Photoisomerization of Tri-*t*-butylbenzenes. Photochemical Interconversion of Benzvalenes[1]

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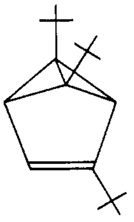
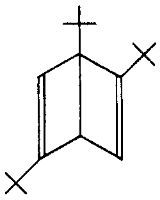
Abstract: The previously unreported 1,2,4-tri-*t*-butylbenzvalene (VI) is formed with a quantum yield of 0.12 as the only initial product in the photolysis of 1,3,5-tri-*t*-butylbenzene (V) in isohexane at 2537 Å. It is also formed, together with 1,2,4-tri-*t*-butylbenzene (IV) and V, by photolysis of 1,3,6-tri-*t*-butylbenzvalene (I). Although it has not been isolated, VI has been found to rearomatize to V with a half-life of 17 min at 24.5°, to react with alcohols to yield 4-alkoxybicyclo[3.1.0]hexenes, and to photolyze to I, IV, and V.

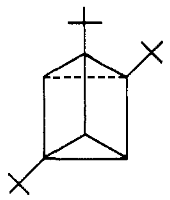
In an earlier communication,[3] photolysis of 1,3,5-tri-*t*-butylbenzene (V) in alkane solvents at 2537 Å was shown to lead to a mixture containing the 1,2,4 isomer (IV) and the three valence isomers I, II, and III.



I

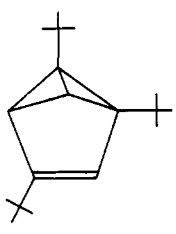


II

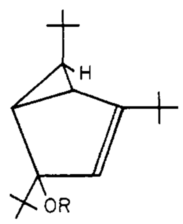


III

In sufficiently dilute solutions, a photostationary state is reached in which the predominant component is the prismane, 1,2,5-tri-*t*-butyltetracyclo[2.2.0.0^{2,6}.0^{3,5}]hexane (III). It is formed by the photolysis of the Dewar benzene, 1,2,4-tri-*t*-butylbicyclo[2.2.0]hexa-2,5-diene (II), which is itself formed[4] by photolysis of IV. The benzvalene I, 1,3,6-tri-*t*-butyltricyclo[3.1.0.0^{2,6}]hex-3-ene, is also formed by photolysis of IV; it is observed, as well, together with IV, in early stages of the photolysis of V. Since I is photolyzed to a mixture of IV and V, it may be considered to be an intermediate in the photochemical interconversion of the aromatic isomers. The formation of I from IV is readily visualized, since it requires no rupture of the σ bond framework; its formation from V, however, involves a more extensive rearrangement.

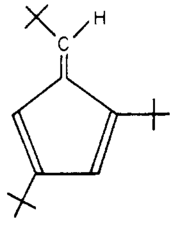


VI



VIIa, R = CH_3

VIIb, c, R = CH_2CF_3



VIII

The subsequent finding[5] that photolysis of V in methanol does not lead to isomerization, but gives, instead, high yields of an adduct, 4-methoxy-2,4,6-*exo*-tri-*t*-butylbicyclo[3.1.0]hex-2-ene (VIIa), suggested that a reactive species might be a precursor of I and IV. The structure of the adduct VIIa led to the speculation[5] that the intermediate might be another benzvalene, the 1,2,4 isomer (VI), or an excited state related to it. This postulate gained support when unsubstituted benzvalene was found[6] to react with acidified methanol to yield as the predominant product an adduct similar to VIIa. In the present study, very early stages in the photolysis of V were investigated by flash techniques and brief steady irradiation in an attempt to detect formation or decay of an intermediate and to determine its structure and properties.

Experimental Section

Light Sources and Cells. Flash experiments were performed using the apparatus of Grossweiner and Matheson.[7] The total duration of the flash from the xenon lamp, using a 22.5-μF condenser charged to 12 kV, was about 100 μsec. Cylindrical quartz cells were mounted parallel to the axis of the flash lamp. A cell 25 cm long × 13 mm i.d. received about 3 × 10^{19} quanta, between 2000 and 5000 Å, per flash. For some flash experiments, a 10-cm spectrophotometer cell with a volume of 30 ml was used.

