Table I. Gas Chromatographic and Mass Spectrometric Data for *B. hamifera* Components

Compound[a]	Retention time[b]	Mass spectral fragment,[a] *m/e* (no. of halogens) (relative intensity)[c] [precise mass][d] M$^+$	a$^+$	b$^+$	c$^+$	d$^+$	e$^+$
1	0.44	270 (Br_2) (0)	214 (Br_2) (8)	177 (Br) (2)	121 (Br) (19)	149 (Br) (9)	93 (Br) (8)
2	0.66	348 (Br_3) (0)	292 (Br_3) (1)	177 (Br) (3)	199 (Br_2) (1)	149 (Br) (12)	171 (Br_2) (2)
3	0.77	348 (Br_3) (0)	292 (Br_3) (2)		121 (Br) (68)	227 (Br_2) (10)	93 (Br) (13)
4[e]	1.00	426 (Br_4) (0)	370 (Br_4) (1) [373.6795 (- 0.5)]	255 (Br_2) (3) [256.8998 (0.2)]	199 (Br_2) (8) [200.8372 (- 0.3)]	227 (Br_2) (17) [228.9045 (- 0.3)]	171 (Br_2) (10) [172.8424 (- 0.1)]
5[f]	1.02	396 (Br_2I) (0) [397.8201 (+ 0.1)]	340 (Br_2I) (1)		169 (I) (84) [168.9148 (0.1)]	227 (Br_2) (12)	141 (I) (17) [140.9200 (0.0)]

[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 (Br_4) and triplets (Br_2), the lower mass peak of doublets (Br), except as noted. Figures in parentheses indicate mmu deviation from calculated values. [e] Additional peaks measured: *m/e* 188.9916 (+ 0.1), $C_7H_{10}BrO$ (M - Br_3), *m/e* 148.9789 (0.0), $C_5H_8{}^{81}Br$ (d - HBr). [f] Additional peaks measured: *m/e* 316.9036 (- 0.1), $C_7H_{11}BrIO$ (M - Br); *m/e* 148.9786 (- 0.3), $C_5H_8{}^{81}Br$ (d - HBr); *m/e* 127.9121 (0.1), HI; *m/e* 126.9043 (0.0), I; *m/e* 111.0806 (- 0.4), $C_7H_{11}O$ (M - Br_2I).

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 Br_2 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 $HI^{+\cdot}$). 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

(1) Presented in part at the 168th National Meeting of the American Chemical Society, Atlantic City, N.J., Sept 8–15, 1974, ANAL-61.

(2) The alga was identified by comparison of a pressed herbarium sample and a sample preserved in 3% formaldehyde with the reported description: E. Y. Dawson, "Marine Red Algae of Pacific Mexico. Part I. Bangiales to Corallinaceae Subf. Corallinoideae," in *Allan Hancock Pacific Expeditions*, **17**, 1 (1953).

(3) L. P. Hager et al., *Proc. Nat. Acad. Sci. U. S. A.*, submitted.

(4) C. Rappe and K. Andersson, *Ark. Kemi*, **24**, 303 (1965).

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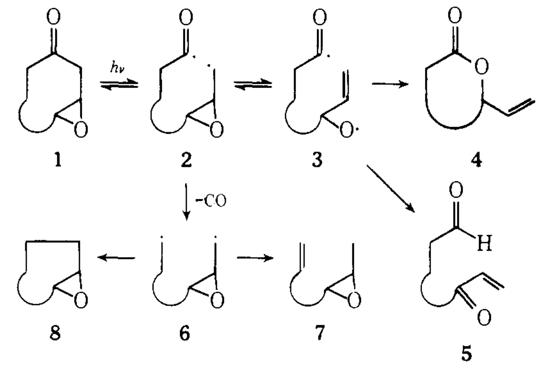
The Photochemistry of β,γ-Epoxy Cyclic Ketones

