Photochemical Addition of Benzene to Cyclopentene

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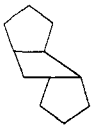
Abstract: Irradiation of solutions of benzene in cyclopentene at 254 nm led to the formation of cyclopentene dimers and two 1,3 photoadducts of benzene to cyclopentene. The major adduct (IV) was shown to have the structure 3,7-*endo*-tetracyclo[6.3.0.0^{2,11}.0^{3,7}]undecene-9 while the minor adduct (V) was the 3,7-exo isomer of IV. These structures which were based on spectroscopic evidence were confirmed by the hydration of the compounds to the corresponding alcohols, *syn*- and *anti*-2-hydroxytricyclo[6.3.0.0^{3,7}]undecene-4, the structures of which were established by nmr studies as well as by oxidation. Quantum yields for the 1,3 addition of benzene to cyclopentene in cyclohexane solution were obtained as a function of the concentration of the olefin. These results when compared to corresponding data for other olefins indicate that cyclopentene is one of the most reactive of olefins in this addition. A mechanism that involves the addition of the olefin directly to the singlet (B_{2u}) state of benzene rather than an (isomeric) intermediate state derived from it would be consistent with these observations.

Although the photochemical 1,3 addition of benzene to olefins has been the subject of many investigations[1-6] over the past 6 years, systematic studies have been limited to the addition of benzene to 2-butenes,[4] cyclobutene,[5] and norbornene.[7] As a result, it is not known what factors control some of the intriguing features of these reactions such as: (i) the preference for the formation of the more strained endo adduct over the exo isomer in some cases[1a,5] but not in others;[7] (ii) the predominance of one mode of addition out of the 1,2, 1,3, and 1,4 paths even though all three seem to originate from the same excited state of benzene;[1c,5] and (iii) the preferential location of an alkyl substituent on the benzene ring at one position in the 1,3 adduct.[8]

Wilzbach and Kaplan, who published the first report[1a] of the photochemical 1,3 addition of benzene to olefins, listed cyclopentene as one of the olefins to which addition was observed but did not publish any details concerning the identity of the product. The present study constitutes a systematic investigation of the benzene–cyclopentene system. Cyclopentene exemplifies a small, cyclic olefin with a minimum of strain. The results reported here when combined with earlier work on more strained or bulkier olefinic systems allow some significant generalizations concerning the mechanism of the process. It will also be shown that these photoadducts can be cleaved stereospecifically to the tricyclo[6.3.0.0^{3,7}]undecane systems I and II. The chemistry and synthesis of the natural products, hirsutic acid[9] and coriolin,[10] which incorporate I have recently attracted considerably interest. The syn isomer II is incorporated in the "peristylane" system which was recently synthesized[11] and offers an alternative route to this molecule.


I


II

Results

Products. Irradiation of a solution (18%) of cyclopentene in benzene at 254 nm resulted in the formation of three products in significant yield. One of these (24% of product mixture) was identified to be a dimer (possibly more than one) of cyclopentene from its mass spectrum. Its nmr spectrum was consistent with structure III which has been described by Scharf and Korte,[12] but positive identification was not possible from these data.

The remainder of the product mixture consisted of two compounds which analyzed for 1:1 adducts of benzene to cyclopentene. Their mass spectra corresponded to the molecular composition $C_{11}H_{14}$. The infrared spectra of both compounds exhibited absorptions at 3007 and 1600 cm^{-1} which could be attributed to a double bond in a cyclopentene ring.[13] The ultraviolet spectrum of the major adduct had a maximum at 220 nm (ϵ_{max} 2300 l. mol^{-1} cm^{-1}) while the minor adduct had a shoulder at 210 nm (ϵ 4500 l. mol^{-1} cm^{-1}). The nmr spectra of both adducts indicated the presence of two olefinic protons in the region δ 5.4–5.7. These data showed that both adducts were tetracyclic in nature and contained the vinylcyclopropane chromophore that is characteristic[1a,5,7] of the 1,3 photoadducts of benzene to olefins. The structures IV and V which correspond to the 1,3 photoadducts of benzene to cyclopentene would be consistent with these data and also with the rest of the nmr spectra (see the Experimental Section). Confirmatory evidence was obtained by the examination of the nmr spectrum of the major

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(1) (a) K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, **88**, 2066 (1966); (b) K. E. Wilzbach, A. L. Harkness, and L. Kaplan, *ibid.*, **90**, 1116 (1968); (c) K. E. Wilzbach and L. Kaplan, *ibid.*, **93**, 2073 (1971).