Monochromatic 2537-Å light was obtained from a General Electric G8T5 germicidal lamp fitted with a cylindrical Vycor 7910 shield to filter out 1849-Å radiation. Most irradiations were carried out in a 3-ml 1-cm cylindrical spectrophotometer cell. A potassium ferrioxalate actinometer solution in this cell received 2 × 10^{16} quanta per second. Where larger volumes were required, a 20-ml 1-cm rectangular quartz cell, which received 7 × 10^{16} quanta per second, was used. For some preparations, an annular vessel with a path length of 1.4 mm and a volume of 35 ml was mounted around the lamp and shield.

Solvents. 2-Methylpentane (isohexane) was Phillips Pure Grade. 2,2,4-Trimethylpentane ("isooctane") and methanol were Eastman Spectro Grade. Ethanol was U.S.I. Reagent Quality absolute alcohol. Trifluoroethanol (TFE) was a Pennsalt Chemicals Corp. product.

1,3,5-Tri-*t*-butylbenzene (V) was prepared[8] from *p*-di-*t*-butylbenzene and recrystallized from methanol, mp 75°. Its uv absorption (Figure 2) was identical with the published spectrum.[9] Impurities detectable by gas chromatography totaled less than 0.05%.

1,3,6-Tri-*t*-butylbenzvalene (I). A solution of 100 mg of V in isohexane was irradiated in the annular vessel for 4 hr, while being flushed with a slow stream of N_2. The solution was concentrated to 0.5 ml and subjected to gas chromatography on a column,

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

[2] PACE participant, 1966; Department of Chemistry, Bowling Green State University, Bowling Green, Ohio.

[3] K. E. Wilzbach and L. Kaplan, *J. Am. Chem. Soc.*, **87**, 4004 (1965).

[4] E. E. van Tamelen and S. P. Pappas, *ibid.*, **84**, 3789 (1962).

[5] L. Kaplan, J. S. Ritscher, and K. E. Wilzbach, *ibid.*, **88**, 2881 (1966).

[6] K. E. Wilzbach, J. S. Ritscher, and L. Kaplan, *ibid.*, **89**, 1031 (1967).

[7] L. I. Grossweiner and M. S. Matheson, *J. Phys. Chem.*, **61**, 1089 (1957).

[8] R. C. Barclay and E. E. Betts, *Can. J. Chem.*, **33**, 672 (1955).

[9] J. Dale, *Chem. Ber.*, **94**, 2821 (1961).

9 ft × $^3/_8$ in o.d., packed with QF-1 (5%) on Chromosorb G (60–70 mesh), maintained at 110°. The "peak" eluting at *ca.* one-half the retention volume of V was rechromatographed to yield 1.5 mg of I and 6 mg of II. A peak eluting at *ca.* three times the volume of V contained 30 mg of IV. The uv spectrum of I is shown in Figure 2. Other properties are detailed in ref 3; the name 2,5,6-tri-*t*-butyltricyclo[2.1.1.0^{5,6}]hex-2-ene assigned to it there is not in accord with IUPAC rules.

4-Methoxy-2,4,6-*exo*-tri-*t*-butylbicyclo[3.1.0]hex-2-ene (VIIIa).[5] A solution of 100 mg of V in methanol was irradiated for 2.5 hr in the annular vessel. It was diluted to 100 ml with H_2O and extracted with three 15-ml portions of isohexane. The extract was evaporated to dryness. A portion of the residue, dissolved in CCl_4, exhibited an nmr spectrum corresponding to a mixture of 10% V and 90% VIIa, with no other detectable resonances. Recrystallization from methanol yielded a white solid, mp 35°, with the following spectral properties: nmr, see Table I; uv no maximum above 2000 Å, ϵ_{2200} 2500; ir maxima (C_2Cl_4 solution) at 3066, 3034, 3010, 2960 (vs), 2902, 2868, 2820, 1621, 1477, 1467, 1392, 1369, 1337, 1296, 1277, 1257, 1243, and 1207 cm^{-1}. Upon heating at 200° it decomposes[5] to **1,3,6-tri-*t*-butylfulvene (VIII)** which has been identified on the basis of the following properties: uv maxima at 2595 (ϵ 17,000) and 3660 Å (ϵ 480); nmr resonances at τ 8.86 (9 H, s), 8.73 (9 H, s), 8.72 (9 H, s), 4.02 (2 H, m), 3.54 (1 H, s). It exhibits ir absorptions (neat) at 2900, 1621, 1590, 1457, 1389, 1357, 1321, 1297, 1248, 1205, 1149, and 1000 cm^{-1}. Fulvene VIII has also been isolated[3] from photolyses of V in alkane solutions.

