.2. Finally, the purified pentane (~50 cc) was placed into ampules and degassed, sealed, and stored in a refrigerator. Immediately prior to use, the required amount was filtered again through $AgNO_3/Al_2O_3$.

Compounds. Azoxycyclopropane.[78] A 250-mL three-neck flask was equipped with a mechanical stirrer, thermometer, addition funnel, and N_2 inlet. A solution of 10 g (0.18 mol) of cyclopropylamine and 1.4 g of sodium tungstate in 25 cc of water was added to the flask. The mixture was cooled to 15 °C, and 62.3 g of 30% H_2O_2 was added over 1.25 h. The blue mixture was then stirred for 15 min at 15 °C and 30 min at room temperature and then extracted with ether. The ether extracts were combined, dried over $MgSO_4$, and concentrated. Vacuum distillation of the residue gave 5.5 g (50%) of azoxycyclopropane: bp 80–83 °C/(10 mm)[lit.[79] bp 104–107 °C/(40 mm)]; ^1H NMR ($CDCl_3$) δ 0.9 (m, 6 H), 1.45 (m, 2 H), 3.9 (m, 2 H).

Azocyclopropane (1t).[78] A 1.03-g portion of $LiAlH_4$ was added to 1.5 g of azoxycyclopropane in 50 mL of dry ether. This mixture was stirred and refluxed for 24 h. The excess $LiAlH_4$ was destroyed with 0.4 mL of H_2O, 0.4 mL of 15% NaOH, and 0.8 mL of H_2O. The solid was filtered off, and the ether solution was dried over $MgSO_4$. Concentration of the ether layer by distillation followed by vacuum distillation gave 46% azocyclopropane, bp 130 °C. GC analysis (column M, 61 °C) of this material revealed two shorter retention time impurities that were identified as (cyclopropylazo)-*n*-propane and azo-*n*-propane. Small amounts of pure **1t** could be isolated by preparative GC on column B at 90 °C while larger amounts were obtained by multiple recrystallizations from pentane at −78 °C. ^1H NMR ($CDCl_3$) δ 0.64–0.86 (m, 4 H), 1.22–1.40 (m, 4 H), 3.51 (m, 2 H); (C_6D_6) δ 0.69 (H_A, m, 4 H), 1.27 (H_B, m, 4 H), 3.46 (H_X, m, 2 H). Spin decoupling



1t

experiments showed $J_{AX} = 7.0$ Hz and $J_{BX} = 3.1$ Hz; ^{13}C NMR (C_6D_6) δ 8.50, 49.62; UV (pentane) λ_{max} 213 (ϵ 10^4), 332 nm (ϵ 51.5); (vapor) λ_{max} 206–8 nm; *m/e* (relative abundance) 110 (4), 109 (5), 83 (6), 82 (7), 68 (13), 67 (6), 56 (7), 55 (24), 54 (22), 44 (7), 42 (8), 41 (100), 40 (13), 39 (91), 38 (9), 29 (6), 28 (69), 27 (47), 26 (31). Anal. Calcd for $C_6H_{10}N_2$: 110.08439. Found: 110.0845.

(Cyclopropylazo)-*n*-propane was isolated by preparative GC (column B, 90 °C) from the LAH reduction of azoxycyclopropane: ^1H NMR ($CDCl_3$) δ 0.96 (t, 3 H), 1.1–1.3 (m, 4 H), 1.79 (m, 2 H), 3.42 (m, 1 H), 3.68 (t, 2 H); (C_6D_6) δ 0.7–0.9 (m, 2 H), 0.95 (t, 3 H), 1.2–1.5 (m, 2 H), 1.81 (sextet, 2 H), 3.57 (m, 1 H), 3.78 (t, 2 H); (DMSO-d_6) δ 0.88 (t, 3 H), 1.0–1.2 (m, 4 H), 1.70 (m, 2 H), 3.42 (m, 1 H), 3.62 (t, 2 H); ^{13}C NMR (C_6D_6) δ 8.50, 12.46, 21.94, 49.95, 70.70.

