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Photochemical Addition of Benzene to Cyclobutene

Abstract: The major products of the photochemical addition at 253.7 nm of benzene to cyclobutene in solution were found to be tetracyclo[5.3.0.$0^{2,10}0^{3,6}$]-decene-8 and tricyclo[4.2.2.$0^{2,5}$]deca-7,9-diene, which arise from 1,3- and 1,4-additions. The quantum yields for both reactions were independent of benzene concentration below 2*M* but decreased at higher concentrations. The maximum quantum yields that were obtained are 0.81 and 0.09 for the 1,3- and 1,4-reactions, respectively, indicating that the former reaction is a very efficient process.

The 1,3-addition may occur from the singlet ($^1B_{2u}$) state of benzene, as has been suggested in the literature. The origin of the 1,4-addition is not clear, but it seems unlikely that it occurs from the triplet state of benzene.

Introduction

The facile addition of benzene to a number of olefins under the influence of light has been studied by several groups [1–5]. Wilzbach and Kaplan [4(a)] first showed that the major product of these additions has a structure corresponding to the 1,3-addition of benzene to the olefin, with retention of the stereochemistry of the olefin. This structure was later corroborated by others [1, 5]. The occurrence of other adducts in lesser yield has been reported for many of the olefins [1, 4, 5] but their structures were not elucidated. The kinetics of these reactions were studied in only one instance, namely, the gas phase addition of benzene to *cis*- and *trans*-2-butene [5].

We report here the results of qualitative and quantitative investigations of the solution-phase photochemical addition of benzene to cyclobutene. This system is unusual in that there is a 1,3-adduct as well as a second adduct in significant amounts; the addition is photochemically very efficient. We also discuss new evidence that establishes clearly the stereochemistry of the 1,3-adducts for the first time, thus resolving an earlier controversy [6].

Experiments

• *Materials*

Cyclobutene was prepared by the photoisomerization of 1, 3-butadiene in solution as described by Sonntag and Srinivasan [7]. The material was more than 93% pure, the impurities being 1,3-butadiene (3%), bicyclobutane (3%) and traces of three unidentified C_4 hydrocarbons. In view of the high efficiency of the addition reaction between benzene and cyclobutene, the presence of these impurities is believed to have a negligible effect on the reaction. This premise was confirmed by using a purer (99%) sample of cyclobutene in one experiment. Benzene and cyclohexane of research grade were distilled under nitrogen before use. Deuteriobenzene (Bio-Rad Laboratories) was used as obtained.

• *Apparatus*

Preparative scale irradiations were carried out in a Rayonet RPR-208 reactor [8] fitted with 254-nm lamps. Quantitative studies were carried out in a Rayonet RPR-100 reactor [8] fitted with four 254-nm lamps. The absorbed intensity as calibrated with a ferrioxalate actinometer was 5.9×10^{-9} Einstein/ml-sec. Quantitative analyses were made in an F & M model 500 gas chromatograph fitted with a silicone column (8 ft; UCON-550X) and programmed from 50° to 150°. The column was calibrated with known amounts of the sample materials.

• *Procedure*

A standard solution of benzene and cyclobutene was made by the addition of a weighed quantity of benzene (stored under nitrogen) to a weighed quantity of cyclobutene. This solution was diluted to required concentrations by the addition of further measured quantities of benzene. Since the volatility of cyclobutene may introduce errors in sampling the solution before and after photolysis, about 0.4% cyclooctane was added to the solution as an internal reference. Control experiments showed that the cyclooctane at this concentration did not undergo any photoreaction in this system. All of the experiments in one series (i.e., those in which one parameter was varied) were run simultaneously using the usual rotary arrange-

