crystallization was methylated with ethereal diazomethane at 0°. The *endo*- and *exo*-methyl esters were separated[11] by glpc through a 0.25 in. × 15 ft column of Carbowax at 160°. Retention times for the *endo* and *exo* isomers were 47 and 39 min, respectively.

Spectra were obtained on a Varian HR60 spectrometer, modified by the inclusion of an internal field-frequency control system,[20] and equipped with an NMR Specialties decoupler. The calculated spectra were obtained by means of the LAOCOON II program[21] on an IBM 7094 computer. The 100-Mcps spectrum was obtained without deuterium decoupling on a Varian HA100 spectrometer, through the kindness of Professor D. T. Sawyer, University of California, Riverside, Calif.

Acknowledgment. This research was supported by a research grant from the University of California.

(20) F. A. L. Anet and A. J. R. Bourn, *J. Am. Chem. Soc.*, **89**, 760 (1967).

(21) S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3863 (1964). We wish to thank Dr. Bothner-By for providing us with a copy of this program.

Photochemical Cyclobutanol Formation of an Aryl Ketone. The Scope and Mechanism of the Reaction[1-3]

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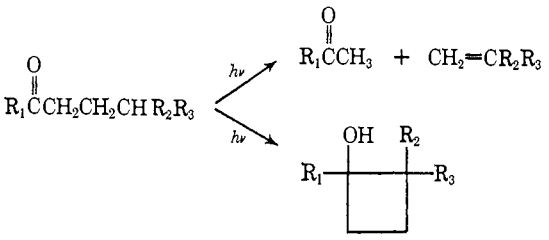
Abstract: The photochemistry of *trans*-1,4-diphenyl-3,4-epoxybutan-1-one (II) was investigated. The photolysis in benzene of II has been found to afford four products. The structures have been assigned as acetophenone, phenylacetic acid, dibenzoylethane, and *cis*-1,2-diphenyl-2,3-epoxy-1-cyclobutanol. Evidence is reported for the structure of the cyclobutanol epoxide. A mechanism involving intramolecular hydrogen transfer from carbon to the p_y orbital of oxygen of the n–π* excited state to produce a spin-unpaired 1,4-biradical intermediate is postulated and discussed.

Studies of the photochemistry of ketones that possess a hydrogen-bearing γ carbon have shown that two major reaction pathways are available. The first involves a photoelimination reaction, commonly called the Norrish type-II cleavage,[6] to yield olefins and smaller carbonyl compounds, and the second involves the formation of cyclobutanols[7] (eq 1). Both reactions appear to be intramolecular with little or no detectable side reactions and have been visualized as arising from a common biradical intermediate.[8]



(1)

Recent studies[9-12] have verified Noyes' suggestion[13] that the Norrish type-II process proceeds by intramolecular hydrogen transfer to yield an olefin and an enol. Although the identification of the excited states responsible for the Norrish type-II process is now well established, considerable controversy exists as to the exact mechanism and nature of the excited state responsible for cyclobutanol formation. Two mechanisms have been considered to account for the photochemical formation of cyclobutanols, one a concerted mechanism and the other a stepwise process. In the original mechanism suggested by Yang,[7] a two-step reaction of hydrogen abstraction followed by ring closure was postulated. More recently, Yang has provided further proof that ketones containing γ hydrogens undergo cyclobutanol formation from their triplet states.[14] The extension of this photochemical reaction to aliphatic optically active starting materials with a single asymmetric carbon atom in a γ position to the carbonyl group has been realized in the work of Jeger[15] and Schulte-Elte and Ohloff.[16] The direct irradiation of (6*S*)-(+)-2,5-dimethyloct-7-en-3-one was found to result in cyclobutanol formation with retention of optical activity. The fact that only one of the possible stereoisomers was formed led

(1) Support of this research by a grant from the Air Force Office of Scientific Research (Grant No. AF-AFOSR-1213-67) is acknowledged with appreciation.

(2) Photochemical Transformation of Small Ring Carbonyl Compounds. XIV. For part XIII, see A. Padwa and L. Hamilton, *J. Heterocyclic Chem.*, **4**, 118 (1967).

(3) For a preliminary report of this work, see A. Padwa, *J. Am. Chem. Soc.*, **87**, 4205 (1965). This work was presented in part at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965.

(4) To whom inquiries should be directed at the Department of Chemistry, State University of New York at Buffalo, Buffalo, N. Y. 14214.

(5) (a) National Science Foundation Undergraduate Research participant, summer 1965; (b) National Science Foundation Predoctoral Fellow, 1963–1965; National Institutes of Health Predoctoral Fellow, 1965–1966; (c) National Institutes of Health Predoctoral Fellow, 1966–present.

(6) C. H. Bamford and R. G. W. Norrish, *J. Chem. Soc.*, 1504 (1935).

(7) N. C. Yang and D. D. H. Yang, *J. Am. Chem. Soc.*, **80**, 2913 (1958).

(8) H. E. Zimmerman, Abstracts, 17th National Organic Chemistry Symposium, Bloomington, Ind., June 1961, p 31.

(9) R. Srinivasan, *J. Am. Chem. Soc.*, **81**, 5061 (1959).

(10) G. R. McMillan, J. G. Calvert, and J. N. Pitts, Jr., *ibid.*, **86**, 3620 (1964).

(11) P. J. Wagner and G. S. Hammond, *ibid.*, **88**, 1245 (1966).

(12) T. J. Dougherty, *ibid.*, **87**, 4011 (1965).

(13) W. Davis, Jr., and W. A. Noyes, Jr., *ibid.*, **69**, 2153 (1947).

(14) N. C. Yang, A. Morduchowitz, and D. H. Yang, *ibid.*, **85**, 1017 (1963).

(15) I. Orban, K. Schaffner, and O. Jeger, *ibid.*, **85**, 3034 (1963).

(16) K. Schulte-Elte and G. Ohloff, *Tetrahedron Letters*, 1143 (1964).

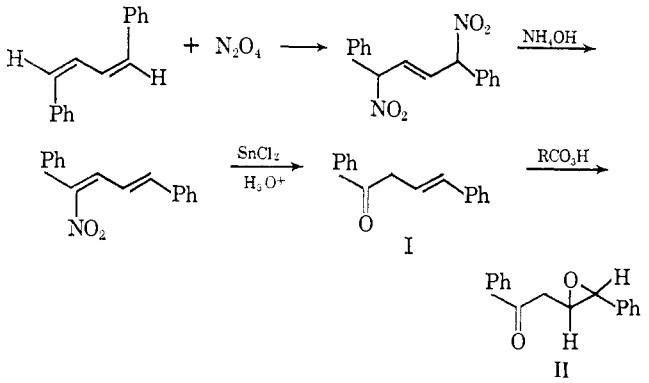
Schulte-Elte and Ohloff to favor a one-step, concerted reaction for cyclobutanol formation. This presumably implies direct reaction of the excited singlet state. The stereochemical results can still be interpreted in terms of a diradical, however, if it is assumed that reversal of electron spin and cyclization proceeds as fast as, or even faster than, rotation about single bonds. This latter interpretation implies that the reactive state responsible for reaction is a triplet n-π^* excited state. On the basis of the previously existing experimental data, these two mechanisms have not yet been fully differentiated.

