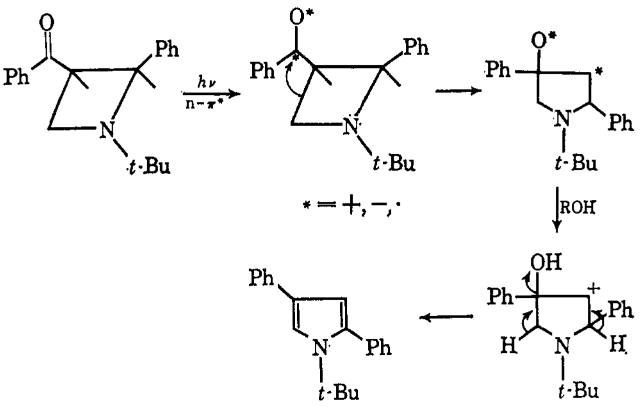
The mechanism by which I undergoes rearrangement and the identification of the excited state(s) responsible for the reaction were deemed of considerable interest. That the n–π* singlet configuration is first populated and is the lowest energy state of this multiplicity seems to be a valid assumption since the absorption spectrum of I showed the n–π* band at 320 mμ, whereas the π–π* transition is at 246 mμ.[8,9] The nature of the lowest lying triplet configuration remains somewhat questionable at this time, although in the present instance the benzoyl group is involved, and the lowest triplet configuration of such a moiety is n–π*. The quantum yield for formation of II in 95% ethanol is 0.046 at 3660 A.[10] In an attempt to determine the rate constant for the unimolecular rearrangement of the excited state, we have studied the variation of quantum yield *vs.* quencher concentration. Surprisingly, the photolysis of I could not be quenched by a moderate concentration (0.3 mole) of piperylene, 1,3-cyclohexadiene, naphthalene, or ferric dipivaloylmethide. The failure to quench could mean that the rearrangement of the n–π* triplet is too rapid for diffusion of the excited state to quencher molecules or that most of the reaction proceeds from the singlet manifold.

With acetophenone present in a concentration so as to absorb 99% of the light a twofold increase in quantum yield resulted, despite the negligible direct excitation of azetidine I. The observation that the same product was obtained in the sensitized photolysis as in the direct irradiation provides proof that the azetidine triplet can rearrange to pyrrole II. Since the quantum yield of II increases by sensitization, we can conclude that either the intersystem crossing efficiency of the n–π* singlet is low or the rate of crossing in this case may be much slower than in benzophenone or acetophenone, thereby allowing for a competing unimolecular rearrangement.[11] The increased quantum yield can also be equally well explained by reaction *via* singlets in the direct irradiation which is less efficient than reaction *via* triplets in the sensitized reaction, both configurations leading to the same product.

These results are consistent with a picture involving reaction of the n–π* state as depicted in terms of the ensuing mechanism.

A possible explanation for the exclusive formation of the 2,4 isomer may be related to the preferred migratory aptitude of methyl *vs.* benzyl toward an electron-deficient center.[14] In view of the uncertainties in the electronic nature of the carbonyl carbon atom, we prefer to postpone further discussion of the reaction mechanism until a more thorough study can be undertaken.



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(8) Pyrex filters were used in all irradiations to remove all light below 300 mμ.

(9) Irradiation of alcohol solutions of I with 2537-A light so as to populate the π–π* manifold produced 2,4-diphenylpyrrole. The effect of different wavelengths of light on I and the photochemistry of the *trans* isomer will be the subject of a future publication.

(10) Quantum yield measurements were carried out on a rotating photochemical assembly in sealed degassed Pyrex ampoules. Irradiation from a 450-w Hanovia lamp was filtered through Corning 7-51 filters. All the light is taken up by I under these conditions.

(11) A similar situation has been noted in the photochemistry of dibenzoylethylene, although in that case reaction proceeded predominantly by way of a n–π* singlet.[12,13]

(12) G. Griffin and E. J. O'Connell, *J. Am. Chem. Soc.*, **84**, 4148 (1962).

(13) H. E. Zimmerman, H. Durr, R. S. Givens, and R. G. Lewis, *ibid.*, **89**, 1863 (1967).

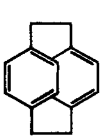
(14) J. R. Owen and W. H. Saunders, Jr., *ibid.*, **88**, 5809 (1966).