Table I. Nmr Spectra of 4-Alkoxytri-*t*-butylbicyclo[3.1.0]hexenes

	VIIa	VIIb	VIIc
	Shift, τ		
H-1	8.86	8.71	8.73
H-3	5.24	5.17	5.08
H-5	8.31	8.37	8.23
H-6	9.27	9.19	9.21
t-Bu	8.87	8.88	8.84
	9.04	9.06	8.97
	9.10	9.10	9.08
OR	7.02	6.20	6.43
		6.22	6.46
	Couplings, cps		
$J_{1,3}$	1.5	1.4	1.4
$J_{1,5}$	5.7	6.3	5.7
$J_{1,6}$	4.6	4.2	4.3
$J_{5,6}$	2.7	3.0	2.8
$J_{H,F}$	...	8.5	8.8
		8.5	8.8

4-Trifluoroethoxy-2,4,6-*exo*-tri-*t*-butylbicyclo[3.1.0]hex-2-enes (VIIb and VIIc). A solution of 65 mg of V and 0.25 ml of trifluoroethanol in 20 ml of isohexane was irradiated for 16 hr in the rectangular cell. Analytical gas chromatography and nmr analysis indicated about 80% conversion of V to VIIb and VIIc. The solution was washed with water, concentrated to 1 ml, and gas chromatographed in two portions on a 9 ft × $^3/_8$ in. column of QF-1 (5% on Chromosorb G) at 125°. Recrhomatography of the crude fractions yielded 10 mg of VIIb and 7 mg of VIIc. Both products exhibit nmr spectra (Table I) which closely resemble that of VIIa with respect to chemical shifts and coupling constants. The major difference in the spectra, the magnetic nonequivalence of the protons in the alkoxy groups, may be ascribed to increased steric hindrance. Both products yield the fulvene VIII at 200° in xylene solution without undergoing any interconversion. The nmr spectra and thermal behavior strongly suggest that they are 4-trifluoroethoxy-2,4,6-*exo*-tri-*t*-butylbicyclo[3.1.0]hex-2-enes, stereoisomeric at C-4.

Photochemical Experiments. Solutions of V in methanol, ethanol, and TFE-saturated isohexane were irradiated at 2537 Å; consumption of V was determined spectrophotometrically, and products were analyzed by gas chromatography. Solutions of V in alkane solvents were irradiated either with the flash lamp or, for varying periods, with the mercury resonance lamp. Post-irradiation changes in uv absorption were followed as a function of time. Some solutions were treated with alcohols (methanol, ethanol, TFE) immediately after irradiation and at later times; changes in absorption were followed, and products were examined by gas chromatography and/or nmr. Solutions of I in isohexane were irradiated at 2537 Å, treated with alcohols, and analyzed by gas chromatography.

Analytical Techniques. Alkane solutions were used directly, or after concentration, for gas chromatographic analysis. The solvent was evaporated, and CCl_4 and TMS were added, for nmr analysis. Solutions containing alcohols were washed with water (after addition of isohexane in the case of pure alcohols), and then treated similarly.

Nmr spectra were taken at 100 Mcps in CCl_4 solution against internal TMS with a Varian HA100 spectrometer equipped with a spin decoupler and a computer of average transients.

