Table I. Dihedral Angles (Degrees) of Selected Cyclic Dipeptides

Angles[a]	*cyclo*(L-Pro-L-Leu) Crystal structure[b]	*cyclo*(L-Pro-L-Pro)		*cyclo*(L-Pro-D-Pro)	
		Calcd	Exptl[c]	Calcd	Exptl[c]
χ_1	−32	−33	−30	−37	−40
χ_2	36	34	42	36	29
χ_3	−25	−23	−21	−22	−12
χ_4	4	2		−1	
ϕ	−42	−16		−6	
ψ	34	26		5	
ω	6	−10		−14	

[a] The reported dihedral angles are for the L-Pro residue and are the negative of the dihedral angles for the D-Pro residue. The conventions followed in this paper are given by: IUPAC–IUB Commission on Biochemical Nomenclature, *Biochemistry*, **9**, 3471 (1970). [b] I. L. Karle, *J. Amer. Chem. Soc.*, **94**, 81 (1972). [c] Calculated from Karplus' equations: M. Karplus (*J. Chem. Phys.*, **30**, 11 (1959)) using the parameters of ref 16b and averaging the values which depend on the same dihedral angle.

near −70°) equilibria between the two ring conformers have been observed. These observations are in accord with a theoretical study.[19]

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Arylcyclopropane Photochemistry. Stereospecific Carbene Elimination from 1,1-Diphenylcyclopropanes

Sir:

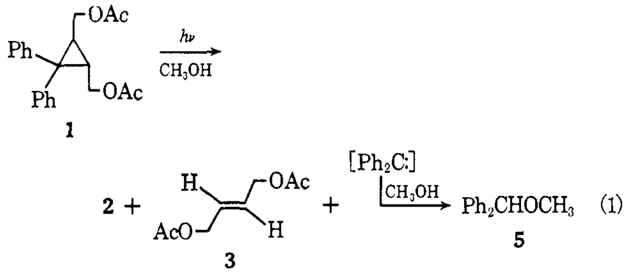
One of the most fascinating of the numerous photochemical reactions undergone by arylcyclopropanes is the fragmentation process leading to carbenes and olefins.[1] The reaction appears to be quite general, though it is often only a minor process since other more efficient reactions frequently predominate. Convincing chemical evidence for the formation of carbenes, *e.g.*, phenylcarbene from 1,2-diphenylcyclopropane[2] and diphenylcarbene from 1,1,2,3-tetraphenylcyclopropane,[3] is found in the isolation of the expected adducts when the cyclopropanes are irradiated in an alcoholic, olefinic, or hydrocarbon medium. Moreover, Griffin has shown that the selectivity of phenylcarbene for insertion into secondary *vs.* primary C–H bonds is the same when the phenylcarbene is produced from diphenylcyclopropane as from other, more usual sources of phenylcarbene.[2a]

The mechanism of this fragmentation is of special interest. Formally, it is a four-electron excited state process and may proceed in a concerted fashion with retention of cyclopropane stereochemistry in the product olefin. However, it has been noted by Griffin[1,4] and others[5] that several of the reactions of excited (singlet and triplet) arylcyclopropanes, diphenylcyclopropane in particular, seem well rationalized as proceeding *via* aryl-substituted trimethylene diradicals, and it has been speculated that excited states (singlet or triplet) having much trimethylene diradical character may be involved in the fragmentations of arylcyclopropanes to carbenes.[1,6] Some support for this idea has been provided by Becker and Griffin who observed long-wavelength phosphorescence from various polyarylcyclopropanes and ascribed this to such radical-like triplet states.[6] Arguments for the existence of corresponding singlet states were presented.

The exact nature of this diradical excited state is of course unknown, though one might expect on the basis of recent calculations[7] that it would be characterized by low barriers to rotation about the terminal carbons. Thus, to provide some concrete evidence about the excited states and possible intermediates involved in the fragmentation we have examined the reaction stereochemistry.

Cyclopropanes **1** and **2** were studied since (a) they are readily prepared[8,9] in stereochemically pure form, (b) they can eliminate the stable carbene diphenylcarbene, and (c) the expected product olefins **3** and **4** are stable and easy to analyze, do not absorb light significantly in the regions where **1** and **2** do, and should have high triplet energies so that they would not isomerize rapidly during the irradiation.

As predicted preparative irradiation of **1** (0.016 *M*) in methanol with Corex-filtered light followed by silica gel chromatography afforded olefins **3** (13%) and **4** (trace), benzhydryl methyl ether (**5**, 11%), and traces of **2** and other unidentified products along with 54% of recovered **1** (eq 1). Similarly, **2** (0.041 *M*) yielded 12% of **3** and **4** (**4**:**3** = 15:1), **5** (14%), **1** (36%), and other unidentified materials together with 17% of re-



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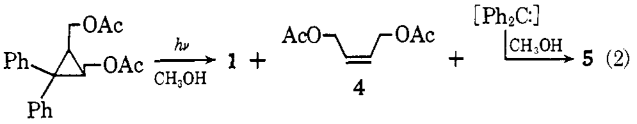
covered **2** (eq 2). The formation of olefins **3** and **4** was also observed in ether and cyclohexane (gc).