(2) (a) D. Bryce-Smith, A. Gilbert, and B. H. Orger, *Chem. Commun.*, 512 (1966); (b) D. Bryce-Smith and H. C. Longuet-Higgins, *ibid.*, 593 (1966); (c) D. Bryce-Smith, *Pure Appl. Chem.*, **16**, 47 (1968); (d) *Chem. Commun.*, 806 (1969).

(3) (a) K. Koltzenburg and K. Kraft, *Tetrahedron Lett.*, 389 (1966); (b) K. Kraft, Doctoral Dissertation, University of Bonn, 1968.

(4) A. Morikawa, S. Brownstein, and R. J. Cvetanovic, *J. Amer. Chem. Soc.*, **92**, 1471 (1970).

(5) R. Srinivasan, *IBM J. Res. Develop.*, **15**, 34 (1971).

(6) H. Morrison and W. I. Ferree, Jr., *Chem. Commun.*, 268 (1969); W. Ferree, Jr., J. B. Grutzner, and H. Morrison, *J. Amer. Chem. Soc.*, **93**, 5502 (1971).

(7) R. Srinivasan, *J. Phys. Chem.*, **76**, 15 (1972).

(8) R. Srinivasan, *J. Amer. Chem. Soc.*, **93**, 3555 (1971).

(9) F. W. Comer, F. McCapra, I. H. Qureshi, and A. I. Scott, *Tetrahedron*, **23**, 4761 (1967); P. T. Lansbury, N. Y. Wang, and J. E. Rhodes, *Tetrahedron Lett.*, 1829 (1971); 2053 (1972); F. Sakan, H. Hashimoto, A. Ichihara, H. Shirihama, and T. Matsumoto, *ibid.*, 3703 (1971).

(10) S. Takahashi, H. Iinuma, T. Takita, K. Maeda, and H. Umezawa, *ibid.*, 4663 (1969); 1637 (1970); S. Takahashi, H. Naganawa, H. Iinuma, and T. Takita, *ibid.*, 1955 (1971).

(11) P. E. Eaton and R. H. Mueller, *J. Amer. Chem. Soc.*, **94**, 1014 (1972).

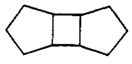
(12) H.-D. Scharf and F. Korte, *Chem. Ber.*, **97**, 2425 (1964).

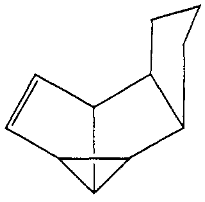
(13) L. J. Bellamy, "Infrared Spectra of Complex Molecules," Wiley, New York, N. Y., 1959, p 37.

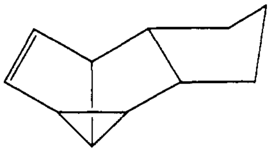
Table I. Values (ppm) for Protons in VIIIa

	H_A	H_B	H_C	H_D	H_E	H_F	H_G	H_H	H_I	-OH
Uncomplexed	2.26	2.26	5.60	5.71	2.26	2.90	2.26	2.90	4.31	~2.29
Complexed[a]	7.26	8.36	9.00	10.01	17.46	20.10	18.56	18.10	~30.3	98–104

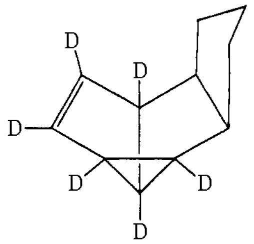
[a] Data from several scans with varying proportions of shift reagents were plotted and the resulting lines extrapolated to a 1:1 complex. The values reported above are for the 1:1 complex.


III


IV


V

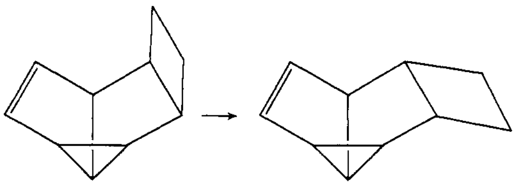
adduct from the irradiation of perdeuteriobenzene and cyclopentene (VI). This compound had absorptions



VI

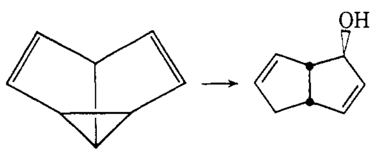
at δ 1.2–2.0 (6 H) and 2.7–3.4 (2 H), which can be attributed to the -CH$_2$CH$_2$CH$_2$- group and the bridgehead protons in VI, respectively.

A tentative assignment of the stereochemistry of IV and V was possible from the observation that the major adduct IV, on heating to 280° under vacuum, was converted (80% yield) to the minor adduct V. This reaction is analogous to the endo → exo isomerization (reaction I) between the 1,3 adducts of benzene to cyclobutene.[14] Therefore, the major adduct may have the endo stereochemistry (IV) in this instance as well.


