

titration against standard base.¹⁸ Solutions of approximately 1% of either methylcyclopropanone or dimethylcyclopropanone and 1% of tetramethylammonium chloride in each of the aforementioned solutions were examined in the nmr. The separation be-

tween the methyl peak of the cyclopropanone and the center peak of the methyl triplet of tetramethylammonium chloride was measured. A mixture of approximately equal amounts of methylcyclopropanone and dimethylcyclopropanone was prepared and solutions of approximately 1% of this mixture were prepared. The separation between the two methyl peaks was measured. The data are summarized in Table I and presented in Figures 1-4.

(18) M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957); N. J. Orgenson and D. R. Hartter, *J. Am. Chem. Soc.*, **85**, 878 (1963).

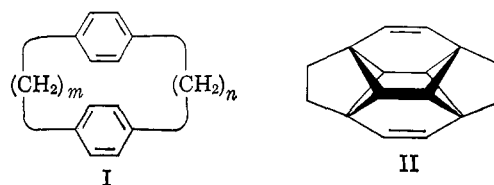
Macro Rings. XXXII. Photochemistry of [2.2]Paracyclophane¹

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Abstract: Irradiation of [2.2]paracyclophane in methanol in a quartz vessel with a 200-w medium-pressure lamp produced *p*-methyl-*p*'-methoxymethylenebiphenyl (IV), *p*-ethylbiphenyl (V), *p*,*p*'-dimethylbiphenyl (VI), *p*-methyl-*p*'-β-hydroxyethylbiphenyl (VII), and β-*p*-methylphenylethyl alcohol (VIII). When carried out in methanol-*O-d* one atom of deuterium was observed in the *p*-methyl group of IV. Similar products were observed when the irradiation was carried out in ethyl alcohol. Use of a low-pressure mercury lamp (90% of its emission is at 2537 Å) and ethanol as solvent in a quartz vessel produced only *p*-methyl-*p*-ethoxymethylenebiphenyl (IX) as product. Use of the medium-pressure lamp in methanol or ethanol as solvent and a Corex filter produced only *p*-ethylbiphenyl (V). The rate of photolysis of [2.2]paracyclophane to give hydrocarbon V was found to correlate roughly with the relative ease with which these solvents provide hydrogen atoms to radicals (2-propanol > ethanol > methanol > cyclohexane in rate). Use of acetone as a photosensitizer and solvent produced only hydrocarbon V. Photolysis in ethanol with a Vycor filter produced a 21% yield of hydrocarbon V and a 16% yield of ether IX. In an identical experiment, except that the solution was 0.01 *M* in naphthalene (quencher), only ether IX was produced. These experiments suggest that ethers IV and IX arise by solvolysis of a zwitterion produced from a charge-transfer excited singlet state which is generated when [2.2]paracyclophane absorbs light in the 2500-Å region. Hydrocarbon V appears to arise from a low-energy triplet-singlet-triplet intersystem crossover that involves an absorption of light in the 2800-3000-Å region, or is produced by triplet-triplet energy transfer from triplet acetone. Hydrocarbon VI and alcohols VII and VIII seem to arise from a biradical produced by cleavage of a high-energy singlet associated with light absorption in the region below 2400 Å. These conclusions are in harmony with interpretations of the ultraviolet absorption and the fluorescence and phosphorescence spectra of [2.2]paracyclophane.

Previous studies of the [*m.n*]paracyclophanes (I) have demonstrated the presence of transannular effects in their ultraviolet,^{2a} infrared,^{2b} and nuclear magnetic resonance^{2c} (nmr) spectra, in their π-base strength,^{2c,3} in their electrophilic substitution reactions,⁴ and in their molecular geometries.⁵ These examples of transannular effects suggested that the photochemistry of the smallest homolog, [2.2]paracyclophane, might involve transannular bond formation. This type of phenomenon has been encountered in the dianthracene analog of [2.2]paracyclophane.⁶ Specifically it was anticipated that [2.2]paracyclophane might undergo a multiple Diels-Alder reaction under the influence of light to give the polycyclic substance II.



Results

Light Sources. Direct irradiation, photosensitization, and quenching techniques were all employed. Most of the irradiations were carried out in an immersion-well apparatus with a Hanovia 200-w medium-pressure mercury lamp as light source, and under an atmosphere of purified nitrogen. The wavelength of absorbed light was varied through use of commercial filter sleeves placed around the light source. Without these filters, the quartz vessel transmitted all of the ultraviolet light. The Vycor filter transmitted light only above 230 mμ, and the Corex filter transmitted light only above 270 mμ. In one experiment (see below), a low-pressure mercury lamp was used, 90% of whose emission is at 253.7 mμ. The very insoluble starting material went into solution as reaction occurred in all experiments.

(1) The authors wish to thank the National Science Foundation for a grant used in support of this research, and Drs. M. A. El-Sayed and G. S. Hammond for enlightening conversations concerning this work.