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-

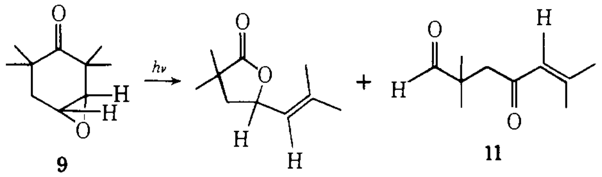
Scheme I



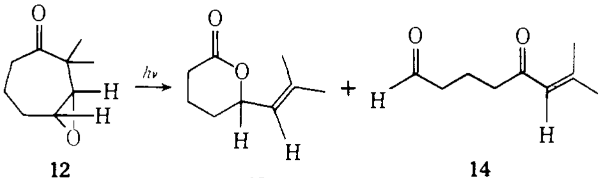
try of β,γ-epoxy ketones.[2-7] We now wish to suggest a general scheme which summarizes the photochemistry of β,γ-epoxy *cyclic* ketones and to present experimental evidence which supports this scheme.[8,9]

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**.

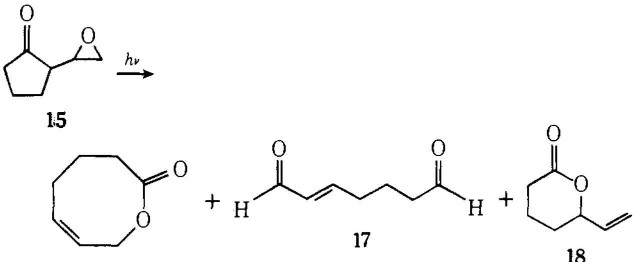
β,γ-Epoxy cyclic ketones **9**, **12**, and **15** possess no unusual molecular constraints (relative to Scheme I) and thus the photochemistry of these compounds should be typical of the "normal" photochemical behavior of β,γ-epoxy cyclic ketones. Previously, we have noted that irradiation of **9** through 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 moieties leads to analogous results. Carlson and his coworkers have shown[5] that irradiation of **15** to 70% conversion gives in ca. 50% yield a 65:25:8 mixture of **16:17:18.**[13]



9 **10** **11**

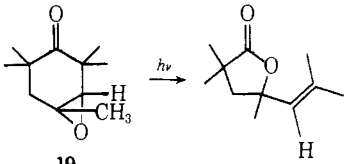


12 **13** **14**

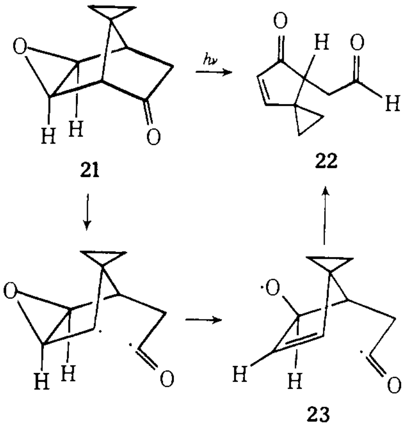


15 **16** **17** **18**

The consequences of preventing *either* **3** → **4** *or* **3** → **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** → **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.

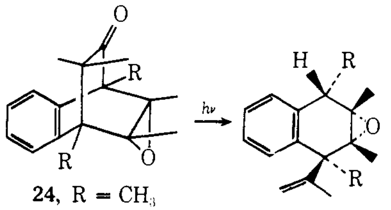


19 **20**



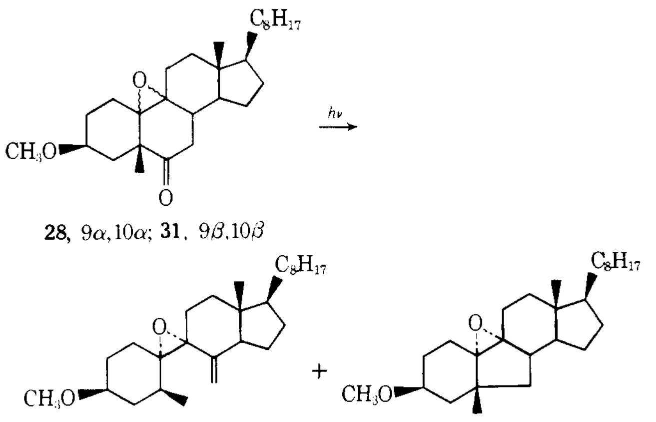
21 **22** **23**

The consequences of preventing *both* **3** → **4** *and* **3** → **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 $9\alpha,10\alpha$-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-