1-Cyclopropyl-2-pyrazoline (2). A 1 M solution of **1t** in hexadecane was degassed and sealed in a glass ampule and then heated at 200 °C for 3 days. The pyrazoline **2** was then isolated

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by preparative GC (column B): ^{1}H NMR ($CDCl_3$) δ 0.6–0.8 (m, 4 H), 2.1 (m, 1 H), 2.6 (split t, 2 H), 3.1 (split t, 2 H), 6.8 (t, 1 H); (C_6D_6) δ 0.4–0.6 (m, 2 H), 0.8–1.0 (m, 2 H), 2.1 (m, 3 H), 2.8 (t, 2 H), 6.5 (t, 1 H); UV (pentane) λ_{max} 240 nm (ϵ 4200); *m/e* (relative abundance) 110 (4), 109 (2), 108 (6), 107 (6), 83 (16), 82 (9), 81 (10), 69 (10), 68 (19), 67 (6), 57 (8), 54 (29), 53 (9), 52 (6), 51 (6), 44 (6), 43 (6), 42 (8), 41 (41), 40 (12), 39 (27), 38 (9), 28 (100), 27 (45), 26 (31).

***cis*-Azocyclopropane (1c).** A 0.7-g portion 95% pure **1t** in 75 mL of pentane was placed in a pyrex tube and irradiated at 313 nm with a Hanovia medium-pressure mercury lamp and K_2CrO_4 filter solution. The irradiation was continued until the trans–cis ratio remained constant (GC on column H). The cis isomer was collected by filtering the mixture through ~7 mL of alumina in a Pasteur pipette. Reirradiation of the filtrate and collection of **1c** was repeated twice more. The combined alumina was washed with EtOAc until no more **1c** eluted. The washings contained **1c** and **1t** in a ratio of ~4–5:1. After removal of the EtOAc, the resulting oil was sublimed under vacuum onto a cold finger at 8 °C to obtain 43 mg of pure, white, solid **1c**: ^{1}H NMR ($CDCl_3$) δ 1.0–1.4 (m, 4 H), 3.69 (m, 1 H); (C_6D_6) δ 0.71 (m, 4 H), 1.32 (m, 4 H), 3.21 (m, 2 H); ^{13}C NMR (C_6D_6) δ 8.93, 41.39; UV (pentane) λ_{max} 204 (ϵ 10^4), 343 nm (ϵ 273).

2-Pyrazoline (9).[25] A 4.6 mL (4.8-g, 0.094-mol) portion of 100% hydrazine hydrate was added to 5 cc of ether in a round-bottom flask equipped with a magnetic stirring bar, dropping funnel, and nitrogen inlet. The mixture was mildly chilled with ice and was rapidly stirred. Freshly distilled acrolein (5 g, 0.089 mol) was added dropwise over 50 min, and the mixture was stirred for an additional 30 min without cooling. The aqueous layer was separated and distilled at atmospheric pressure through a short-path column to remove the water. The resulting residual oil appeared by NMR to be a mixture of acrolein hydrazone and **9**, which was isolated by preparative GC (column B): ^{1}H NMR ($CDCl_3$) δ 1.4–2.4 (br, 1 H), 2.67 (t, 2 H), 3.32 (t, 2 H), 6.88 (s, 1 H). A chloroform solution of **9** decomposed over about 24 h.

Propanal *N*-Cyclopropylhydrazone (21). A small amount of cyclopropylazo-*n*-propane was dissolved in about 0.5 mL of C_6D_6 along with a small crystal of 18-crown-6. The initial solution was checked by NMR then transferred to a half dram vial. After purging with argon for several minutes, a crushed pellet of potassium hydroxide was added, and the vial was capped. Again, the reaction was monitored by NMR. After the azoalkane was half converted to **21** (~5 h), the solution was decanted from the KOH. The ^{1}H and ^{13}C NMR signals of **21** were deduced by comparison of initial and reacted solutions: ^{1}H NMR (C_6D_6) δ 0.3–0.6 (m, 4 H), 1.10 (t, 3 H), 1.98–2.42 (m, 3 H), ~5.1 (br, 1 H), 7.00 (t, 1 H); ^{13}C NMR (C_6D_6) δ 6.7, 12.2, 29.2, 49.2, 140.6.