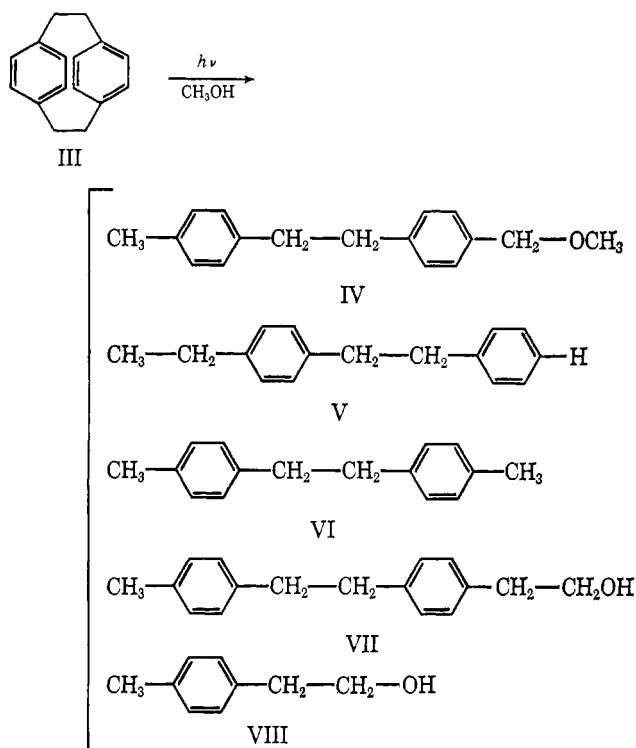
(2) (a) D. J. Cram, R. H. Bauer, N. L. Allinger, R. A. Reeves, W. J. Wechter, and E. Heilbronner, *J. Am. Chem. Soc.*, **81**, 5977 (1959); (b) D. J. Cram, N. L. Allinger, and H. Steinberg, *ibid.*, **76**, 6132 (1954); (c) D. J. Cram and L. A. Singer, *ibid.*, **85**, 1084 (1963); (d) L. A. Singer and D. J. Cram, *ibid.*, **85**, 1080 (1963).

(3) D. J. Cram and R. H. Bauer, *ibid.*, **81**, 5971 (1959).

(4) (a) D. J. Cram, W. J. Wechter, and R. W. Kierstead, *ibid.*, **80**, 3126 (1958); (b) D. J. Cram and L. A. Singer, *ibid.*, **85**, 1075 (1963).

(5) (a) C. J. Brown, *J. Chem. Soc.*, 3265, 3279 (1953); (b) C. L. Coulter and K. N. Trueblood, *Acta Cryst.*, **16**, 667 (1963); (c) K. N. Trueblood, P. K. Gantzel, and D. A. Bekoe, private communication.

(6) J. H. Golden, *J. Chem. Soc.*, 3741 (1961).



Irradiation in Methanol. Irradiation of [2.2]paracyclophane (III) in methanol in a quartz vessel produced compounds IV–VIII. No other products could be detected with vapor phase chromatography (vpc), nmr spectroscopy, or thin layer chromatography (tlc), even when the reaction mixture was examined after short exposure times. Thus, the products listed seem to arise directly from III, rather than from one another, or from an initially detectable intermediate.

Table I records the yields of compounds IV–VIII obtained when the reactions were conducted both with and without filters. Appropriate analytical control

Table I. Products of Irradiation of [2.2]Paracyclophane in Methanol

| Run no. | Time, days | Filter | % yield or recovery ^a | | | | | III |
|---------|------------|--------|----------------------------------|---|------|------|------|-----|
| | | | IV | V | VI | VII | VIII | |
| 1 | 2 | Quartz | 19 | 1 | 4 | 2 | 2 | 38 |
| 2 | 5 | Quartz | 31 | 2 | 6 | 3 | 3 | 21 |
| 3 | 5 | Vycor | 16 | 2 | <1 | <1 | <1 | 44 |
| 4 | 5 | Corex | <0.5 | 3 | <0.5 | <0.5 | <0.5 | 70 |

^a Determined by vpc.

experiments with authentic samples of IV and VI–VIII demonstrated that less than 0.5% yields of these compounds could be detected with vpc analytical techniques. Insoluble polymer always was produced in the reactions.

Compounds IV to VIII were identified as follows. Ether IV, isolated from irradiation experiments, exhibited a series of singlets as follows: three protons at τ 7.77 (*p*-methyl group), four protons at τ 3.08 (aromatic protons of tolyl ring), four protons at τ 7.22 (methylene–methylene protons), four protons at τ 2.93 (aromatic protons of the benzyl ether ring), two protons at τ 5.68 (benzyl protons of the benzyl ether), three protons at τ 6.78 (protons of the methoxyl group). It possessed λ_{\max} values in its ultraviolet spec-

trum characteristic of *p*-disubstituted dialkylbenzenes: 221 $m\mu$ (ϵ 18,600), 252 (466), 259 (633), 264 (680), 267 (640), 273 (593). The infrared spectrum of IV gave a strong band at 9.1 μ characteristic of an alkyl ether. The substance gave a correct analysis, and was reduced with sodium and liquid ammonia to give VI, identified by mixture melting point with an authentic sample.⁷

Hydrocarbon V was characterized by combustion and spectral analysis. The nmr spectra contained the following bands: five protons at τ 2.90 as a singlet (phenyl protons), four protons at τ 3.03 as a singlet (aromatic protons of *p*-dialkylbenzene ring), four protons at τ 7.22 as a singlet (methylene–methylene protons), two protons centered at τ 7.42 as a quartet (methylene of the ethyl group), three protons centered at τ 8.79 as a triplet (methyl group). The ultraviolet spectrum of V gave λ_{\max} as follows: 219 $m\mu$ (ϵ 15,580), 253 (595), 259 (719), 264 (743), 267 (617), 273 (495).

Hydrocarbon VI was identified by mixture melting point, vpc retention time, tlc R_f values, and nmr spectral comparisons with an authentic sample.⁷ The nmr spectrum gave singlets as follows: eight protons at τ 3.05 (aromatic), four protons at τ 7.23 (methylene), six protons at τ 7.74 (methyl).

Alcohol VIII was identified by comparison of its vpc retention time, tlc R_f value, and nmr and infrared spectra with that of an authentic sample,⁸ prepared by lithium aluminum hydride reduction of *p*-methylphenylacetic acid. All properties of the two samples matched identically. The nmr spectrum exhibited the following bands: four protons at τ 3.02 as a singlet (aromatic), two protons centered at τ 6.32 as a triplet (hydroxymethylene), two protons centered at τ 7.28 as a triplet (benzyl), three protons at τ 7.71 as a singlet (methyl), one proton as a singlet at τ 8.73 (hydroxyl).