Racemization, Ring Opening, and Ring Expansion of the [2.2]Paracyclophane Nucleus through a Diradical Intermediate[1]

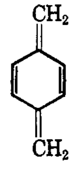
Sir:

The smallest of the [*m.n*]paracyclophanes in which $m = n = 2$ (I) exhibits a strain energy of 31.3 kcal/mole[2a] which is reflected in the highly deformed crystal structure of the molecule.[2b] The photochemical ring opening of [2.2]paracyclophane by both heterolytic and homolytic cleavage of the benzyl–benzyl bond results in release of this compression energy.[3] The thermal ring opening of the substance at 400° to give *p,p'*-dimethylbibenzyl and *p,p'*-dimethylstilbene[4] and at 600° to give *p*-xylylene[5] (II) also reflect the innate instability of the system. Octamethyl[2.2]paracyclophane is much more thermally unstable, a property attributed to diradical formation followed by polymerization.[6]

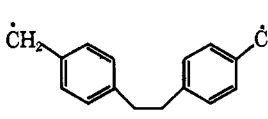
We wish to report the results of three types of experiments, all of which point to thermal cleavage of [2.2]paracyclophane to the *p,p'*-dimethylenebibenzyl diradical (III) whose fate depends on the medium.



I



II



III

When 40 mg of (−)-4-carbomethoxy[2.2]paracyclophane[7] (IV), mp 174–175°, $[\alpha]^{25}_{436}$ −583° (*c* 1, chloro-

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(1) The authors wish to thank the National Science Foundation for a grant used in support of this research.

(2) (a) R. H. Boyd, *Tetrahedron*, **22**, 119 (1966); (b) P. K. Gantzel and K. N. Trueblood, *Acta Cryst.*, **18**, 958 (1965).

(3) R. C. Helgeson and D. J. Cram, *J. Am. Chem. Soc.*, **88**, 509 (1966).

(4) J. R. Schaefgen, *J. Polymer Sci.*, **15**, 203 (1955).

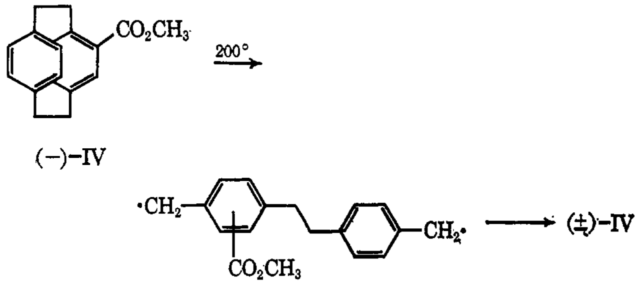
(5) W. F. Gorham, *ibid.*, **4** (A-1), 3027 (1966).

(6) D. T. Longone and L. H. Simanyi, *J. Org. Chem.*, **29**, 3245 (1964).

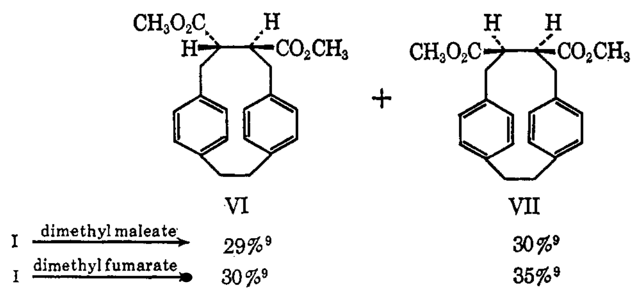
(7) (a) Elemental analyses, nmr, and infrared spectra of all new compounds were in accord with the assigned structures. (b) Optically pure (−)-4-carboxy[2.2]paracyclophane [D. J. Cram and N. L. Allinger, *J. Am. Chem. Soc.*, 77, 6289 (1955)] was previously reported.

form here and elsewhere), was heated in 0.96 g of dimethyl sulfone for 13.3 hr at 200°, 33 mg of ester with $[\alpha]^{25}_{436}$ $-77.5°$ (13% optically pure) was isolated after purification by column chromatography and sublimation. A reaction conducted under identical conditions in *n*-tridecane gave 33 mg of material, $[\alpha]^{25}_{436}$ $-32.5°$ (5.6% optically pure). The ratio of one-point first-order rate constants calculated from these data is $k_{DS}/k_{TD} = 0.7$. The constrictions of the ring system of IV preclude racemization as occurring by a path which does not involve ring cleavage. The insensitivity of the rate to solvent polarity suggests either the derived *p*-xylylene (carbomethoxy derivative of II) or diradical[3] (carbomethoxy derivative V) rather than a zwitterion as a reaction intermediate in the racemization.

