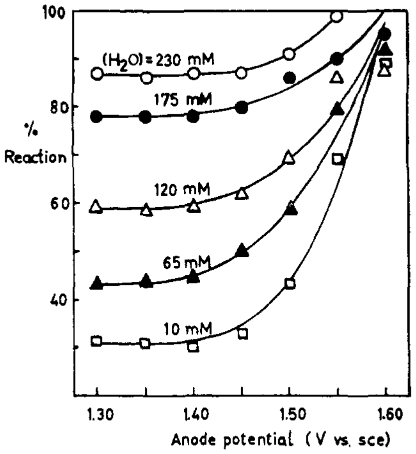

Figure 1. Extent of hydroxylation of thianthrene as a function of anode potential and water concentration.

about 200 mV beyond the peak potential for the oxidation of substrate. In this potential interval, the dication concentration increased by approximately 3000. At potentials greater than (E_1 + 200 mV), the extent of reaction (and hence the reaction rate) increased markedly with increasing potential and at E_1 + 350 mV (E_2) the reaction went to completion at all water concentrations. From these results we can conclusively say that the cation radical is the kinetically active species during hydroxylations at potentials less than (E_1 + 200 mV). We can also estimate that the dication is about 10^3 times as reactive as the cation radical. However, since the cation-radical concentration is about 10^6 times that of the dication in solutions of $Th\cdot^{+}$ in acetonitrile, Th^{2+} would have to be 10^8 times as reactive as the cation radical in order that 99% of the hydroxylation reaction follow the dication mechanism.

Similar conclusions may be drawn from a rotating disk electrode study of the anodic hydroxylation of thianthrene. Likewise, the results from the anodic pyridination of anthracenes[2] are not consistent with the dication mechanism.

Although our results only apply directly to the anodic reactions of cation radicals, there is no evidence that the homogeneous reactions should differ markedly. A mechanism similar to the ECE process (eq 6–8) may also account for the data previously presented[1] and should thus be considered for the reaction of thianthrene cation radical with water.

Disproportionation of cation radicals to dications has been postulated in other systems, for example during the anodic hydroxylation of phenothiazines.[10]

Further studies on these and other systems will be reported soon.

(10) F. H. Merkle and C. A. Discher, *Anal. Chem.*, **36**, 1639 (1964).

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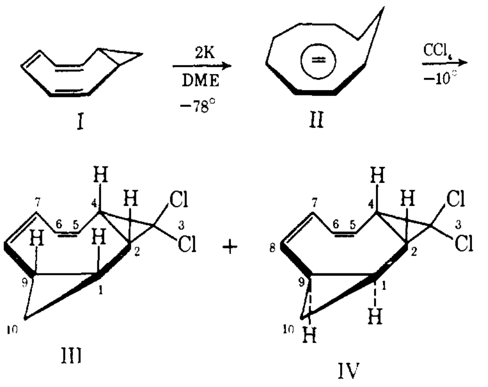
Reaction of the Monohomocyclooctatetraene Dianion

Sir:

Reaction of the recently reported 10π-electron monohomocyclooctatetraene dianion (II)[1] as a nucleophile[2] has proved to be interesting and useful. We now describe additional information on the chemical behavior of II, specifically its behavior upon reaction with carbon tetrachloride. The results obtained from this reaction are also useful in discussing the mechanism of the reaction of the alkali metal cyclooctatetraenides with gem dihalides, and the stereochemistry of the products formed.[3]

Generation of the potassium salt of I was accomplished initially[1] by allowing a solution of *ca.* 25 mg of bicyclo[6.1.0]nona-2,4,6-triene (monohomocyclooctatetraene (I)) in *ca.* 1.5 ml of 1,2-dimethoxyethane (DME) to stand under high vacuum at −80° over a mirror of excess K. Although this procedure produces the dianion, it was cumbersome, requiring the use of a vacuum line, and only small amounts of I could be reduced at one time. Recently, however, we have been able to reduce larger quantities, *ca.* 1–15 g, of the starting material with K under argon at low temperatures. This procedure produces the dianion in amounts much more suitable for synthetic use. The technique employed for this large-scale reduction requires the use of a high-speed stirrer and a Morton flask (indented sides), so that the starting material can be completely reduced within a short time, before the initially produced dianion begins to decompose.