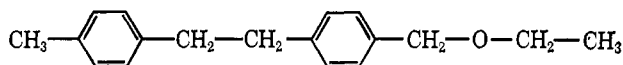
Alcohol VII was identified by its nmr, ultraviolet, and infrared spectra. The nmr spectrum exhibited bands as follows: four protons at τ 2.98 as a singlet (*p*-tolyl aromatic), four protons at τ 3.02 as a singlet (*p*-xylyl aromatic), two protons centered at τ 6.32 as a triplet (hydroxymethylene), four protons at τ 7.22 as a singlet (methylene–methylene), two protons centered at τ 7.28 as a triplet (methylene flanked by aryl and hydroxymethylene), three protons at τ 7.71 as a singlet (methyl), one proton at τ 8.73 as a singlet (hydroxyl). The ultraviolet spectrum gave λ_{\max} as follows: 220 $m\mu$ (ϵ 17,800), 253 (434), 259 (608), 264 (757), 267 (696), 273 (725). The infrared spectrum gave a hydroxyl group absorption at 2.8 μ . These spectra, when compared with those of the simpler alcohol VIII, clearly require the structure written for compound VII. Furthermore, VII gave vpc retention times and tlc R_f values consistent with its molecular weight and polarity (see the Experimental Section).

Irradiation in Methanol-O-*d*. To help determine the mode of formation of ether IV, [2.2]paracyclophane was irradiated in methanol-O-*d* (99% of one atom of deuterium) in a quartz test tube. Ether IV was isolated and its nmr spectrum proved identical with that of ether IV prepared in ordinary methanol except for the methyl absorption band. The singlet in the protio product was split into a triplet by the

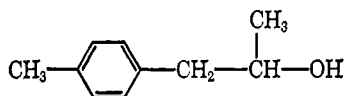
(7) D. J. Cram and H. Steinberg, *J. Am. Chem. Soc.*, **73**, 5691 (1951).

(8) H. Pines and J. Shabtai, *J. Org. Chem.*, **26**, 4220 (1961).

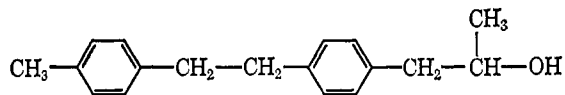
deuterium⁹ in the deuterio product. Integration of this peak indicated that the molecule contained $95 \pm 5\%$ of one atom of deuterium in the methyl group. Clearly ether IV was formed by addition of the elements of methanol to [2.2]paracyclophane cleaved at the 1,2 position.



IX



X



XI

Irradiation in Ethanol. The hydrocarbon products of irradiation in ethanol were the same as those in methanol (V and VI), but, as expected, the ether (IX) and alcohol products (X and XI) were analogous but different. Table II records the yields as the filter was

Table II. Products of Irradiation of [2.2]Paracyclophane in Ethanol

| Run no. | Filter | IX | V | VI | X | XI | III |
|---------|--------|------|----|------|------|------|-----|
| 5 | Quartz | 33 | 12 | 5 | 2 | 1 | 15 |
| 6 | Vycor | 16 | 21 | 2 | <1 | <1 | 30 |
| 7 | Corex | <0.5 | 29 | <0.5 | <0.5 | <0.5 | 50 |

changed from quartz to Vycor to Corex. The only marked difference in the pattern of results from those in methanol is the increase in yield of *p*-ethylbibenzyl (V).

Ether IX was characterized by combustion analysis, as well as by its nmr, ultraviolet, and infrared spectra. The nmr spectrum exhibited the following bands: four protons as a doublet at τ 2.92 (aromatic, *p*-xylyl ring), four protons as a singlet at τ 3.05 (aromatic *p*-tolyl ring), two protons as a singlet at τ 5.65 (benzyl ether), two protons as a quartet at τ 6.06 (methylene of ethyl), four protons as a singlet at τ 7.22 (methylene-methylene), three protons as a singlet at τ 7.75 (tolyl methyl), three protons as a triplet at τ 8.33 (methyl of ethyl). The ultraviolet spectrum was very similar to that of ether IV, and the infrared spectrum possessed a strong absorption at 9.1μ associated with carbon-oxygen stretch.

Alcohol X was identified by its nmr, infrared, and chromatographic properties. Its nmr spectrum possessed the following bands: four protons as a singlet at τ 2.98 (aromatic), one proton as a multiplet at τ 6.14 (methine), three hydrogens as a singlet at τ 7.71 (arylmethyl), two protons as a doublet at τ 7.39 (benzyl), one proton as a singlet at τ 8.27 (hydroxyl), three protons as a doublet at τ 8.88 (methine-methyl). The infrared spectrum possessed hydroxyl absorption at 2.8

μ . The vpc retention time and tlc R_f values were consistent with its molecular weight and polarity.

Alcohol XI was not isolated in a pure state, but its nmr spectrum, vpc retention time, and infrared spectrum support the structural assignment. The substance possessed an nmr spectrum with the same bands as alcohol X, except for the new aryl and methylene bands. The substance was eluted in column chromatography with the same solvent mixture as was X.

Variation in Yields of *p*-Ethylbibenzyl (V) with Solvent. In Table III are compared the yields of hydrocarbon V under a standard set of conditions (Corex

Table III. Effect of Solvent on Yield of *p*-Ethylbibenzyl (V) by Irradiation of [2.2]Paracyclophane (III) in Corex

| Solvent | Relative solubility of III | % yield of V | % yield of recovered III |
|-------------|----------------------------|--------------|--------------------------|
| 2-Propanol | 2 | 30 | 34 |
| Ethanol | 2 | 22 | 51 |
| Methanol | 1 | 3 | 75 |
| Cyclohexane | 20 | 3 | 68 |

filter) as solvent is changed from 2-propanol to ethanol to methanol to cyclohexane. The reactions were heterogeneous and, therefore, the relative solubility of [2.2]paracyclophane is also listed. The results clearly indicate that the rate of production of hydrocarbon V from III correlates with the ease with which the solvent can provide hydrogen atoms to substrate, i.e., 2-propanol > ethanol > methanol > cyclohexane.

