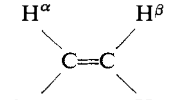
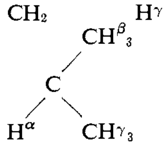
Table I. Correlation of Nmr Sense of Nonequivalence with Absolute Configuration for Some Partially Resolved Type **1** Sulfoxides[a,b]

R	Δδ, Hz[c] R	Δδ, Hz[c] CH$_3$	Nonequivalence sense R[d]	Nonequivalence sense CH$_3$	% optical purity[e]
CD_3[f]		1.7		Low	28
$CH^{\alpha}_2CH^{\beta}_3$	2.4, 2.5	2.5	High	Low	29
	0.8, 1.3, 1.8	1.9	High	Low	30
	2.6, 1.1, 3.0	3.1	High	Low	37
$C(CH_3)_3$	1.2	2.6	High	Low	24
$CH_2C_6H_5$		2.5		Low	31
C_6H_5		1.2		Low	28
p-$CH_3C_6H_4$		1.4		Low	30
p-$CH_3^{\alpha}O$-$C_6H^{\beta}_4$	0.8, 2.5[g]	1.8	High	Low	29
α-Napthyl		1.3		Low	31

[a] The sulfoxides were prepared[7b] from a single batch of (−)-(*R*)-menthyl methanesulfinate of 28% diastereomeric purity,[7b] in each case using *ca.* 1 mol excess of the appropriate Grignard reagent except for dimethyl-1,1,1-d_3 sulfoxide, where a 20% excess of methyl-d_3-magnesium iodide was employed. The sulfoxides have physical and spectral properties consistent with their assigned structures. [b] Nmr spectra were measured on a Varian HA-100 spectrometer at 28° using samples composed of 2:1:*ca.* 3 mol ratios of alcohol:sulfoxide:carbon tetrachloride or fluorotrichloromethane, respectively. [c] Chemical shift differences (±0.1 Hz) are for the α, β, ... protons, respectively. Proton resonances for which no Δδ is reported were either obscured by other resonances or exhibited unresolvable chemical shift differences. [d] In each case where more than one proton in the alkyl (or aryl) group exhibits a chemical shift difference, the sense of nonequivalence is the same as that for other protons within the group. [e] Optical purities (±1%) calculated from the relative peak heights of the enantiomeric methanesulfinyl resonances. [f] Dimethyl-1,1,1-d_3 sulfoxide, previously unreported, was characterized by its elemental analysis, its infrared spectrum, and its proton and deuterium nmr spectra. Based on its observed optical rotation, enantiomerically pure material would have an $[\alpha]^{25}D$ −3.8° (neat). This sample was shown by vpc to contain less than 0.05% menthol, menthone, or menthyl methanesulfinate, and to contain less than 0.1% of any impurity other than water. [g] Observed for the high-field portion of the AA'BB' aromatic multiplet.

arises by the formation of short-lived, hydrogen-bonded diastereomeric solvates.[10] When (−)-(*S*)-α-methylbenzylcarbinol (**4**), less acidic than **2**,[11] is used as a solvent for methyl *t*-butyl sulfoxide, the magnitude of nonequivalence is reduced by a factor of *ca.* 1.5, consistent with weaker solvent–solute association, although other factors may also be involved.

The nonequivalence of the nmr spectra of the enantiomers of type **1** sulfoxides in optically active **2** is quite general, as shown by Table I. The power of the method is strikingly demonstrated by the direct determination of the optical purity of a partially resolved sample of dimethyl-1,1,1-d_3 sulfoxide, a compound which is asymmetric only by virtue of isotopic substitution.[12]

An inspection of Table I suggests that the degree of spectral nonequivalence depends upon the extent of association and upon relative population levels of various conformers.[13] For example, the alkyl aryl sulfoxides generally show a smaller Δδ for the methanesulfinyl group than do the more basic dialkyl sulfoxides, while among the substituted methyl phenyl sulfoxides studied, an increasing $\Delta\delta_{SOCH_3}$ is observed in the order of increasing basicity.[14]

Since the partially resolved sulfoxides in Table I were prepared by the action of an excess of the appropriate Grignard reagent upon portions of a single batch of a 1.78:1.00 mixture of the diastereomeric (*R* configuration at sulfur in excess)[15] (−)-menthyl methanesulfinates (**3**), all of the major enantiomers should have the same absolute configuration (*i.e.*, *R*),[15] although they need not necessarily have identical optical purities.[16]