Gas chromatographic analyses were carried out on a 6 ft × 0.25 in. o.d. column, packed with QF-1 (2.5%) on Chromosorb G, operated at 100°, using a flame ionization detector. Retention volumes, relative to V, are I, 0.57; II, 0.68; IV, 3.15; VIIb, 3.63; VIIc, 4.16; VIII, 1.20. Two products, presumably adducts, formed by photolysis of V in ethanol have relative retention volumes of 1.97 and 2.23. The latter undergoes partial decomposition during chromatography. Decomposition of VIIa is so extensive that no discrete peak is visible in chromatograms.

Uv absorption was measured using either the apparatus for flash spectrophotometry which has been described[7] or a Cary Model 14 spectrophotometer with a thermostated cell compartment.

Results and Discussion

Photolysis of V at 2537 Å in Alcoholic Solutions. Irradiation of a 0.006 *M* solution of V in methanol for 10 min resulted in a 10% decrease in absorbance at 2620 Å. Since the adduct VIIa does not absorb at this wavelength, and no other products are detectable by gas chromatography or nmr, it can be concluded that 10% of V was consumed, corresponding to a quantum yield, $\Phi_{-V} = 0.12$. A 0.006 *M* solution of V in isohexane saturated with trifluoroethanol (TFE) and irradiated similarly showed a 10.7% decrease in absorbance, corresponding to $\Phi_{-V} = 0.13$. Gas chromatographic analysis showed the presence of VIIb (7.3% of V), VIIc (4.8% of V) and only traces of I and IV. The combined yield of adducts, 10.8% of the initial V, is essentially equal to the amount of V consumed. Disappearance of V in ethanol could not be followed optically because of the formation of absorbing products. Gas chromatography of a 0.006 *M* solution irradiated for 10 min showed the presence of I (0.07% of V) and IV (0.7% of V). Two additional products eluted at 1.97 and 2.23 times V, with peak areas 0.8 and 3% of V, respectively. The second of these undergoes partial decomposition on the chromatographic column; they are probably adducts, but have not been definitely characterized.

The almost complete suppression by methanol and TFE of the isomerization of V to I and IV, with quantitative formation of characteristic addition products, has led us to use these alcohols in a search for a reactive intermediate in the photolysis of V. Ethanol is evidently less reactive, but we have used it in some cases, because the chromatographic detection of reaction products is convenient.

An Unstable Photoproduct of V. To investigate the possible formation of a short-lived absorbing intermediate, solutions of V in isooctane were irradiated with 100-μ sec flashes from the xenon lamp, and the absorption at 2400 Å was monitored over periods ranging from 1 msec to several hours. A 10^{-4} *M* solution of V, flashed in the 25-cm cell, showed an

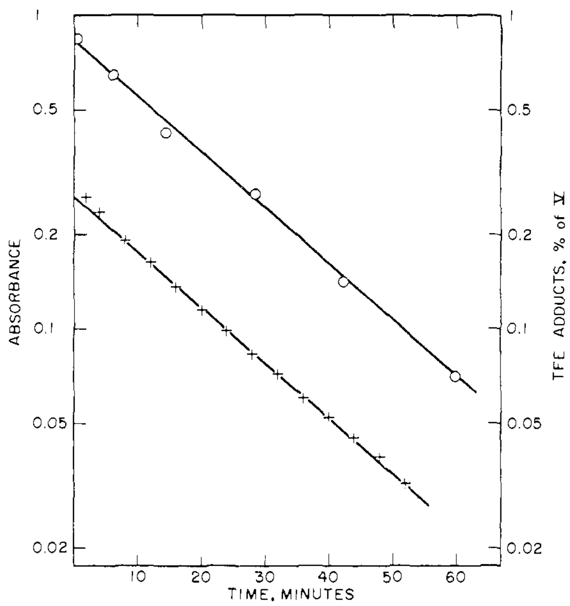

Figure 1. Decay at 24.5° of photoproduct formed by 2537-Å irradiation of a 0.006 *M* solution of 1,3,5-tri-*t*-butylbenzene (V) in isohexane: +, absorbance at 2350 Å after 3-min irradiation, measured against aged, similarly irradiated solution; O, combined yields of VIIb and VIIc found in TFE-treated aliquots of a solution irradiated for 2 min.

