$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		Retention		Mass spectral	fragment, $a_{,} m/e$ (no. of halo	idens) (relative intensity) ^c {pi	recise mass] ^d	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Compound ^a	timeb	+W	a ⁺	p+	c+	d+	e+
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1	0.44	270 (Br.,) (0)	214 (Br,) (8)	177 (Br) (2)	121 (Br) (19)	149 (Br) (9)	93 (Br) (8)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	2	0.66	348 (Br,) (0)	292 (Br,) (1)	177 (Br) (3)	199 (Br,) (1)	149 (Br) (12)	171 (Br,) (2)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4^{e} 1.00 426 (Br ₄) (0) 370 (Br ₄) (1) 255 (Br ₂) (3) 199 (Br ₁) (8) 227 (Br ₂) (17) 171 (Br ₂) (10) $5f$ 1.02 396 (Br ₂) (0) 373.6795 (-0.5)] 1256.8998 (-0.2)] 1290.8372 (-0.3)] 1228.9045 (-0.3)] 1172.8424 (-0.1)] $5f$ 1.02 396 (Br ₂) (0) 340 (Br ₂) (1) 1256.8998 (-0.2)] 169 (1) (84) 227 (Br ₂) (12) 141 (1) (17) $5f$ 1.02 396 (Br ₂) (0) 340 (Br ₂) (1) 1256.8998 (-0.2) 169 (1) (84) 227 (Br ₂) (12) 141 (1) (17) 616 (1) 69 (1) (84) 227 (Br ₂) (12) 141 (1) (17) 141 (1) (17) $7f$ 1.02 396 (Br ₂) (10.1) 340 (Br ₂) (10) 340 (Br ₂) (10) 169 (1) (84) 227 (Br ₂) (12) 141 (1) (17) 616 (1) (12) 1168.9148 (-0.1) 0.1) 120.69200 (0.0) 1140.92200 (0.0) 1140.92200 (0.0) 1140.92200 (0.0) 1140.9200 (0.0) 1140.9200 (0.0) 1140.9200 (0.0) 1146.9876 (-0.1) 128.9916 ($+0.1$). Cr ₁ H ₀ , BrO (M - Br ₂), m/e 148.978 10.6 ($+18n$). 10.6 ($+10.1$). Cr ₁ , H ₁₀ , BrO (M - Br ₂), M/e 148.978	3	0.77	348 (Br,) (0)	292 (Br.) (2)		121 (Br) (68)	227 (Br ₃) (10)	93 (Br) (13)
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \frac{1373.6795 (-0.5)}{56 (Br_2 I) (0)} \frac{1256.8998 (-0.2)}{340 (Br_2 I) (1)} \frac{1256.8998 (-0.2)}{1200.8372 (-0.3)} \frac{1228.9045 (-0.3)}{1228.9045 (-0.3)} \frac{1172.8424 (-0.1)}{141 (1) (17)} \frac{117}{141 (1) (17)} \frac{111}{140.9200 (0.0)} \frac{1168.9148 (-0.1)}{1140.9200 (0.0)} \frac{1168.9148 (-0.1)}{1140.9200 (0.0)} \frac{1140.9200 (0.0)}{1140.9200 (0.0)} \frac{1168.9148 (-0.1)}{1140.9200 (0.0)} \frac{1140.9200 (0.0)}{1140.9200 (0.0)} \frac{1100.5 Hz}{1100 (-0.1)} \frac{1100.5 Hz}{1100 (-0.1)} \frac{1100.5 Hz}{110 (-0.1)} 11$	4e	1.00	426 (Br ₄) (0)	$370 (Br_{\bullet}) (1)$	255 (Br ₂) (3)	$199 (Br_2) (8)$	$227 (Br_2) (17)$	$171 (Br_2) (10)$
	$ \frac{5f}{1.02} \frac{1.02}{396} (Br_2 I) (0) \frac{340 (Br_2 I) (1)}{140.9200 (0.0)} \frac{169 (1) (84)}{168.9148 (-0.1)} \frac{227 (Br_2) (12)}{1140.9200 (0.0)} \frac{141 (1) (17)}{1140.9200 (0.0)} \frac{1}{1140.9200 (0.0$				[373.6795 (- 0.5)]	[256.8998 (0.2)]	[200.8372(-0.3)]	[228.9045 (= 0.3)]	[172.8424 (= 0.1)]
[397.8201 (+ 0.1)] [168.9148 (0.1)] [168.9148 (0.1)]	$[168.9148 (-0.1)] \qquad [140.9200 (0.0)]$ ^{<i>a</i>} For structures, see Figure 1. <i>b</i> Relative to compound 4 equal 1.00. <i>c</i> Per cent of base peak. <i>d</i> Measured (by peak matching) on the center peak of quintuplets (Br ₄) and triplets (Br ₄), the lower mass as of doublets (Br), except as noted. Figures in parentheses indicate mmu deviation from calculated values. <i>e</i> Additional peaks measured: <i>m/e</i> 188.9916 (+0.1), C ₇ H ₁₀ BrO (M - Br ₃), <i>m/e</i> 148.978(0.0), C ₈ H ₈ ^a Br (d - HBr). <i>f</i> Additional peaks measured: <i>m/e</i> 126.9043 (0.0), 1; <i>m/e</i> 148.978(d - 0.3), C ₈ H ₈ ^a Br (d - HBr).	Sf	1.02	396 (Br, I) (0)	$340 (Br_2 I) (1)$		169 (1) (84)	$227 (Br_2) (12)$	141 (1) (17)
	^a For structures, see Figure 1. ^b Relative to compound 4 equal 1.00. ^c Per cent of base peak. ^d Measured (by peak matching) on the center peak of quintuplets (B_{r_4}) and triplets (B_{r_4}), the lower mass ak of doublets (B_{1}), except as noted. Figures in parentheses indicate mmu deviation from calculated values. ^e Additional peaks measured: m/e 188,9916 (+ 0.1), C_{r_4} H ₁₀ BrO (M - B_{r_3}), m/e 148,978 (0), C_{s_4} H ₈ ^{a1} Br (d - HBr). ^f Additional peaks measured: m/e 127.9121 (-0.1), HI: m/e 126.9043 (0.0), 1; $m/$			[397.8201 (+ 0.1)]	I		[168.9148 (0.1)]		[140.9200 (0.0)]