As part of a broad program on the photochemical transformations of small-ring carbonyl compounds,[17] an investigation was initiated to determine whether a triplet biradical state was an essential intermediate in photochemical cyclobutanol formation. The present investigation is concerned with the photochemical properties of a β,γ-epoxy ketone and the structural modifications that have been made to provide further insight into the mechanism of the photoreaction. In this paper we describe results pertaining to the as yet unresolved problem of elucidating the nature of the primary photochemical process occurring in cyclobutanol formation.

Results and Discussion

trans-1,4-Diphenyl-3,4-epoxybutan-1-one (II) was chosen for the present study. In contrast to the exhaustive studies concerned with the photochemistry of α,β-epoxy ketones[18] there has been no attempt to examine the phototransformations of the related β,γ-acyl oxide system. We were led to investigate the photochemistry of this particular compound in an attempt not only to ascertain the available photolytic pathways but also to elucidate the details of cyclobutanol formation. The four-step synthesis of *trans*-1,4-diphenyl-3,4-epoxybutan-1-one (II) illustrated in Chart I employs a modification of the sequence used by Wieland and Stenzl for the preparation of *trans*-1,4-diphenyl-3-buten-1-one (I).[19] Stereospecific epoxidation of *trans*-keto olefin I with *m*-chloroperbenzoic acid in methylene

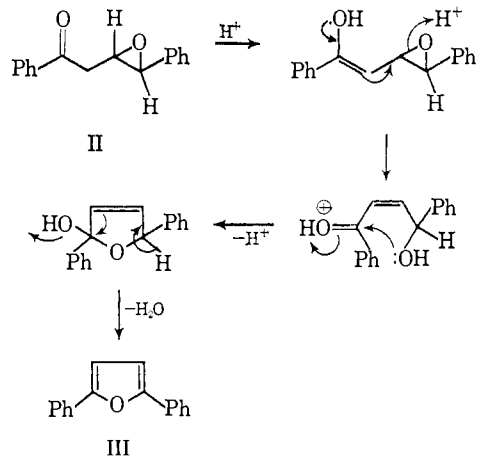
Chart I



chloride afforded in excellent yield the desired starting material. The spectra data (infrared, ultraviolet, nmr) and elemental analysis were consistent with structure II and are summarized in the Experimental Section.

The irradiation of II was conducted using an internal water-cooled mercury arc lamp (Hanovia, Type L, 450 w) with a Pyrex filter to eliminate wavelengths below 280 mμ. The photolysis was followed by withdrawal of small samples at fixed intervals and examination of these by thin layer chromatography. Upon irradiation of 1.0 g of II in benzene for 8 hr, the spot on a thin layer plate due to II had completely disappeared, and several new spots had appeared in its place. Chromatography of the crude photolysis mixture on Woelm alumina (activity II) afforded acetophenone, 2,5-diphenylfuran (III), and dibenzoylethane (IV). The formation of 2,5-diphenylfuran (III) was shown by control experiments to be the result of a ground-state acid-catalyzed rearrangement of II, which presumably arose *via* the mechanistic path shown in Chart II.

Chart II



When the photolysis apparatus was thoroughly cleansed and then washed with dilute base prior to use, no 2,5-diphenylfuran was detected. By using scanning liquid–liquid partition chromatography,[20] the crude photolysis mixture could be resolved into five peaks. In addition to unreacted II, four new compounds were obtained. The major products were identified as dibenzoylethane (IV), mp 142–143°, and *cis*-1,2-diphenyl-2,3-epoxy-1-cyclobutanol (V), mp 141–142°. The two minor components were shown to be acetophenone and phenylacetic acid. In a typical run the irradiation of 1.0 g of II afforded 0.08 g of phenylacetic acid, 0.07 g of acetophenone, 0.24 g of IV, and 0.36 g of V.

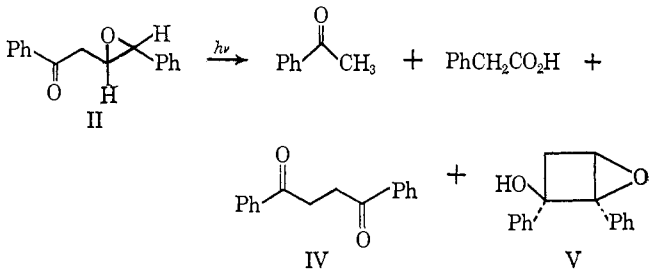
The structure of V was elucidated by elemental analysis, infrared, ultraviolet, nmr, and chemical degradation. The pure cyclobutanol V was a solid (white needles from ethanol), mp 141–142°. The elemental analysis of this component (*Anal.* Calcd for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92. Found: C, 80.47; H, 5.90) indicates that it is an isomer of II. The molecular weight (calcd 238, found 226) is consistent with a monomeric unit. The high-dilution infrared spectrum ($CHCl_3$) of V shows a sharp strong intramolecular hydrogen bond (3559 cm^{-1}); the infrared band corresponding to a nonbonded hydroxyl stretching frequency

(17) A. Padwa in "Organic Photochemistry," Vol. I, O. L. Chapman, Ed., Marcel Dekker, Inc., New York, N. Y., 1967, p 92.

(18) (a) C. K. Johnson, B. Dominy, and W. Reusch, *J. Am. Chem. Soc.*, **85**, 3894 (1963); (b) H. E. Zimmerman, R. B. Cowley, C. Y. Tseng, and J. W. Wilson, *ibid.*, **86**, 947 (1964); (c) O. Jeger, K. Schaffner, and H. Wehrli, *Pure Appl. Chem.*, **9**, 555 (1964); (d) E. F. Ullman, *J. Am. Chem. Soc.*, **85**, 3529 (1963); (e) J. M. Dunston and P. Yates, *Tetrahedron Letters*, 505 (1964); (f) H. E. Zimmerman and R. D. Simkin, *ibid.*, 1847 (1964).

(19) G. Wieland and R. Stenzl, *Ber.*, **40**, 4825 (1907).