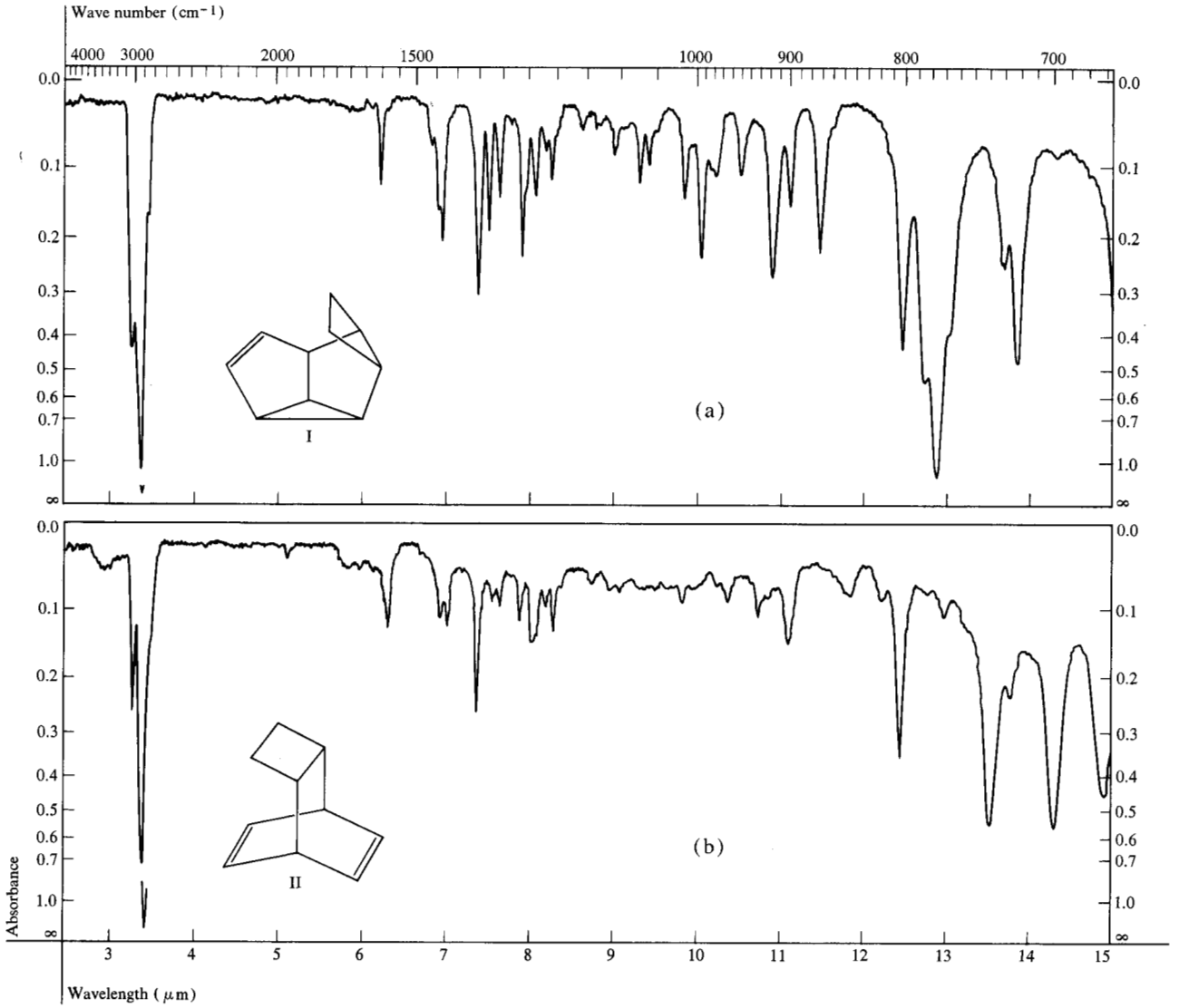


Figure 1 Infrared absorption spectra of photoadducts obtained using neat liquids: (a) Product I; (b) Product II.

ment. Each cylindrical quartz irradiation tube (0.6-cm i.d.) contained an irradiated volume of 2.5 ml. The tubes were filled in a nitrogen atmosphere. During irradiation the vapor above the solution was shielded from the light.

Results

The irradiation of a solution of cyclobutene in benzene gave rise to significant amounts of two products and minor amounts of three others. All of these were compounds of molecular weight greater than that of benzene. There was no evidence for the formation of low molecular weight products (e.g., isomers of cyclobutene) in these experiments. On prolonged irradiation the solution turned intensely yellow and secondary decomposition of the primary products was noticed. At the same time, a polymer film was formed on the walls of the cell.