and cochromatographed (GC) with 1-3 obtained from B. hamifera.

Among the compounds identified by GC-mass spectra is 1-iodo-3,3-dibromo-2-heptanone (5), which gave peaks at m/e 396 (M, symmetrical Br₂ triplet at 396, 398, 400) and at m/e 340, 169, 227, and 141 (a, c, d, and e, respectively) as well as peaks at m/e 127 and 128 (I⁺ and HI^{+.}). High resolution mass spectrometric data (Table I) agreed with these assignments. Compound 5 is especially significant among those in Table I since it represents the first example of a natural product containing both iodine and bromine and also structurally departs from the only other known iodinated natural substances, which are thyroxine related compounds.5

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References and Notes

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The Photochemistry of β , γ -Epoxy Cyclic Ketones

Sir:

In striking contrast to the extensive investigation of the photochemistry of α,β -epoxy ketones,¹ only scattered reports have appeared concerning aspects of the photochemis-

(-0.4), $C_7 H_{11} O (M - Br_2 I)$.

Scheme I



try of β , γ -epoxy ketones.²⁻⁷ We now wish to suggest a general scheme which summarizes the photochemistry of β , γ -epoxy *cyclic* ketones and to present experimental evidence which supports this scheme.^{8,9}

We propose that irradiation of a β , γ -epoxy cyclic ketone (1) (Scheme I) initially leads to Norrish type I bond cleavage and the formation of an apparent diradical species 2 which undergoes subsequent ring opening to give the acylalkoxy diradical 3. Unless specific substituent and/or skeletal constraints are present, product formation proceeds from 3 by *competitive* ring closure to give lactone 4 and hydrogen transfer to provide aldehyde 5. If the formation of *either* 4 or 5 is prevented, then the other product predominates. If the formation of *both* 4 and 5 is precluded, then decarbonylation occurs to give diradical 6 which undergoes disproportionation to provide 7 and/or ring closure to afford 8.

 β , γ -Epoxy cyclic ketones 9, 12, and 15 possess no unusual molecular constraints (relative to Scheme I) and thus the photochemistry of these compounds should be typical of the "normal" photochemical behavior of β , γ -epoxy cyclic ketones. Previously, we have noted that irradiation of 9 through a Corex filter with a Hanovia L 450-W lamp to 95% conversion gives 10 and 11 in yields of ca. 50 and 20%,



respectively.⁷ Expanding the size of the ketone ring does not significantly affect the overall photochemical result. Thus, irradiation of $12^{10,12}$ under comparable conditions affords 13 and 14 in yields of ca. 65 and 10%, respectively. Even



more drastic changes in the geometric relationship of the carbonyl and epoxide moleties leads to analogous results. Carlson and his coworkers have shown⁵ that irradiation of 15 to 70% conversion gives in ca. 50% yield a 65:25:8 mixture of 16:17:18.¹³

The consequences of preventing either $3 \rightarrow 4$ or $3 \rightarrow 5$ from occurring have been investigated. If the hydrogen at the γ -carbon in the β , γ -epoxy ketone moiety of 1 is replaced by an alkyl substituent, then the formation of aldehyde 5 is precluded. In order to explore the ramifications of



this constraint, we have examined the photochemistry of $19.^{14}$ Irradiation of an ether solution of epoxy ketone 19 through a Corex filter gives lactone 20 as the only major reaction product in ca. 35% yield.¹⁵ By the introduction of



suitable geometric constraints in 1, it is possible to prohibit $3 \rightarrow 5$. Such is the case in β , γ -epoxy cyclic ketone 21.¹⁶ Irradiation of an ether solution of 21 through a Corex filter gives aldehyde 22 as the only major reaction product in ca. 50% yield. If the photorearrangement of 21 proceeds by the mechanism outlined in Scheme I, then product formation occurs from diradical 23. Of course, lactone formation from 23 is disfavored by the geometric relationship of the acyl and alkoxy radicals.



