about the C_3–C_4 and C_4–C_5 bonds. The diaxial chair and conformations $\mathbf{3b}_{210}$ through $\mathbf{3b}_{330}$ (as for **1**)[7] are severely strained and, therefore, negligibly populated. For $\mathbf{3b}_0$ through $\mathbf{3b}_{120}$, we expect $0 \lesssim J_{\mathrm{CX}} < 4$ Hz. A total population of more than 4% of $\mathbf{3b}_0$ through $\mathbf{3b}_{120}$ would be detected as a significant decrease in W compared to **5** and/or as an increase in $|J_{\mathrm{AX}} - J_{\mathrm{CX}}|$ and/or $|J_{\mathrm{BX}} - J_{\mathrm{DX}}|$. Estimating for $\mathbf{3t}_{150}$, $\Delta J_1 = J_{\mathrm{AX}} - J_{\mathrm{CX}} > 2.6$ Hz and $\Delta J_2 = J_{\mathrm{DX}} - J_{\mathrm{BX}} > 2.6$ Hz, then a population of 15% or more of $\mathbf{3t}_{150}$ would give $\Delta J_1 \approx \Delta J_2 \gtrsim 0.4$ Hz, which is *not* observed. Furthermore, computer analysis shows that 10% or more of $\mathbf{3t}_{150}$ would produce a detectable change in line shape within the X-proton multiplet, which is *not* observed. Since steric interactions present in boat $\mathbf{3b}_{180}$ are relaxed upon pseudorotation to $\mathbf{3t}_{150}$, the population of $\mathbf{3b}_{180}$ should be much *less* than the 10% limit set for $\mathbf{3t}_{150}$.[12] Therefore, the nonchair population of **3** is *small*, probably less than 10%.

The *trans* isomer **4** gives a quintet for the C_4 X-proton resonance, $W = 12.0 \pm 0.2$ Hz, in methanol-d_4 solution. Computer analysis shows the spectrum to be consistent with $J_{\mathrm{AX}} = J_{\mathrm{CX}} = 2.7$ Hz, $J_{\mathrm{BX}} = 3.2$ Hz, and $J_{\mathrm{DX}} = 3.4$ Hz.[9] One could compare **4** with *cis*-4-*t*-butylcyclohexanol-3,3,4,5,5-d_5 (**6**), which gives $W = 11.4$ Hz for the C_1 proton band width in carbon tetrachloride solution.[13] If W were 11.4 Hz for the chair conformation of **4** with hydroxyl axial (illustrated above), then, for the other chair and $\mathbf{4b}_{120}$ through $\mathbf{4b}_{240}$ ($W > 25$ Hz), the total population would be *less* than 6%. As for **2**, above,[7] $\mathbf{4b}_0$ through $\mathbf{4t}_{90}$ are populated negligibly (no hydrogen bond, or severe strain). For $\mathbf{4t}_{270}$ through $\mathbf{4t}_{330}$, we expect $J_{\mathrm{CX}} > 6.0$ Hz. Since $J_{\mathrm{CX}} = 2.7 \pm 0.2$ Hz, observed for **4**, is not larger than the corresponding coupling constant for **6**,[13] then the total population of $\mathbf{4t}_{270}$ through $\mathbf{4t}_{330}$ should be less than 10%. The negligible values observed for $|J_{\mathrm{AX}} - J_{\mathrm{CX}}|$ and $|J_{\mathrm{BX}} - J_{\mathrm{DX}}|$ confirm this limit. Therefore, the nonchair population of **4** is *small*, probably less than 10%. We suggest extension of this conclusion to 2-*t*-butylcyclohexanone.

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[12] It would be unreasonable to suggest special stability for $\mathbf{3b}_{180}$, since it differs from $\mathbf{2b}_0$ only in configuration at C_4, and the latter, which could be stabilized further by intramolecular hydrogen bonding, was not detected in infrared studies of **2** (see above).

