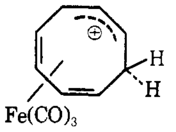
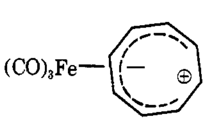
$-80°$ shows a one-proton triplet (J = 7 Hz) at τ 3.23 assigned to H_3, a four-proton multiplet at τ 4.12 assigned to H_2, H_4, H_6, and H_7, a two-proton multiplet at τ 5.46 for H_1 and H_5, and a two-proton multiplet at τ 7.15 assigned to the methylene protons at C_8. If the protonation is carried out in $FSO_3D-SO_2F_2$, the band at τ 7.15 is reduced to a relative intensity corresponding to one proton, confirming the assignment of this band to the methylene protons.

When the temperature of the $FSO_3H-SO_2F_2$ solution is raised, ion II undergoes a clean first-order ring closure to the previously reported[2] bicyclo[5.1.0]octadienyliron complex III. The first-order rate constant for appearance of III at $-60°$ is 3×10^{-4} sec^{-1}, corresponding to $\Delta F^{\ddagger} = 15.7$ kcal/mol.

The nmr spectrum of the intermediate complex clearly indicates that its structure is best described as II, in which the ligand contains a "free" double bond and a five-carbon pentadienyl system complexed to iron,[6] and not alternative structures such as IV, in which the ligand contains a free allylic cation and a diene moiety complexed to iron, or V, in which the iron is symmetrically disposed with respect to the ligand. The position and difference in chemical shifts of H_1, H_5 and H_2, H_4 are in accord with other cyclic pentadienyliron tricarbonyl complexes,[8-10] while the chemical shift of H_3 (τ 3.23) and the H_3-H_2 and H_3-H_4 coupling constants (7 Hz) are quite characteristic of the central proton in cationic pentadienyliron tricarbonyl complexes.[8,9,11] The chemical shift of protons H_6 and H_7 (*ca.* τ 4.12) is also appropriate for the protons on the unbound vinyl group, considering the chemical shift (*ca.* τ 4.5) of the protons of the free vinyl group in cyclooctatrieneiron tricarbonyl.[9,12]



IV



V

There has been much current interest and speculation about the effects which transition metals may have upon symmetry-controlled transformations of organic systems.[14] The present observation appears to be the first unambiguous case of an electrocyclic ring closure of an organic ligand bound to a transition metal.[15] The closure involves a six-π-electron system, and, therefore, the disrotatory mode of closure is symmetry allowed in the free ligand and is the mode observed[17] in the complex II. It is difficult to assess the exact effect of the metal on the activation energy for ring closure in this case since the analogous transformation of the unbound ligand has not been observed. (The free ligand is the nonclassical monohomotropylium ion.) Several disrotatory ring closures have been reported for cyclic trienes;[18] while the free energies of activation are generally higher (*ca.* 25 kcal/mol) than that observed for II, these neutral trienes serve as poor reference compounds.

Studies are currently in progress on the low-temperature protonations of derivatives of I, and the thermal isomerization of III at higher temperatures, as well as other symmetry-controlled isomerizations of organic molecules bound to transition metals.

Acknowledgments. The authors are grateful to the Research Corporation and the University of North Carolina Research Council for partial support of this work and to Badische Anilin- und Soda-Fabrik for a gift of cyclooctatetraene. M. B. thanks the University of North Carolina for a faculty summer research stipend.

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[6] Since signals for II are sharp at -40, no rapid 1,3 oscillations of iron are occurring with $\Delta F^{\ddagger} <$ *ca.* 11 kcal/mol to average H_1 with H_7, H_2 with H_6, and H_3 with H_5. The bonding in tropyliumiron tricarbonyl is postulated[7] to be similar to that in II (iron bound to a pentadienyl unit with a free double bond); however, the nmr of this complex shows all proton signals averaged to a singlet. This averaging probably occurs by 1,2 iron shifts rather than shifts of other orders (*e.g.*, 1,3).

