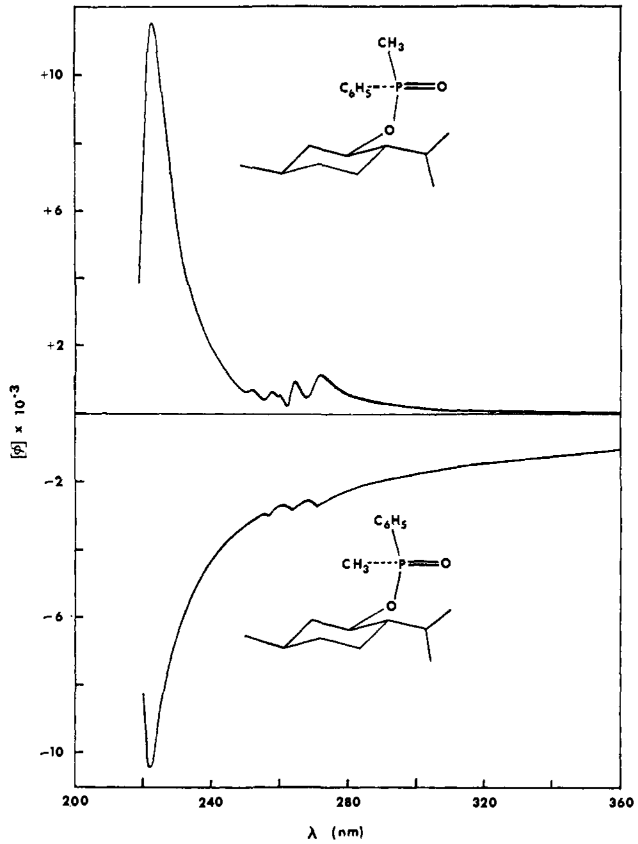

Figure 1.

The ord curves (Figure 1) of **2A** and **2B** are enantiomeric in type, the positive and negative Cotton effects corresponding to the *R* and *S* configurations at phosphorus, respectively. The chirality of the benzenephosphoryl chromophore (λ_{max} 210 nm (ϵ 8300), 217 nm (ϵ 7800)) dominates the ord, as previously found[10] for the analogous *p*-iodobenzenesulfinyl chromophore in the diastereomeric menthyl *p*-iodobenzenesulfinates. Further studies on the correlation of configuration and ord of phosphinates and phosphine oxides[11] are in progress.

(10) K. Mislow, M. M. Green, P. Laur, J. T. Melillo, T. Simmons, and A. L. Ternay, Jr., *J. Am. Chem. Soc.*, **87**, 1958 (1965).

(11) See also L. Horner and H. Winkler, *Tetrahedron Letters*, 3265 (1964); O. Červinka and O. Kříž, *Collection Czech. Chem. Commun.*, **31**, 1910 (1966).

(12) U. S. Public Health Service Predoctoral Fellow, 1966–1967.

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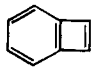
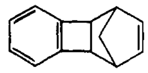
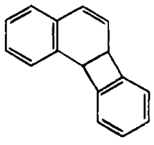
Oxidative Degradation of (Benzocyclobutadiene)iron Tricarbonyl

Sir:

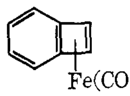
Previous work by Cava[1] and by Nenitzescu[2] and their collaborators has indicated that benzocyclobutadiene (I) is produced upon dehalogenation of dihalobenzocyclobutene with zinc or lithium amalgam. When conducted in the presence of cyclopentadiene, this reaction produces the Diels-Alder adduct II whereas, in the absence of added diene, the hydrocarbon III is formed.[2,3] Compound III is reasoned to be the stable rearrangement product of the intermediate Diels-Alder type dimer of benzocyclobutadiene.

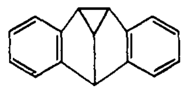

I


II


III

Our previous studies have indicated that cyclobutadiene is liberated upon oxidative degradation of cyclobutadieneiron tricarbonyl.[4] However, as also reported earlier, oxidative decomposition of (benzocyclobutadiene)iron tricarbonyl (IV) using silver ions as the oxidant produced none of the normal dimerization product of I, *viz.* III, but instead gave rise to the isomeric hydrocarbon V;[5] oxidation with ceric ion produced polymeric material. This has then raised the important question as to whether free benzocyclobutadiene is liberated in these oxidative decompositions. In this paper we wish to report evidence indicating that I is indeed produced upon oxidation of IV and to rationalize the anomaly presented by the formation of V.


IV


V

It is now found that oxidative degradation of the complex IV in the presence of cyclopentadiene, using lead tetraacetate in pyridine, produces the hydrocarbon II identical with an authentic sample prepared by the method of Nenitzescu.[2] In the absence of cyclopentadiene this oxidation also produces the normal dimer III in good yield, and none of the isomeric compound V can be detected. Identical behavior is found when ferric nitrate in aqueous ethanol is used as the oxidant. These products parallel exactly the pattern found in the earlier dehalogenation reactions and support the contention that the benzocyclobutadiene is implicated in their formation.