(I)

As additional chemical evidence for the stereochemistry of these adducts, it seemed desirable to functionalize the central cyclopentane ring in each instance and observe the nature of the nmr absorptions of the bridgehead protons. A series of derivatives of each isomer was prepared and their chemical and spectral properties were compared.

From the work of Moriarty and Yeh,[15] it is known that solvolysis of semibullvalene (VII) proceeds according to reaction II. The resulting bicyclic alcohol was found to be very suited for examination in the presence of the nmr shift reagent Eu(DPM)$_3$. Since the 1,3 photoadducts of benzene to olefins may be viewed as dihydrosemibullvalenes, a similar reaction was attempted.



(II)

Hydration of the endo adduct (IV) in aqueous acetone in the presence of an acid catalyst proceeded smoothly to give a single alcohol. Although either HCl or *p*-toluenesulfonic acid served as a catalyst, the former was significantly more advantageous, since the addition of the sulfonic acid to the photoadduct competed successfully with hydration.

The alcohol which was obtained as the product on analysis fit the formula $C_{11}H_{16}O$ and formed a crystalline *p*-nitrobenzoate (mp 140–141°). Its infrared spectrum showed hydroxyl absorptions at 3650 and 3500–3350 cm^{-1} [16] as well as a weak absorption at 1640 cm^{-1} which indicated that an olefinic bond was present. The nmr spectrum (60 MHz) was not particularly informative since only the vinyl protons (δ 5.4–5.8, 2 H, m) and the methine proton adjacent to the -OH group (δ 4.44, 1 H, s) were readily assignable. The signal from the proton on the hydroxy group shifted in position with variations in concentration and disappeared *via* deuterium exchange on the addition of CDCl$_3$ (without added acid). The -OH proton appeared in the range δ 1.7–4.2. Other complex absorptions appeared at δ 1.0–1.9 (6 H) and 2.0–3.3 (6 H).

In order to ascertain whether the alcohol was allylic in nature or not, activated manganese dioxide was used as an oxidizing agent. This reagent, which is capable of oxidizing allylic alcohols selectively to unsaturated ketones,[17] proved totally unreactive in this instance, the unchanged alcohol being recovered essentially quantitatively.

The hydration, since it is an electrophilic addition,[15] can theoretically give any one or all of six possible products as shown in scheme A. Since the product is not an allylic alcohol, possibilities IXa–d can be ruled out. In view of the steric hindrance to attack on the inside of structures VIII, the most likely representation seemed to be as in VIIIa. Initial attack at the olefinic group to give a cyclopropyl carbinyl ion would appear to be the favored pathway.

The chemical shifts in the nmr spectrum of the alcohol on the addition of Eu(DPM)$_3$ allowed for the unequivocal assignment of structure VIIIa to the compound. In Table I, the δ values (ppm) for the protons in VIIIa both before and after complexing to the shift reagent are listed. The spectrum of the complex indicated a molecule with four protons located close enough to the hydroxy group to cause changes in the chemical shifts of 15–17 ppm. This may be compared to the shift

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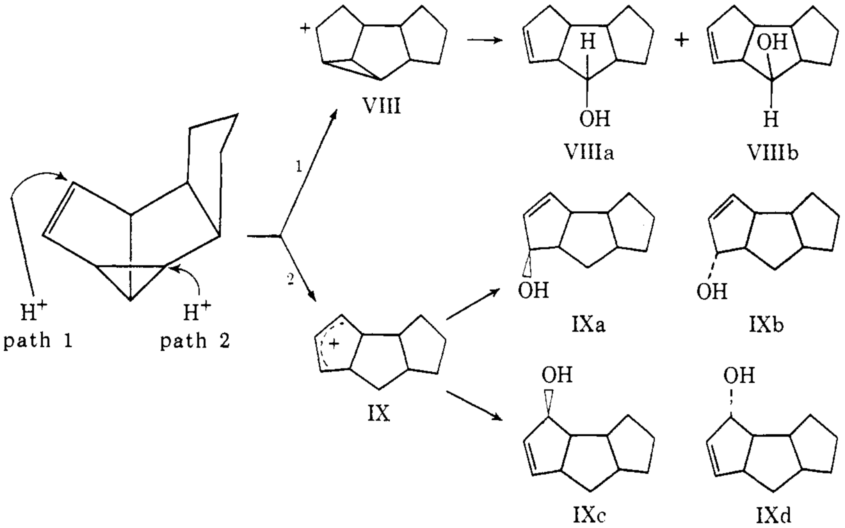
(14) R. Srinivasan, *J. Amer. Chem. Soc.*, **92**, 7542 (1970).