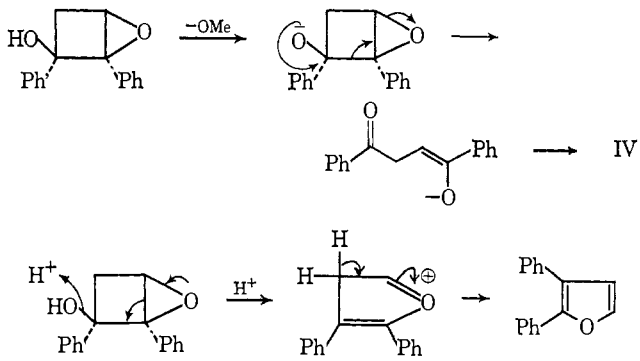
(20) H. E. Zimmerman and D. Schuster, *J. Am. Chem. Soc.*, **84**, 4527 (1962).



was absent. Increasing the concentration by factors up to 50 causes little change in the peak shape or position. The infrared spectrum of related model systems, in which the tertiary hydroxyl group has a similar steric environment, revealed the presence of extensive polymeric association. The fact that the absorption due to this bond is strong and is invariant with concentration suggests that the hydroxyl group of V is *cis* to the oxide ring. The ultraviolet spectrum (95% ethanol) with maxima at 260 and 265 mμ (ϵ 525 and 440) is characteristic of two isolated benzene rings. The nmr in deuteriochloroform shows the methylene hydrogens as a pair of doublets at τ 7.87 and 7.32 (J = 13 cps), the hydroxyl proton as a singlet at τ 6.51, the tertiary hydrogen as a singlet at τ 5.40, and the aromatic hydrogens as a multiplet centered at τ 2.69. The peak areas are in the ratio of 1:1:1:10. It is noteworthy that the tertiary oxide hydrogen does not couple individually with the neighboring cyclobutane protons. Karplus has shown that the mutual spin–spin interaction experienced by the protons of an HCCH system is a function of the dihedral angle defined by that system.[21] The relevant dihedral angles are seen from models to be approximately 40 and 90°. The lack of coupling between the two protons whose dihedral angle is 90° is to be expected based on the Karplus correlation.[21] The fact that no spin–spin coupling was observed for the other set may be attributed to the fact that the coupling constant is not a function of the dihedral angle alone, and other variables such as bond length and electronegativity, as well as hybridization, must be taken into account if reliable quantitative predictions are to be made. Thus, Karplus has cautioned against the indiscriminate use of these equations without the proper cognizance of structural discrepancies.[22]

We found that V is converted rapidly to dibenzoylethane by chromatography on Woelm base-washed alumina but can be recovered unchanged from liquid–liquid partition chromatography. Further evidence for the cyclobutanol oxide structure was provided by the observation that V was quantitatively converted with base to dibenzoylethane, whereas treatment with acid gave 2,3-diphenylfuran[23] as the major product.[24] A reasonable mechanism for these transformations is presented below.

(21) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).
(22) M. Karplus, *J. Am. Chem. Soc.*, **85**, 2870 (1963).
(23) A. Padwa, *Tetrahedron Letters*, 1049 (1965).
(24) An alternate mechanism for the acid-catalyzed dehydration of V to 2,3-diphenylfuran which involves the transient existence of 1,2-diphenyl-5-oxabicyclo[2.1.0]pent-2-ene is not favored, primarily because all attempts to trap the reactive olefin with various dienes failed. Also, the dehydration of V could be followed spectroscopically by scanning the ultraviolet spectrum of the reaction mixture at 4° in a thermostated quartz cell. Analysis of the spectral curves obtained after 2 min showed that they were composed of overlapping spectra of V and 2,3-diphenylfuran. No absorption attributable to a transient Dewar furan was discernible. These data suggest that a diphenyl-substituted Dewar furan is not formed in the dehydration of V.

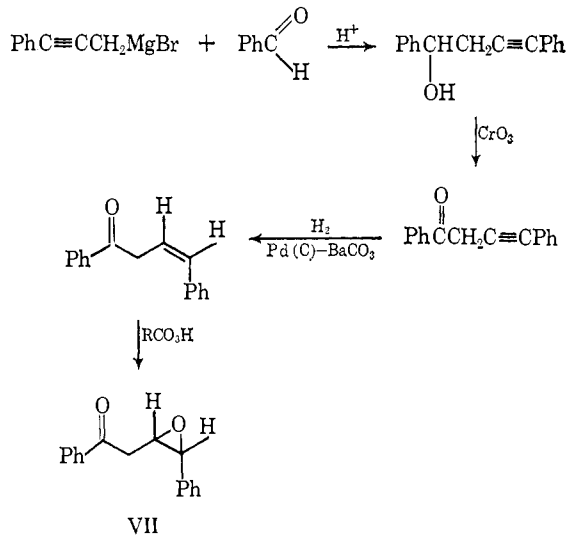


Several questions arise as a result of the observations just described. The first was whether dibenzoylethane is a primary photoproduct or instead arose from V, either photochemically or under "work-up" conditions. The question was resolved quickly by the finding that V can be recovered unchanged when subjected to the same photolytic conditions that were used for II. Furthermore, it was noted that neither II nor V afforded dibenzoylethane when subjected to liquid–liquid partition chromatography. This clearly indicates that IV is a primary reaction product.

The second question is whether a common precursor is responsible for the formation of both IV and V. It was found that in the 2537-A photolysis of styrene oxide one could obtain yields of 30–40% of phenylacetaldehyde. Similarly, Griffin has observed that 2537-A irradiation of β-methylstyrene oxide afforded phenylacetone.[25] These results suggest that IV may be formed by intramolecular energy transfer from the excited carbonyl chromophore to the epoxide ring followed by hydrogen migration. This mechanism does not appear attractive, however, in view of the failure of propiophenone or benzophenone to photosensitize the rearrangement of styrene oxide when light of greater than 290-mμ wavelength was used. To further answer this question and to provide information needed to substantiate the mechanism to be outlined later, the irradiation of *cis*-1,4-diphenyl-3,4-epoxybutan-1-one (VII) was studied.

A direct approach to the synthesis of VII involves four steps as is illustrated in Chart III. The spectral

Chart III



(25) G. Griffin, private communication.

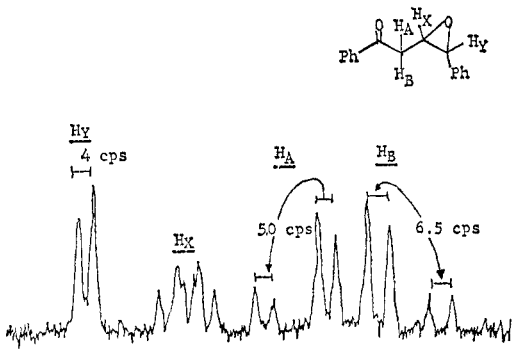
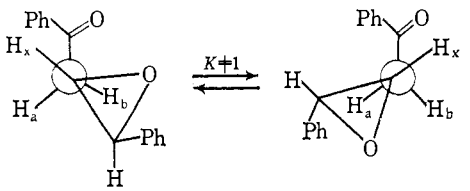


Figure 1. Partial nmr spectrum (60 Mc) of *cis*-1,4-diphenyl-3,4-epoxybutan-1-one (VII), showing multiplet arising from magnetically nonequivalent methylene protons.

data (infrared, ultraviolet) and elemental analyses were consistent with structure VII and are summarized in the Experimental Section. Epoxide VII showed the expected magnetic nonequivalence of the methylene protons adjacent to the epoxide ring, there being the predicted eight-line multiplet (AB part of an ABX spectrum) centered at τ 7.22 with δ_{AB} 0.44 ppm and J_{AB} = 17 cps. An interesting feature of the octet is the fact that the vicinal coupling constants J_{AX} and J_{BX} are different, as seen in Figure 1.