Further inspection of Table I reveals that in (−)-**2** the partially resolved methyl-substituted sulfoxides all exhibit low-field senses of nonequivalence for the methanesulfinyl resonances and high-field senses of nonequivalence for the resonances of the remaining alkyl or aryl substituents.[17] Contrasting senses of nonequivalence have been previously observed and rationalized[1,18] for other solutes in optically active solvents. In the present instances, the reliability of the correlation between the senses of nmr nonequivalence and sulfoxide absolute configuration suggests that the method may be safely extended and used to assign absolute configurations to methyl sulfoxides of unknown stereochemistry similar to those in Table I. The effect which added functional groups in the sulfoxides will have upon nonequivalence sense has not yet been ascertained.

Acknowledgments. This work was supported by Grant No. GM 14518 from the U. S. Public Health Service. We wish to thank Dr. R. W. Woody for obtaining the ORD spectrum of dimethyl-1,1,1-d_3 sulfoxide.

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(10) A similar explanation has been recently proposed [F. A. L. Anet, L. M. Sweeting, T. A. Whitney, and D. J. Cram, *Tetrahedron Lett.*, 2617 (1968)] to account for the nmr spectral nonequivalence of enantiomeric alkylarylcarbinols in suitable optically active sulfoxides.

(11) The pK_a of **2** is 11.9 [R. Stewart and R. Van der Linden, *Can. J. Chem.*, **38**, 399 (1960)].

(12) Isotopic exchange of dimethyl-1,1,1-d_3 sulfoxide with alcohol **2** is negligible, since no change in optical purity (by nmr) was observed for the partially resolved sulfoxide in (−)-**2** over a period of several weeks.

(13) The magnitudes of the enantiomeric chemical shift differences may be enhanced by lowering the temperature or by increasing the alcohol concentration.

(14) K. K. Andersen, W. H. Edmonds, J. Biasotti, and R. A. Strecker, *J. Org. Chem.*, **31**, 2859 (1966), have determined the apparent pK_a values for several substituted methyl phenyl sulfoxides, obtaining values of −0.488, 0.014, and 0.55 for phenyl, *p*-tolyl, and *p*-anisyl methyl sulfoxides, respectively. The pK_a for dimethyl sulfoxide is 0.911.

(15) M. Axelrod, P. Bickart, J. Jacobus, M. M. Green, and K. Mislow, *J. Amer. Chem. Soc.*, **90**, 4835 (1968).

(16) In view of the recent work of Mislow and coworkers[15] demonstrating the nearly complete stereospecificity of the Andersen synthesis, it would appear that kinetic resolution is responsible for any significant deviations of optical purities of the sulfoxides in Table I from the 28% diastereomeric purity of sulfinate ester **3**.

(17) Significantly, these same senses of nonequivalence are also observed in (−)-**4**, which is known to have the same stereochemistry as does (−)-**2**.[18]

(18) W. H. Pirkle and S. D. Beare, *J. Amer. Chem. Soc.*, **89**, 5485 (1967), and references cited therein.

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Received August 2, 1968

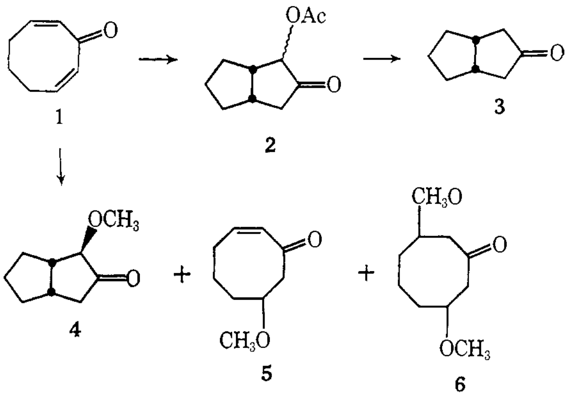
The Photochemistry of 2,7-Cyclooctadienone

Sir:

Cross-conjugated cyclohexadienones have received great attention as photochemical substrates in both qualitative and quantitative experimentation.[1] By comparison we wish to divulge some initial observations on the photochemical behavior of 2,7-cyclooctadienone[2] (**1**), a variant of the above system in which the cross-conjugated carbonyl moiety is situated within a medium-ring carbocycle. Of particular significance is the demonstration that a *ground-state intermediate* intervenes between **1** and its isolated photoproducts.