(15) R. M. Moriarty and C.-L. Yeh, *Tetrahedron Lett.*, 383 (1972).

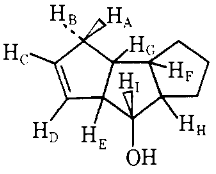
(16) Reference 13, p 95.

(17) (a) S. Ball, T. W. Goodwin, and R. A. Morton, *Biochem. J.*, **42**, 516 (1948); (b) J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Herns, A. B. A. Jansen, and T. Walker, *J. Chem. Soc.*, 1094 (1952).

Scheme A



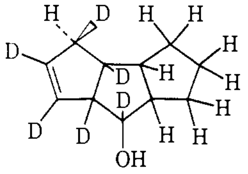
in the hydroxyl proton (96–102 ppm) and the methine proton, H_I (26 ppm). Double resonance studies confirmed the assignments listed in Table I. The coupling between H_I and either H_G or H_H was negligible, since H_I appeared as a singlet. This supported the trans-diaxial arrangement.



VIIIa

As a further proof of the structure of VIIIa, it was oxidized with Jones reagent[18] to an unconjugated ketone ($\nu_{C=O}$ = 1750 cm^{-1}). Its nmr spectrum showed the loss of the -OH group and H_I. Subsequently, this ketone was reduced with $LiAlH_4$ to an alcohol which proved to be identical with VIIIa. In view of the known tendency for this reagent to attack from the less hindered side of the molecule, it is appropriate to represent the -OH group in VIIIa to be on the "outside" of the tricyclic system.

The partially deuterated adduct VI, when similarly hydrated, gave a product (VIIIc) which contained a



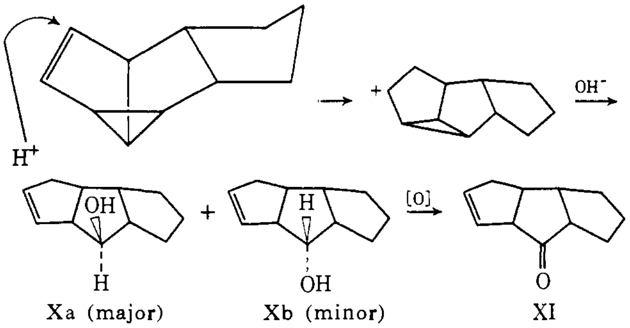
VIIIc

proton uniquely in position "B" of VIIIa. This showed that attack by H^+ as well as the subsequent addition of OH^- were stereospecific in nature.

Hydration of the exo adduct V gave a mixture (3:1) of two alcohols. These could not be separated cleanly from each other by vapor phase chromatography. Neither compound was identical with VIIIa. Both were inert to oxidation by activated manganese dioxide. Oxidation of the mixture with chromic acid gave a single ketone ($\nu_{C=O}$ = 1750 cm^{-1}) which was different from the ketone obtained from VIIIa.

The hydration and the oxidation of the exo adduct V may be expected to proceed according to scheme B.

Scheme B



In the nmr spectrum of the major component (Xa) there was a signal (δ 4.08) which could be assigned to a methine proton adjacent to a hydroxyl group and vinyl protons at δ 5.4–5.8. The minor component gave a corresponding single proton signal at δ 4.29 and vinyl proton absorptions at 5.0–5.3 ppm. Since the methine proton in Xb lies over the C=C band, a diamagnetic shift of 0.1–0.2 ppm was expected[19] and therefore the minor adduct was assigned this structure. It can be reasoned that the addition of OH^- to the intermediate ion in scheme B would be less hindered on the side which contains the cyclopentene ring than on the opposite side with the saturated cyclopentane ring. Therefore, the formation of Xa would be favored over Xb.

Rate Studies. As in the cases of the photochemical 1,3 addition of benzene to cyclobutene[5] or norbornene,[7] the efficiency of the photochemical addition of benzene to cyclopentene fell off rapidly with conversion. Only results obtained in the initial stages of the reaction, when the conversion ranged from 0 to 5%, gave a linear time-yield relationship. These data were used exclusively to compute the quantum yields.

Quantum yields for the formation of the adducts IV and V and the dimer of cyclopentene are plotted as

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[18] J. Meinwald, J. K. Crandall, and W. E. Hymans, *Org. Syn.*, **45**, 77 (1965).

[19] J. N. Shoolery and M. T. Rogers, *J. Amer. Chem. Soc.*, **80**, 5121 (1958).