The two predominant products were found to be adducts of benzene to cyclobutene ($C_{10}H_{12}$; mol wt from mass spectrum, 132). The major one of the pair showed infrared absorption [Fig. 1(a)] at 3050 and 1600 cm^{-1}, which correspond to an olefin group in a cyclopentane ring [9]. The NMR spectrum [Fig. 2(a)] indicated the presence of only two olefinic protons. On hydrogenation with Adams' catalyst at a pressure of 500 Torr, each mole of the compound took up one mole of hydrogen to give a product ($C_{10}H_{14}$) that had no absorption due to olefinic protons in its NMR spectrum. This photoadduct thus had only one carbon-carbon double bond and, according to the formula, should be tetracyclic. The ultraviolet spectrum showed a maximum at 220 nm ($\epsilon \approx 2500$ cm^2/mole) which, in a monoolefinic hydrocarbon, is attributable to a vinylcyclopropane chromophore. The spectrum indicated

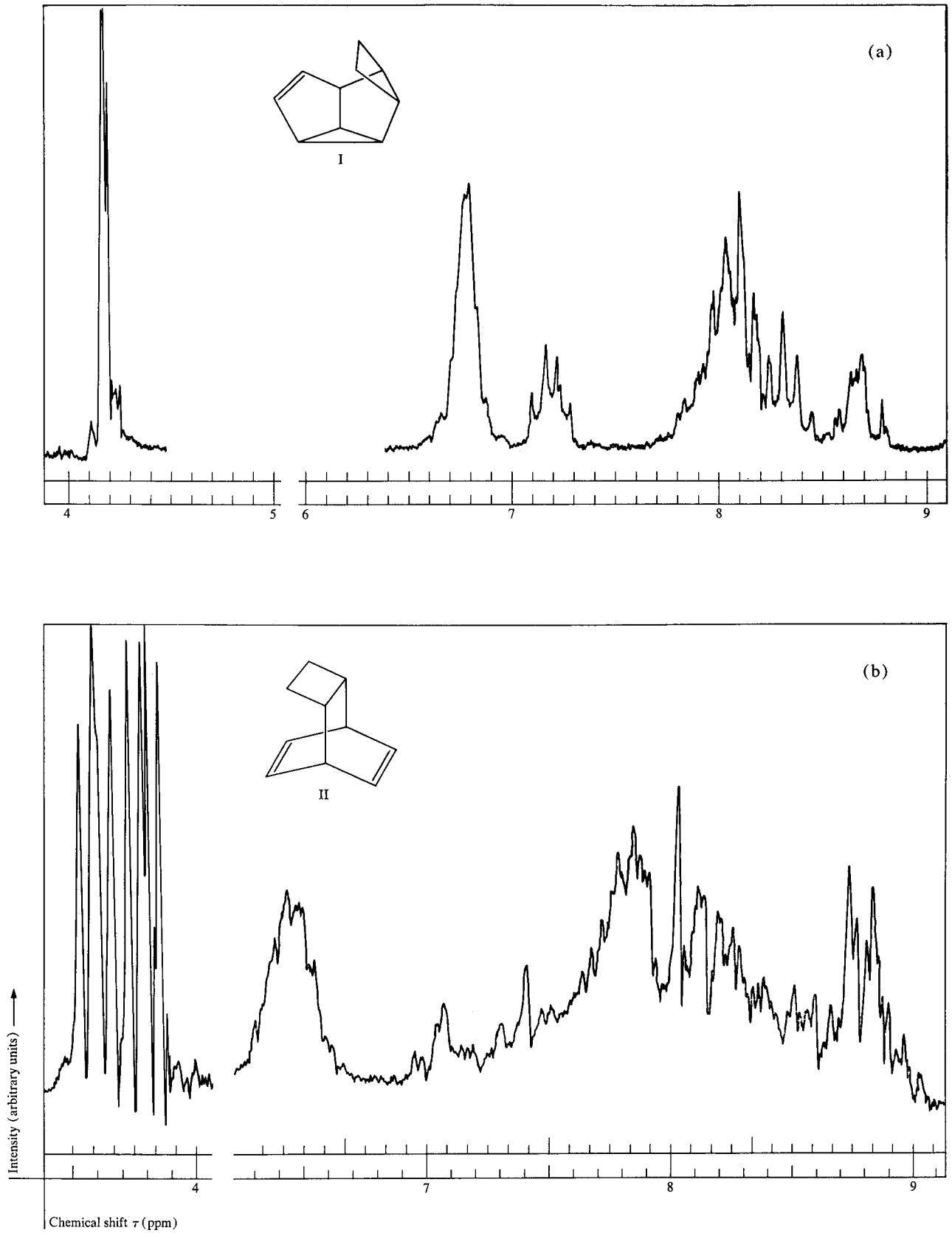
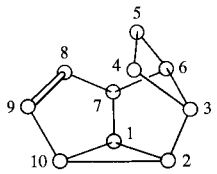


Figure 2 NMR spectra of photoadducts: (a) Product I (Varian HA-100 spectrometer); (b) Product II (Varian HA-60 spectrometer). Tetramethylsilane was used as the internal reference in both spectrometers.

that this product had a structure (I) analogous to that proposed (and later observed [10]) by Wilzbach and Kaplan [4(a)] for the photoadducts of benzene to many olefins.