Allylcyclopropane.[22] A 1 mL portion of 1,5-hexadiene (Aldrich) was filtered through alumina to remove peroxides and was diluted with 5 mL of spectrophotometric grade methanol. The solution was purged with nitrogen and was irradiated at 193 nm in a Suprasil tube with an excimer laser. After the conversion had reached 30%, 1 mL of saturated NaCl solution was added, and the mixture was extracted with pentane. Allylcyclopropane[24,80] was isolated by preparative GC (column D) of the pentane extract: ^{1}H NMR ($CDCl_3$) δ 0.0–1.0 (m, 5 H), 1.97 (br t, 2 H), 5.05 (m, 2 H), 5.08 (m, 1 H); *m/e* (relative abundance) 82 (0), 81 (4), 79 (3), 77 (2), 68 (3), 67 (47), 65 (4), 55 (7), 54 (100), 53 (16), 52 (4), 51 (6), 41 (59), 39 (64).

***tert*-Butylcyclopropane.**[23] Several microliters of (*tert*-butylazo)cyclopropane[78] sealed in a melting point capillary tube were irradiated at 366 nm for 1 h with a high-pressure mercury lamp. The neat product solution was analyzed by GC (column C programmed from 35 to 140 °C at 4 °C/min) and GC/MS. Four GC product peaks were assigned to ethylene, isobutane, cyclopropane, and isobutylene by comparison with authentic materials. The GC peak assigned to *tert*-butylcyclopropane (12.3 min retention time) yielded the following mass spectral data: *m/e* (relative abundance) 98 (0), 83 (8), 71 (6), 70 (95), 69 (11), 67 (8), 57 (11), 56 (17), 55 (100), 53 (9), 43 (8), 42 (24), 41 (71), 40 (6), 39 (53).

***trans*-[2,3,3-$^2H_3$]Cyclopropanecarboxylic Acid (25).**[73,74] To a three-neck 5-L round-bottom flask equipped with a mechanical stirrer (Teflon blade) was added 23.5 g (0.191 mol) of *trans*-[2,3,3-$^2H_3$]phenylcyclopropane,[72] 615 g (2.67 mol, 14.0 equiv) of KIO_4, 0.967 g (0.0047 mol, 2.4 mol %) of $RuCl_3 \cdot H_2O$, 1200 mL of water, 760 mL of acetonitrile, and 760 mL of carbon tetrachloride. The mixture was stirred vigorously at room temperature, and the extent of reaction was determined by GC analysis (column H, 110 °C) of the lower organic phase. The reaction was stopped after 61.5 h by adding enough saturated Na_2CO_3 (100–150 mL) to bring the mixture to approximately pH 9. After stirring for an additional 10 min, the solid was removed by vacuum filtration. The solids were washed with 4 × 200 mL portions of water followed by 3 × 100 mL portions of dichloromethane. The two layers in the filtrate were separated, and the aqueous phase was washed with 100 mL of methylene chloride to remove any residual organics. The aqueous phase was then acidified to pH ~4 with concentrated HCl. The bright yellow, clear solution was divided into portions for continuous extraction with Et_2O. During extraction, the aqueous phase turned dark red in color. The dark red Et_2O extracts were combined and distilled to remove the Et_2O. The concentrate was then vacuum distilled to remove acetic acid byproduct and an unidentified dark red material which solidified in the condenser. The remaining material in the pot was bulb-to-bulb distilled, leaving behind a dark tar. This distillate was then redistilled at 0.7 mm until most of the red color had been removed to leave 9.57 g (0.108 mol, 56% yield) of **25**: ^{1}H NMR ($CDCl_3$) δ 1.03 (d, 1 H, J = 4.7 Hz), 1.58 (d, 1 H, J = 4.7 Hz).