Irradiation of [2.2]Paracyclophane (III) in Acetone. The use of acetone as a photosensitizer-solvent for the irradiation of III was also investigated.¹⁰ The very limited solubility of [2.2]paracyclophane in acetone (10^{-3} to 10^{-4} M) ensured that virtually all of the irradiating light was absorbed by the solvent. In the reaction, a 23% yield of *p*-ethylbibenzyl was obtained, along with 30% of unreacted starting material and some polymer. Other compounds of low molecular weight were not produced in detectable quantity.

Quenching Experiment. In an attempt to gain information regarding the multiplicity of the excited states that gave rise to the various products, naphthalene was used as a quencher in an irradiation of [2.2]paracyclophane in ethanol with a Vycor filter. In the absence of naphthalene, a 21% yield of *p*-ethylbibenzyl (V), a 16% yield of ether IX, and a 2% yield of *p,p'*-dimethylbibenzyl (VI) were obtained. When the same reaction was conducted in ethanol, 0.01 M in naphthalene, no detectable amount (<0.5%) of V was produced, whereas ether IX and hydrocarbon VI were produced in the same yields as obtained without the naphthalene present (16 and 2%, respectively). Clearly, the naphthalene acted as a quencher for the excited state involved in the production of V, but not for that for VI or IX.

When the same reaction was carried out in the presence of air but in the absence of naphthalene, hydrocarbon V was not detected, although starting material was consumed.

(9) L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press Inc., New York, N. Y., 1960, p 23.

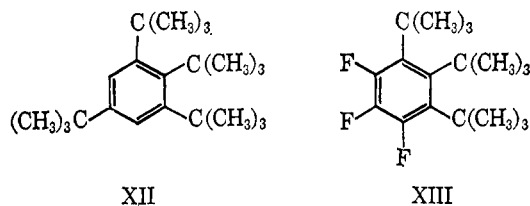
(10) This photosensitizer was suggested by Professor George S. Hammond.

Irradiation at 2537 Å. The low-pressure mercury lamp, 90% of whose emission is at 2537 Å, was used as a light source in an experiment conducted in ethanol in a quartz vessel. The only product formed in detectable amount (<0.5%) was ether IX, which was obtained in 15% yield.

Discussion

Distinct products seem to be associated with particular irradiation conditions. The hydrocarbon, *p,p'*-dimethylbibenzyl (VI), and alcohols VII, VIII, X, and XI were produced by the highest energy radiation, clearly below 2537 Å and probably in the 2250-Å region. Ethers IV and IX were generated with irradiation in the 2537-Å region. The hydrocarbon, *p*-ethylbibenzyl (V), involved radiation of lower energy, probably of 2800- to 3000-Å wavelength. Each of these sets of wavelengths corresponds roughly to absorption bands in the ultraviolet spectrum of [2.2]paracyclophane, which exhibits absorption maxima or points of inflection at about 2250, 2440, 2860, and 3020 Å. The ultraviolet, fluorescence, and phosphorescence spectra of [2.2]paracyclophane will first be discussed, followed by an interpretation of the photochemistry associated with each of the sets of products observed.

Ultraviolet, Fluorescence, and Phosphorescence Spectra of [2.2]Paracyclophane (III). Comparisons of the ultraviolet spectra of the [2.2]-, [2.3]-, [3.3]-, [3.4]-, and [4.4]paracyclophanes, the [8]-, [9]-, [10]-, [11]-, and [12]paracyclophanes and open-chain models (*p*-dialkylbenzenes) led to the following conclusions.^{2a,3} (1) The abnormal spectrum of [2.2]paracyclophane (III) is due to both transannular electronic effects and to effects associated with the nonplanar benzene rings. (2) The shift in the normal 2230-Å band to 2440 Å in III is associated with transannular electronic effects. (3) The shift in the normal 2650-Å band to 2860 Å is mainly due to the nonplanarity of the benzene rings. (4) The shift of the normal 2730-Å band to 3020 Å is associated with both the distorted benzene rings and transannular electronic effects. Conclusion 3 is further supported by the types of abnormalities observed in the spectra of nonplanar aromatic compounds such as XII and XIII.¹¹



A number of theoretical treatments of the spectra have appeared,¹² which are, in general, in harmony with the above conclusions based on empirical grounds. In particular, Vala and Rice¹³ recently have presented strong evidence that the abnormal shifts in the ultraviolet spectra of the smaller [*m.n*]paracyclophanes are caused by configurational mixing of neutral and charge-

transfer excited states. Inclusion of charge-transfer terms in the wave functions of the excited states gave calculated spectra in excellent agreement with those observed for [2.2]-, [2.3]-, [3.3]-, and [3.4]paracyclophanes.

Both Ron and Schnepf,¹⁴ and Vala, Haebig, and Rice¹⁵ studied the fluorescence spectrum of [2.2]paracyclophane, which exhibited a broad band with a maximum at 3500 Å. The position of this band was consistent with charge-transfer interactions in the emitting state although ring-bending effects were also operative. The fluorescence spectrum of [4.4]paracyclophane also was taken,¹⁵ which gave a maximum at 3400 Å in contrast to the expected mirror image fluorescence at about 2850 Å. This anomalous effect was explained in terms of vibrationally induced interactions of the benzene rings after absorption of light had occurred, and which are associated with molecules in which the interbenzenoid distance has decreased to allow electronic coupling between the rings. These authors, as well as others,¹⁶ have demonstrated that the shift to longer wavelength in the fluorescence emission of the dimer state relative to the monomer (non-interacting) state can only be satisfactorily accounted for by the inclusion of charge-transfer states mixing with neutral electronic states. The larger [*m.n*]paracyclophanes gave normal fluorescence spectra. It seems reasonable to conclude that charge-transfer interaction should be present in the absorption spectrum of [2.2]paracyclophane since the benzene rings are separated by only about 3 Å in the ground state.¹⁷

The phosphorescence spectrum of [2.2]paracyclophane has been taken in an ether-isopentane-ethanol (5:5:2) glass (EPA) by El-Sayed.¹⁸ The emission was broad (4100 to 5600 Å) with a maximum at about 4700 Å. This emission is different from that of benzene which phosphoresces in the 3400-Å region.¹⁹ The emission was strong and the lifetime was 3.3 sec compared to 6 sec for benzene phosphorescence. The strong emission and lifetime indicate a favorable intersystem crossing from the lowest singlet to the emitting triplet state. The emission spectrum indicates that interaction between the rings exists in the triplet state, but this could be either bonding or only spin interaction.