24, R = CH_3
26, R = H

25, R = CH_3
27, R = H



28, 9α,10α; 31, 9β,10β

29

30

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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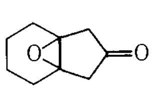
(6) R. K. Murray, Jr., T. K. Morgan, Jr., H. Hart, and V. J. Hull, *J. Org. Chem.*, **38,** 3805 (1973).

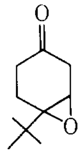
(7) R. K. Murray, Jr., and D. L. Goff, *J. Chem. Soc., Chem. Commun.*, 881 (1973).

(8) For a detailed investigation of the photochemistry of an *acyclic* β,γ-epoxy ketone see ref 2.

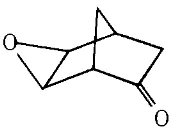
(9) The dearth of information concerning the photochemistry of β,γ-epoxy cyclic ketones may follow from the observation of Starr and Eastman[3] that irradiation of cyclohexane or methanol solutions of i "gave small amounts (less than 0.2 mol/mol of ketone) of a mixture of carbon mon-



i



ii



iii

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 similarly 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 moiety 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-3-enone[11] with *m*-chloroperbenzoic acid.

(11) L. A. Paquette, R. F. Eizember, and O. Cox, *J. Am. Chem. Soc.*, **90,** 5153 (1968).

(12) All new compounds reported gave analytical data and had spectroscopic properties consistent with the proposed structures.

(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 exhaustive 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 ketone[17] with *m*-chloroperbenzoic acid.

(17) J. Ipaktschi, *Chem. Ber.*, **105,** 1840 (1972); K. Alder, H.-J. Ache, and F. H. Flock, *ibid.*, **93,** 1888 (1960).

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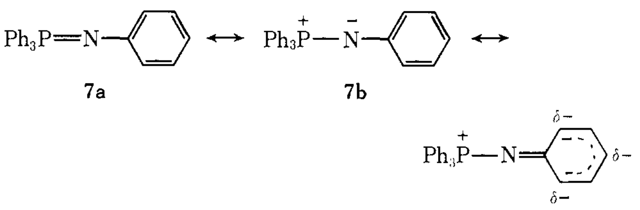
Nuclear Magnetic Resonance Studies. III. Carbon Nuclear Magnetic Resonance of Triphenylphosphonium Ylides

Sir:

We wish to report the preliminary results of a ^{13}C 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 ^{13}C NMR of several stabilized ylides[1] 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 ^{13}C chemical shift and P-^{13}C coupling data can provide sensitive tests for models which propose[3] d orbital participation in these compounds. Contribution from the following resonance structures are considered in this study.

$$\underset{\textbf{3a}}{Ph_3P{=}CH_2} \longleftrightarrow \underset{\textbf{3b}}{Ph_3\overset{+}{P}{-}\overset{-}{C}H_2}$$



7a

7b

7c

$$\underset{\textbf{9a}}{Ph_3P{=}N{-}N{=}CH_2} \longleftrightarrow \underset{\textbf{9b}}{Ph_3\overset{+}{P}{-}\overset{-}{N}{-}N{=}CH_2} \longleftrightarrow$$

$$\underset{\textbf{9c}}{Ph_3\overset{+}{P}{-}N{=}N{-}\overset{-}{C}H_2}$$

Bart[4] has determined by means of the X-ray structure of methylenetriphenylphosphorane, that the methylene carbon is trigonally hybridized. In addition, other X-ray studies[4-6] 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 dπ-pπ overlap may be relatively small between phosphorus and carbon.

Due to the rather limited NMR studies dealing with carbon involved in dπ-pπ bonding with second-row elements, we wish to examine the above effects of such interactions on