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Photolysis of Benzene Vapor. Benzvalene Formation at Wavelengths 2537–2370 Å[1]

Sir:

Although benzene irradiated at 2537 Å in the liquid phase and in solution is known to undergo isomerizations to yield fulvene[2] and benzvalene[3] (tricyclo[3.1.0.0^{2,6}]hex-3-ene), benzene vapor has been considered[4] to be virtually inert to radiation of this wavelength. We have recently shown,[5] however, that benzene-1,3,5-d_3 rearranges to the 1,2,4 isomer at 2537 Å in the vapor phase and have suggested an excited benzvalene intermediate, formed with $\Phi = 0.03$. We now wish to report that benzvalene is indeed formed by photolysis of benzene vapor at 2537 Å and that, in the presence of additives which facilitate its vibrational relaxation and prevent its benzene-photosensitized destruction, steady-state concentrations greater than 1% of the benzene can be attained.

We have investigated the photolysis of benzvalene and benzene in the presence of added gases at 2537 Å and have studied the wavelength dependence of benzvalene formation and other processes in benzene. Photolyses were performed in a cylindrical quartz cell, 2 cm in diameter and 10 cm long, fitted with Teflon stopcocks. The cell was filled by flushing with the appropriate gas or gas mixture; benzvalene samples were introduced as effluent from a gas-chromatographic column.[3] Benzene (*ca.* 4 μl) was added from a microsyringe just before closing the stopcocks. For 2537-Å irradiations, a General Electric G8T5 lamp fitted with a Vycor 7910 shield was mounted parallel to the axis of the cell. For other wavelengths, a Bausch and Lomb SP-200 super pressure mercury lamp and high-intensity grating monochromator (nominal bandpass 32 Å) was used.

A difficulty encountered in working with benzvalene vapor was its rapid isomerization to fulvene in freshly flamed quartz cells. In a cell previously conditioned with benzvalene, *e.g.*, by photolysis of benzene under appropriate conditions, benzvalene was stable, however, and exhibited a characteristic banded absorption spectrum with peaks at 2172, 2182, 2212, 2222, 2256, and 2266 Å ($\epsilon_{2172} \sim 4000$, $\epsilon_{2573} \sim 300$). Irradiation of benzvalene (0.1 torr) in 1 atm of N_2 at 2537 Å results in conversion ($\Phi \sim 0.4$) to benzene and fulvene in a ratio ~3:1. Under our conditions one-third was consumed in 5 min. In the presence of 20 torr of benzene, the benzvalene disappeared 50 times as rapidly, $\Phi \sim 0.3$, indicating very efficient energy transfer from benzene to benzvalene. Addition of 25 torr of *cis*-2-butene resulted in a 20-fold decrease in the rate of the benzene-sensitized disappearance. Since butene at this pressure does not quench benzene fluorescence,[6] the benzvalene disappearance must be triplet-sensitized; benzene triplets apparently transfer their energy to benzvalene about ten times as efficiently as to butene.

When benzene vapor is irradiated at 2537 Å in the absence of triplet quenchers, benzvalene is barely detectable[3] by gas chromatography. Its steady-state concentration, relative to benzene, is only 0.002% for 25 torr of benzene in 1 atm of N_2 and 0.004% in 1 atm of neopentane. In the presence of 25 torr of *cis*-2-butene, the steady-state concentrations increase markedly, to 0.04% in N_2 and 0.3% in neopentane. At these concentrations it was possible to confirm that the product was benzvalene, both by its characteristic vapor-phase uv absorption and by its reaction[3] with acidified methanol to form 4- and 6-methoxybicyclo[3.1.0]hex-2-enes. In the neopentane–butene mixture, benzvalene production measured by gas chromatography at an early stage corresponds to $\Phi \sim 0.02$. When benzene is irradiated in 1

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

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[4] J. N. Pitts, Jr., J. K. Foote, and J. K. S. Wan, *Photochem. Photobiol.*, **4**, 323 (1965).

[5] K. E. Wilzbach, A. L. Harkness, and L. Kaplan, *J. Am. Chem. Soc.*, **90**, 1116 (1968).

[6] W. A. Noyes, Jr., and D. A. Harter, *J. Chem. Phys.*, **46**, 674 (1967).

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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[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.

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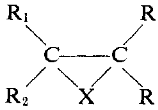
Spectroscopy and Photochemistry of Phenyloxiranes

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

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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