A reasonable explanation for the unequal coupling of H_X with the adjacent nonequivalent methylene protons H_A and H_B is that preferred conformations I and II (below) are unequally populated, due to the asymmetry of the oxide ring. Thus δ_{AB} would be expected to be large because of the preferential shielding of either H_A or H_B by the oxide ring.[26] Furthermore, it can be seen that the less shielded methylene proton would be essentially *gauche* to H_X (on a time-average basis),

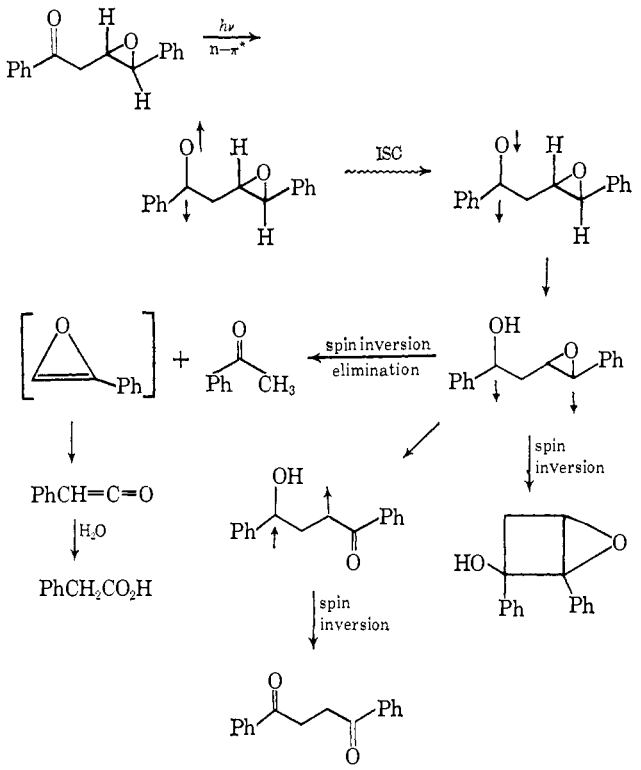


whereas the more highly shielded proton is *trans*. This should result in the low-field proton having a smaller vicinal coupling constant, exactly[21] as is observed (Figure 1).

In an attempt to ascertain the reality of a mechanism for the formation of IV involving energy transfer to the epoxide ring followed by ring opening and subsequent hydrogen migration, we studied the photochemistry of *cis*-epoxide VII. The close resemblance in structure of VII to II prompted this attempt. It was felt that the mechanism described above should be independent of the relative position of the substituents on the three-membered ring. Experimentally, prolonged irradiation of VII afforded only recovered starting material. This observation is not compatible with the above mechanism and instead adds credence to the supposition that a common precursor is responsible for the formation of both IV and V.

Among the several mechanistic schemes that might be considered adequate to explain the formation of the photoproducts formed from II, we currently favor the one outlined below. It is based on the knowledge that hydrogen abstraction of aryl ketones proceeds by way of their n–π* triplet state. Thus, Hammond and coworkers clearly demonstrated the role of benzophenone triplet in the hydrogen-abstraction dimerization reaction giving benzopinacol.[27] Furthermore, they adequately showed that the Norrish type-II cleavage occurs exclusively from triplet states of the phenyl ketones examined[11] (Chart IV). In this postulated mechanism,

Chart IV



intramolecular hydrogen transfer from carbon to the p_y orbital of oxygen of the n–π* excited state produces a spin-unpaired 1,4-biradical intermediate. In the case of VII, the excited n–π* state is geometrically incapable of internal hydrogen abstraction, thereby accounting for the lack of reactivity. The 1,4 biradical has to undergo spin inversion prior to ring closure (or elimination) in order to produce products in their singlet ground states. Photoelimination yields the enol form of acetophenone and phenyloxirene as a transient intermediate. Rearrangement of the oxirene to phenylketene followed by reaction with water accounts for the presence of phenylacetic acid.[28]

The isolation of dibenzoylethane in addition to acetophenone and cyclobutanol V makes the intermediacy of a 1,4 biradical, from which both types of product could result, especially appealing. Opening of the three-membered oxide ring should occur with considerable ease. The demonstrated free-radical ring opening of propylene oxide to produce a keto radical provides

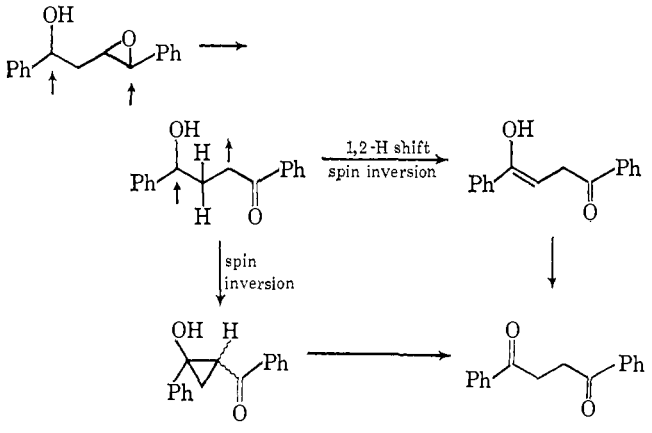
(26) K. Tori, K. Kitahonoki, Y. Takano, H. Tanida, and T. Tsuji, *Tetrahedron Letters*, 559 (1964).

(27) G. S. Hammond, W. P. Baker, and W. M. Moore, *J. Am. Chem. Soc.*, **83**, 2795 (1961).

(28) It has been shown that, in the peracid oxidation of acetylenes, substituted oxirenes serve as intermediates.[29] It has been suggested that one of the dominant pathways of these species involves rearrangement to produce ketenes.