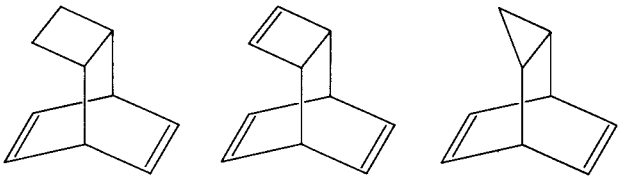
I

Confirmatory evidence was obtained from the following data: The NMR spectrum of the major product from the photochemical addition of deuteriobenzene to cyclobutene showed complex absorption centered at 6.9τ (2H), 8.1τ (3H) and 8.75τ (1H). [Here τ is the chemical shift (expressed in ppm) and 2H denotes two protons.] This indicated that in the NMR spectrum of structure I, the protons that originally belonged to the benzene molecule absorbed at 4.25τ (2H), approximately 6.9τ (1H), 7.30τ (1H) and approximately 8.4τ (2H). These absorptions presumably correspond to C_9, C_8, C_7, C_1, C_{10} and C_2, respectively, on the basis of the assignments previously made to the photoadduct of benzene and *cis*-2-butene [4(a)]. Double-irradiation experiments demonstrated that, as in the latter instance, the proton absorbing at 7.30τ (C_1) was strongly coupled to the protons absorbing at about 8.4τ (C_{10} and C_2) [11]. The lone proton absorbing at 8.75τ, which was derived from the cyclobutene moiety, was coupled to the proton(s) absorbing at 6.9τ. More extensive decoupling studies were hindered by the weak coupling between the olefinic and the aliphatic protons. The latter point is in contrast to the observations of Wilzbach and Kaplan on the adducts made by them and is discussed at the end of this section [12].

The adduct resisted pyrolysis in the vapor phase at temperatures up to 200°C, which rules out a structure that corresponds to the 1,2-addition of benzene to the olefin.

The second most important product was a labile compound that had strong infrared absorption [Fig. 1(b)] at 3080 and 1580 cm^{-1}. The NMR spectrum [Fig. 2(b)] showed two strongly coupled patterns at 3.60 and 3.80τ due to two protons each, a broad absorption at 6.4τ (2H) and a complex pattern in the range 7.0 to 9.0τ (6H). The NMR spectrum of the same product (when made from deuteriobenzene and cyclobutene) showed only the last of these four absorptions, which indicated the location of the protons derived from the cyclobutene. After decomposition of this partly deuterated adduct at about 200°C in an NMR sample tube, its spectrum was completely replaced by the spectrum of 1,3-butadiene. The undeuterated adduct, when pyrolyzed in the vapor phase, gave a mixture of benzene and 1,3-butadiene as the only products.

The structure that seems consistent with these data is structure II, which corresponds to the 1,4-addition of

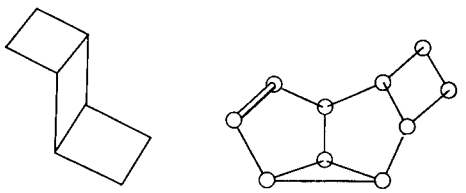


II III IV

benzene to cyclobutene. When the pattern produced by the olefinic protons in the NMR spectrum of structure II is compared to those of the olefinic protons in structure IV and the 1,4-cyclohexadiene ring in structure III [13], it can be seen that in all of these there are two very similar absorptions made up of doublets of doublets. The primary coupling in II is at 4.0 to 4.2 Hz, whereas in III and IV the couplings are at 5.5 and 4.5 Hz, respectively. Again, the secondary couplings in this pattern in II range from 2.5 to 3.0 Hz; the range is the same for the corresponding quantities in III and IV. It may also be noted that the chemical shifts of the olefinic protons in IV are 3.4 and 4.0τ, and are 3.6 and 4.0τ in III, which agree closely with the values in II. The chemical shift of the allylic bridgehead protons in IV is 6.4τ, which compares favorably with the corresponding value in II.

The thermal lability of derivatives of bicyclo[2.2.2]octa-2, 5-diene is well documented [14]. In the present case the decomposition of II to give benzene and cyclobutene and the decomposition of the latter in turn to 1,3-butadiene would agree with the proposed structure.