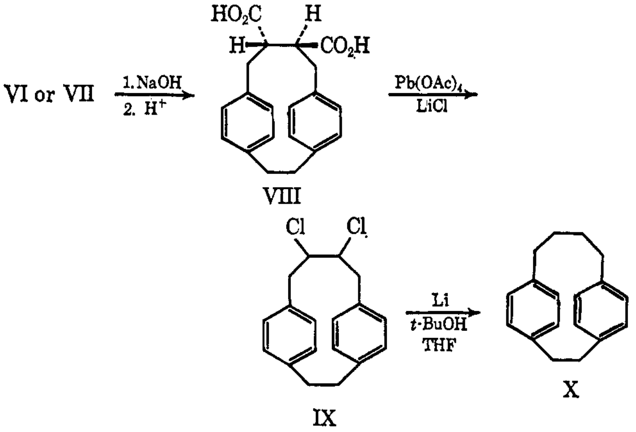
When 1.0 g of [2.2]paracyclophane (I) was heated at 250° in 30 ml of *p*-diisopropylbenzene, 211 mg (21% yield) of *p,p'*-dimethylbibenzyl (mp 81–82°, undepressed by admixture with an authentic sample[3]) was isolated by column chromatography. This product suggested that diradical III intervened as the intermediate in this reduction, and that V was the intermediate in the above racemization reaction.



Dimethyl maleate and dimethyl fumarate esters exhibit particularly favorable tendencies to form ABAB copolymers in styrene radical polymerization under conditions that produce little homopolymerization.[8] Thus, it seemed possible that if diradical III were an intermediate in the thermolysis of I, then I might ring expand to a diester of [2.4]paracyclophane (VI) or VII) when heated with either of the two esters. Accordingly, 3.0 g of I was heated in 8.0 g of dimethyl fumarate in the absence of air at 200° for 40 hr. The product was subjected to silica gel chromatography and fractional crystallization; 0.902 g of starting material (I) was recovered, and 0.867 g of VI (mp 202.5–203.5°)[7a] and 0.800 g of VII (mp 88–89°)[7a] were isolated. A parallel experiment conducted in dimethyl maleate gave similar results.



The nmr spectra of VI and VII exhibit high-field aromatic absorption bands (above τ 3.3) characteristic of the smaller [*m.n*]paracyclophanes.[10] The ultraviolet spectra of VI and VII are similar to that of [2.4]paracyclophane but distinctly different from other [*m.n*]-paracyclophanes and open-chain materials.[11] Both VI and VII have carbonyl absorptions at 5.79 μ in their infrared spectra. Unambiguous proof that VI and VII possess the indicated ring structure is provided by degradation experiments. The diacid VIII[7a] derived from either VI or VII by alkaline hydrolysis was decarboxylated[12] with lead tetraacetate and lithium chloride in pyridine to give a 15–35% yield of dichloride IX,[7a] mp 147–148°. Treatment of IX with lithium in refluxing *t*-butyl alcohol–tetrahydrofuran[13] gave a 57% yield of [2.4]paracyclophane (X), identical with authentic material[11a] (melting point, mixture melting point, and nmr comparisons).



The assignment of the *trans* structure to VI and the *cis* structure to VII was made as follows. Treatment of VII with sodium methoxide in refluxing methanol–dimethoxyethane gave a high yield of VI (less than 0.5% of VII by nmr analysis remained). Thus, VI is more thermodynamically stable than VII by at least 3.5 kcal/mole. Molecular models indicate unambiguously that the *cis* structure is highly compressed compared to the *trans*. The rigid geometry of the ring system forces one of the carbomethoxy groups between the two benzene rings in the *cis* isomer.