(29) (a) R. N. McDonald and P. A. Schwab, *J. Am. Chem. Soc.*, **86**, 4866 (1964); (b) J. K. Stille and D. D. Whitehurst, *ibid.*, **86**, 4871 (1964).

reasonable analogy.[30] The 1,3 diradical thus formed easily accommodates formation of dibenzoylethane by an unusual but not unprecedented 1,2 hydrogen migration. Schuster and Krull invoked such a mechanism to explain the photochemistry of spiro[2.5]octa-4,7-dien-6-one-1,1,2,2-d_4.[31] Similarly, Griffin and co-workers have postulated 1,2 hydrogen shifts in the photochemical interconversions of various phenyl- and benzoyl-substituted cyclopropanes and propenes in solution.[32] Alternatively, it may be argued that ring closure of the 1,3 diradical occurs to produce 1-phenyl-2-benzoylcyclopropanol followed by a ground-state ring opening.[33]



With the evidence that has now been presented, we might conclude that this establishes a 1,4-biradical intermediate as the species initially responsible for product formation. This is a reasonable but not rigorous conclusion. Additional evidence in support of this mechanism is obtained from experiments using methanol-d_1. When a solution of II in CH_3OD was irradiated with a 450-w Hanovia source, the recovered IV was found to contain 0.9–1.1 atoms of deuterium per molecule. The recovered starting material was examined by infrared and nmr; the spectra obtained gave no evidence for any incorporation of deuterium. Control experiments demonstrated that no exchange of dibenzoylethane occurred under comparable conditions. Furthermore, the possibility of exchange owing to some photolytically produced catalyst was eliminated by irradiating II for 6 hr, removing a third of the solution, and allowing the remainder to stand in the dark for 24 hr. Work-up of both solutions gave IV with identical deuterium incorporation. Finally, under the experimental conditions chosen, V did not rearrange to IV. The results are reasonably understood by assuming that the formation of IV proceeds either by a 1,2-hydrogen shift or by ring closure of a 1,3-biradical intermediate.

In order to demonstrate conclusively that a triplet n–π^* state was involved in the reactions of II, quenching experiments were run using piperylene as the quencher. Energy transfer from the triplet state of the carbonyl compound to piperylene is sufficiently exothermic to ensure diffusion control of triplet destruction.[34] The quantum yields for appearance of products are summarized in Table I. The only reaction observed in the samples containing piperylene was photodimerization of the quencher. Although the data could not be subjected to quantitative analysis, they showed very clearly that formation of all products occurs exclusively from the triplet state of the ketone.

Table I. Representative Quantum Yields [a,b]

Piperylene, moles	Quantum yields: Aceto-phenone	Phenyl-acetic Acid	IV	V
...	0.004	0.005	0.017	0.024
0.5	...	...	...	...
2.0	...	...	...	...

[a] The filter combination used has a maximum transmission of 62.8% at 313 mμ and transmits less than 1% below 290 mμ and above 436 mμ. [b] All runs carried out in 600 ml of anhydrous benzene.

With the same objective in mind, that of determining multiplicity, we have examined the phosphorescence of II at 77°K. The 0–0 band of II in EPA corresponds to a triplet energy of 74.2 kcal. The vibrational spacing between the 0–0 and 0–1 band is 1643 cm^{-1}. The spectrum of II in a methylcyclohexane–isopentane (MCIP) glass shows the 0–0 band at 71.5 kcal. The higher energy in the more polar glass and the 1643-cm^{-1} gap between the first and second bands are highly indicative that the emission is from the n–π^* triplet.

Conclusion

It is apparent that the evidence presented in the present paper has served to demonstrate that cyclobutanol formation, photoelimination, and rearrangement proceed from a common biradical intermediate. The isolation of both IV and V in the present investigation adds strong support for Yang's stepwise mechanism. It also indicates that the reactive state responsible for this reaction is an n–π^* triplet. It should be pointed out that on the basis of the data available to date, we cannot exclude a concerted mechanism as a possible alternative for *aliphatic ketones*. As mentioned earlier, more than one kind of excited n–π^* state may be involved in cyclobutanol formation of these species.

Experimental Section[35]

Preparation of *trans*-1,4-Diphenyl-3-buten-1-one (I). The procedure of Wieland and Stenzl was adopted to the present case.[19] To 50 g of a suspension of 1,4-diphenyl-1,3-butadiene in 80 ml of ether was added 25 g of nitrogen tetroxide in 70 ml of hexane. The mixture was allowed to stir at room temperature for 2 hr. The yellow crystalline solid was separated by filtration and dried to give 65 g of 1,4-diphenyl-1,4-dinitro-2-butene.

(30) R. J. Gritter and T. J. Wallace, *J. Org. Chem.*, **26**, 282 (1961).
(31) D. I. Schuster and I. S. Krull, *J. Am. Chem. Soc.*, **88**, 3456 (1966).
(32) G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Close, *ibid.*, **87**, 1410 (1965).
(33) Depuy and Breitbeil have amply demonstrated the facile ring opening of substituted cyclopropanols under a variety of experimental conditions: C. H. Depuy and F. W. Breitbeil, *ibid.*, **85**, 2176 (1963).
(34) G. Porter and F. Wilkinson, *Proc. Roy. Soc.* (London), **A264**, 1 (1964).
(35) All melting points are corrected and boiling points uncorrected. Elemental analyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark, and Alfred Bernhardt Laboratories, Hohenweg, Germany. The infrared absorption spectra were determined on a Perkin-Elmer Infracord spectrophotometer, Model 137. The ultraviolet absorption spectra were measured with a Cary recording spectrophotometer, using 1-cm matched cells. The nuclear magnetic resonance spectra were determined at 60 Mc with the Varian Associates high-resolution spectrophotometer. Tetramethylsilane was used as an internal standard.

The above dinitroolefin was dissolved in 300 ml of ether. To the mixture was added 50 ml of concentrated ammonium hydroxide. The solution was allowed to stir at room temperature for 30 min and was then diluted with water. The aqueous layer was removed and the ether extracts were dried over sodium sulfate. Removal of the solvent left 42 g (68%) of a solid, mp 98–107°. Recrystallization from ethanol afforded 36 g of *trans*-1-nitro-1,4-diphenyl-1,3-butadiene, mp 110–112°.

To a mixture of 5.0 g of the above nitrodiene and 15 g of stannous chloride was added 12.5 ml of concentrated hydrochloric acid and 5 ml of 95% ethanol. The mixture was subsequently stirred for 1 hr in an ice bath and for 45 min at room temperature. At the end of this time, 15 ml of 95% ethanol was added and the solution was heated on a steam bath for 5 min. The mixture was cooled, poured onto ice, and extracted with ether. The ethereal extracts were washed with four 50-ml portions of 10% sodium carbonate and washed once with water. The organic layer was dried over sodium sulfate, and evaporation left 3.2 g of a solid, mp 79–88°. Recrystallization from hexane–ether gave pure *trans*-1,4-diphenyl-3-buten-1-one, mp 92–93° (lit.[19] mp 93°).

Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.41; H, 6.30.