Photochemistry Leading to *p*-Ethylbibenzyl (V). This hydrocarbon was the exclusive product when light of wavelengths longer than 2700 Å was employed. The rate of generation of the substance correlated well with the hydrogen atom donating ability of the solvent, a fact which suggests radical intermediates. That a triplet state was involved was indicated by the facts that oxygen inhibited the formation of V, and that naphthalene served as an efficient quencher for the reaction. The singlet of naphthalene corresponds to 90 kcal and the triplet to 60 kcal,¹⁹ whereas [2.2]paracyclophane has a triplet at 69 kcal¹⁸ and a singlet

(14) A. Ron and O. Schnepf, *J. Chem. Phys.*, **37**, 2540 (1962).

(15) M. T. Vala, Jr., J. Haebig, and S. A. Rice, private communication.

(16) (a) J. N. Murrell and J. Tanaka, *Mol. Phys.*, **4**, 363 (1964); (b) T. Azumi, A. T. Armstrong, and S. P. McGlynn, *J. Chem. Phys.*, **41**, 3839 (1964).

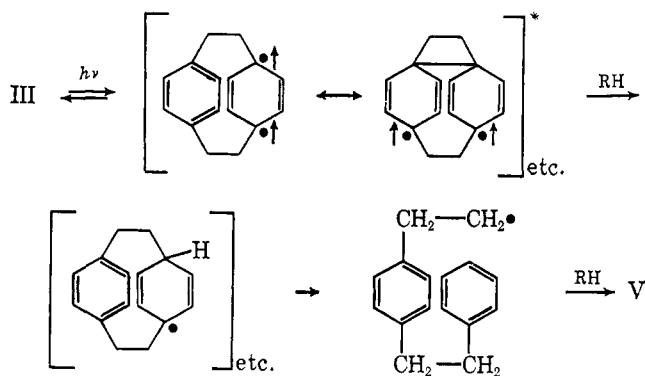
(17) C. J. Brown, *J. Chem. Soc.*, 3265, 3279 (1953).

(18) M. A. El-Sayed, *Nature*, **197**, 481 (1963).

(19) E. J. Bowen, "Advances in Photochemistry," Vol. 1, W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 2.

at 87 kcal.¹⁴ These energy relationships should make singlet-singlet energy transfer inefficient, but triplet-triplet transfer very efficient. The inhibition of production of V by naphthalene indicates that V is generated from the lowest energy triplet of [2.2]paracyclophane.

The results of photolysis of III in acetone point to the same conclusion. The singlet and triplet energies of acetone are not known exactly because the phosphorescence and fluorescence emission spectra strongly overlap. However, the singlet energy is not greater than 84 kcal and the triplet not less than 75 kcal.²⁰ Thus, acetone has a triplet energy higher than that of [2.2]paracyclophane by at least 6 kcal, and triplet energy transfer from acetone to the cycle should be favorable. The fact that acetone has a lower singlet energy than [2.2]paracyclophane should make singlet energy transfer from acetone to the cycle unfavorable. These energy relationships coupled with the observation that *p*-ethylbibenzyl (V) was the sole volatile product in acetone as solvent indicates that this substance arises from the lowest triplet of [2.2]paracyclophane, and that the other photolysis products must come from other excited states. The ring-opening stage in the production of V is undoubtedly facilitated by the release of strain inherent in the ring system. The probable mechanism is formulated

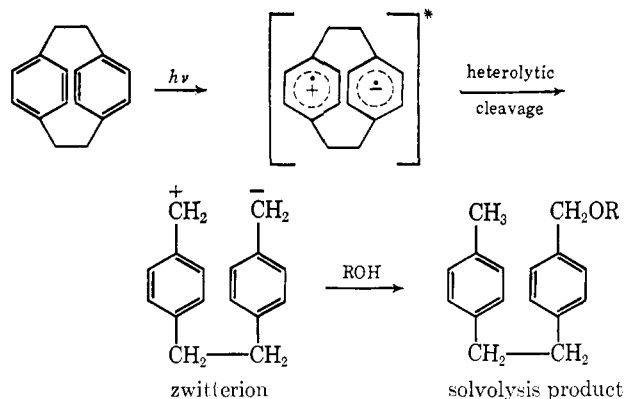


Photochemistry Leading to Solvolysis Products.