increase of absorbance of 0.25 immediately after the flash. It decayed to 0.22 in 10 msec, but this decay could be attributed to the solvent. (Isooctane alone flashed similarly, exhibited an increase of 0.07 followed by a decay to 0.04.) Very little further decay was observed on the oscilloscope within 1 min. To permit observations over longer periods a 3×10^{-4} *M* solution of V was flashed in the 10-cm cell and its absorbance was compared with that of an unirradiated solution in the spectrophotometer. An absorbance of 0.29 2 min after the flash decreased to a final value of 0.11 with a half-time of 16 min. Gas chromatographic analysis of the freshly irradiated and of the aged solution showed only I (0.4% of V) and IV (1.1% of V), in addition to V. A solution similarly flashed, but stirred with 0.25 ml of TFE immediately afterward, had an absorbance of only 0.11 2 min later. Gas chromatographic analysis of this solution showed, in addition to I and IV, a product (1.4% of V) and another (0.3% of V) having retention volumes indistinguishable from those of VIIb and VIIc, respectively. The nmr spectrum of the TFE-treated material exhibited resonances corresponding to the *t*-butyl resonances of IV and VIIb with areas, relative to V, of 1 and 2%, respectively. The flash experiments thus demonstrated the formation, within the duration of the flash, of a thermally unstable, uv-absorbing species which reacts with TFE.

The relatively long lifetime of this species made it feasible to continue the investigation with monochromatic light. Solutions of V in isohexane, irradiated briefly at 2537 Å, were found to behave similarly to the flash-irradiated solutions. A 0.006 *M* solution, irradiated for 3 min in the 3-ml cell, had an absorbance at 2350 Å of 0.3 relative to a solution similarly irradiated 2 hr earlier. This absorbance decayed in first-order fashion, with a half-time of 17 min at 24.5°, as shown in Figure 1. Addition of small amounts of alcohols accelerated the decay markedly. The half-times were 6 min in 0.6 *M* ethanol, 1.4 min in 0.5 *M* methanol, and less than 10 sec in 0.1 *M* TFE. Examination of the TFE- and ethanol-treated solutions by gas chromatography showed the presence of two reaction products in each case. Retentions were indistinguishable from those of products formed on photolysis of V in the respective alcohols. Gas chromatography of the methanol-treated solution showed no discrete product peak. The presence of a product, however, was demonstrated by nmr: 20 ml of the 0.006 *M* isohexane solution was irradiated for 6 min, the solvent was rapidly removed *in vacuo* at low temperature, methanol was distilled in, and the mixture was warmed to room temperature. A CCl_4 extract of the diluted solution showed only four resonances in the *t*-butyl region—a large peak corresponding to V and three equal peaks (total area 0.02 that of V) with chemical shifts identical with those of the *t*-butyl groups of VIIa.

To establish whether these adducts are derived from the unstable, uv-absorbing species, yields were investigated as a function of time after irradiation. Aliquots from 20 ml of a 0.006 *M* solution of V in isohexane which had been irradiated for 2 min were treated periodically with TFE and analyzed by gas chromatography. The first sample, treated 10 sec after irradiation, contained, relative to V, I, 0.06%; IV, 0.14%; VIIb, 0.55%; and VIIc, 0.30%. In aliquots treated subsequently, amounts of I and IV were unchanged, but the yields of both adducts decreased with time. As shown in Figure 1, a plot of the combined yields of adducts followed a first-order decay with the same half-time, 17 min at 24.5°, as the optical absorption. The correspondence in lifetimes shows clearly that the yield of TFE adducts, measured by gas chromatography, is proportional to the amount of unstable photoproduct. The correspondence between the yield of adducts and the disappearance of V, when the latter is photolyzed in TFE, suggests that TFE treatment followed by gas chromatography provides a quantitative measure of the unstable photoproduct. On this basis, we have obtained its absorption spectrum and have investigated its photochemical formation and behavior.