[7] J. E. Mahler, D. A. K. Jones, and R. Pettit, *J. Amer. Chem. Soc.*, **86**, 3589 (1964).

[8] H. J. Dauben, Jr., and D. J. Bertelli, *ibid.*, **83**, 497 (1961).

[9] W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 2162 (1963).

[10] The assignment of H_1, H_5 to the signal at τ 5.46 is further strengthened by the fact that H_3 appears as a clean triplet. In III, in which H_2, H_6 and H_3, H_5 have the same chemical shifts, H_4 appears as a quintet. This quintet, although originally interpreted[2] as equal coupling of H_4 to H_2, H_3, H_5, and H_6 is best explained by "virtual coupling" between H_4 and H_2, H_6 in the AA'BB'X system. If H_1, H_5 had the same chemical shift as H_2, H_4 in II, virtual coupling would again be expected to alter the triplet structure of H_3. We thank Dr. D. L. Harris for calling this to our attention.

[11] (a) J. E. Mahler and R. Pettit, *J. Amer. Chem. Soc.*, **85**, 3955 (1963); (b) J. E. Mahler, D. H. Gibson, and R. Pettit, *ibid.*, **85**, 3959 (1963).

[12] A referee has suggested that structure IV remains a possibility for the low-temperature intermediate if the τ-3.23 resonance is assigned to the central proton of the free allylic cation, the τ-5.46 band to the terminal allylic protons, and the τ-4.12 band to the bound diene protons. Such an assignment can be ruled out by comparison of the assignments of the allylic protons to shifts of protons bound to other cyclic allylic cations. Typically, terminal allylic protons are at *ca.* τ 0 and to *low fields* of the central proton at *ca.* τ 2.[13]

[13] (a) A. F. Diaz, D. L. Harris, M. Sakai, and S. Winstein, *Tetrahedron Lett.*, in press; (b) P. M. Warner, Ph.D. Thesis, UCLA, 1970.

[14] (a) F. D. Mango and J. H. Schachtschneider, *J. Amer. Chem. Soc.*, **89**, 2484 (1967); (b) W. Merk and R. Pettit, *ibid.*, **89**, 4787, 4788 (1967); (c) R. Pettit, H. Sugahara, J. Wristers, and W. Merk, *Discuss. Faraday Soc.*, **47**, 71 (1969); (d) F. D. Mango, *Advan. Catal.*, **20**, 291 (1969); (e) L. Cassar, P. E. Eaton, and J. Halpern, *J. Amer. Chem. Soc.*, **92**, 3515 (1970).

[15] The present results and the limited data available[16] suggest that bicyclo[4.2.0]octadieneiron tricarbonyl may be formed by electrocyclic ring closure of cyclooctatrieneiron tricarbonyl.

[16] (a) T. A. Manuel and F. G. A. Stone, *J. Amer. Chem. Soc.*, **82**, 6240 (1960); (b) W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 2162 (1963).

[17] The disrotatory closure of II may proceed in either of two ways to yield the cyclopropane ring cis or trans to the $Fe(CO)_3$. As in previous papers, the complex III is written with a *trans*-cyclopropane, but this stereochemistry has not been proved.

[18] (a) D. S. Glass, J. W. H. Wattley, and S. Winstein, *Tetrahedron Lett.*, 377 (1965); (b) A. C. Cope, A. C. Haven, F. C. Ramp, and E. R. Trumbull, *J. Amer. Chem. Soc.*, **74**, 4867 (1952).

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Photoracemization of Optically Active Derivatives of [2.2]Paracyclophane[1]

Sir:

Earlier work[2] demonstrated that [2.2]paracyclophane underwent photolytic ring opening to give open-chain

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[1] The authors thank the National Science Foundation for a grant used in support of this research. M. H. Delton thanks the Regents of the University of California for a First Year Fellowship.

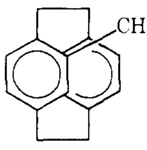
[2] (a) R. C. Helgeson and D. J. Cram, *J. Amer. Chem. Soc.*, **88**, 509 (1966); (b) H. J. Reich and D. J. Cram, *ibid.*, **91**, 3517 (1969).