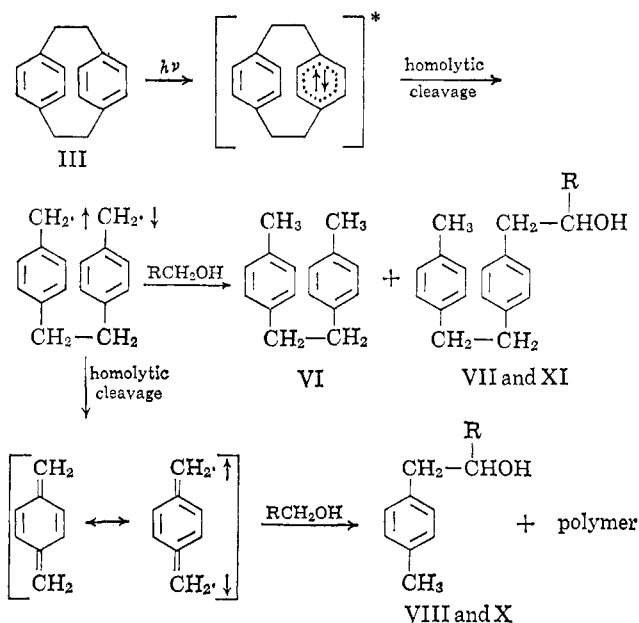
When [2.2]paracyclophane was photolyzed in methanol-*O-d*, the methyl of the *p*-tolyl group of ether IV contained one atom of deuterium. This experiment demonstrated that ethers IV and IX must have arisen by addition of two adjacent benzyl groups of [2.2]paracyclophane across the O-H bond of methanol and ethanol, respectively. Additions of radicals across the O-H bond are unknown, whereas polar additions of alcohols in fragmentation solvolysis reactions are common.²¹ Thus, production of ethers IV and IX from [2.2]paracyclophane (III) and alcohols resembles solvolytic fragmentation reactions known to involve polar intermediates or transition states.

Ether IX was the exclusive product when III was photolyzed with light at 2537 Å. This wavelength is close to an absorption band in the ultraviolet spectrum of [2.2]paracyclophane which occurs at about 2440 Å, and seems to involve charge transfer in the singlet excited state. The character of the product suggests that the excited state cleaves to produce a zwitterion

which, in turn, reacts with solvent. Alternatively, the excited state could react directly with solvent as the benzyl-benzyl bond cleaves. The phenomenon of electron transfer between the rings is not without precedent as Weissman has measured the rate of electron exchange between rings in the radical anions derived from the smaller [*m,n*]paracyclophanes.²² Although the proposed zwitterion is a high-energy species, the energy of the light combined with the strain released on ring cleavage could be enough to produce the proposed zwitterion in a little-solvated state, although the evidence is far from conclusive.



Photochemistry Leading to *p,p'*-Dimethylbibenzyl (VI) and the Various Alcohols (VII, VIII, X, and XI). These products were produced only by radiation below 2537 Å, and so must arise from an excitation of higher energy than either the first singlet or first triplet. Since loss of vibrational energy in higher electronic states is much faster than intersystem crossing, it is unlikely that a triplet is an intermediate here.¹⁹ In all probability, a high singlet is involved, and this excited state undergoes homolytic dissociation before the molecule undergoes any loss of vibrational energy. The resulting biradical then might partition between reaction with alcohol and further homolytic dissociation.

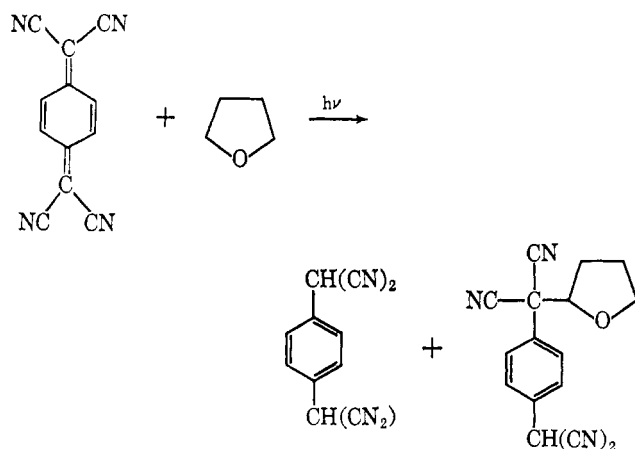


(20) W. A. Noyes, Jr., G. B. Porter, and J. E. Jolley, *Chem. Rev.*, **56**, 49 (1956).

(21) C. A. Grob, W. Schwarz, and H. P. Fischer, *Helv. Chim. Acta*, **45**, 1385 (1964), and references cited therein.

(22) S. I. Weissman, *J. Am. Chem. Soc.*, **80**, 5342 (1958).

Some analogy for the photolytic cleavage of III to *p*-xylene is found in the report that a pyrolytic cleavage occurs at about 550°. The postulated 1,6-radical addition to *p*-xylene is similar to the photolytic addition of tetrahydrofuran to 7,7,8,8-tetracyanoquinodimethane.²⁴



Experimental Section

Materials. Recrystallization of commercial [2.2]paracyclophane (III) from chloroform gave material, mp 286–287°. Naphthalene, reagent grade, was recrystallized from ethanol, mp 79.5–80°. Spectroscopic grade methanol, ethanol, 2-propanol, acetone, and cyclohexane were employed as solvents. Melting points were taken on a Fisher-Johns melting point block and are uncorrected.

Spectra. All ultraviolet spectra were taken at 25° in a 1-cm cell with a Cary Model 14 spectrophotometer in 95% ethanol. The nmr spectra were taken on a Varian Associates A-60 instrument with carbon tetrachloride as solvent and tetramethylsilane as internal standard. Infrared spectra were run on a Beckman spectrophotometer, Model IR-5.

Chromatography. Silica Gel G layers, 0.25 mm thick, on glass plates were used in the thin layer chromatography. The plates were developed in an iodine chamber.

Analytical vapor phase chromatography was performed on an F and M temperature program Model 720 machine. A 3-ft column, 0.25 in. in diameter, packed with 20% silicone gum (SE-30) on 60–80 firebrick was used in all analytical work. The temperature was isothermal at 225°, and a helium pressure of 35 psi was used. The retention times in minutes were as follows: alcohol VIII, 1.4; alcohol X, 2.0; hydrocarbon V, 6.7; hydrocarbon VI, 7.2; hydrocarbon III, 8.8; ether IV, 14.0; ether IX, 18.5; alcohol VII, 21.0; alcohol XI, 27.6. Preparative vpc was performed on a homemade (flame detector) machine with a 6-ft long column, 0.5 in. in diameter, with the same packing as the analytical column. The column temperature was 180°, the preheater 220°, and 15 psi of helium pressure was employed.