***trans*-[2,3,3-$^2H_3$]Cyclopropanecarboxamide.**[81,82] To a 0.5-L three-neck round-bottom flask equipped with thermometer, mechanical stirrer, and nitrogen inlet was added 14.5 g (0.134 mol) of ethyl chloroformate in 130 mL of dichloromethane. The solution was cooled in an ice bath to ~4 °C and was stirred vigorously while a prechilled solution of 11.83 g (0.133 mol) of **25** and 13.4 g (0.133 mol) of triethylamine in 130 mL of dichloromethane was added dropwise over 50 min. After the addition was complete, the solution was stirred for an additional 70 min at 4 °C. The solution was then purged with NH_3, causing it to turn milky white almost immediately. The NH_3 flow was controlled so as to keep the temperature below 15 °C. After 35 min, the NH_3 flow was stopped, the ice bath was removed, and the stirred slurry was allowed to warm to room temperature over 1 h. The white solid was collected and extracted with three portions of hot dichloromethane. The clear, cream-colored solution was then concentrated to cloudiness by rotory evaporation, and the fine, white crystaline product was collected by vacuum filtration. The filtrate afforded an additional amount of product, for a total yield of 9.03 g (77.2%): ^{1}H NMR ($CDCl_3$) δ 0.95 (d, 1 H, J = 4.4 Hz), 1.39 (d, 1 H, J = 4.4 Hz), 5.6 (br s, 2 H).

***trans*-[2,3,3-$^2H_3$]Cyclopropylamine (26).**[83] In a three-neck 250-mL Morton flask equipped with thermometer, nitrogen inlet, mechanical stirrer, and additional funnel was mixed 9.03 g (0.103 mol) of the above amide and 25 mL of water. The mixture was vigorously stirred and chilled to 4–5 °C with an ice bath. A concentrated NaOCl solution[84] (41.4 g, 18.5 % by weight, with a 1.2% excess of NaOH) was prepared by bubbling Cl_2 into a tared flask containing 8.3 g (0.21 mol) of NaOH and 25.8 g of H_2O (1 part ice, 2 parts liquid) until 7.3 g (0.10 mol) had been absorbed. The hypochlorite was then added dropwise over 10–15 min to the amide solution. The temperature rose to 10–11 °C during the addition and then fell back to 3 °C as the solution stirred for another hour. The clear, colorless solution of *N*-chloroamide was then transferred to an Erlenmeyer flask, stoppered, and stored in a refrigerator for ~30 min while preparations for the next step were made. The Morton flask was next equipped with a Teflon stirring bar, jacketed dropping funnel (with no pressure equalizing arm), and empty 8 mm × 6 in. distillation column with condenser and collection flask. The flask was charged with 17.4 g of 50% NaOH, which was brought to reflux at ~110 °C with an oil bath. The chlorinated amide solution was placed into the ice-cooled

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dropping funnel and added dropwise over about 30 min with vigorous stirring. Shortly after the addition began, material began to distill at 90–95 °C. After the addition was complete, the distillation was continued for another 10 min at which time the head temperature was 99 °C. The collection flask contained 9.99 g of an amine–water mixture. Titration with aqueous HCl (methyl red pH indicator) showed that the mixture was 45.4% amine for a yield of 4.54 g (0.0756 mol, 74%); NMR analysis showed only trideuteriocyclopropylamine and water: ^{1}H NMR ($CDCl_3$) δ 0.26 (s, 1 H), 1.5 (br s, 2 H), 2.28 (s, 1 H).

***trans*-Azoxy[2,3,3-$^2H_3$]cyclopropane (27).** The amine–water solution from above (4.54 g, 0.076 mol amine) was mixed with 5 mL of water and was oxidized as in the nondeuteriated compound with 0.6 g of Na_2WO_4 and 86.1 g of 30% H_2O_2. Vacuum distillation of the crude product at 8–9 mm yielded a total of 2.24 g (0.017 mol) of azoxycyclopropane-d_6 (47% yield): ^{1}H NMR ($CDCl_3$) δ 0.90 (br s, 1 H), 1.43 (br s, 1 H), 3.82 (br s, 1 H), 3.93 (br s, 1 H).