Table I. Photolytic Racemization Experiments at 25° of Optically Pure Compounds under Nitrogen[a]

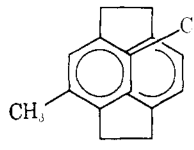
Run no.	Substrate Nature	Substrate Concn, $M \times 10^3$	Medium	λ, nm	Time, hr	Recovered paracyclophane %	Recovered paracyclophane % optical purity
1	(−)-I	0.69	AcOH	254[b]	0.5	42	<1
2	(−)-I	0.66	CH$_3$OH	254[b]	0.5	78	<1
3	(−)-I	0.55	CH$_3$OH	254[b]	0.17	97	5
4	(−)-I	0.67	(CH$_3$)$_2$CHOH	254[b]	0.5	43	<1
5	(−)-I	0.78	C$_6$H$_6$	254[b]	0.5	75	28
6	(−)-I	45	CH$_3$COCH$_3$	>270[c]	4.0	92	4
7	(−)-I	43	C$_6$H$_5$COCH$_3$	350[d]	5.75	55	54
8	(−)-II	0.50	CH$_3$OH	254[b]	0.5	68	<1
9	(−)-III	0.42	CH$_3$OH	254[b]	0.5	87	<1
10	(+)-IV	42	CH$_3$COCH$_3$	>270[c]	4.0	76	43

[a] Solvent was flushed with and irradiated under a blanket of pure nitrogen. [b] Radiation source was a quartz U-tube, low-pressure mercury arc of *ca.* 2 W at 254 nm. Emission characteristics (as per cent of output) were 86% at 254 nm; 8.5% at 578 nm; 2.5% at 185 nm; and less than 1% each at 313, 365, and 436 nm. Irradiated solution was in direct contact with lamp. [c] Rayonet RPR-100 reactor equipped with lamps of 350-nm emission. [d] Medium-pressure, 450-W Hanovia lamp with Corex filter in an immersion apparatus.

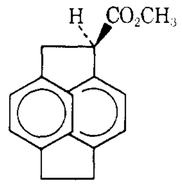
materials.[2a] Optically active [2.2]paracyclophanes were observed to undergo thermal racemization at about 200°.[2b] We now report the photoracemization of optically active compounds (−)-I, (−)-II, (−)-III, and (+)-IV. Optically pure (−)-I was prepared[3] (61% overall) from optically pure (−)-4-carboxy[2.2]paracyclophane[4] to give material,[5] mp 152.5–153°, $[\alpha]^{25}_{546}$ −114° (*c* 1.0, CHCl$_3$). Acetylation of racemic I gave *p*-acetylmethyl[2.2]paracyclophane[5] (75%), mp 116–117°, which was oxidized[4] to *p*-carboxymethyl[2.2]-paracyclophane[5] (82%), mp 258–259°, and resolved through its brucine salt to give (−)-acid[5] (71%), mp 213.5–214°, $[\alpha]^{25}_{546}$ −284° (*c* 0.76, CHCl$_3$), and (+)-acid[5] (33%), mp 213.5–214.5°, $[\alpha]^{25}_{546}$ +280° (*c* 0.78, CHCl$_3$). Reduction of (−)-acid with lithium aluminum hydride gave the alcohol, which was brominated and reduced with lithium aluminum hydride to (−)-II[5] (75% overall), mp 138–139°, $[\alpha]^{25}_{546}$ −198° (*c* 0.58, CCl$_4$). Bromination of optically pure (−)-I followed by metalation with butyllithium and alkylation with dimethyl sulfate also gave, after preparative glc, (−)-II (24% overall), mp 137–138.5°, $[\alpha]^{25}_{546}$ −189° (*c* 0.15, CCl$_4$). From [2.2]paracyclophane was prepared[6] racemic III[5] (32%), mp 95.5–96.5°, hydrolysis of which gave 1-carboxy[2.2]paracyclophane[5] (90%), mp 186–187°.[6] This material was resolved through its α-phenylethylamine salts to give optically pure (−)-acid[5] (36%), mp 187–188°, $[\alpha]^{25}_{546}$ −44.1° (*c* 0.54, CHCl$_3$), and (+)-acid[5] (29%), mp 187–188°, $[\alpha]^{25}_{546}$ +42.0° (*c* 0.56, CHCl$_3$). With diazomethane, (−)-acid gave (−)-III[5] (100%), mp 115.5–116.5° (after recrystallization), $[\alpha]^{25}_{546}$ −51.2° (*c* 0.5, CHCl$_3$), and (+)-acid gave (+)-III (100%), mp 115.5–116.5°, $[\alpha]^{25}_{546}$ +49.2° (*c* 0.6, CHCl$_3$). Reduction of (−)-acid with lithium aluminum hydride gave (+)-IV[5] (100%), mp 122–123°, $[\alpha]^{25}_{546}$ +51.2° (*c* 0.56, CHCl$_3$). Compounds I, II, and IV possessed ultraviolet spectra very similar to that of [2.2]paracyclophane.