Irradiation of dilute solutions of **1** with 3500-Å lamps resulted in rapid depletion of starting material, but the use of inert solvents afforded only insoluble, polymeric products. However, hydroxylic solvents profoundly influenced the course of reaction. In acetic acid a 4:1 mixture of *exo*- and *endo*-2-acetoxy-*cis*-bicyclo[3.3.0]octane-3-ones (**2**) was obtained. The structures of these compounds were assigned on the basis of spectroscopic data, including 5.68- and 5.74 μ carbonyl bands in the ir,[3] zinc–acetic acid reduction to *cis*-bicyclo[3.3.0]octan-3-one[4] (**3**), and alternate synthesis from **3** by epoxidation of the corresponding enol acetate followed by thermal isomerization of the resulting epoxide.[5]

In methanol a more complex product mixture was obtained in which *exo*-2-methoxy-*cis*-bicyclo[3.3.0]-octan-3-one (**4**) was the major component and minor constituents included ketone **3**, 7-methoxy-2-cyclooctenone (**5**), and 3,7-dimethoxycyclooctanones[6] (**6**).

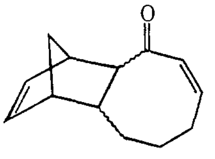


1 **2** **3** **4** **5** **6**

Bicyclooctanone **3** was shown to be a secondary photoproduct derived from **4** by a type-II photoelimination of formaldehyde.[7] Finally, an unambiguous synthesis of **4** was performed by hydroboration of 2-methoxy-*cis*-bicyclo[3.3.0]oct-2-ene, followed by chromic acid oxidation of the resulting alcohol.[8]

In contrast to its lack of interaction with simple olefins, irradiation of **1** in the presence of cyclopentadiene yields a mixture of two adducts which are assigned as stereoisomers of formula **7** on the basis of spectroscopic information: ir, 6.02 (C=O), 6.15 (C=C), 13.1 and 13.9 μ (*cis* CH=CH); nmr, δ 6.7–5.4 (m, 4), 3.3–0.9 (m, 12); *m/e* 188 (25), 122 (21), 66 (100). This behavior is similar to that of *cis*-2-cyclooctenone which yields adducts with dienes *via* the reactive *trans* isomer.[9]

In the presence of furan an entirely different type of photoadduct is formed which is tentatively assigned structure **8** on the basis of spectral evidence, particularly its very simple and distinctive nmr spectrum: δ 6.25 (s, 2, C*H*=C*H*), 4.62 (d, 2, J = 3.5 Hz, OC*H*), 2.58 (m, 2, C*H*), 2.1 (d, 2, J = 3.5 Hz, COC*H*), and 2.0–0.8 (m, 6, CH_2). The ir spectrum displays a cyclopentanone carbonyl at 5.73 μ and a 14.4-μ *cis*-disubstituted olefin band. The stereochemical structure illustrated for **8** is the only one compatible with the experimental nmr coupling parameters. Catalytic hydrogenation of **8** gave a dihydro adduct with the expected properties. The genesis of this material, as well as the bicyclic ketones discussed above, is best visualized, as involving a species related to zwitterion **9**.



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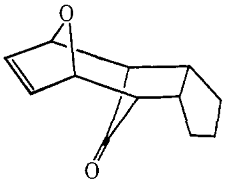

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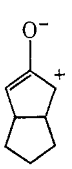

9

Finally, the involvement of a reactive ground-state intermediate in all of the above reactions was demonstrated by low-temperature (−78°) studies in inert solvents. Samples were irradiated under these conditions for a given period, the light source was turned off, and *after several minutes* reagent (acetic acid, methanol, cyclopentadiene, or furan) was added. Upon warming to room temperature, glpc analysis showed the respective photoproducts to be present. The use of an internal standard confirmed that the material balance was quantitative. Evidently photoequilibrium is established between **1** and the reactive intermediate, since *ca.* 10% photoproduct was uniformly obtained with each of the reagents, and extending the irradiation time neither increased the proportion of product nor decreased the material balance. The intermediate also apparently thermally reverts to **1** because glpc shows only starting material in undiminished quantity after low-temperature irradiation in the absence of reactive reagents.

We conclude on the basis of the above experiments that a ground-state intermediate is the reactive precursor of the products from photolysis of **1**, since survival of an excited-state species for the time between cessation of irradiation and addition of reagent is extraordinarily unlikely. However, the exact nature of this species is uncertain. The close analogy provided by cyclooctenone[9] suggests strong consideration of the *cis,trans* isomer of **1**, but **9** and a number of other valence isomers and zwitterionic counterparts of **1** can also

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(1) For a review, see P. J. Kropp in "Organic Photochemistry," Vol. 1, O. Chapman, Ed., Marcel Dekker, Inc., New York, N. Y., 1967, p 1. A more recent paper is H. E. Zimmerman and J. S. Swenton, *J. Amer. Chem. Soc.*, **89**, 906 (1967).