Two of the minor products of the photoaddition were identified as the dimer of cyclobutene, tricyclo[4.2.0.$0^{2,5}$] octane (V), and a second 1,3-adduct (VI) of benzene to cyclobutene. It has been shown elsewhere [15] that I undergoes pyrolysis to give VI as one of the products.



V VI

This thermal stability of VI with respect to I, as well as the thermal isomerization of I to tricyclo[5.2.1.$0^{4,10}$]deca-2, 5-diene [15], shows that I is the 3,6-*endo* adduct and VI is the corresponding *exo* adduct.

Since this result is the first case for which there is independent evidence to show the stereochemistry about the 3,6-bond, an interesting fact concerning the stereo-

Table 1 Quantum-yield data for products resulting from the photochemical addition of benzene to cyclobutene [wavelength, 254 nm; intensity, 5.9×10^{-9} Einstein/ml-sec; room temperature; solvent (runs 8 through 16), cyclohexane].

	Cyclobutene		*Benzene*		*Quantum yield*		[I]
Run	*Wt %*	*M*	*Wt %*	*M*	Φ_I	Φ_{II}	[II]
1	54.0	8.60	46.0	5.1	0.66	0.05	13.2
2	41.0	6.90	59.0	6.6	0.69	0.06	11.5
3	26.0	4.30	74.0	8.5	0.64	0.06	10.6
4	16.0	2.50	84.0	9.5	0.61	0.03	20.3
5	8.2	1.30	91.7	10.0	0.56	0.05	11.2
6	5.6	0.98	94.4	10.3	0.48	0.03	16.0
7	2.7	0.46	97.3	10.7	0.27		
8	4.2	0.64	59.5	6.1	0.46	0.04	11.5
9	1.1	0.16	31.7	3.3	0.23	0.02	11.5
10	0.6	0.09	27.1	2.7	0.15	0.02	7.5
11	6.2	0.93	4.3	0.5	0.72	0.07	10.2
12	6.0	0.88	8.7	0.9	0.81	0.09	9.0
13	6.0	0.88	13.0	1.3	0.80	0.07	11.4
14	5.9	0.88	21.5	2.2	0.81	0.07	11.5
15	6.1	0.95	31.2	3.3	0.61	0.05	12.2
16	5.8	0.88	42.0	4.5	0.67	0.05	13.1
17	7.8	1.3	92.2	9.84	0.68	0.04	17.0
18	3.4	0.51	96.6	10.6	0.37	0.03	12.3

chemistry of these 1,3-adducts can be pointed out. It can be seen [Fig. 2(a)] that in the NMR spectrum of I (the *endo* adduct), the pattern from the two olefinic protons indicates relatively weak coupling to other protons, whereas in the spectrum of VI [15], these protons are strongly coupled to others. Similarly, the addition of benzene to 1,2-dimethylcyclobutene yields two 1,3-adducts [16], the olefinic protons of one showing a strong coupling and of the other, a weak coupling. However, more examples are needed to establish that the stereochemistry of the 1,3-adducts can be inferred from this information.

Quantum yield data for the formation of products I and II at 253.7 nm are given in Table 1. The first section in this table covers mixtures of cyclobutene and benzene; the second and third sections, those experiments in which cyclohexane was used as a diluent; and the fourth section, mixtures of cyclobutene and deuteriobenzene. In all of these experiments the solutions were sampled at frequent intervals starting from time zero, and the results were averaged over the linear portion of the product formation curve. Thus errors due to secondary photolysis or depletion of the starting material should be negligible.

Discussion

The photochemistry of benzene has been the subject of numerous studies. The results have been analyzed theoretically by Bryce-Smith and Longuet-Higgins [1(b)] and by Bryce-Smith [1(d)]. Both experiment and theory support the idea that the photochemical 1,3-addition takes place from the $^1B_{2u}$ state of benzene when the exciting radiation is of 253.7 nm wavelength. For the specific case of reaction of benzene (B) with cyclobutene (C), it is possible to write the following steps:

$$B + h\nu \rightarrow {}^1B; \quad (1)$$

$$^1B \rightarrow B; \quad (2)$$

$$^1B + C \rightarrow I; \quad (3)$$

$$^1B \rightarrow {}^3B. \quad (4)$$

Here B is also used to denote the benzene ground state; ^1B is the benzene singlet state and ^3B is the benzene triplet state. Step (2) refers to all of the unimolecular decay reactions of the singlet state except intersystem crossing. It can be derived from these reactions that

$$\frac{1}{\Phi_I} = 1 + \frac{k_2 + k_4}{k_3[C]}, \quad (5)$$

where Φ denotes quantum yield, k is a rate constant, and [ ] denotes concentration. A plot of the experimental values of $1/\Phi_I$ vs $1/[C]$ shows a satisfactorily straight line at low concentrations of benzene, but the intercept is 1.2 rather than 1.0, which suggests that the bimolecular reaction (3) may not give product I at every encounter; i.e., it may lead to other addition product(s) or deactivation, or to both of these.