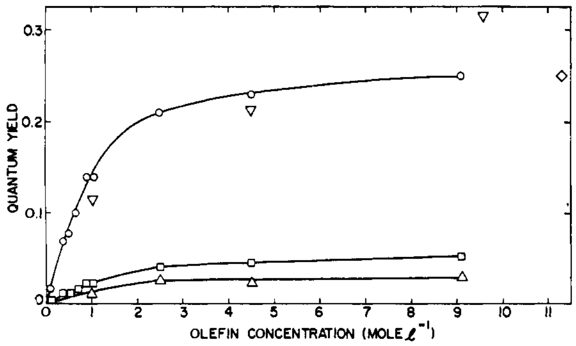


Figure 1. Quantum yields for products as a function of molarity of cyclopentene: solvent, cyclohexane and benzene; concentration, 1.7 *M;* (○) endo 1,3 adduct; (□) exo 1,3 adduct; (△) dimers of cyclopentene; (▽) total 1,1 adducts from ref 3b; (◇) total 1,3 adducts from ref 1c. The last two studies were carried out in the absence of any solvent.

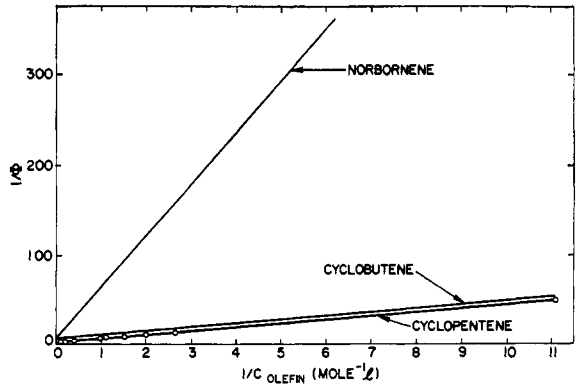


Figure 2. Plot of reciprocal of quantum yield (endo + exo) *vs.* reciprocal of olefin concentration. Data on cyclobutene from ref 5. Data on norbornene from ref 7.

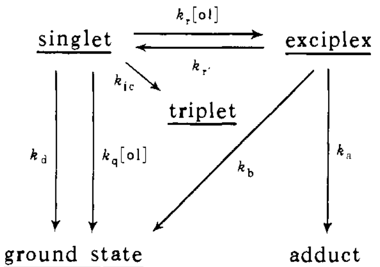
functions of concentration in Figure 1. Values that were obtained using undegassed solutions indicated that the presence of air had no detectable effect on the yields. This is similar to earlier results[5,7] on other olefins. The endo adduct constituted 80–85% of the adduct mixture. There was no indication that the ratio of the endo to the exo adduct (IV/V) was a function of reaction conditions.

There are fragmentary results in the literature on the photochemical 1,3 addition of benzene to cyclopentene to which the present data may be compared. The three values reported by Kraft[3b] for the quantum yield of the adduct (endo + exo?) in *pure benzene* agree reasonably well with the present work, if it is borne in mind that values in pure benzene are observably lower than quantum yields that are obtained in cyclohexane (*i.e.*, at low benzene concentration).[5] The single value reported by Wilzbach and Kaplan[1b] (also in pure benzene) but at a high concentration of olefin is also in agreement (see Figure 1).

Discussion

Since earlier work[1b,2d,4,5] has excluded the possibility that the photoaddition reactions of benzene to olefins involve the triplet state of the former, it is necessary to consider only those mechanisms which originate from the singlet (B_{2u}) state of benzene.

A scheme which incorporates a number of reasonable reactions from the singlet is as follows.



Arguments have been presented elsewhere[20] which rule out the intermediacy of a valence isomer of benzene as a precursor to the adducts. Therefore, the valence isomerization (which is, in any case, an inefficient process) is not explicitly indicated in the scheme.

The most attractive mechanism for the addition is one first proposed by Wilzbach and Kaplan[1c] that involves the initial formation of an exciplex between singlet benzene and an olefin. The exciplex can subsequently give a stable adduct (path a) or decompose as in paths b or r′. Note that the former is equivalent to the quenching by a direct bimolecular process (path q).

With the usual steady-state assumptions, it can be derived that

$$1/\Phi_{\text{adduct}} = (k_d + k_{ic})(k_{r'} + k_a + k_b)/k_a k_r[\text{ol}] + (k_q + k_r)(k_{r'} + k_a + k_b) - k_r k_{r'}/k_a k_r \quad (1)$$

The plot of 1/Φ *vs.* 1/[ol] should be a straight line according to (1). The experimental points which are shown in Figure 2 fit a satisfactory straight line. For comparison, the corresponding plots for cyclobutene and norbornene are also included in the figure.[21] The reciprocals of the intercepts which correspond to the limiting quantum yields at [ol] → ∞ are 0.45, 0.14, and 0.13 respectively for cyclopentene, cyclobutene, and norbornene. If the bimolecular quenching of the excited benzene (step q) is discarded as a separate step, the intercept of the plot equals $(k_a + k_b)/k_a$, which is the inverse of the partitioning of the exciplex between addition and deactivation. These values show that even in the case of cyclopentene, which is the most efficient partner in the addition reaction, as many exciplexes undergo deactivation as addition. The ratio is much less in favor of addition in cyclobutene and norbornene.