(2) E. W. Garbisch, *J. Org. Chem.*, **30**, 2109 (1965).

(3) All new materials have been characterized by acceptable combustion analysis or high-resolution mass spectrometric determination of molecular formula. Detailed spectroscopic characterization has been performed, and the data are in complete accord with the assigned structures. The partial information provided herein will be supplemented in the full paper.

(4) H. C. Brown and W. Hammar, *J. Amer. Chem. Soc.*, **89**, 6378 (1967).

(5) K. L. Williamson and W. S. Johnson, *J. Org. Chem.*, **26**, 4563 (1961). The major product from the epoxide rearrangement should be the *endo* isomer; this material was identical with the minor photoproduct.

(6) The photochemically induced addition of alcohols has been noted in several instances. See, for example, B. J. Ramey and P. D. Gardner, *J. Amer. Chem. Soc.*, **89**, 3949 (1967); H. Nozaki, M. Kurita, and R. Noyori, *Tetrahedron Lett.*, 2025 (1968).

(7) A similar transformation has been noted for methoxyacetone by P. J. Wagner and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 1245 (1966). Prolonged irradiation of **1** led to a number of other secondary products.

(8) This sequence gave a mixture of **4** and its epimer (which does not appear to be an important *initial* photoproduct of **1**).

(9) P. E. Eaton and K. Lin, *J. Amer. Chem. Soc.*, **86**, 2087 (1964).

be visualized. Whatever its structure, the intermediate possesses the interesting ability to generate products with, and without, bond formation between the β carbon atoms of the original cross-conjugated dienone system of **1**. Further characterization of this species is the goal of our continuing research.[10]

Acknowledgment. This work was supported by the U. S. Public Health Service.

(10) Hydroxylic solvent adducts similar to those described herein have been recently reported for 2,6-cycloheptadienone: H. Nozaki, M. Kurita, and R. Noyori, *Tetrahedron Lett.*, 3635 (1968).

(11) (a) Alfred P. Sloan Research Fellow, 1968–1970; (b) NASA Predoctoral Fellow, 1965–1968.

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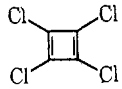
Received August 2, 1968

Interception of Transient Tetrachlorocyclobutadiene[1]

Sir:

We report here the generation and trapping of a reactive species which we believe is tetrachlorocyclobutadiene (I). Reaction of 2-chloro-3,3,4,4-tetrafluorocyclobutene[2] (II) with aluminum trichloride in dichloromethane[3] gave, as the sole product in 74–86% yield, 3-H-pentachlorocyclobutene[4] (IV), $\nu_{C=C}$ 1637 cm^{-1}, τ 4.78 (s). None of the 1-H isomer (III) was detected in the reaction mixture although the conditions would undoubtedly cause equilibration of III and IV; the greater stability of IV was expected by analogy[5] but stands in contrast to the behavior of trichlorocyclopropene, where the 1-H isomer is favored.[6] Compound III rearranges to 1-H-pentachlorobutadiene-1,3[7] above *ca.* 160°, but may conveniently be purified by vacuum distillation through a spinning-band[8] column, bp 89–90° (19 mm).



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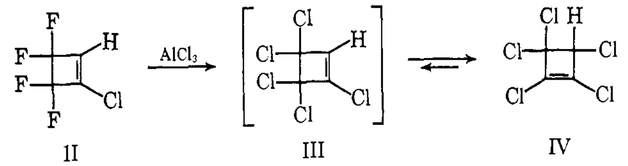
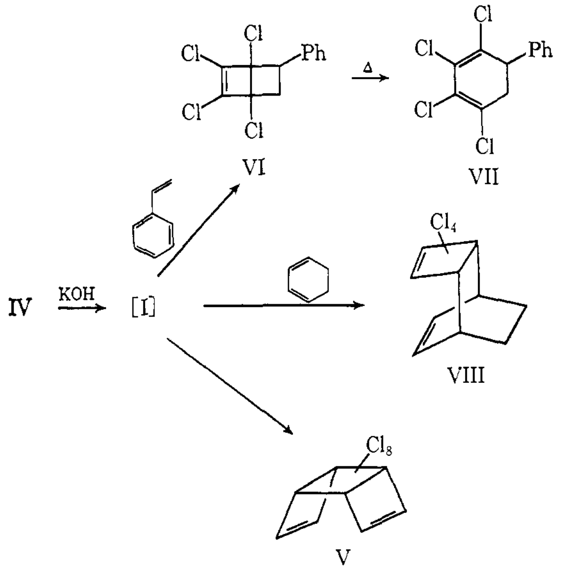