Addition of a DME solution of the dianion II, prepared by the above procedure, to carbon tetrachloride at −10° produced an immediate color change from dark brown to light yellow with no further change as the solution was allowed to come to room temperature. Work-up of the reaction mixture and vacuum distillation produced a colorless liquid which was shown to be a mixture of two products by vpc. Separation and collection by preparative vpc afforded two of the four products possible from this reaction, the 3,3-dichloro-*cis*- and -*trans*-tricyclo[7.1.0.0^{2,4}]deca-5,7-dienes (III and IV) in 60 and 30% yields, respectively;[4] 3,3-dichloro-*cis*-tricyclo[7.1.0.0^{2,4}]deca-5,7-diene (III): nmr (CCl$_4$) τ 4.10 (m, 2, inner vinyl H$_{6,7}$), 4.65 (m, 2, outer vinyl H$_{5,8}$), 8.10–8.85 (m centered at 8.52, 2, allylic H$_{4,9}$), 8.87–9.63 (m centered at 9.21, 3, nonallylic tertiary H$_{1,2}$ and anti methylene H at C$_{10}$), 9.85 (m, 1, syn methylene H at C$_{10}$); 3,3-dichloro-*trans*-tricyclo[7.1.0.0^{2,4}]deca-5,7-diene (IV): nmr (CCl$_4$)



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(1) M. Ogliaruso, R. Rieke, and S. Winstein, *J. Amer. Chem. Soc.*, **88**, 4731 (1966).

(2) M. Ogliaruso and S. Winstein, *ibid.*, **89**, 5290 (1967).

(3) T. J. Katz and P. J. Garratt, *ibid.*, **85**, 2852 (1963); *ibid.*, **86**, 4876, 5194 (1964).

(4) All compounds prepared gave satisfactory carbon, hydrogen, and chlorine analyses.

τ 4.01 (m, 2, inner vinyl $H_{6,7}$), 4.60 (m, 2, outer vinyl $H_{5,8}$), 8.10–8.85 (m centered at 8.46, 2, allylic $H_{4,9}$), 8.85–9.50 (m centered at 9.10, 3, nonallylic tertiary $H_{1,2}$ and anti methylene H at C_{10}), 9.86 (m, 1, syn methylene H at C_{10}).

The assignment of the stereochemistry of the products is based on the greater chemical-shift differences in the nmr between "inner" ($H_{6,7}$) and "outer" ($H_{5,8}$) vinyl protons expected in the trans compound IV.[5] The high-field protons of the vinyl multiplet adjacent to the cyclopropane ring are also further shielded by the ring current in the trans isomer IV.

It should be noted that in the reaction of II with carbon tetrachloride the *only* products obtained resulted from adjacent biscyclopropanation with the cis isomer predominating. The fact that the cis isomer predominates in this reaction is contrary to the results expected. By using steric considerations we are lead to the prediction that the second cyclopropyl ring would be more stable and more easily formed if it were oriented trans to the cyclopropyl ring already present in the molecule. However, in the reaction of II with carbon tetrachloride there is a preference for the cyclopropyl rings to be oriented cis to each other by a factor of 2:1 based on the yields of the two products. In view of this, and in view of the predominating stereochemistry of the products obtained from the reaction of alkali metal cyclooctatetraenides with gem dihalides,[3] it is likely that the cyclooctatetraenyl dianion and the monohomocyclooctatetraenyl dianion react with carbon tetrachloride *via* the same mechanism, and that this mechanism does involve the generation of a divalent carbon species which then combines with bicyclo[6.1.0]-nonatriene (I). However, still unexplained in both dianion reactions is what determines the stereochemistry of the products.

Reactions of the dianion II with other organic compounds are now under investigation.

Acknowledgments. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We thank the Badische Anilin und Sodafabrink, A. G., for a generous gift of cyclooctatetraene.

[5] This assignment is based on analogous adjacent bishomocyclooctatetraene compounds which will be discussed in a future paper.