To obtain the absorption spectrum of the unstable photoproduct, the 0.006 *M* solution of V in isohexane was irradiated for 1.5 min and compared immediately with a similarly irradiated solution which had aged for 2 hr. The spectrum so obtained showed a maximum at 2300 Å, with an absorbance of 0.19. A value of ϵ_{max} 3400 was calculated from the observation that the combined yield of VIIb and VIIc in an identically irradiated solution treated with TFE was 0.9% of V. The absorption spectrum is shown as curve VI of Figure 2; absorbance below 2280 Å could not be measured because of interference by V. The resemblance of this spectrum to those of the benzvalene I and of benzvalene[6] itself suggests that the photoproduct is also a benzvalene. The fact that it, like benzvalene,[6] undergoes a dark reaction with alcohols to yield 4-alkoxybicyclo[3.1.0]hexenes supports this conclusion. The only benzvalene from which adducts VIIa, b, and c can be derived without rearrangement is 1,2,4-tri-*t*-butyltricyclo[3.1.0.$0^{2,6}$]hex-3-ene (VI).

The Role of Benzvalenes in the Interconversion of Tri-*t*-butylbenzenes. In order to determine the primary

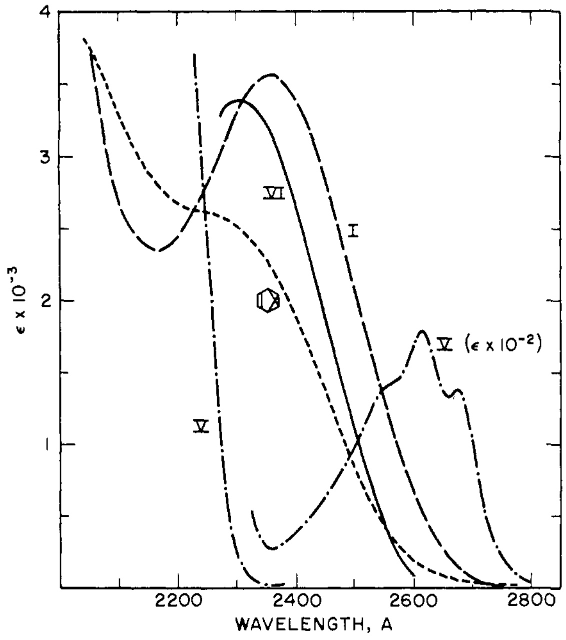

Figure 2. Uv absorption spectra in isohexane of benzvalene; 1,3,6-tri-*t*-butylbenzvalene (I); 1,2,4-tri-*t*-butylbenzvalene (VI); and 1,3,5-tri-*t*-butylbenzene (V).

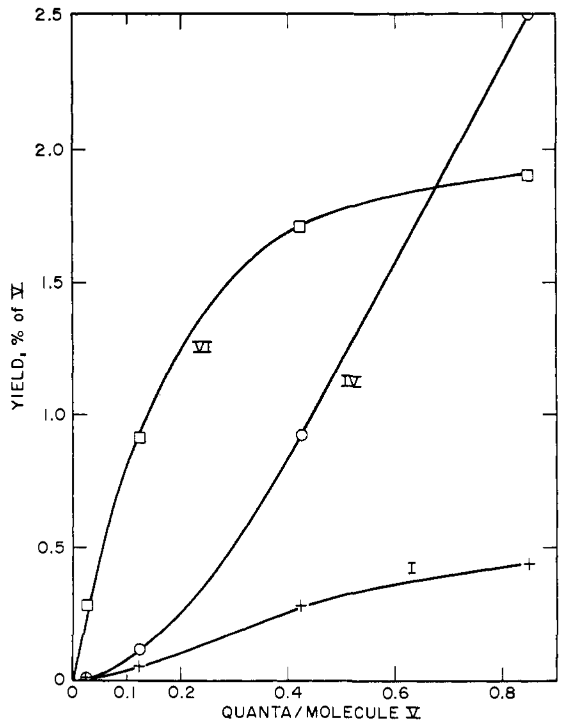

Figure 3. Dependence of yields of products from 1,3,5-tri-*t*-butylbenzene upon extent of irradiation at 2537 Å in isohexane solutions: I, 1,3,6-tri-*t*-butylbenzvalene; IV, 1,2,4-tri-*t*-butylbenzene; VI, 1,2,4-tri-*t*-butylbenzvalene, measured as combined yield of TFE adducts. The number of quanta/molecule, the molarity, and the time of irradiation are given, respectively, as follows: 0.025, 0.034 *M*, 1.5 min; 0.125, 0.034 *M*, 7.5 min; 0.125, 0.006 *M*, 1.5 min; 0.42, 0.006 *M*, 5 min; 0.84, 0.006 *M*, 10 min.