Irradiation Apparatus. In most of the experiments, a Hanovia immersion well reactor was used. The light source was a Hanovia medium-pressure Type 54A36 200-w lamp. Cylindrical filter sleeves were placed around the light source for the irradiations in Corex and Vycor. For the irradiations in methanol-*O-d* and acetone, quartz test tubes were suspended around the light source. All experiments were performed in an atmosphere of purified nitrogen, and the solution was swept with nitrogen for 15 min. before it was illuminated. The mixture was stirred magnetically during the reaction.

A Nester Faust Model NFUV-300 low-pressure lamp was used with an emission, 90% of which is at 2537 Å.

Irradiation in Methanol. Irradiation was performed on 0.700 g of [2.2]paracyclophane in 700 ml of methanol. The solution was heterogeneous initially, and the paracyclophane gradually dissolved as it reacted. In initial runs, aliquots were removed and analyzed by vpc, nmr, and tlc after 6, 12, and 24 hr. The distribution of products was independent of the reaction time. Irradiations in which products were isolated were run for 5 days. After reaction

was complete, the mixture was filtered to remove starting material and polymer. The filtrate was evaporated under reduced pressure to about 75 ml, the [2.2]paracyclophane that had crystallized was filtered, and the remaining solvent was evaporated at 25°. The residue was dissolved in 25 ml of benzene. The resulting solution was chromatographed on a 100-g silica gel column made up in pentane. Elution of the column with pentane (3 l.) produced hydrocarbon V (R_f 0.60 on tlc, pentane developer), hydrocarbon VI (R_f 0.55 on tlc, pentane developer), and unreacted III (R_f 0.38, pentane developer). Hydrocarbons V and VI did not completely separate, but the nmr spectra of the mixed fractions were used to distinguish the amounts of the components (integration of peak areas). The yield of V was 0.015 g (2%), of VI was 0.040 g (6%), and of unreacted III was 0.145 g (21%). Elution of the column with 5% ether–95% pentane provided 0.250 g (31%) of ether IV. Elution of the column with 10% ether–90% pentane produced only traces of compound. Elution with 20% ether–80% pentane gave 0.030 g (3%) of alcohol VIII (R_f 0.30, 40% ether–60% pentane developer) and 0.025 g (3%) of alcohol VII with R_f 0.20, 40% ether–60% pentane developer. More polar solvent mixtures up to 10% methanol–90% ether gave only traces of insoluble, nonsublimable material.

Hydrocarbon VI was purified by crystallization from ether–hexane and sublimation at 70° (0.05 mm). The melting point of sublimed material was 78–80°, undepressed by admixture with an authentic sample of mp 79–80°. The vpc, nmr, and tlc of the irradiation product were identical with those of the authentic sample. Hydrocarbon V, a liquid with bp 292°, was identical in all respects (vpc, nmr, and tlc) with the product obtained by irradiation of III in ethanol where larger quantities were obtained.

Anal. Calcd for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.50; H, 8.61.

Unreacted III was identified by vpc, tlc, and nmr.

Ether IV was purified by molecular distillation at 90° (0.05 mm), mp 45–46°.

Anal. Calcd for $C_{17}H_{20}O$: C, 84.96; H, 8.39. Found: C, 84.96; H, 8.37.

Alcohol VIII was identical (tlc, nmr, and vpc) with an authentic sample (see below). Alcohol VII, pure to vpc and tlc, was sublimed at 90° (0.05 mm), mp 94–96°.

Anal. Calcd for $C_{17}H_{20}O$: C, 84.96; H, 8.39. Found: C, 83.85; H, 8.53.

The same techniques were applied to the products of irradiation in methanol with Corex and Vycor filters. The results are tabulated in Table I.

Irradiation in methanol-*O-d* (99.8% of one atom of deuterium, prepared from trimethyl orthoformate and deuterium oxide)²⁵ was conducted in a quartz test tube suspended at the side of the light source with a clamp under purified nitrogen. Ether IV was isolated by the above procedure (23% yield), and was pure to vpc and tlc. Deuterium analysis was performed by integration procedures on the nmr spectrum of this material, and is good to an estimated $\pm 5\%$.

Reduction of Ether IV to Hydrocarbon VI. To a mixture of 0.10 g of ether IV in 100 ml of ether and 50 ml of liquid ammonia at its boiling point were added small pieces of sodium metal until a dark blue color persisted. After 4 hr, the solution was neutralized with ammonium chloride, the ammonia was allowed to evaporate, and ether was added. The salts that separated were filtered, the solution was evaporated, and the residual solid was sublimed to give 0.08 g of hydrocarbon VI, mp 78–80°, undepressed by admixture with product from irradiation. This compound possessed the same spectral properties as authentic material.

β -*p*-Methylphenylethyl Alcohol (VIII). To a solution of 2.0 g of lithium aluminum hydride in 100 ml of ether was cautiously added 5.0 g of *p*-tolylacetic acid dissolved in 100 ml of ether. After 10 hr, water was added cautiously, and the product isolated by the usual extraction procedures. Preparative vpc gave 4.0 g (83%) of VIII, which was pure to vpc and tlc.

Irradiations in Ethanol. The procedures paralleled those carried out in methanol. Ether X was eluted from the chromatogram with 5% ether–95% pentane, and alcohols X and XI were eluted with 20% ether–80% pentane. X was purified by preparative vpc.

Anal. Calcd for $C_{18}H_{22}O$: C, 84.99; H, 8.72. Found: C, 85.15; H, 8.66.

Alcohols X and XI were not separated, but were analyzed as a

(23) W. F. Gorhan, German Patent 1,085,673 (1960); *Chem. Abstr.*, 55, 22920 (1961).

(24) J. Dieckmann and C. J. Pedersen, *J. Org. Chem.*, 28, 2879 (1963).