2

Triplet sensitization of **1** and **2** with xanthone afforded no detectable amounts of **3** and **4**. Net isomerization of each cyclopropane to the other isomer was observed, indicating transfer of triplet energy from the xanthone to the cyclopropanes had occurred. This indicates that the pathways leading to fragmentation of **1** and **2** do not involve the triplet states of these molecules.

The preparative irradiations gave an indication of reaction stereospecificity. This was confirmed by low conversion experiments. Irradiation of 0.13 *M* ether solutions of **1** and **2** were carried out to give less than 1% conversion to the other cyclopropane stereoisomer. At this point analyses for olefins **3** and **4** were carried out.[10] These revealed that cyclopropane **1** yielded olefin consisting of at least 99% **3**. Similarly, **2** produced >99% **4** at these very low conversions. As the photolyses proceeded further and the amount of the other cyclopropane stereoisomer increased, the percentage of the other olefin likewise increased as expected. Thus, the fragmentations of **1** and **2** are essentially completely stereospecific.[11]

Relative quantum yields for isomerization and cleavage of **1** and **2** were measured on a merry-go-round apparatus at the same very low (<1%) conversions. These experiments yielded for *cis*-cyclopropane **2** $\phi_{\text{isom}}/\phi_{\text{cleav}} = 4.6 \pm 0.2$, and for *trans*-cyclopropane **1** $\phi_{\text{isom}}/\phi_{\text{cleav}} = 1.1 \pm 0.1$. The data also reveal that **2** cleaves more efficiently than does **1**: $\phi_2/\phi_1 = 2.6 \pm 0.2$. It should be noted that these ratios of quantum yields for isomerization *vs.* fragmentation for each cyclopropane isomer are maximum figures for the relative rates of the two processes from the singlet states of **2** and **1**, since the triplet contribution to isomerization is not known in either case.

These results indicate that the fragmentation process proceeds *via* the singlet state bypassing any long-lived intermediate diradical (excited state or ground state) species having free rotation about the terminal carbons. Similarly, carbene formation *via* thermal cleavage of diradicals with the 0,0 geometry formed by disrotatory photochemical ring opening[1] cannot account for the product stereochemistry. Instead, the reaction appears to be a concerted, allowed excited state process. It is conceivable that fragmentation occurs from a singlet state other than the spectroscopic one—a state[6] having one or more ring bonds considerably stretched relative to the ground state. Our results then provide certain restrictions on this state with respect to geometry, rotational barriers, and mode of cleavage.

We note that this stereospecificity is especially interesting in light of the fact that the thermal reverse of the fragmentation—the addition of singlet carbenes to olefins[12]—is likewise highly stereospecific and probably concerted. The difference between the thermal and photochemical reactions would appear to lie in the relative orientation of carbene and olefin during reaction.[7a,13]

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[10] Analyses for olefins and cyclopropanes were carried out with a Perkin-Elmer Model 990 gas chromatograph equipped with a flame ionization detector. For 3 and 4 a 7 ft × 1/8 in. stainless steel column packed with 10% C-6 diethylene glycol succinate on Anakrom S.D., 90–100 mesh operated at 130°, was used. Cyclopropanes were analyzed on a 5 ft × 1/8 in. stainless steel column packed with 3% XE-60 on Varaport 30, 100–120 mesh operated at 195°. Yields were determined with an internal standard.

[11] Experiments in which 4 was added to 1 and 3 to 2 prior to photolysis showed no detectable loss of 4 or 3, respectively. Thus the observed stereospecificity cannot be due to selective destruction or isomerization of the nonobserved olefin.

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^{14}C Isotope Effects in the 1,3-Dipolar Addition of *N*,α-Diphenylnitrone and Styrene. A Concerted Cyclic Process[1]

Sir:

We find that the primary carbon-14 kinetic isotope effects[2] in the 1,3-dipolar addition of *N*,α-diphenylnitrone[3,4] and styrene to yield 2,3,5-triphenylisoxazolidine are consistent with Huisgen's[5,6] concerted, cyclic mechanism and inconsistent with the diradical mechanism.[7–9]

Inter-[10] and intramolecular[11] deuterium isotope effects have been used in attempts to answer the question of concerted *vs.* diradical addition during 1,3-dipolar additions, but with indifferent results.

We prepared Ph*C*H=N(O)Ph, Ph*C*H=CH$_2$, and PhCH=*C*H$_2$ by standard methods[3,12] and, in separate experiments, determined the isotope effects during the additions. In these measurements, the method of competing reactions and low conversion[13] was employed, except during the experiments with *N*-α-diphenylnitrone and styrene-α-^{14}C, for which a variation of the differential method[14] was used. The reactions all took place in boiling ethanol containing a trace of hydroquinone to suppress styrene polymerization. The results are shown in Figure 1 and leave no doubt, we believe, that the reaction must proceed through a

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[1] Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

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