Alkaline hydrolysis of either VI or VII gave the same diacid, VIII, which when reesterified gave only VI. Apparently VII isomerized during hydrolysis. Diacid VIII, when heated in acetic anhydride, readily formed the stable cyclic anhydride XI,[7a] 87% yield, mp 234.5–235.5°, carbonyl frequencies at 5.37 and 5.62 μ in the infrared. A sample of XI was hydrolyzed 25% in benzene with brucine hydrate at 80° for 20 min. The recovered anhydride gave $[\alpha]^{25}_{365}$ 0.67° (*c* 8, dichloromethane). The diacid formed was reconverted to anhydride, which had $[\alpha]^{25}_{365}$ $-2.68°$ (*c* 8, dichloromethane). These experiments demonstrate unambiguously that XI, VIII, and VI possess the *trans* structures and are racemates, and that VII has the *cis* structure and is a *meso* form.

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[8] (a) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 132; (b) F. R. Mayo and C. Walling, *Chem. Rev.*, **46**, 191 (1950).

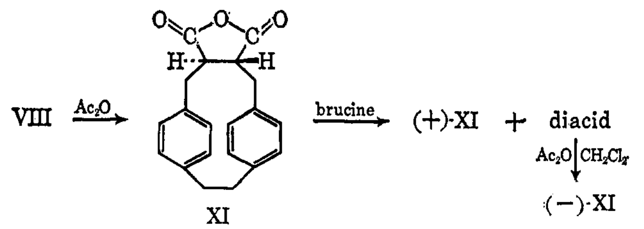
[9] These yields were determined by a combination of gravimetric and nmr procedures.

[10] (a) L. A. Singer and D. J. Cram, *J. Am. Chem. Soc.*, **85**, 1080 (1963); (b) D. J. Cram and R. C. Helgeson, *ibid.*, **88**, 3515 (1966).

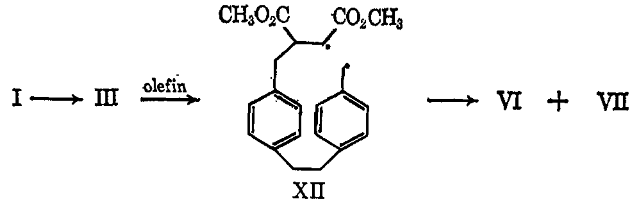
[11] (a) D. J. Cram and H. Steinberg, *ibid.*, **73**, 5691 (1951); (b) D. J. Cram, *Record Chem. Progr.*, **20**, 71 (1959).

[12] J. K. Kochi, *J. Am. Chem. Soc.*, **87**, 2500 (1965).

[13] P. Bruck, D. Thompson, and S. Winstein, *Chem. Ind.* (London), 405 (1960).



The olefin insertion reaction undoubtedly involves production of the diradical III, one benzyl carbon atom of which adds to olefin to produce a second diradical, XII, which in turn ring closes to give VI and VII. Intermediate XII must have a sufficient lifetime to destroy the stereochemical memory of the adding olefin before ring closure. The lack of stereospecificity[14] of the insertion reaction precludes any concerted addition to the diradical III or to [2.2]paracyclophane itself.



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[14] Appropriate control experiments demonstrated that dimethyl maleate, dimethyl fumarate, and VII are essentially configurationally stable under the reaction conditions.

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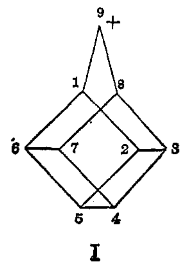
Stereospecific Rearrangements in the Homocubyl Cation

Sir:

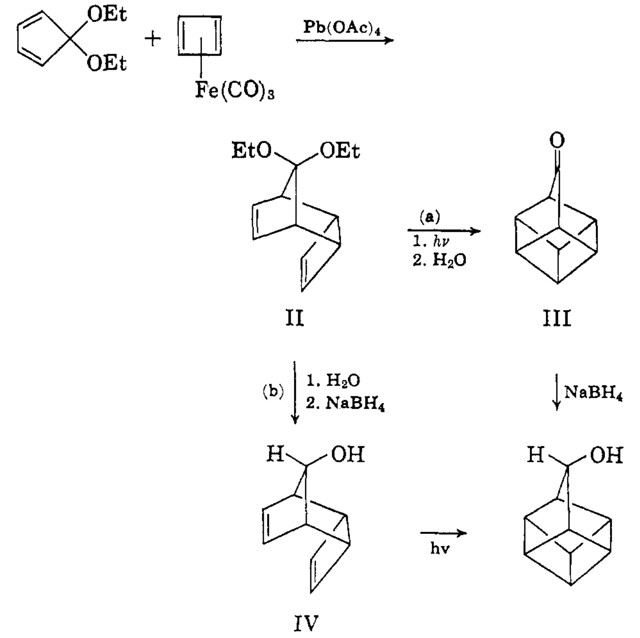
Of the fluctional molecules now known, bullvalene remains the most remarkable in that *via* a series of Cope rearrangements the system can undergo degenerate valence tautomerism which ultimately leads to complete scrambling of the carbon atoms in the framework.[1] Among other systems which can, in principle, behave similarly is the 9-homocubyl cation I; in this case, a succession of Wagner-Meerwein rearrangements continually regenerates the 9-homocubyl cation and results in scrambling of the nine methine units.



I

In a recent communication, Schleyer and co-workers[2] have reported preliminary studies dealing with the synthesis and rearrangement of the homocubyl cation. We have independently been investigating this same problem and wish to report our initial results at this time. These results, based upon both a different synthesis and method of rearrangement detection, are in agreement with those of Schleyer, *et al.*,[2] in showing that the homocubyl cation when generated in acetic acid does undergo several degenerate rearrangements before forming the acetate. In addition, evidence indicates the reaction to be stereospecific and that much of the scrambling proceeds *via* internal return of the tosylate employed.

9-Homocubyl tosylate was prepared by two related pathways. Oxidative decomposition of cyclobutadieneiron tricarbonyl with lead tetraacetate in pyridine in the presence of cyclopentadienone diethyl ketal[3] afforded the adduct II.[4] In path a irradiation of II in acetone gave 9,9-diethoxyhomocubane which upon hydrolysis yielded homocubanone III. Reduction of III with sodium borohydride produced 9-homocubanol which was converted to the tosylate in the usual manner. The tosylate (mp 73–73.5°) displayed absorptions in the nmr at τ 2.42 (area 4), 5.12 (1), 6.33–7.00 (8), and 7.56 (3).[6] In path b, hydrolysis of the ketal II followed by reduction with $NaBH_4$ afforded predominantly the alcohol IV in which the stereochemistry of the hydroxyl group is as indicated.[7] Irradiation of IV gave homocubanol.



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[1] W. von E. Doering and W. Roth, *Tetrahedron*, **19**, 715 (1963); G. Schröder, J. F. M. Oth, and R. Merenyi, *Angew. Chem. Intern. Ed. Engl.*, **4**, 752 (1965).

[2] P. von R. Schleyer, J. J. Harper, G. L. Dunn, V. J. Di Pasquo, and J. R. E. Hoover, *J. Am. Chem. Soc.*, **89**, 698 (1967).

[3] P. E. Eaton and R. A. Hudson, *ibid.*, **87**, 2769 (1965).

[4] Decomposition with ceric ion[5] was unsatisfactory in that the ketal was rapidly hydrolyzed and dimerized to dicyclopentadienone.

[5] J. C. Barborak, L. Watts, and R. Pettit, *J. Am. Chem. Soc.*, **88**, 1328 (1966).

[6] The physical properties of 9-homocubanol and its acetate and tosylate were identical with those reported by Schleyer and co-workers.[2]

[7] This isomer is formed in better than 90% yield. The stereochemistry is indicated by the nmr pattern of the 7,8-olefinic protons (triplet) characteristic of 7-antisubstituted norbornenes [see E. I. Snyder and B. Franzus, *J. Am. Chem. Soc.*, **86**, 1166 (1964)]. In addition, in the mixture of tetradeuterated 9-homocubyl tosylates made *via* pathway a (see text) there exists two distinct regions of absorptions for the ring protons other than C_9; these occur in the regions τ 6.4–6.6 and 6.6–7.0 of areas 1:3, respectively. The lower field set (τ 6.4–6.6) must therefore be associated with those protons situated beneath the tosylate group rather than those β to the tosylate group. In the d_4 tosylate made *via* path b there is no absorption in the region τ 6.4–6.6 but all four protons appear at τ 6.65–6.9; therefore, the tosylate must be *syn* to two deuterium atoms, which requires the stereochemistry shown in IV.