Reaction of compound IV with an excess of powdered 85% potassium hydroxide in refluxing benzene, best with high-speed stirring, effects dehydrohalogenation and in the absence of a reactive diene or dienophile gives up to 43% of a compound C_8Cl_8,[4] assigned structure V. If excess styrene is present, I is trapped as its Diels–Alder adduct VI,[4] formed in 18–20% yield along with a comparable amount of V. In the presence of excess cyclohexa-1,3-diene, adduct VIII[4] is formed in 22% yield, accompanied by traces of V. The structure of VI, mp 35.5–37°, $\nu_{C=C}$ 1603 cm^{-1}, follows from its composition, its ir and nmr spectra, and its ready thermal isomerization to the known 1,2-dihydro-3,4,5,6-tetrachlorobiphenyl[9] (VII) identified by comparison (ir spectra, mixture melting point) with an authentic sample. Only a single isomer of VI has been found in the reaction mixture, but we have no evidence for the stereochemistry of the phenyl group.



The structure of VIII, mp 101–103°, $\nu_{C=C}$ 1626 cm^{-1}, was assigned largely on the basis of its nmr spectrum. Three centrosymmetric multiplets are observed at 3.84 (2 H), 7.15 (2 H), and 7.6–8.8 (4 H), and the vinyl proton signal at lowest field collapses to a singlet on irradiation of the τ 7.15 peak. The *syn* disposition of the four-membered ring is assigned by analogy (Alder rule).

The structure of V, mp 161–163° dec, was initially assigned from its spectroscopic properties: ir, $\nu_{C=C}^{C_2Cl_4}$ 1606 and 1580 cm^{-1}, with other medium-to-strong bands at 1164, 1060, 1012, 991, 792, 663, and 596 cm^{-1} (in CS$_2$); uv, $\lambda_{\max}^{\mathrm{EtOH}}$ 238 mμ (ϵ 5700). The ultraviolet spectrum is inconsistent with either noninteracting double bonds (in the *anti* isomer)—*cf.* $\lambda_{\max}$ 210 mμ (ϵ 1000) for IV—or a perchlorinated conjugated diene—*cf.* $\lambda_{\max}$ 287 mμ (ϵ 7000) for VII—and may be rationalized by postulating excited-state interaction of the adjacent but nonconjugated double bonds. An X-ray study of V has been undertaken by Dodge and Templeton, who report[10] good (R = 9%) refinement to octachlorocubane! Examination of a molecular model of V indicates that the eight chlorines lie very near the corners of a cube, and we believe the X-ray results are consistent with packing of V in the cubane lattice with random orientation of the C$_2$ axis

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(1) Presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 3, 1968, Abstract P180. Grateful acknowledgment is made to the donors of the Petroleum Research Fund and the National Institutes of Health for grants (PRF 2191-A1,4, GM-12731, and GM-15678) in partial support of this work.

(2) D. J. Burton and R. L. Johnson, *J. Amer. Chem. Soc.*, **86**, 5361 (1964).

(3) W. C. Soloman, L. A. Dee, and D. W. Schultz, *J. Org. Chem.*, **31**, 1551 (1966).

(4) Elemental composition of new compounds was established by satisfactory C, H, and Cl analyses and by mass spectrometry.

(5) J. D. Park, J. R. Lacher, and J. R. Dick, *J. Org. Chem.*, **31**, 1116 (1966).

(6) R. Breslow and G. Ryan, *J. Amer. Chem. Soc.*, **89**, 3073 (1967); R. Breslow, paper presented at the International Symposium on the Chemistry and Applications of Small Ring Compounds, Louvain, Belgium, Sept 1967.

(7) A. Roedig, R. Kohlhaupt, and G. Markl, *Ber.*, **99**, 698 (1966).

(8) Auto-Annular still, Nester-Faust Manufacturing Corp. Newark, Del.

(9) E. T. McBee, W. R. Diveley, and J. E. Burch, *J. Amer. Chem. Soc.*, **77**, 385 (1955).

(10) R. P. Dodge and D. H. Templeton, private communication.