yield of VI and the source of I and IV, photolysis of V in isohexane solution was studied as a function of extent of irradiation. The yields of products, obtained by gas chromatographic analysis of TFE-treated solutions, are shown in Figure 3. At the lowest exposure (0.025 quantum per molecule in 1.5-min irradiation of a 0.034 *M* solution) I and IV are each 0.004% of V; the combined yield of TFE reaction products is 0.28% of V, corresponding to an apparent quantum yield of 0.11 for formation of the unstable benzvalene VI. At an exposure of 0.125 quantum per molecule, both in 0.034 *M* and in 0.006 *M* solution, the yields relative to V are I, 0.06%; IV, 0.11%; VI, 0.91%. With continued irradiation of the 0.006 *M* solution, the concentration of IV continues to grow, while those of I and VI approach limiting values. The rapid early increase in the rate of formation of I and IV indicates that they are produced in large part by a process other than the direct photolysis of V. The decrease in the rate of growth of VI suggests that it may be a precursor of I and IV. It is evident that I and IV are not formed thermally from VI, since the quantities are in no case higher in aged solutions than in those treated immediately with TFE. It can be deduced from the results in Figure 3 that I and IV are formed entirely by photolysis of VI. The fall-off in the growth curve of VI is much greater than can be accounted for by its thermal decay, and must therefore be attributed to its photochemical disappearance. The absence of a photosensitized reaction, indicated by the correspondence of the percentage yields of products for the same exposure at different concentrations of V, permits the calculation of a quantum yield for consumption of VI. The value, calculated from the limiting concentration of VI and the relative molar extinctions of VI and V (Figure 2), is close to unity. Taking into account the known photochemical behavior of IV[3] and I (see below), and the virtual absence of polymer formation in this system, we calculate that VI photolyzes to I, IV, and V in the ratio 1:1:3. The small amount of I and IV present at the lowest exposure is completely accounted for by photolysis of VI, leading to the conclusion that VI is the sole product[10] of the photolysis of V at 2537 Å and is formed with a quantum yield of 0.12. The conclusion that V photolyzes only to VI, which is in turn the precursor of I and IV, is supported by the findings that I and IV are absent from solutions of V photolyzed in methanol and in TFE, which react rapidly with VI, but are present in ethanol solutions in which VI is sufficiently stable to permit an appreciable concentration to accumulate. Since the quantum yield for formation of VI in isohexane is essentially equal to those for the disappearance of V and formation of adducts in methanol and TFE, it is unnecessary to invoke reactions of excited species to explain the addition of alcohols to V.

In order to investigate whether the photochemical transformation of benzvalene VI to benzvalene I is reversible, a 0.002 *M* solution of I in isohexane was irradiated for 4 min and aliquots were treated with TFE and with ethanol. Gas chromatographic analysis of the TFE-treated solution revealed the presence of I, 50%; V, 2.4%; IV, 43%; and two products indistinguishable from VIIb and VIIc, 3.5 and 1.3%, respectively. The ethanol-treated sample contained, in addition to I, IV, and V, two products with elution volumes identical with those of the photolysis products

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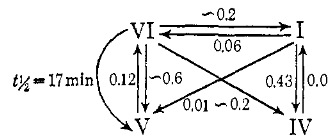
[10] It is not clear whether the formation of I and IV in the flash experiments is the result of shorter wavelength irradiation, or whether the VI initially formed undergoes secondary photolysis within the duration of the flash.

of V in ethanol. TFE treatment of the 2-hr-old photolyzed solution gave a mixture containing only I, 50%; IV, 43%, and V, 6.7%. The observations that a photoproduct of I decays to V within 2 hr, and that the four products it yields on treatment with TFE and ethanol have elution times identical with those of the corresponding products from VI, leave little doubt that it is indeed VI. By correcting the results for the thermal decay and photolysis of VI, we estimate that I, which disappears with a quantum yield of 0.5, yields IV, 86%; V, 2%; and VI, 12%.