The infrared spectrum of this material showed strong bands at 5.98 and 10.31 μ. The ultraviolet spectrum (95% ethanol) has $\lambda\lambda_{max}$ at 249 mμ (ϵ 28,600), 277 (4100), and 287 (2300). The nmr spectrum in deuteriochloroform shows multiplets at τ 6.12, 3.42, 2.51, and 1.89. The peak areas are in the ratio of 1:1:4:1.

***trans*-1,4-Diphenyl-3,4-epoxybutan-1-one (II).** A solution of 10.0 g of *trans*-1,4-diphenyl-3-buten-1-one and 9.2 g of *m*-chloroperbenzoic acid in 400 ml of methylene chloride was allowed to stand at room temperature for 12 hr. At the end of this time, the precipitate of *m*-chlorobenzoic acid was removed by filtration and the solution was washed with saturated sodium carbonate and dried over sodium sulfate. The solvent was removed *in vacuo* to leave a white solid. Recrystallization from hexane–benzene gave a white, crystalline solid (II), mp 112–113°, yield 5.7 g (51%).

Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92. Found: C, 80.66; H, 5.89.

The infrared spectrum in a potassium bromide pellet is characterized by bands at 5.93 and 11.25 μ. The ultraviolet spectrum in 95% ethanol has $\lambda\lambda_{max}$ 243 mμ (ϵ 14,000) and 277 mμ (ϵ 1000). The nmr spectrum is in excellent agreement with the structure. There is a multiplet centered at τ 6.62, a doublet at τ 6.26 (J = 1.5 cps), and multiplets at τ 2.62 and 2.01. The peak areas are in the ratio of 3:1:8:2.

Irradiation of *trans*-1,4-Diphenyl-3,4-epoxybutan-1-one. A solution of *trans*-1,4-diphenyl-3,4-epoxybutan-1-one (1.0 g) in anhydrous benzene (1 l.) was irradiated with a Hanovia 450-w mercury arc lamp using a Pyrex filter to eliminate wavelengths below 280 mμ. The photolysis was followed by withdrawing small samples at fixed intervals without interrupting the system. The samples were analyzed by thin layer chromatography. After 8 hr, the spot on a thin layer plate due to II had completely disappeared, and three new spots had appeared in its place. After the irradiation was completed, the solution was evaporated to dryness to give an orange oil. The crude residue was dissolved in 200 ml of ether; the ethereal solution was extracted with three portions of 3% sodium hydroxide solution and then dried over sodium sulfate. The ether was removed *in vacuo* and the residual "neutral" fraction was treated as described below. The basic extracts were made strongly acidic with 10% sulfuric acid, and the acidic solution was extracted three times with ether. These extracts were dried over sodium sulfate, and the ether was removed *in vacuo* to give 75 mg of a solid, mp 72–76°. Recrystallization from ethanol gave pure phenylacetic acid, mp 75–76°.

The "neutral" fraction was chromatographed on a 3 × 98 cm alumina (Woelm, acid, grade II) column. The column was eluted with 500 ml of 1% ethyl acetate–benzene. The eluent, in 50-ml fractions, was concentrated and dried *in vacuo*. Fractions 1–4 contained 68 mg of a liquid whose infrared spectrum was identical in every respect with that of acetophenone. Fractions 4–8 contained 280 mg of 2,5-diphenylfuran (III), mp 88–89°. 2,5-Diphenylfuran was identified by comparison with an authentic sample prepared by a procedure described by Nowlin.[36]

Further elution of the column with 2% ethyl acetate–benzene gave 350 mg of dibenzoylethane (IV), mp 142–143°. Proof of structure IV was obtained by comparison with an authentic sample.[37] Further elution of the column afforded intractable material. The formation of 2,5-diphenylfuran was shown by control experiments to be the result of a ground-state acid-catalyzed rearrangement of starting material. When the photolysis apparatus was thoroughly cleaned and then washed with dilute base prior to use, no 2,5-diphenylfuran was detected.

By using scanning liquid–liquid partition chromatography the crude photolysis mixture could be resolved into three major components. The separation was carried out in a water-jacketed column (150 × 3.5 cm) which was kept at a constant temperature of 29.0 ± 0.05°. The two-phase system (prepared from 1000 ml of cyclohexane, 400 ml of dimethylformamide, 250 ml of ethyl acetate, and 30 ml of water) was allowed to equilibrate for at least 30 min before use. The liquid–liquid apparatus used in these experiments and the processing of the fractions has been described in detail elsewhere.[10] The chromatogram showed three major peaks with retention volumes of 1200, 1500, and 1700 ml of mobile phase. The first peak (73 mg) was identified as acetophenone. The second peak (240 mg) was shown to be dibenzoylethane.

***cis*-1,2-Diphenyl-2,3-epoxy-1-cyclobutanol (V).** The third fraction from the liquid–liquid chromatogram contained 260 mg of a white solid, mp 136–142°. Recrystallization from hexane–ether afforded a crystalline solid, mp 142–143°. The structure of this material is assigned as *cis*-1,2-diphenyl-2,3-epoxy-1-cyclobutanol (V) on the basis of the following observations.

Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92. Found: C, 80.59; H, 5.92.

The molecular weight (calcd 238, found 226) is consistent with a monomeric unit. The high-dilution infrared spectrum ($CHCl_3$) of V shows a sharp strong intramolecular hydrogen bond (3559 cm^{-1}); the infrared band corresponding to a nonbonded hydroxyl stretching frequency was absent. Increasing the concentration by factors up to 50 caused little change in the peak shape or position. The infrared spectrum of related model systems, in which the tertiary hydroxyl group has a similar steric environment, revealed the presence of extensive polymeric association. The fact that absorption due to this bond is strong and invariant with concentration suggests that the hydroxyl group of V is *cis* to the oxide ring. The ultraviolet spectrum (95% ethanol) with maxima at 260 and 265 mμ (ϵ 525 and 440) is characteristic of two isolated benzene rings. The nmr in deuteriochloroform shows the methylene hydrogens as a pair of doublets at τ 7.87 and 7.32 (J = 13 cps), the hydroxyl proton as a singlet at τ 6.51, the tertiary hydrogen as a broad singlet at τ 5.40, and the aromatic hydrogens as a multiplet centered at τ 2.69. The peak areas are in the ratio of 1:1:1:10.

Structure V was further confirmed by its reactions with acid and base. To a solution of 50 mg of V in 5 ml of benzene was added 2 mg of *p*-toluenesulfonic acid. The solution was allowed to reflux for 10 hr. The solvent was removed *in vacuo*, and the crude residue was analyzed by vapor phase chromatography on an Aerograph A-90 instrument. The products were separated on a column of Dow 710 silicone oil (0.1% on glass beads) at 170° at a flow rate of 50 cc/min. The material of retention time 3.8 min was collected in a liquid nitrogen trap connected to the gas outlet. The colorless liquid obtained had an infrared spectrum and retention time identical with that of an authentic sample of 2,3-diphenylfuran[23] (68%).

