atm of *cis*-2-butene, benzvalene is produced at the same rate, but attains a higher steady-state concentration, 1.3%. These results are readily interpreted in terms of two factors, the effectiveness of added gases in promoting the production of benzvalene, and in quenching its sensitized disappearance. Neopentane and *cis*-butene, at 1 atm, each appear to increase the rate of benzvalene production sevenfold relative to N_2. The low steady-state concentration of benzvalene in 1 atm of neopentane is attributable to the high rate of its benzene-triplet-sensitized disappearance. (At 2370 Å, where benzene triplets appear to be virtually absent,[6] the growth of benzvalene is still almost linear at a concentration ten times the steady state at 2537 Å.) Increasing the ratio of butene to neopentane results in progressively more effective quenching of the sensitized disappearance of benzvalene, and correspondingly higher steady-state concentrations. The attainment of a concentration significantly higher than that found in 1 atm of butene is precluded by unsensitized photolysis of benzvalene.

The facile formation of benzvalene in the presence of butene indicates that it is not formed from those benzene triplets which are measured[6] by energy transfer to butene. Photolyses of benzene in 1 atm of butene at varying wavelength (Table I) show that the benzvalene is not derived entirely from the fluorescing state of benzene: the yield of benzvalene increases with increasing energy of the exciting radiation while fluorescence yield does not. (Fluorescence in the presence of 50 torr of cyclohexane decreases[6] as shown in Table I. That in cyclohexane solution is independent of wavelength in this region.[7]) As the excitation energy increases, therefore, increasing amounts of benzvalene must come, on a very short time scale, from upper vibrational levels of the benzene.[8] The same conclusion, with respect to the "hot" benzvalene intermediate in the rearrangement of 1,3,5- to 1,2,4-trideuteriobenzene, has been drawn[5] from studies at 2537 and 2480 Å and is supported, as shown in Table I, by additional results at shorter wavelengths obtained during the present investigation. It is clear that the enhancement of benzvalene production by addition of foreign gases is not the result of collisional deactivation of excited benzene, but is rather attributable to vibrational relaxation of "hot" benzvalene. The finding that the ratio of stable to "hot" benzvalene increases with wavelength is in accord with the expectation that molecules with less excess energy would be stabilized more effectively by collision.

Table I. Quantum Yields in Benzene Vapor

	2530 A	2480 Å	2420 A	2370 Å
Benzvalene[a]	0.016	0.022	0.024	0.037
"Hot benzvalene"[b]	0.03[c,d]	0.07,[d] 0.06[e]		0.16[e]
Butene adduct[a]	0.010	0.008	0.006	0.003
Fluorescence[f]	0.18	0.10	0	0
Triplets[f]	0.6	0.6	Small	

[a] In 1 atm of *cis*-2-butene, 25 torr of benzene. [b] Assumed intermediate in the rearrangement of 1,3,5- to 1,2,4-benzene-d_3. [c] At 2537 Å. [d] Reference 5. [e] In 1 atm of He, 25 torr of benzene. [f] From data in ref 6.

Vapor-phase photolysis of benzene in *cis*-2-butene produces, along with benzvalene, small yields of the same 1,3-cycloaddition product[9] (6,7-dimethyltricyclo-[3.3.0.0^{2,8}]oct-3-ene) which is formed in the liquid phase. Bryce-Smith and Longuet-Higgins have suggested[10] that these products (as well as fulvene) have a common precursor, a singlet diradical. As shown in Table I, however, yields of benzvalene and of the adduct have opposite wavelength dependences. These results seem to require at least some qualification of their postulate. If there is a common intermediate, the ratio of products must vary with its energy content.

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[7] C. L. Braun, S. Kato, and S. Lipsky, *J. Chem. Phys.*, **39**, 1645 (1963).

[8] Our unpublished observations that the yield of benzvalene in solution is essentially independent of wavelength between 2540 and 2380 Å suggest that in the condensed phase most of the benzvalene is formed *via* the lowest vibrational level of the excited benzene.

[9] K. E. Wilzbach and L. Kaplan, *J. Am. Chem. Soc.*, **88**, 2066 (1966).

[10] D. Bryce-Smith and H. C. Longuet-Higgins, *Chem. Commun.*, 593 (1966).

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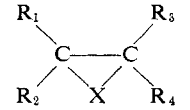
Spectroscopy and Photochemistry of Phenyloxiranes

Sir:

There has been considerable interest in the photolysis of some phenyloxiranes.[1-3] We have investigated the spectroscopy and photochemistry of diphenyloxirane (I), triphenyloxirane (II), tetraphenyloxirane (III), tetraphenyl episulfide (IV), and di-α-naphthyloxirane (V) in rigid 3-methylpentane (3MeP) at 77°K. The



I, $R_2 = R_3 = Ph$; $R_1 = R_4 = H$; $X = O$
II, $R_1 = R_2 = R_3 = Ph$; $R_4 = H$; $X = O$
III, $R_1 = R_2 = R_3 = R_4 = Ph$; $X = O$
IV, $R_1 = R_2 = R_3 = R_4 = Ph$; $X = S$
V, $R_1 = R_3 = \alpha$-naphthyl; $R_2 = R_4 = H$, $X = O$

principal results of this investigation include: (1) the observation of colored intermediates created in the primary photochemical process, (2) the observation of two separate one-photon processes, (3) the nature of the final photoproducts, (4) the spectroscopy of phenylmethylene and its involvement in the photochemistry, and (5) the nature of some of the nonphotochemical reactions of methylenes.

