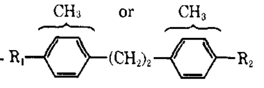
Table II. Products of 254-nm Irradiation of ~4 × 10^{-3} *M* Solutions of I[a]



Run no.	Solvent	Atmosphere[b]	R_1	R_2	% yield	R_1	R_2	% yield	R_1	R_2	% yield
11	AcOH	N_2	CH_3	CH_2OAc	3–9						
12	AcOH	O_2	CHO	CH_2OAc	4	Dimer[d]		~3			
13	CH_3OH	N_2	CH_3	CH_2OCH_3	6						
14	CH_3OH	O_2	CH_3	CH_2OCH_3	6	Aldehyde[e]		2			
15	$(CH_3)_2CHOH$	N_2	CH_3	$CH_2OCH(CH_3)_2$	4	C_2H_5	H	3	CH_3	$CH_2C(CH_3)_2OH$	~3

[a] See footnote *b*, Table I. [b] Solution saturated with gas and blanketed by it. [c] Trace amounts (glc) of xylylene-type cleavage products were also produced, and much polymer. Products listed have methyl on one or other ring. Yields varied with reaction time but are in most cases optimal. [d] Polar, nonvolatile open-chain compound with C=O, *m/e* 562. [e] 4-Aldehydo[2.2]paracyclophane.

Although photoracemization of (−)-I *via* V finds some analogy in other studies,[7] this alternative is eliminated by the facts that both (−)-II and (−)-III photoracemize under the same conditions (runs 2, 8, and 9). The double Diels–Alder intermediate VIa, although formable in the paracyclonaphthane system,[8] is ruled out in the present case. The intermediate from (−)-II in run 8 would have been VIb which, unlike VIa, is asymmetric and in principle could give either (−)-II back or optically active pseudo-*o*-dimethyl[2.2]paracyclophane, but not racemic II. The product from run 8 gave a mass spectrum that demonstrated that both methyl groups were still in the same ring. Had VIb been produced, some of the product should have had one methyl in one ring and the other methyl in the other.[9] Furthermore, the adduct derived from ester (−)-III (run 9) is asymmetric and would not produce (±)-III. Benzvalene[10] intermediate VIIa possesses the requisite plane of symmetry required for (−)-I ⇄ (±)-I. However, VIIb that would be produced in run 8 is asymmetric although it could in principle equilibrate with its enantiomer. No *m*-dimethyl[2.2]paracyclophane, a probable product of VIIb, was observed in run 8. Run 9, in which ester (−)-III racemized, eliminates the benzvalene route, since such an intermediate does not possess a plane of symmetry, nor can enantiomeric intermediates equilibrate through such intermediates.

The pattern of products produced in runs 11–15 suggests that racemization of (−)-I at 254 nm takes place mainly through VIII as intermediate, most likely in the zwitterionic form. In run 15, a small amount of product that might have involved diradical X was observed, but it could have been produced from the small amount of longer wavelength light.[2a] The results of runs 1–4 and 8–10 that involved 254-nm irradiation are all explainable on the basis of either IX or X. The possibility of racemizing through the xylylene fragments, IX, has some analogy in the fact that [2.2]paracyclophane gives *p*-xylylene at 550°.[11] The absence of disproportionation products might reflect an efficient recombination reaction of the two reorganized tetraenes within the solvent cage. The photosensitized runs, 5–7 and 10, were made under conditions that produced *p*-ethylbibenzyl in an earlier investigation.[2a] If the racemization of (−)-I and production of open-chain products both involved the same intermediate, that intermediate would be diradical X. The photosensitized racemization of (+)-IV eliminates structures such as V, VI, and VII as intermediates.

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(8) H. H. Wasserman and P. M. Keehn, *ibid.*, **89**, 2770 (1967).

(9) H. J. Reich and D. J. Cram, *ibid.*, **91**, 3534 (1969).

(10) K. E. Wilzbach, A. L. Harkness, and L. Kaplan, *ibid.*, **90**, 1116 (1968), and previous papers and references.

(11) (a) W. F. Gorham, *J. Polym. Sci.*, **4**, 3027 (1966); (b) Y. L. Yeh and W. F. Gorham, *J. Org. Chem.*, **34**, 2366 (1969).