***trans,trans*-1*H*,2*H*-Azo[2,3,3-$^2H_3$]cyclopropane (1tHt).** A 1.95-g (0.014–0.015-mol) portion of **27** was added to 120 cc of distilled chloroform in a 250-cc three-neck round-bottom flask equipped with magnetic stirring bar, nitrogen inlet, thermometer, and addition funnel. After chilling the solution to ~4 °C with an ice bath, 3.82 g (0.0141 mol) of Si_2Cl_6 (Aldrich, freshly opened) was added dropwise over 15 min. The temperature rose to 8–10 °C during the addition and then fell back to 5 °C. The mixture was stirred cold for 5 min and then allowed to warm to room temperature. After the yellow solution was stirred for an additional 80 min, the reaction mixture was quenched with an excess of 1 N NaOH. The organic phase was decanted off a yellow solid, which was rinsed with chloroform. The combined organic phases were washed with 25 cc of water and then dried over $MgSO_4$. The dried solution was then concentrated to ~5 cc by distillation at 1 atm. The orange concentrate showed signs of degradation. Vacuum distillation at ~35 mm allowed collection of 0.332 g (2.86 mmol, 20% yield) of pure **1tHt**. A little more product was recovered from the vacuum trap as a mixture suitable for preparative GC: ^{1}H NMR ($CDCl_3$) δ 1.23 (br s, 2 H), 3.33 (br s, 2 H); (C_6D_6) δ 1.24 (br s, 2 H), 3.44 (s, 2 H). An NMR peak at 0.7 ppm (C_6D_6) with $^1/_8$ the area of the δ 1.23 peak is attributed to **1tHc** or to incompletely deuteriated azocyclopropane.

Gas-Phase Photolysis. A Pyrex vessel in the shape of a rectangular loop with a section of vycor tubing was constructed for irradiation of **1t** at 254 nm.[85] The apparatus contained a glass paddle wheel attached to a glass-encased magnet for continuous circulation of the gaseous mixture. One stopcock was installed for evacuation and filling the vessel while another had a straight bore and was fitted with a septum to allow removal of GC samples. A 32.4-mg (0.294-mmol) sample of **1t** was injected through the septum into the evacuated vessel, and the pressure was brought up to 700 mm with isobutane. The vessel was placed in the center of a triangle consisting of three GE 30-W low-pressure mercury lamps. After 8-h irradiation at 45–50 °C, GC monitoring (columns C, E, and M) showed the conversion to be 70%, and the volatile gases were distilled into a 500-cc bulb. The yellow film that coated the vycor section of the irradiation vessel was partly washed out with $CDCl_3$ and was checked by NMR. No identifiable signals were observed and no 2-pyrazoline (**9**) was detected. To facilitate further GC analysis, (columns C, D, and F) the gaseous products were concentrated by distilling them into a 15-cc bulb and then distilling much of the isobutane from the 15-cc bulb held at −78 °C back to the 500-cc bulb held at 196 °C. Most of the products were identified by GC/MS and by co-injection with authentic materials, giving the results shown in Table I. At least four peaks accounting for 5–10% of the reacted **1t** remain unknown. A control irradiation of isobutane alone under the same conditions showed no photochemistry to have taken place.

Irradiation at 366 and 313 nm. A Hanovia 450-W mercury lamp in a photochemical merry-go-round was equipped with 2,7-dimethyl-3,6-diazacyclohepta-1,6-diene perchlorate and Corning 7-60 UV filters (366 nm) or potassium chromate (313 nm) filter solutions. Samples were degassed and sealed into Pyrex NMR tubes or 1-cm cylindrical tubes that fit closely into a black metal sleeve with a window to allow exposure of a fixed area of the sample. Actinometry at 366 nm was based on nitrogen evolution from the benzophenone sensitized deazatation of 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH, Φ = 1.0),[86] while the 313-nm irradiations in NMR tubes used the photolysis of butyrophenone as an actinometer.[87,88] Evolved gases were collected with a Toepler pump and gas buret and were analyzed by GC on column G at −78 °C. Relative amounts of each component were calculated by correcting the peak area on the TC detector for differences in thermal conductivity. Since these GC conditions separated oxygen and nitrogen, leakage of air into the sample was readily revealed by the presence of oxygen.

Experiments run in C_6D_6 in NMR tubes normally gave only a mixture of **1t** and **1c**, whose ratio was determined by integration of the multiplets at δ 3.46 and δ 3.21, respectively. If the total amount of azocyclopropane at any time was assumed to equal the initial amount, the concentration of each isomer was readily calculable.