The inclusion of an exciplex in the mechanism will serve to rationalize some of the qualitative features of the addition such as the selective orientation of the substituents on the aromatic ring[8] and the preference for an endo adduct. But it also makes it difficult to compare the reactivities of the olefins in any direct way. Thus, the limiting quantum yields for both cyclobutene and norbornene are nearly the same, although the slopes of their plots of 1/Φ *vs.* 1/[ol] are quite different. The slope of these plots is given by

$$\text{slope} = \left[\frac{k_d + k_{ic}}{k_r}\right]\left[\frac{k_{r'} + k_a + k_b}{k_a}\right] \quad (2)$$

wherein the first term on the right denotes the ratio of

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[20] J. Cornelisse and R. Srinivasan, *Chem. Phys. Lett.*, **20**, 278 (1973).

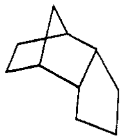
[21] The quantum yield data for both cyclobutene[5] and norbornene[7] are too large due to a systematic error in the calibration of the light intensity. The corrected values are shown in this plot.

the unimolecular decay of the singlet benzene to its tendency to form the exciplex and the second term denotes the partitioning of the exciplex among various pathways. Since either or both terms may control the slope of the plot, it is difficult to reconcile the slope for cyclobutene (which is nearly the same as for cyclopentene but widely different from the value for norbornene) to its intercept.

Qualitatively, it may be noted that cyclobutene gives predominantly the endo adduct (as cyclopentene does) but also leads to a significant quantity of a 1,4 adduct.[5] Norbornene seems to give predominantly an exo adduct[7] but no 1,4 adduct was observed.

It is clear that it is not possible to generalize on the course of all 1,3 additions from these three systems.

Although the dimerization of cyclopentene was not a significant reaction in the benzene–cyclopentene system, a curious feature of this reaction may be noted. Any mechanism for the dimerization if it occurred by photosensitization would require a dependence on a power of olefin concentration greater than 1. The detailed equations for the instance in which triplet benzene is a sensitizer are given elsewhere.[7] In this case, the quantum yield for the dimer would show a maximum at a fairly low concentration of the olefin (the value is 0.06 *M* for norbornene) and decreases thereafter with an increase in [ol]. In the present study, the yield of the dimeric product rises steadily with the concentration of the olefin and the ratio [adduct]/[dimer] changes by a factor <2 over a 100-fold change in concentration. These observations cannot be reconciled with any simple sensitized dimerization reaction. The observation of Scharf and Korte[12] that no more than 30% of the dimer was III when acetone was the photosensitizer and that XII was one of the products suggests that a radical chain mechanism may play a part in that system as well. Nmr analysis suggested that dimer XII was also included in the dimer fraction in the present study.



XII

Experimental Section

Infrared spectra were determined on a Perkin-Elmer infracord spectrophotometer. Mass spectra were recorded on a Hitachi Perkin-Elmer RMS-4 mass spectrometer. Ultraviolet spectra were measured on a Cary 14 spectrophotometer. Nuclear magnetic resonance spectra at 60, 90, and 220 MHz were run on a JEOL Minimar, a Bruker HFX-10, and a Varian HR-220 spectrometer, respectively. The last was operated by the Consortium at The Rockefeller University in New York. Microanalysis were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn. Benzene, cyclopentene, and cyclohexane of greater than 99% purity were obtained commercially and used as such.

Photoaddition of Benzene to Cyclopentene. Preparative scale irradiations were carried out in a Rayone Type RS preparative photochemical reactor[22] fitted with four RPR-208 modules (254 nm). The cylindrical quartz irradiation tubes measured 12 in. × 1 in. (o.d.) and their capacity was 100 ml of solution. Each tube was filled with cyclopentene (50 ml), benzene (25 ml), and cyclohexane (25 m) and sealed by means of a rubber serum cap, through which samples could be removed using a syringe. The reaction was monitored by vpc (0.25 in. × 12 ft 10% UCON 550X, ~160°, He pressure 40 psi) at 24, 48, 60, and 72 hr, and the irradiations were terminated when the formation of adducts began to level off (usually ~60 hr). The photolysis solutions were distilled at reduced pressures to remove solvent and unreacted starting materials, in each case limiting the bath temperature to less than 80–85°. The residues were further distilled under high vacuum (~10 μ), condensing with liquid nitrogen to separate the product mixture from polymeric materials. The neat products were stored at −80° due to their tendency to polymerize.