Solvolyses with Retention of Configuration and Cis Polar Additions in the Side-Chain Chemistry of [2.2]Paracyclophane[1]

Sir:

Usually solvolytic reactions at secondary benzyl carbon in the absence of neighboring-group participation proceed with varying amounts of net inversion, depending on the character of the solvent. For example, methanolysis of optically active α-phenylethyl chloride at 70° occurred with 32% net inversion.[2] Furthermore, little if any neighboring-phenyl participation is expected in solvolysis of ordinary phenylbenzylcarbinyl systems.[3] We wish to report the unusual stereochemical course of reactions in the side chain of the [2.2]paracyclophane system. The alcohol, 1-hydroxy[2.2]paracyclophane (I),[4] mp 228–231°, was resolved through the brucine salt of its acid phthalate[5] to give (+)-I[5] (14% overall), mp 228–231°, $[\alpha]^{25}_{546}$ +76.9° (*c* 1.0, $CHCl_3$), maximum rotation; and (−)-I of 93% optical purity (20%), $[\alpha]^{25}_{546}$ −71.7° (*c* 1.0, $CHCl_3$). Conversion of this sample of (−)-I to its acetate (88%) gave as a total sublimed sample, mp 104–110°, $[\alpha]^{25}_{546}$ −66.9° (*c* 0.93, $CHCl_3$), which fractionally crystallized to give (−)-II, mp 110–111 °,[5] $[\alpha]^{25}_{546}$ −69.1° (*c* 0.37, $CHCl_3$). The same sample of

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

(2) H. M. R. Hoffman and E. D. Hughes, *J. Chem. Soc.*, 1244 (1964).

(3) D. J. Cram in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 260.

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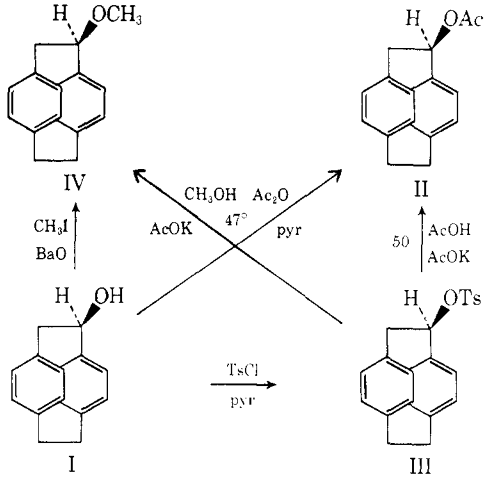
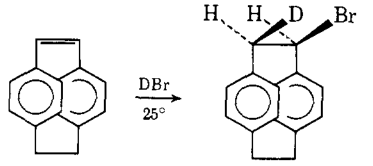
(5) All new compounds gave carbon and hydrogen analyses within 0.3% of theory.

(−)-I gave tosylate (−)-III (83%),[5] mp 85–87° dec, $[\alpha]^{25}{}_{546}$ −92.0° (*c* 0.25, CS_2) after one crystallization. The methyl ether[5] (+)-IV of optically pure (+)-I was prepared with methyl iodide and base (32%), mp 114–117° (sublimed sample), $[\alpha]^{25}{}_{546}$ +168° (*c* 0.60, $CHCl_3$).

Two triligostatic stereochemical reaction cycles[6] were completed, each of which contained three reactions and three chiromers. Direct preparations of acetate, tosylate, and methyl ether from I did not involve C–O bond cleavage and went with retention of configuration. Acetolysis of (−)-III (93% optically pure) gave (−)-II (83%, total sample) with 99% retention of configuration. Methanolysis of optically pure (+)-III at 47° in the presence of potassium acetate gave (82%) ether (+)-IV, mp 113.5–117° (sublimation of total sample), $[\alpha]^{25}{}_{546}$ +168° (*c* 0.61, $CHCl_3$). This reaction occurred with 100% retention. The titrimetric acetolysis rate constants in unbuffered acetic acid at 25 and 50° were 8.49 ± 0.06 × 10^{-6} and 2.28 ± 0.07 × 10^{-4} sec^{-1} (two standard deviations), respectively.

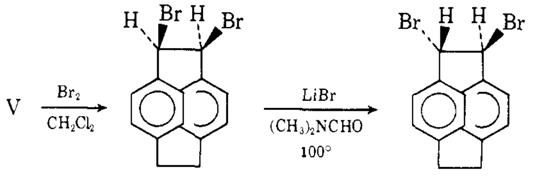


The stereochemical course of addition reactions of 1,2-dehydro[2.2]paracyclophane[4] (V) was examined. Deuterium bromide in benzene–pentane (2:1 by volume) at 25° added to V to give within error exclusively the product of cis addition, VI-*d* (48%), mp 121–123°. In the nmr spectrum of 1 bromo[2.2]-paracyclophane,[4] the substituted bridge provides an ABX pattern with the highest field proton cis-vicinal to the bromine on the adjacent carbon. The cis and trans coupling constants for such conformations are reported as 8.85 and 7.40 Hz, respectively.[7] In the 100-MHz nmr spectra, the highest field proton band present in VI-*h* is absent in VI-*d*, and the rest of the spectrum associated with the substituted bridge has been reduced to an AB quartet, J_{AB} = 9 Hz. Thus both the chemical shifts and coupling constants point to cis addition.