Direct 366-nm irradiation of 0.128 M **1t** in pentane in a 1-cm tube was monitored by UV from 330 to 360 nm. The absorbance at each of four wavelengths was converted to concentration of **1c** from the known extinction coefficients. A plot of concentration versus time resembled the one from triplet sensitization (see below) except that the data were less scattered, and the reaction was 10-times faster due to the larger sample area and the higher light intensity at 366 nm than 313 nm. From the known light intensity and the initial slope, the quantum yield **1t** → **1c** was calculated as 0.60. The Lamola treatment of these data gave a good straight line corresponding to Φ = 0.53.

Irradiation at 254 nm. The reactor was the same one used for gas-phase photolysis but the samples were placed either into 5-mm Amersil NMR tubes or 1.0-cm o.d. quartz tubes. A vycor sleeve surrounded the tube to prevent penetration of 185-nm light. DBH–benzophenone actinometry showed the light intensity to be 0.25 mE/h in the 1.0-cm tubes while azobenzene actinometry[89] gave a value of 0.16 mE/h in the NMR tubes. Since no provision was made for precise sample placement within the reactor, the actual intensity may have deviated as much as ±20% from these values. The products were analyzed by GC on columns C, H, J, and M.

Irradiation at 248 and 193 nm. Pentane solutions of **1t** were degassed and sealed in 2.5 cm o.d. round Suprasil tubes equipped with a 1 cm square UV cell sidearm and a breakseal. The solution was stirred magnetically during irradiation by means of a small Teflon stirring bar. The round tube was placed into a black aluminum sample block with a horizontal 2.0-cm round hole bored all the way through the block. Light from a Lambda Physik EMG101 pulsed excimer laser passing through the hole first struck the liquid sample and then a Scientech Model 380103 laser power meter. The absolute pulse energy was measured with no cell in the block. In order to monitor the relative pulse energy over the course of time, a small portion of the laser beam was reflected onto a photodiode connected to a gated integrator and PDP 11/03 computer. The computer was programmed to count laser pulses and to store the relative pulse energies. The progress of the photolyses was monitored by UV, and the end products were analyzed by means of a Toepler pump and GC of both the gases (column G) and the liquid (columns C and E).

Triplet-Sensitized Irradiation of 1t. A 7.8-mg portion of **1t** and 3.8 mg of xanthone were dissolved in 0.5 mL of C_6D_6, and the solution was degassed and sealed in a Pyrex NMR tube. At these concentrations, the sensitizer absorbed 96% of the 313-nm light. The sample was irradiated with the Hanovia 450-W lamp and K_2CrO_4 filter described above, producing a light intensity of 0.0064 mE/h at 313 nm. After 66-h irradiation with periodic NMR monitoring, the solution had reached a pss composition of 20% **1c**. A plot of the mole fraction of **1c** versus time for the xanthone sensitized 313-nm irradiation of **1t** is shown in Figure 3. The initial slope of this curve, though not very precise, corresponds to a quantum yield for **1t** → **1c** of 0.18 while correction

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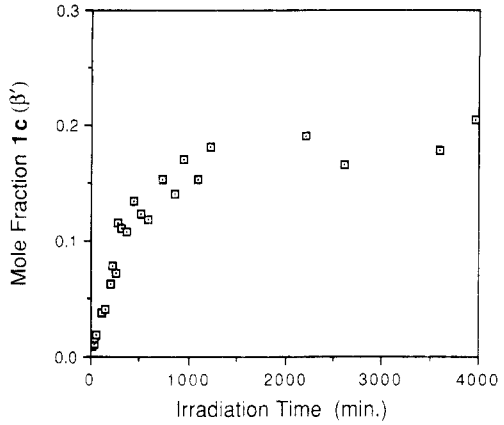

Figure 3. Experimental conversion (by NMR) to **1c** (β') vs irradiation time for xanthone sensitization of **1t**.

of these data for back reaction according to Lamola,[31] gave a Φ of 0.23.