A 50-mg sample of V was heated with 5 mg of sodium methoxide in 5 mg of anhydrous methyl alcohol for 20 min at gentle reflux. The mixture was cooled and diluted with 15 ml of water. The aqueous solution was extracted with ether, and the extracts were dried over sodium sulfate. Evaporation of the solvent left 47 mg of a pale yellow solid. The infrared spectrum of this material was identical in all respects with 1,2-dibenzoylethane. The mixture melting point of these two materials was undepressed at 142–143°.

Photolysis of II in Methanol-d_1. A solution of 500 mg of II in 150 ml of benzene and 380 ml of methanol-d_1 was irradiated with an internal water-cooled mercury arc lamp (450 w) with a soft glass filter to eliminate wavelengths below 300 mμ. Purified nitrogen was passed through the solution for at least 45 min before irradiation commenced and a positive pressure was maintained throughout. The nitrogen atmosphere was purified by the vanadous ion method of Meites.[38] Concentration of the solution left an oil. The crude residue was chromatographed on a liquid–liquid partition column using a 4.5 × 150 cm thermostated column. There were three major peaks in the chromatogram. The first fraction was identified as acetophenone. The second peak (retention volume of 1520 ml) was identified as monodeuteriodibenzoylethane. That

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Table II. Quantum Yields of Products from Irradiation of *trans*-1,4-Diphenyl-3,4-epoxybutan-1-one[a,b]

Run[c]	Piperylene, moles	$10^{-18}I$, quantum sec^{-1}	$10^{8}t$, min	% conversion	Quantum yields[d] Aceto-phenone	Phenylacetic acid	IV	V
1	...	1.3	3.0	11	0.004	0.005	0.017	0.024
2	...	1.8	2.4	13	0.003	0.004	0.018	0.026
3	2	1.3	3.0	...	...	...	...	...
4	0.5	1.8	2.4	...	...	...	...	...

[a] The filter combination used has a maximum transmission of 62.8% at 313 mμ and transmits less than 1% below 290 mμ and above 436 mμ. [b] 2.0 g of *trans*-epoxide II. [c] All runs in 600 ml of anhydrous benzene. [d] Large uncertainty (±20%) in acetophenone and phenylacetic acid quantum yields due to small amount of material produced.

deuterium incorporation occurs specifically at C-2 was confirmed by an nmr spectrum which showed a ratio of 0.3 for the methylene to aromatic protons. Control experiments demonstrated that no exchange of either starting material or dibenzoylethane occurred in the dark under comparable conditions. The third peak from the chromatogram was identified as V. Under the experimental conditions chosen, V did not rearrange to IV.

Preparation of *cis*-1,4-Diphenyl-3-buten-1-one (VI). Phenylpropargyl bromide[39] was prepared from phenylpropargyl alcohol[40] by action of phosphorus tribromide and pyridine in ether. The product boiled at 110–120° (8 mm) and had $n^{26}D$ 1.6176.[41] To a solution of the Grignard reagent prepared from 5.1 g of magnesium and 10.1 g of phenylpropargyl bromide in 200 ml of anhydrous ether was added slowly and with stirring 5.5 g of benzaldehyde in 50 ml of ether. After standing overnight, the mixture was decomposed by ice and a saturated solution of ammonium chloride. The ether layer was separated, washed once with water, then dried over anhydrous sodium carbonate, and fractionated through an 8-in. Vigreux column. The product (6.8 g) boiled at 155–165° (0.2 mm) and had $n^{25}D$ 1.5913. The colorless oil slowly solidified upon standing for several days. Recrystallization from hexane–ether gave a white solid, mp 55–56°. The formula 1,4-diphenyl-3-butyn-1-ol was indicated by analysis.

Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.66; H, 6.48.

The infrared spectrum of the alcohol in carbon tetrachloride has bands at 2.8-3.0 and 9.5 μ.

To 5.0 g of the above 1,4-diphenyl-3-butyn-1-ol in 25 ml of acetone was added 2.2 g of chromium trioxide in 12 ml of 23% sulfuric acid. The reaction mixture was stirred for 2 hr at 0°. The reaction mixture was poured into water (200 ml), and the aqueous layer was extracted four times with ether. The ethereal extracts were washed successively with aqueous sodium carbonate, aqueous potassium iodide and twice with water and dried. Removal of the solvent left a white solid which was recrystallized from hexane–ethyl acetate to give 3.6 g (72%) of a white, crystalline solid, mp 75–76°.

Anal. Calcd for $C_{16}H_{12}O$: C, 87.24; H, 5.49. Found: C, 87.09; H, 5.56.

The infrared spectrum of 1,4-diphenyl-3-butyn-1-one shows a carbonyl band at 5.93 μ. The nmr spectrum has a singlet at τ 6.02 and a multiplet centered at τ 2.71. The peak areas are in the ratio of 1:5.

1,4-Diphenyl-3-butyn-1-one, 2.15 g, was hydrogenated with 52 mg of palladium on barium carbonate in 35 ml of ethyl acetate to which was added four drops of quinoline. One equivalent of hydrogen was taken up in 45 min, whereupon the hydrogen uptake abruptly ceased. The solution was filtered free of catalyst, and the solvent was removed *in vacuo*. The colorless oil was taken up in pentane–benzene and a solid soon precipitated. The solid amounted to 1.96 g (90%), mp 50–53°, and was repeatedly recrystallized from pentane–benzene to give *cis*-1,4-diphenyl-3-buten-1-one (VI), mp 53–54°.

Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.44; H, 6.42.

The infrared spectrum of the crystalline compound in carbon tetrachloride is characterized by a carbonyl band at 5.92 μ. The nmr spectrum in deuteriochloroform is in excellent agreement with the proposed structure and consisted of a multiplet at τ 2.55 (10 H); the remaining part of the spectrum consisted of an ABX_2 system. The A proton of the ABX_2 system was centered at τ 3.47 (7 H) and consisted of a triplet of doublets. The B proton was centered at τ 4.08 (1 H) and consisted of two overlapping triplets. The X portion of the system was centered at τ 6.20 (2 H) and consisted of a doublet of doublets. The coupling constants for the ABX_2 system were J_{AB} = 12, J_{BX} = 7, and J_{AX} = 1.5 cps. Further proof of structure was shown by the following degradation reaction.

Palladium–charcoal catalyst (20 mg) was suspended in ethyl acetate (10 ml), stirred with a magnetic stirrer, and equilibrated with hydrogen gas at atmospheric pressure. The *cis*-ketoolefin VI (100 mg), dissolved in ethyl acetate (5 ml), was added to the catalyst suspension and the hydrogenation continued. The olefin absorbed 11.2 ml of hydrogen (calculated value: 11.8 ml for 1 equiv). The catalyst was filtered off through a bed of Celite and the solvent evaporated. The partially crystalline oil which remained was recrystallized from pentane–ether. The yield was 86 mg of solid (85%), which melted at 53–54° and did not depress the melting point on an authentic sample of 1,4-diphenyl-1-butanone.[42] The infrared spectrum of the solid was identical in every detail with that of 1,4-diphenyl-1-butanone.