V VI-*d*

Addition of bromine in methylene dichloride at 25° gave (74%) a single dibromide, *cis*-VII,[5] mp 161–163° dec. When the addition was conducted in acetic acid–sodium acetate at 25°, *cis*-VII (35%) and *cis*-1-bromo-2-acetoxy[2.2]paracyclophane (*cis*-VIII)[5] (31%), mp 169–171°, were the only products isolable. Control experiments employing nmr demonstrated that less than 2% of the respective trans isomers could have been detected in the reaction product. When heated in dimethylformamide–lithium bromide at 100°, *cis*-VII isomerized to *trans*-VII[5] (58%), mp 244–246°. The nmr spectrum of the reaction mixture after crystallization of *trans*-VII coupled with control experiments demonstrated that $(trans\text{-VII}/cis\text{-VII})_{equil} > 100$. The structural assignments of *cis*- and *trans*-VII were confirmed by asymmetric destruction experiments. Each dibromide was heated with brucine in chloroform at 100° and recovered. The trans isomer showed a rotation of $\alpha^{25}{}_{546}$ +0.106° (obsd, 1 dm, *c* 1.13, $CHCl_3$), whereas the *cis* isomer was optically inactive.



cis-VII *trans*-VII

When heated at 75° in acetic acid–silver acetate, *trans*-VII gave starting material (31%), *trans*-VIII (22%),[5] mp 148–150.5°, and *trans*-IX (36%),[5] mp 149–151°. At 100°, the reaction gave only *trans*-IX (75%). At 75° in the same mixture, *cis*-VII gave a mixture of hydroxyacetate and diacetate, acetylation of which produced only diacetate *cis*-IX (96%),[5] mp 187–189°. In these and other conversions of dibromides to bromoacetates to diacetates, in no case were trans produced from cis or cis produced from trans isomers (1% could have been detected). The stereostructural assignment of *cis*- and *trans*-VII and *cis*- and *trans*-IX rested on nmr spectral comparisons.

These results indicate that within limits of detection the solvolysis reactions occur with complete retention of configuration, and the addition reactions exclusively follow a cis stereochemical course. The results correlate if one assumes that both classes of reactions involve participation of the β-phenyl group in formation of phenonium ion A (or substituted A) as intermediate. Although A is highly strained, some of the 31-kcal/mol strain of the [2.2]paracyclophane system[8] possibly is released on forming A. A partial positive charge in the system should decrease the π–π repulsions between the two rings by dispersing charge in inter-ring bonding. Thus the α ring might carry some charge by relay. The fact that [2.2]paracyclophane itself is slightly skewed from a completely eclipsed state[9] indicates that the ground-state molecule has some tendency to assume the geometry envisioned in A.

The unique geometry of tosylate III makes it difficult to make quantitative comparisons of solvolysis rates. The α-phenyl in a classical ion derivable from III

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(6) D. J. Cram and D. C. Garwood, *J. Amer. Chem. Soc.*, 92, 4575 (1970).

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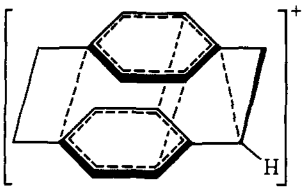

A

should provide little or no delocalization of charge because of its unfavorable geometry. The inductive and steric inhibition of solvation effects of the two phenyl groups should decrease the solvolysis rate in the absence of anchimeric assistance by the β-phenyl group. The fact that the acetolysis rate of III is about 10^2 times faster than that of aliphatic secondary tosylates[10] is not incompatible with a blend of deeclipsing and β-aryl participation in ionization effects which enhance the rate, and steric inhibition of delocalization and solvation and of inductive effects which decelerate the rate.

(10) S. Winstein and H. Marshall, *J. Amer. Chem. Soc.*, **74**, 1120 (1952).

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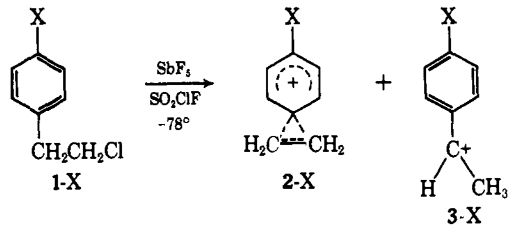
Stable Carbonium Ions. CXV.[1a] The Ethylenephenonium and Ethylene-*p*-toluonium Ions[1b]

Sir:

There has been considerable interest in recent years in β-phenylethyl systems especially as related to the fundamental studies of Cram[2] with regard to the suggested phenonium ion intermediates in their solvolysis reactions. Stable, long-lived phenonium ions have been particularly elusive in strong acid media with the exception of those strongly stabilized by ring substituents (methoxy, trimethyl, and pentamethyl).[3] We report now our success in preparing the parent ethylenephenonium ion **2**-H and the ethylene-*p*-toluonium ion **2**-CH_3. These ions were prepared from their chloride precursors **1**-H and **1**-CH_3, respectively, in SbF_5–SO_2ClF solution at $-78°$. In all cases they are accompanied by the formation of the substituted styryl cations **3**-X.[4] The ratio of **2**-X to **3**-X once observed, does not change over a period of 40 hr at $-60°$. Quenching solutions of the ions with a slurry of a buffered solution of water in SO_2ClF at $-78°$ gave α- and β-phenylethyl alcohols in a 1:3 ratio[5] as the only identifiable products. Overall yield in the quenching experiments, however, was low due to obvious polymerization under the reaction conditions.



X = H, CH_3

Pmr spectra of **2**-H and **2**-CH_3 consist of a sharp singlet for the methylene protons at δ 4.80 and 4.42, respectively, at considerably higher field than found in previously studied substituted ethylenearylonium ions.[6] This indicates the expected larger amount of charge delocalization into the cyclopropyl ring because of the lesser charge delocalizing ability of the aryl system. Figure 1 shows the pmr spectrum of **2**-H with absorptions due to **3**-H deleted. The downfield "aromatic" region contains overlapping absorptions for both **2**-H

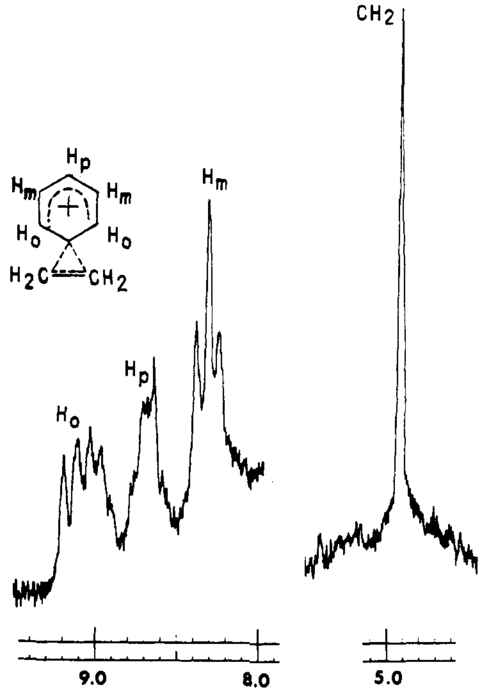


Figure 1. Pmr spectrum (100 MHz) of ethylenephenonium ion **2**-H in SbF_5–SO_2ClF solution at $-78°$.

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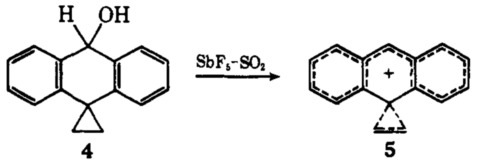
[1] (a) Part CXIV: G. A. Olah, C. L. Jeuell, D. P. Kelly, and R. D. Porter, *J. Amer. Chem. Soc.*, in press. (b) Presented in part at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970.

[2] (a) D. J. Cram, *J. Amer. Chem. Soc.*, **71**, 3683 (1949); (b) D. J. Cram, *ibid.*, **74**, 2129 (1952); (c) for a summary, see D. J. Cram, *ibid.*, **86**, 3767 (1964).

[3] G. A. Olah, M. B. Comisarow, E. Namanworth, and B. Ramsey, *ibid.*, **89**, 5259 (1967). The first observation of a stable phenonium ion (reported by L. Eberson and S. Winstein, *J. Amer. Chem. Soc.*, **87**, 3506 (1965)) was the case of the ethylene-9-anthracenonium ion **5** obtained from the alcohol **4**, but the ion was not obtained *via* aryl participation.



[4] (a) G. A. Olah, R. D. Porter, and D. P. Kelly, *J. Amer. Chem. Soc.*, in press. (b) The pmr spectrum of **3**-H is given in ref 4a. No detailed analysis was possible and assignment of protons in the aromatic region was precluded by low ion concentration and polymeric impurities.

[5] Based on the nmr spectrum of the ion quenched, the anticipated ratio of α- to β-phenylethyl alcohol would have been about 1:2 The higher proportion of β-phenylethyl alcohol is probably due to competition from reaction of **3**-H to form polystyrenes during the quenching process. Analysis by glpc was accomplished with a Carbowax K 20-M on Anakron ABS 12 ft × $^1/_8$ in. column at 140°.

[6] For comparison, methylene proton chemical shifts for other ethylenarylonium systems are: aryl = 2,4-dimethylphenyl, δ 4.16; mesityl, δ 3.77; pentamethylphenyl, δ 3.61; *p*-anisyl, δ 3.45.