At high concentrations of benzene the slopes of the plots of $1/\Phi_I$ vs $1/[C]$ tend to increase, which suggests

that it is necessary to consider the role of the excimer (D) in this system. The excimer can be formed [17] by the reaction

$$^1B + B \rightarrow D, \tag{6}$$

and can decay by the reactions

$$D \rightarrow {}^1B + B; \tag{7}$$

$$D \rightarrow 2B + h\nu. \tag{8}$$

The presence of the excimer, as denoted by its emission at 515 nm, is significant even in a 10% solution of benzene in cyclohexane [18]. Since reaction (7) restores the singlet-state products that are used by (6), the net loss of singlet states is only via reaction (8). This step probably accounts for the decrease in the quantum yield of product I when the concentration of benzene is increased at constant cyclobutene concentration.

The quantum yields for the 1,3-cycloadditions of benzene to 2-butene and tetramethylethylene were reported [4(a)] to be 0.04 and 0.005, respectively. At the same concentration (10% olefin) the quantum yield for cyclobutene from the present study, by extrapolation, would be 0.6. It has also been stated [4(b)] that the quantum yield for 1,3-addition to cyclopentene is 0.25, but this value was measured in a 5% solution of benzene in the olefin. It would appear that the quantum yields for the 1,3-reaction increase with strain and in any case are considerably larger for cyclic olefins. More data are needed to confirm these points but, if they are correct, the implications may prove interesting.

The isolation and identification of product II indicate that benzene is capable of 1,4-photochemical addition to olefins as well. In the literature it has been stated [1(c)] that cyclooctene gives a second adduct (in addition to the 1,3-adduct), which proved too labile to be identified. It is possible that this adduct is also a 1,4-adduct and that the photoreaction is a more general one than has been realized for benzene with olefins. The identity of the excited state of benzene that gives rise to this product is obscure at present. If this role is assigned to the triplet ($^3B_{1u}$) state, one can add the following elementary steps to the reaction scheme:

$$^3B + C \rightarrow II; \tag{9}$$

$$^3B \rightarrow B. \tag{10}$$

Here (10) would represent the unimolecular decay of benzene by internal conversion or phosphorescence. For dilute solutions of benzene (i.e., benzene concentration $< 2M$) the involvement of the excimer can be neglected and one can derive that

$$\frac{\Phi_I}{\Phi_{II}} = \frac{k_3}{k_4}\left(\frac{k_{10}}{k_9} + [C]\right). \tag{11}$$

The data in Table 1 show that within the uncertainties in the quantum yields of product II, the experimental values of the ratio Φ_I/Φ_{II} change little over a ten-fold change in the concentration of cyclobutene, although the absolute magnitudes of the quantum yields change by a factor of three. This observation is compatible with Eq. (11) only if k_{10}/k_9 is very large in comparison to [C]. While this condition may obtain, it seems unlikely that a constant fraction of the singlet molecules would cross over to the triplet state and react to give product II under all experimental conditions.

From a purely kinetic viewpoint, it is possible to accommodate the results of the present study by postulating that II and I are formed from the same excited state of benzene by parallel processes. Thus the replacement of (9) by (12),

$$^1B + C \rightarrow II, \tag{12}$$

would give

$$\frac{\Phi_I}{\Phi_{II}} = \frac{k_3}{k_{12}},$$

which would readily explain the relative invariance of the ratio of the quantum yields even though the absolute values may change considerably. Similar parallel additions undoubtedly account for the formation of the *exo* isomer of I. This formation would be consistent with the statement made previously in the discussion, based on the analysis of the values for Φ_I, that step (3) may not lead exclusively to product I.

A study of the photoaddition of benzene to cyclobutene in the vapor phase might provide detailed information concerning the role (or lack of one) of the triplet state of benzene in this system.

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10. In a private communication Drs. Wilzbach and Kaplan informed the author that they have also observed the formation of this product in the benzene:cyclobutene system.
11. The numbering of the carbon atoms is that of structure I, rather than that of Ref. 4(a).
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