The mixture of products, as a thick viscous yellow oil, was separated into pure components by means of gas chromatography on a SE-30 (6 ft) column at 125°. The isolated yields of III, IV, and V were 2, 5, and 1%, respectively. The low yields merely reflect the loss of cyclopentene during work-up. From considerations of mass balance and earlier results with cyclobutene[5] it can be predicted that optimum yields which are tenfold greater can be obtained.

3,7-*endo*-Tetracyclo[6.3.0.0^{2,11}.0^{3,7}]undecene-9 (IV): mass spectrum, parent peak 146; other intense peaks at 117, 91, 78, 67, 51, 39 and 27; ir spectrum (liquid film) 3008, 2975, 2900, 1600, 1468, 1443, 1353, 980, 800, 781, 774, 750, and 720 cm^{-1}; uv spectrum (pentane) max at 220 nm (ϵ 2300); nmr spectrum ($CDCl_3$ solution, TMS as internal reference) δ 1.22–2.00 (8 H), 2.58–3.41 (4 H), and 5.44–5.70 (2 H).

3,7-*exo*-Tetracyclo[6.3.0.0^{2,11}.0^{3,7}]undecene-9 (V): mass spectrum parent peak 146; other intense peaks at 131, 117, 91, 81, 79, 78, 68, 67, 51, 39, and 27; ir spectrum (liquid film) 3007, 2970, 2900, 1600, 1449, 1352, 913, 790, 753, and 728 cm^{-1}; uv spectrum (pentane) shoulder ~210 nm (ϵ 4500); nmr spectrum (CCl_4 solution) δ 1.15–1.95 (8 H), 1.95–3.13 (4 H), and 5.38–5.60 (2 H). *Anal.* (IV + V). Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.21; H, 9.60.

Hydration of IV. A sample of IV (0.45 g, 3.1 mmol) purified by gas chromatography was added to 80% aqueous acetone (20 ml), acetone (5 ml), and concentrated HCl (1 ml) (or *p*-toluenesulfonic acid, 0.16 g). The mixture was refluxed overnight under nitrogen. The light green solution was neutralized with 50% K_2CO_3 and extracted with methylene chloride. The extract was dried over sodium sulfate and filtered and the solvent removed on a rotary evaporator. The residue (0.5 g, 3.1 mmol) slowly crystallized. Analytical samples were obtained by purification on a gas chromatograph (12 ft SE-30 column; 150°). The hydration of V was carried out analogously.

***syn*-2-Hydroxytricyclo[6.3.0.0^{3,7}]undecene-4 (VIIa):** mass spectrum parent peak at 164; other intense peaks at 147, 146, 131, 118, 117, 105, 104, 81, 80, 78, and 68; ir spectrum (liquid film) 3650, 3350–3500, 3050, 2970, 2900, 1640, 1448, 1074, 760, 716, and 695 cm^{-1}; nmr spectrum (see text); *p*-nitrobenzoate mp 140–141°.

Anal. Calcd for $C_{18}H_{19}NO_4$: C, 69.00; H, 6.11; N, 4.47; mol wt 313.34. Found: C, 69.07; H, 6.30; N, 4.39; mol wt 314.

***anti*-2-Hydroxytricyclo[6.3.0.0^{3,7}]undecene-4 (Mixture of Xa and Xb):** mass spectrum parent peak at 164; ir spectrum (liquid film) 3500, 3060, 2960, and 1640 cm^{-1}; nmr spectrum (see text).

Attempted Oxidation of VIIIa with Activated Manganese Dioxide. Active MnO_2 was prepared according to ref 17b. A sample of VIIIa (0.25 g, 1.5 mmol) was stirred for 30 min with a suspension of freshly prepared activated MnO_2 (1.0 g) in light petroleum ether (40–60°, 5 ml) and the mixture was quickly filtered without suction. The precipitate was washed with solvent and the combined filtrate was evaporated to yield an oily residue (0.25 g) which was identical (ir, nmr, vpc) with VIIIa.

Oxidation of VIIIa with Jones reagent. The procedure in ref 18 was followed exactly. A sample of VIIIa (0.25 g, 1.5 mmol) yielded 0.22 g (90%) of ketone.

***syn*-Tricyclo[6.3.0.0^{3,7}]undecen-4-one-2:** mass spectrum parent peak at 162; ir spectrum (liquid film) 2980, 1442, 1750, 1442, 1260, 1110, 790, and 720 cm^{-1}; mass spectrum (CCl_4 solution) δ 1.4–2.1 (6 H), 2.1–2.7 (4 H), 2.6–2.9 (2 H), and 5.7–5.9 (2 H); 2.4-DNP mp 190° (dec); semicarbazone mp 212–214° (dec).

Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 8.137; H, 8.62.

***anti*-Tricyclo[6.3.0.0^{3,7}]undecen-4-one-2 (XI):** mass spectrum parent peak at 162; ir spectrum (liquid film) 2990, 1750, 1440, 1260, 1180, 1100, and 800 cm^{-1}; nmr spectrum (CCl_4 solution) δ 1.1–3.0 (12 H) and 5.3–6.2 (2 H); semicarbazone mp 197–208° (dec).

Quantum Yield Measurements. These were carried out in a Rayonet RPR-100 photochemical reactor[22] (with a turntable arrangement) fitted with two 254-nm lamps. Light intensities were determined with a potassium ferrioxalate actinometer. The

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[22] This unit is available from the Southern New England Ultraviolet Co., Middletown, Conn.

cylindrical quartz irradiation tubes (~0.75 mm i.d.) contained an irradiated volume of 1 ml. Solutions were degassed by the freeze–pump–thaw cycle. Irradiation times were chosen so that the degree of conversion never exceeded 5%. Quantitative analyses were made on a Hewlett-Packard Model 5750 gas chromatograph fitted with a polypropylene glycol column (12 ft, UCON-50LB-550X, 20%) at 160°.

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The Optical Rotation of α-Bromopropionitrile and 3-Methyl-5-bromo-1-cyanoadamantane from Polarizability Theory

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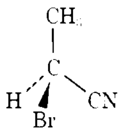
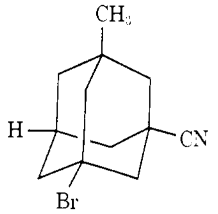
Abstract: The optical rotations of α-bromopropionitrile (BPN) and 3-methyl-5-bromo-1-cyanoadamantane (MBCA) at 5893 Å are calculated from polarizability theory, assigning isotropic polarizabilities to all atoms and, alternatively, single isotropic or anisotropic polarizabilities to the CN group. The calculations make use of (i) modified polarizability data based on the dipole interaction model and (ii) the exact calculation of the relay tensors. These modifications lead to a much better agreement with experiment than earlier calculations for both compounds. The isotropic atom model for CN gives intrinsic molar rotations of L-BPN in the range −55 to −74 deg cm^2/dmol (experimental value −19) and of MBCA of the same configuration in the range −0.29 to −0.94 (experimental value −0.82 for unknown configuration). The other models for CN show ambiguity of sign for BPN but not for MBCA. Displacement of the N atom in a manner approximating electrostatic repulsion by Br reverses the sign of rotation for MBCA but not for BPN. Rotation of the CH$_3$ group produces significant changes in optical rotation, but the thermal average optical rotation assuming reasonable energy barriers is not significantly different from the rotation of the staggered form.

A previous attempt[1] to account for the optical rotations of α-bromopropionitrile (BPN) and 3-methyl-5-bromo-1-cyanoadamantane (MBCA) by means of a polarizability theory which included all atoms was unsatisfactory for two reasons that were evident at the time: (i) the sign of the rotation calculated for BPN was inconsistent with the known absolute configuration, and (ii) the perturbation series used to calculate the rotations did not converge rapidly. In a subsequent study[2] it was found that the additive atom polarizabilities used in these calculations were invalid for calculating polarizability interactions, and a more valid set of atom polarizabilities and CN group polarizabilities[3] was determined. In addition, it has been found[4,5] that the perturbation approximation can be avoided by using an exact treatment of dipole–dipole interactions to calculate the set of "relay tensors" which determine both the optical rotation and molecular polarizability. The object of this paper is to show how these developments affect the rotations calculated for BPN and MBCA.



L-BPN



MBCA

We are confined in this study to calculations at the sodium D line, 5893 Å, since our polarizability data apply only at this wavelength. However, the calculations serve as a more realistic test of the polarizability theory than previous attempts because of the modifications noted above. While we do not obtain information on rotatory dispersion, the present theory treats intramolecular interactions which are generally omitted in the quantum mechanical calculations of rotatory dispersion. This approach should therefore serve as a useful supplement to quantum mechanical methods in general and particularly in cases such as the present ones, where the available information needed for a quantum mechanical calculation is very limited.

The molecules studied here serve as useful test cases because they have simple, essentially unstrained structures, and because their lack of conformational freedom minimizes the need for conformational averaging. In addition, the L configuration of BPN has been identified as the levorotatory form,[1,6] though the configuration of MBCA has not been related to sign of rotation.

Calculations

The molecule is regarded as being made up of N units which interact by means of the fields of their

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