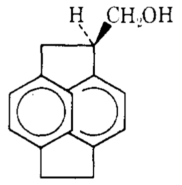
I



II

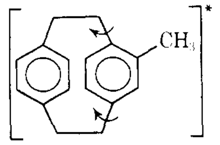


III

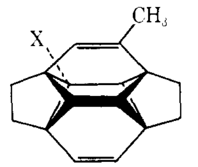


IV

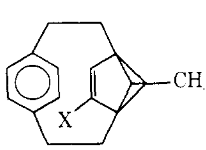
When irradiated in various media with several light sources, (−)-I, (−)-II, (−)-III, and (+)-IV underwent racemization (see Table I) with much greater efficiency than their racemates underwent other reactions (see Table II). In each run the products were separated by column chromatography (silica gel) or preparative glc (20% SE-30 on 60–80 firebrick column in an F and M Model 720 instrument). In each solvent, (−)-I was >99% racemized after only 0.5 hr of irradiation. Irradiation for 24 hr gave at most 9% open-chain products of reaction with medium.



V

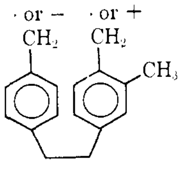


VIa, X = H
VIb, X = CH$_3$

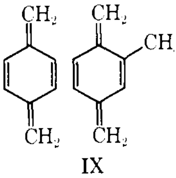


VIIa, X = H
VIIb, X = CH$_3$

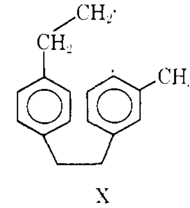
Intermediates V, VI, VII, VIII, IX, and X can



VIII



IX



X

formally be envisioned as accommodating the photolytic racemization reaction of (−)-I at 254 nm.

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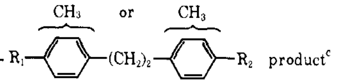
(3) M. J. Nugent and O. E. Weigang, Jr., *J. Amer. Chem. Soc.*, 91, 4556 (1969).

(4) D. J. Cram and N. L. Allinger, *ibid.*, 77, 6289 (1955).

(5) All new compounds gave elemental analyses within ±0.3% of theory.

(6) E. Hedaya and L. M. Kyle, *J. Org. Chem.*, 32, 197 (1967).

Table II. Products of 254-nm Irradiation of $\sim 4 \times 10^{-3}$ *M* Solutions of I[a]



product[c]

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 $\rightleftarrows$ (±)-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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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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[7] K. Mislow and A. J. Gordon, *J. Amer. Chem. Soc.*, **85**, 3521 (1963).

[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).

[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.

[4] K. C. Dewhirst and D. J. Cram, *J. Amer. Chem. Soc.*, **80**, 3185 (1958).

[5] All new compounds gave carbon and hydrogen analyses within 0.3% of theory.