Preparation of *cis*-1,4-Diphenyl-3,4-epoxybutan-1-one (VII). A solution of 5.0 g of V and 4.6 g of *m*-chloroperbenzoic acid in 200 ml of methylene chloride was allowed to stand at room temperature for 10 hr. At the end of this time, the precipitated *m*-chlorobenzoic acid was removed by filtration and the solution was washed with 10% sodium carbonate and dried over magnesium sulfate. The solvent was removed *in vacuo* to leave a white solid. Recrystallization from pentane–ether gave a white, crystalline solid (VII), mp 52–53°, yield 3.6 g (69%).

Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92. Found: C, 80.47; H, 5.96.

The infrared spectrum in a potassium bromide pellet is characterized by bands at 5.92, 8.40, and 10.21 μ. The nmr spectrum is in excellent agreement with the proposed structure. There is a multiplet centered at τ 2.54 (10 H); the remaining part of the spectrum consisted of a ABXY system. The A proton was centered at τ 5.93 (1 H) and consisted of a doublet. The B proton was centered at τ 6.41 (1 H) and consisted of a quartet. The X and Y portions were centered at τ 7.07 (1 H) and 7.44 (1 H). Each consisted of an unsymmetrical quartet. The coupling constants were J_{AB} = 4, J_{BS} = 5, J_{BY} = 6.5, J_{XY} = 17, and J_{AX} and J_{AY} = 0 cps.

Structure VII was further confirmed by the following degradation reactions. A solution of 100 mg of VII in 5 ml of anhydrous methanol containing 20 mg of sodium methoxide was allowed to stand at room temperature for 2 hr. The solution was poured onto 10 ml of water and acidified to pH 7 with dilute hydrochloric acid. The aqueous layer was extracted with ether and dried over sodium sulfate. Removal of the solvent left a white solid, mp 140–143°, whose infrared spectrum was identical with that of an authentic sample of dibenzoylethane.

In 15 ml of anhydrous methanol was dissolved 100 mg of VII. To the mixture was added 0.25 ml of concentrated hydrochloric acid. The mixture was allowed to stand at room temperature for 2 hr and then diluted with water. The oil which separated was extracted with ether, and the extracts were dried over sodium sulfate. Evaporation of the solvent *in vacuo* left 87 mg of a white solid. The infrared spectrum of this material was identical in all respects with 2,5-diphenylfuran. The mixture melting point of these two materials was undepressed at 86–88°.

Irradiation of *cis*-1,4-Diphenyl-3,4-epoxybutan-1-one. A solution of 1.0 g of *cis*-epoxide VII in anhydrous benzene (1 l.) was irradiated with an internal water-cooled mercury arc lamp (Hanovia, type L, 450 w) with a Pyrex filter to eliminate wavelengths below

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280 mμ. Purified nitrogen was passed through the solution for at least 45 min before irradiation commenced, and a positive pressure of nitrogen was maintained throughout. Aliquots were removed without interrupting the photolysis and analyzed by infrared spectroscopy and thin layer chromatography. Even after 72 hr of irradiation, infrared analysis and thin layer chromatography showed only unchanged starting material. Upon work-up, pure crystalline starting material was the only compound present.

Quantum Yield Determinations. The apparatus used was that described earlier using a 200-w Hanovia lamp.[43] It consisted of five borosilicate glass cylinders of 100, 80, 39, and 28 mm joined together by approprirate ring seals and standard taper joints. The two interior tubes with cell spaces of 3 and 8 mm, respectively, contained 10 g of hexahydrated nickel sulfate per 30 ml of aqueous solution and 12.5 g of heptahydrated cobalt sulfate per 30 ml of aqueous solution. Light intensities were monitored just before and just after sample irradiation. Quantum output rates for the 200-w mercury lamp used were determined by potassium ferrioxalate actinometry.[44] Reliably reproducible output rates of 1.5×10^{18} quanta/sec were recorded. After the irradiation the degree of reaction was determined by quantitative column chromatography using a liquid–liquid partition column. The conversions were run to 13% or less. Details of the measurements are given in Table II.

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Electrochemical Preparation of Bicyclobutanes and Other Strained Cycloalkanes

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Abstract: As part of a study on the mechanism of the electrochemical cleavage of carbon–halogen bonds, it was discovered that 1,3-dihalocyclobutanes can be reductively cyclized to give bicyclobutanes in good yields. Thus, 1,3-dimethylbicyclobutane (II) was prepared from 1,3-dibromo-1,3-dimethylcyclobutane (I) in over 90% yield. Bicyclobutanes can be selectively prepared from cyclobutanes containing more than two halogens by controlling the electrode potential. By this technique, 1,1,3,3-tetrachloro-2,2,4,4-tetramethylcyclobutane (III) was electroyzed at -2.0 ± 0.1 v (sce) to give 1,3-dichloro-2,2,4,4-tetramethylbicyclobutane (IV). The method of reductive cyclization is of general utility in the synthesis of small-ring compounds. Cyclopropane and cyclobutane were prepared from the corresponding α,ω-dihalides. Data obtained from polarography, as well as product analysis, suggest that anions are involved in these ring closures.

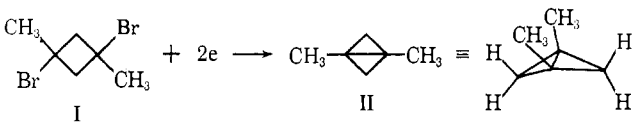
The first authentic bicyclobutane derivative was prepared by Wiberg and Ciula in 1959.[1] Since then, a host of bicyclobutanes have been prepared by numerous routes.[2–12]

We have discovered that bicyclobutanes, as well as cyclopropane, cyclobutane, and spiropentane, can be prepared by the electrochemical reduction of appropriately substituted halides.

While 1,2-dihalides afford olefins upon electrolysis,[13] the electrolytic cyclization of a 1,3- and 1,4-dihalide to the corresponding cyclopropane and cyclobutane has not been reported. Therefore, it was of interest to study the electrolysis of α,ω-dihalides as a general preparative method for small-ring compounds.

Results

The electrolysis of 1-chloro-3-bromocyclobutane[14] in dimethylformamide saturated with lithium bromide afforded a mixture of bicyclobutane (60%), cyclobutene (20%), and cyclobutane (10%). Similarly, 1,3-dibromo-1,3-dimethylcyclobutane[15] was electrolyzed to give 1,3-dimethylbicyclobutane (II).



(*cis* and *trans*)

The structural assignment of II is based on its nmr spectrum which showed singlets at τ 8.67 (area 3), 9.0

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