In a separate experiment, 11.8 mg of **1t** and 50 mg of xanthone were dissolved in 1.5 cc of C_6D_6. One half of this solution was placed into an NMR tube containing 10.1 mg of thiophenol (sample A1) and the other half was placed into an empty NMR tube (sample A2). Both tubes were degassed, sealed, and irradiated together at 366 nm with periodic monitoring by NMR. Sample A1 was irradiated for 6.2 h and A2 for 15 h. The pss of A2 contained 17% **1c**, a lower value than found in the 313-nm irradiation. This discrepancy is probably due to light absorption by **1c**, which competes better with xanthone for light at 366 nm than at 313 nm. GC analysis of A2 showed **1t** and **1c** but no cyclopropane, ethylene, or pyrazoline **2**. Sample A1 showed no **1c** by NMR or GC but instead formed **13**, **21**, and diphenyl disulfide, as demonstrated by NMR and GC comparison with authentic samples (columns H, I, K).

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Registry No. **1t**, 80201-75-8; **1c**, 80201-76-9; **2**, 80201-77-0; **9**, 109-98-8; **13**, 15601-98-6; **21**, 115962-98-6; **25**, 61377-11-5; **26**, 69517-15-3; **27**, 115963-00-3; pentane, 109-66-0; hydrogen, 1333-74-0; azoxycyclopropane, 33425-51-3; cyclopropylamine, 765-30-0; (cyclopropylazo)-*n*-propane, 115962-97-5; allylcyclopropane, 4663-23-4; *tert*-butylcyclopropane, 4741-87-1; *trans*-[2,3,3-$^2H_3$]-cyclopropanecarboxamide, 115962-99-7; acrolein, 107-02-8; 1,5-hexadiene, 592-42-7; (*tert*-butylazo)cyclopropane, 115963-01-4; *trans*-[2,3,3-$^2H_3$]phenylcyclopropane, 61377-10-4; bicyclopropyl, 5685-46-1; ethylene, 74-85-1; cyclopropane, 75-19-4.

Reactivities of Conjugated Dienes to Arylthiyl Radicals

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The rate constants for the addition reactions of the arylthiyl radicals to various conjugated dienes have been determined by the flash photolysis method. For each arylthiyl radical, the absolute rate constant of 1,3-butadiene is close to that of styrene and is larger than that of 1-hexene by a factor of ca. 3500; the formation of the resonance stabilization of the allyl-type radical accelerates the reaction rate. The Hammett relation with varying substituents on the arylthiyl radicals was examined for each diene; the chloro and carboxylic substitutions on diene reduce the electron density of the conjugated double bond due to the inductive effect, vise versa for the methyl and methoxy substituents. The substitution at the terminal carbon of diene decreases the reactivity; the terminal position is predominantly attacked by the arylthiyl radical. The reactivity of 2,3-dimethoxy-1,3-butadiene is considerably lower than that of the 2,3-dimethyl derivative, suggesting an angular conformation for the former diene.

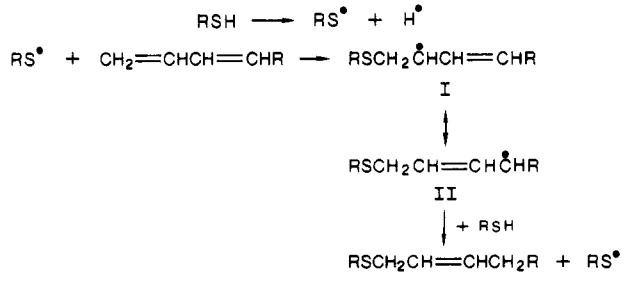
Introduction

Radical addition reactions of thiols to 1,3-conjugated dienes give predominantly 1,4-addition products, i.e., the thiyl radical attacks the terminal position and the carbon radical center at the 4-position of the allyl radical abstracts an hydrogen atom from thiol (Scheme I).[1,2]

In the co-presence of oxygen, 1-sulfide 2-ol compounds (i.e., $RSCH_2CH(OH)CH{=}CHR$) are produced, suggesting that the reaction of oxyggen occurs at the 2-position of the allyl radical (resonance structure I).[3] This finding also indicates that the arylthiyl radicals are not reactive to oxygen, since the sulfonyl or sulfinyl compounds are not found under an ordinal condition.

Although these studies based on the product analyses revealed the regioselectivity of the reactions, any systematic kinetic study for the reactivity of various dienes toward free radicals has not yet been reported. Some reaction rate

Scheme I



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