(25) C. Solis, *Ber.*, 15, 1681 (1882).

(26) D. J. Cram and A. S. Wingrove, *J. Am. Chem. Soc.*, 86, 5490 (1964).

mixture with nmr techniques. The hydrocarbons III, V, and VI were isolated as in the methanol irradiation experiments. Table II records the results.

The quenching experiment with naphthalene was identical with run 6 (Table II) except that the irradiation medium was 0.01 *M* in naphthalene. Naphthalene (0.900 g) appeared in the isolation procedure during elution of the silica gel column with pentane, and came off just ahead of unreacted III.

The quenching experiment with oxygen was identical with run 7 (Table II) except that the system was left open to the air. After 2 days reaction time, 95% of III had undergone reaction, and yet no V or VI could be detected among the products by vpc or tlc analytical techniques.

Irradiation in Acetone. The irradiation experiment was conducted in two quartz test tubes suspended around the immersion well. No filter was used. Each test tube contained 0.075 g of III and 100 ml of acetone. The reaction was run for 5 days, the solution was filtered, and the solvent was evaporated. The residue was extracted with ether, and the extract was evaporated. The residue was submitted to preparative vpc, and 0.035 g (23%) of hydrocar-

bon V was isolated, as well as 30% of the starting material. Hydrocarbon V was identified by vpc, tlc, and nmr comparisons with authentic material.

Effect of Solvent on Yield of *p*-Ethylbibenzyl (V). Irradiations of III (0.700 g) in methanol, ethanol, 2-propanol, and cyclohexane were carried out under identical conditions (Corex for 3 days) for comparative purposes. The hydrocarbon products were separated on preparative vpc, and Table III records the results. The solubilities of III in the four solvents were determined by saturating the solvent with III, and analyzing an aliquot of the saturated solution by vpc.

Irradiation with Low-Pressure Lamp. The apparatus used was the same as in the other experiments except that a Nester Faust Model NFUV-300 low-pressure mercury lamp was used as light source. This lamp has an emission, 90% of which is at 2537 Å. The experiment was conducted with 0.700 g of III in 700 ml of ethanol in quartz for 2 days. The only products detected (vpc, good for detection of less than 0.5% of V, VI, X, and XI) were 55% yield of unreacted III, and a 15% yield of ether IX, isolated by silica gel column chromatography.

Macro Rings. XXXIII. A 1,6 to 1,6 Cycloaddition Reaction, a Diels–Alder Insertion Reaction, and Bent Benzene Rings^{1,2}

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Abstract: The two tetraenes, *p*-xylylene (I) and its furan analog (II), when generated in the presence of one another, underwent 1,6 to 1,6 cycloaddition reactions to give the monofuran analog (III) of [2.2]paracyclophane as the major product, and [2.2]paracyclophane (IV) and its difuran analog (V) as minor products. The monofuran analog (III), when allowed to stand in hexane in the sunlight in contact with air, slowly produced [2.2.2]paracyclophane (VI). The difuran analog (V) underwent a multiple Diels–Alder reaction with dimethyl acetylenedicarboxylate to give the very highly condensed polycyclic compound (VII) which when heated reverted to the starting materials. Treatment of III with zinc and hydrochloric acid gave [8]paracyclophane (X), whose spectral and chemical properties indicated the benzene ring to be seriously deformed from a planar configuration. Hydrolysis of III produced 3,6-diketo[8]paracyclophane (XI), which through formation of its monothioacetal (XIII) and treatment of this substance with Raney nickel, gave 3-keto[8]paracyclophane (XIV), 3-hydroxy[8]paracyclophane (XV), and 3-keto-4-[8]paracyclophane (XVI). The ultraviolet spectrum of the last substance indicated that the two chromophores were somewhat coupled with one another. The tosylate of alcohol XV when acetylated gave 4-[8]paracyclophane (XIX) as the major product, and bridge-aromatic ring alkylated material (XX) as the minor product. The rate of this reaction was 52 times faster than that of cyclohexyl tosylate. Oxidative hydrolysis of monofuran analog III gave *cis*-3,6-diketo-4-[8]paracyclophane (XXIII), which when heated gave the *trans* isomer (XXII). Each of these isomers when treated with butadiene gave the corresponding isomeric adducts (XXVI and XXVII), which resisted attempts at aromatization. The *trans*-enedione (XXII) when treated with *l*-menthyl *N*-aminocarbamate formed the bis-hydrazone (XXIX) in high yield, and the substance appeared to be a single chemical entity (not a mixture of diastereomers). The ultraviolet, infrared, and nuclear magnetic resonance (nmr) spectra of many of these compounds were taken, and the last were particularly useful in making structural assignments.

In previous papers of this series,³ the spectral, π -base strength, and chemical properties of the [*m*]- and [*m.n*]paracyclophanes were compared both with one another and with open-chain model compounds

(1) This investigation was supported in part by grants from the National Science Foundation and the U. S. Army Research Office (Durham). The authors wish to thank these agencies for their interest.

(2) Parts of this paper were reported in communication form: D. J. Cram and G. R. Knox, *J. Am. Chem. Soc.*, **83**, 2204 (1961).

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These comparisons allowed an identification of transannular electronic effects and of benzene ring deformation effects in the [*m.n*]paracyclophanes, particularly since the lower homologs of the [*m*]paracyclophanes contain nonplanar benzene rings without being pressed face to face with a second aromatic nucleus. Since conventional methods of synthesis of the [*m*]paracyclophanes failed when *m* = 9, and the next lower homolog (*m* = 8) was desired, an indirect approach to this substance was developed, inspired by the 1,6 to 1,6 cycloaddition reactions of Winberg, *et al.*⁴ The synthetic

(4) H. E. Winberg, F. S. Fawcett, W. E. Mochel, and C. W. Theobald, *ibid.*, **82**, 1428 (1960).