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Electron Paramagnetic Resonance of CD_2 and CHD. Isotope Effects, Motion, and Geometry of Methylene

Sir:

We have observed that the epr spectra of CD_2 and CHD in a solid matrix differ significantly from the spectrum of CH_2. We assign the changes to differences in zero-point motion. Comparing CH_2 and CD_2 allows the first experimentally based determination of a zero-field parameter for rigid (or gas phase) methylene. Also, the apparent asymmetry of CHD is greater than that of either CH_2 or CD_2. This variation is consistent with methylene and its deuterated derivatives being substantially bent (HCH angle 136°) and rotating about the long axis. The electronic spectra of all three species have been previously observed in the gas phase by Herzberg.[1] These spectra were compatible with a "linear or nearly linear" geometry for the ground state.

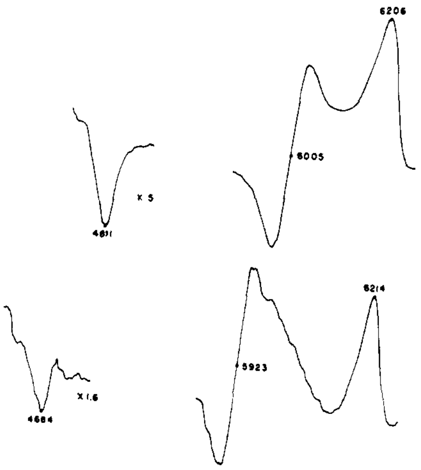

Figure 1. Spectra of CD_2 (top) and CHD (bottom) with $h\nu/g\beta$ = 3279.2 and 3277.4 G, respectively.

The precursors, mono- or dideuteriodiazirene, were condensed with xenon at 77°K and irradiated at 4°K. After irradiation ceased spectra remained unchanged for hours with the sample at 4°K, as expected for ground-state triplets (Figure 1).[2] The zero-field parameters which characterize the spectra[4,5] are D_{HD} = 0.7443, E_{HD} = 0.00640 cm^{-1} for the major triplet of CHD[2] and D_{DD} = 0.7563, E_{DD} = 0.00443 cm^{-1} for CD_2. The values which have been previously observed for CH_2 are D_{HH} = 0.6881, E_{HH} = 0.00346 cm^{-1}.[3,6] The presence of three and only three distinct spectra for the three isomeric precursors shows that the triplet contains two hydrogens.

To extrapolate from the above observations to a rigid methylene we note that $D \propto \langle (3z^2 - r^2)/r^5 \rangle$, while $E \propto \langle (y^2 - x^2)/r^5 \rangle$, where r and its coordinates refer to the distance between the two unpaired electrons.[7] Both parameters are largest for a triplet fixed in space, decrease with increasing motion, and vanish for a randomly tumbling molecule.[8] The 10% decrease in D_{HH} compared to D_{DD} indicates that CH_2 has a significantly larger wobble of the long (z) axis than CD_2. We assume that this motion takes place in a potential

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[1] (a) G. Herzberg, *Proc. Roy. Soc., Ser. A*, **262**, 291 (1961); (b) "Electronic Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1967, p 491.

[2] A second triplet species, which can dominate some CH_2 spectra and which we have assigned to a second crystalline form of the matrix,[3] is less in evidence in CHD and barely detectable in CD_2. This second triplet of CHD is visible on the high-field side of the 5923-G line.

[3] E. Wasserman, W. A. Yager, and V. J. Kuck, *Chem. Phys. Lett.*, 7, 409 (1970).

[4] E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, **41**, 1764 (1964).

[5] P. Kottis and R. Lefebvre, *ibid.*, **41**, 379 (1964).

[6] R. A. Bernheim, H. W. Bernard, P. S. Wang, L. S. Wood, and P. S. Skell, *ibid.*, **53**, 1280 (1970). We are grateful to Dr. Bernheim for making available a preprint of this first publication of an epr of CH_2. We disagree with the geometrical conclusion given.

[7] M. Goutermann and W. Moffitt, *ibid.*, **30**, 1107 (1959).

[8] See, for example, A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper and Row, New York, N. Y., 1967, Chapters 3 and 8.