The low-temperature absorption spectra for all three cases consist of a weak, highly resolved transition with a 0–0 band at 272 ± 1 mμ and a much stronger unresolved transition with a maximum at approximately 230 mμ. Tetraphenyloxirane has very poorly resolved fluorescence and phosphorescence with maxima at approximately 292 and 404 mμ, respectively.

Irradiation into the 0–0 or higher bands of any of the compounds I–V produces a colored intermediate with broad, structureless, visible absorption bands. In the case of I, there is one band with a maximum at 503 mμ;

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[1] H. Kristinnson and G. Griffin, *Angew. Chem. Intern. Ed. Engl.*, **4**, 868 (1965).

[2] H. Kristinnson, R. Mateer, and G. Griffin, *Chem. Commun.*, 415 (1966).

[3] A. Trozzolo, W. Yager, G. Griffin, H. Kristinnson, and I. Sarkar, *J. Am. Chem. Soc.*, **89**, 3357 (1967), and references therein.

for II there are two bands with maxima at 547 and 398; and for III two bands exist with maxima at 605 mμ and two poorly resolved maxima at approximately 435 and 415 mμ. For IV a broad structureless band exists with a maximum at approximately 650 mμ and another with a maximum in the region 400–425 mμ. Finally, for V a strong structureless band exists with a maximum at 575 mμ and shoulders at 485 and 455 mμ. The colored intermediates are stable at 77°K but generally can be eradicated either by warming or by irradiating into a visible absorption band. Trozzolo, *et al.*,[3] while not eliminating a radical intermediate, favored an ionic intermediate formed initially or rapidly from a radical intermediate. Our results on the tetraphenyloxirane (III) and episulfide (IV) indicate that a biradical intermediate resulting from C–S or C–O cleavage is the preferred form. That is, it would be unlikely that the episulfide intermediate resulting from C–S bond cleavage would be of ionic nature. Further, since the spectrum of the oxirane intermediate is similar to that of the episulfide, except for an expected blue shift, a similar structure for this intermediate should prevail. Furthermore, other photoproducts can be formed (see below).

The second point of importance is the existence of two separate one-photon processes. These are the production of the colored intermediate and the subsequent formation of final photoproducts. Irradiation into the visible absorption bands of the intermediate of either the dinaphthyloxirane (V) or the tetraphenyloxirane (III) produces additional final photoproducts (as well as recyclization).

In all cases, final photoproducts were identified by comparison of emission spectra with independent authentic samples. Furthermore, selective excitation of the photoproduct mixture was used to clarify the nature of the components.

For diphenyloxirane (I), the final primary products are *trans*-stilbene, benzaldehyde, and phenylmethylene. In order to establish *trans*-stilbene as a primary product and not the result of phenylmethylene radical reaction, an additional photochemical study was made because 3MeP is a relatively soft glass at 77°K. Another hydrocarbon matrix (isononane–isooctane) with a viscosity some 10^7 times greater than 3MeP was used as a matrix. In this case, radical recombination certainly would not occur and *trans*-stilbene is still formed. Additional subsequent data from the study of triphenyloxirane (see below) indicate that, essentially, radical recombination does not occur in 3MeP at 77°K. Phenylmethylene is inferred from the existence of a highly resolved emission (0–0 band at 388 mμ) which disappears on warming with the consequent formation of additional *trans*-stilbene.

Benzophenone, diphenylmethylene, and tetraphenylethylene are primary products of tetraphenyloxirane (III). The tetraphenylethylene was not considered by Trozzolo, *et al.*[3] The emission of diphenylmethylene was similar to that previously given,[3] although better defined. This emission disappeared upon warming and recooling the solution.

In the case of triphenyloxirane (II), the primary products are diphenylmethylene, phenylmethylene, benzaldehyde, and benzophenone. There is indication of the formation of triphenylethylene. Diphenylmethylene was identified on the basis of its emission spectrum and its disappearance upon warming with consequent formation of tetraphenylethylene. Phenylmethylene was inferred primarily from the fact that photolysis in rigid medium gave no *trans*-stilbene; however, warming the solution resulted in the formation of *trans*-stilbene. This would occur because of phenylmethylene radical recombination in fluid solution but not in a rigid matrix. Previous workers[3] did not find either the benzophenone or the phenylmethylene. Solution photochemistry results in products derived from both diphenyl- and phenylmethylenes.[1]

The nature of the final photoproducts from all three of the phenyloxiranes is such that they arise from splitting of bonds in pairs and where all pair combinations are possible; that is, a C–C bond and one or the other of the C–O bonds split, as well as no C–C bond but both C–O bonds split.

Further details concerning the spectroscopy, the mechanism, the nature of the intermediates, and the relative reaction rates of the photochemistry of oxiranes will appear in the near future.

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The Preparation and Probable Structure of $(CH_3)_2AsC{=}CAs(CH_3)_2CF_2CF_2Fe_3(CO)_{10}$

Sir:

Ditertiary arsines are well known for their ability to form chelate complexes with metal carbonyls.[1] In addition, complexes have recently been obtained in which the ligand acts as a bridging group between two metal carbonyl moieties.[2] The recently discovered cyclobutene derivative $(CH_3)_2AsC{=}CAs(CH_3)_2CF_2CF_2$ (ffars) acts as both a chelating bidentate ligand and a tridentate ligand with the double bond acting as the third electron donor.[3]

We now wish to report the synthesis of a compound ffars$Fe_3(CO)_{10}$ which probably has structure I. In such a compound ffars is acting as a bridging ligand, but more interestingly it is bonded to a fragment of a polynuclear carbonyl, $Fe_3(CO)_{12}$. One similar compound, Fe_3-

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