The consequences of preventing both $3 \rightarrow 4$ and $3 \rightarrow 5$ from occurring are reflected in the photochemistry of 24 and 26. Irradiation of 24 leads to photodecarbonylation and the formation of epoxide 25 in ca. 95% yield.⁶ Similarly, irradiation of 26 gives 27 in ca. 75% yield.⁶ Chambers and



Marples have reported that irradiation of an ether solution of 9α , 10α -epoxy ketone **28** also results in rapid decarbonylation and formation of the unsaturated epoxide **29** (20% yield), the *B*-norepoxide **30** (3%), and several minor prod-



ucts.⁴ By contrast, the 9β , 10β -epoxy ketone **31** remains unchanged when irradiated under comparable conditions.⁴ In view of Scheme I, an examination of molecular models suggests that it would appear to be more likely that epoxy ketone 31 rather than 28 would undergo photodecarbonylation. This point is currently under active investigation.

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- (8) For a detailed investigation of the photochemistry of an acyclic β , γ epoxy ketone see ref 2.
- (9) The dearth of information concerning the photochemistry of β , γ -epoxy cyclic ketones may follow from the observation of Starr and Eastman that irradiation of cyclohexane or methanol solutions of i "gave small amounts (less than 0.2 mol/mol of ketone) of a mixture of carbon mon-



oxide and carbon dioxide. The product consisted of a tarry fraction (ca. 50%) and a volatile fraction containing mainly unreacted ketone along with small amounts of a number of products which were not identified." We have found irradiation of ii and iii in a variety of solvents to be simi-larly unrewarding. It appears that in order for product formation to become significant in the photochemistry of most β , γ -epoxy cyclic ketones that the α -carbon of the β , γ -epoxy ketone molety must be substituted with either two alkyl groups or one exceptionally good radical stabilizing group (e.g., phenyl or cyclopropyl).
(10) Epoxy ketone 12 was prepared by treatment of 2,2-dimethylcyclohept-

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- (13) Carlson et al. have suggested that lactone 18 may arise by initial formation of the thermally unstable E isomer of **16** which undergoes an oxy-Cope rearrangement.⁵
- (14) Epoxy ketone 19 was prepared by m-chloroperbenzoic acid epoxidation of 2,2,4,6,6-pentamethylcyclohex-3-enone which was obtained by ex-

haustive methylation of 2,4-dimethylcyclohex-2-enone with excess methyl iodide and sodium tert-pentoxide in refluxing anhydrous ether

- (15) The disappointing low yield of 20 appears to be a consequence of the extensive competitive photodecomposition of 20 which occurs under the photolysis conditions employed.
- (16) Epoxy ketone 21 was prepared by treatment of the corresponding β,γ-unsaturated ketone¹⁷ with *m*-chloroperbenzoic acid.
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Nuclear Magnetic Resonance Studies. III. **Carbon Nuclear Magnetic Resonance of Triphenylphosphonium Ylides**

Sir:

We wish to report the preliminary results of a ¹³C NMR study of several alkylidene triphenylphosphoranes, triphenylphosphinimines, triphenylphosphazenes, and their corresponding phosphonium salts. Stabilized ylides contain a strong electron withdrawing group adjacent to the carbon bearing the formal negative charge. The ¹³C NMR of several stabilized ylides¹ and only one nonstabilized ylide, methylenetrimethylphosphorane,² have been reported previously. There has been no carbon NMR study of phosphinimines or phosphazenes, which contain formal P=N bonds. Utilization of the ¹³C chemical shift and P-¹³C coupling data can provide sensitive tests for models which propose³ d orbital participation in these compounds. Contribution from the following resonance structures are considered in this study.



Bart⁴ has determined by means of the X-ray structure of methylenetriphenylphosphorane, that the methylene carbon is trigonally hybridized. In addition, other X-ray studies⁴⁻⁶ indicate a shortened ylide bond in nonstabilized ylides. These studies have suggested a bonding picture in which there is some transfer of electronic charge from carbon to phosphorus presumably via d orbitals.7 We recognize that the amount of $d\pi$ -p π overlap may be relatively small between phosphorus and carbon.

Due to the rather limited NMR studies dealing with carbon involved in $d\pi - p\pi$ bonding with second-row elements, we wish to examine the above effects of such interactions on