It is of some interest that the interconversion of benzvalenes I and VI, which involves a valence interchange between double bond and cyclopropane ring, is a transformation of a type envisaged[11] in the naming of this class of compounds. In the present case, such a transformation does occur upon photochemical excitation. That it does not occur thermally is obvious from the facts that VI decays to V, but not to I or IV, and that I on heating yields IV, but not V.

The results of the present study are summarized in the following diagram, in which the numbers represent quantum yields in isohexane solution at 2537 Å and 25°.



Acknowledgment. We are indebted to Miss Gail Norman for nmr analyses and to W. A. Mulac for assistance with the flash photolyses.

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Allylic Cation Promoted Olefinic Cyclizations.[1] The Stereospecific Formation of a Tricyclic System and the Total Synthesis of *dl*-Fichtelite[2]

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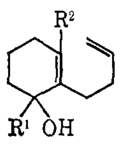
Abstract: The cyclization of the trienol **3** has been studied. It was prepared as follows: the dienic bromide **5** was formed from the alcohol **11** which, in turn, was produced as suggested in the flowsheet, **7** → **8** → **9** → **10** → **11**. Alkylation of the keto ester **4** with the bromide **5** afforded the substance **6**, which upon hydrolysis and decarboxylation gave the trienone **13**. Treatment of this last substance with methyllithium afforded the trienol **3**. When the trienol **3** was shaken with formic acid, at room temperature, it was converted in high yield into a mixture of the carbinol **20** and the hydrocarbons **16**, **17**, **18**, and **19**. All of these substances were shown to belong to the same stereochemical series, having "natural" (*anti*, *trans*) configuration, by interconversion experiments and by their reductive transformation into the natural product, fichtelite (**21**).

In previous work from our laboratory it was shown that the butenylcyclohexenol **1** ($R^1 = R^2 = H$), on treatment with formic acid for a few minutes at room temperature, undergoes a highly stereoselective cyclization to give an excellent yield of the formate of the octalol **2** ($R^1 = R^2 = H$).[3] The process appears to proceed *via* an allylic cationic intermediate. It was also shown[4] that the homologous dienol **1** ($R^1 = H$, $R^2 = CH_3$) cyclized to give the formate of the methyloctalol **2** ($R^1 = CH_3$, $R^2 = H$) along with products derived from the addition of formic acid to the olefinic bond of this bicyclic substance; none of the product **2** ($R^1 = H$, $R^2 = CH_3$) containing an angular methyl group was formed. In connection with his ingenious synthesis of telekin and alantolactone, Marshall[5] had occasion to utilize the cyclization of the next higher homolog **1** ($R^1 = R^2 = CH_3$) which afforded the formate of the dimethyloctalol **2** ($R^1 = R^2 = CH_3$), containing an angular methyl group, in excellent yield. We have now extended our study to include an examination of the behavior of the trienol **3**.



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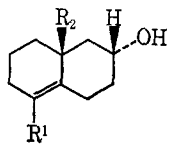

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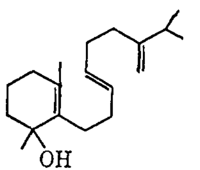

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[1] This represents paper XI of the series on olefinic cyclizations. Part X: W. S. Johnson, A. van der Gen, and J. J. Swoboda, *J. Amer. Chem. Soc.*, **89**, 170 (1967).

[2] For a preliminary account of this work, see W. S. Johnson, N. P. Jensen, and J. Hooz, *ibid.*, **88**, 3859 (1966).

[3] W. S. Johnson, W. H. Lunn, and K. Fitzi, *ibid.*, **86**, 1972 (1964).

[4] W. S. Johnson, P. J. Neustaedter, and K. K. Schmiegel, *ibid.*, **87**, 5148 (1965).

[5] J. A. Marshall, N. Cohen, and A. R. Hochstettler, *ibid.*, **88**, 3408 (1966).