The rate of oxidation of the complex IV is fast and appears to be comparable to that of the oxidation of cyclobutadieneiron tricarbonyl with $Pb(OAc)_4$. Since evidence indicated benzocyclobutadiene to be reactive as a dienophile but not as a diene,[3] this then suggested the intriguing possibility of being able to add cyclobutadiene to benzocyclobutadiene by this technique. This has now proved to be possible; addition of a mixture of cyclobutadieneiron tricarbonyl and the complex IV to $Pb(OAc)_4$ afforded the adduct VI[6] in 75% yield.

(1) M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **79**, 1701 (1957).

(2) C. D. Nenitzescu, M. Avram, and D. Dinu, *Chem. Ber.*, **90**, 2541 (1957).

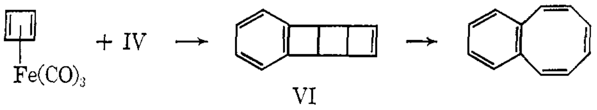
(3) M. P. Cava and M. J. Mitchell, *J. Am. Chem. Soc.*, **81**, 5409 (1959).

(4) J. C. Barborak and R. Pettit, *ibid.*, **89**, 3080 (1967), and references therein.

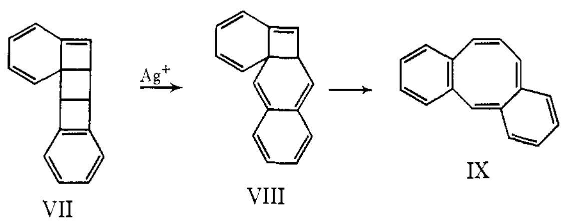
(5) G. F. Emerson, L. Watts, and R. Pettit, *ibid.*, **87**, 131 (1965).

(6) White crystalline solid, mp 17°, nmr absorptions at τ 2.98, 4.28, 6.22–6.77, having areas of 4:2:4, respectively. Elemental analysis and molecular weight are in agreement with the formula $C_{12}H_{10}$.

Compound VI undergoes thermal isomerization to benzocyclooctatetraene in almost quantitative yield.[7]



The question raised by the formation of the hydrocarbon V in the degradation with Ag^+ now clearly implicates involvement (other than mere oxidation) by the silver ion. Confirmation of this is seen in the fact that whereas degradation of IV with ferric nitrate gives only the normal dimer III, when the same oxidation is conducted in the presence of catalytic amounts of silver nitrate (20 molar %) the sole $C_{16}H_{12}$ product is V. Under a variety of conditions we have not been able to effect the isomerization of III to V with silver ion; hence III cannot be the precursor of V. The remarkable facile silver ion catalyzed isomerization of strained benzocyclobutenes to *o*-xylylenes discussed in the accompanying paper[8] now suggests a reasonable role for Ag^+. The dimerization of I produces the unstable Diels–Alder adduct VII which, before it thermally isomerizes to the normal dimer III, could undergo silver ion catalyzed rearrangement to the *o*-xylylene derivative VIII and thence to the cyclooctatetraene derivative IX. Intramolecular Diels–Alder addition of IX would then produce the hydrocarbon V.



[7] The product has properties identical with those reported by G. Wittig, H. Eggers, and P. Duffner, *Ann.*, 619, 10 (1958).

[8] W. Merk and R. Pettit, *J. Am. Chem. Soc.*, **89**, 4788 (1967).

[9] We thank the National Science Foundation, The U. S. Army Research Office (Durham), and the Robert A. Welch Foundation for financial support. We also thank Badische Anilin and Soda Fabrik and General Aniline and Film Corp. for generous gifts of cyclooctatetraene and iron carbonyl, respectively.

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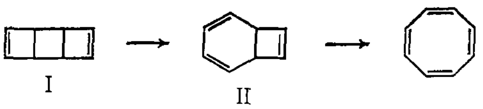
Metal Ion Catalyzed Cyclobutene–Butadiene and Benzocyclobutene–*o*-Xylylene Isomerizations

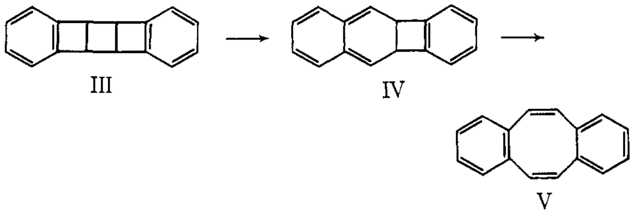
Sir:

We wish to report examples of facile metal ion (Ag^+ and Cu^+) catalyzed isomerizations of derivatives of cyclobutene to those of butadiene. Of particular interest in these reactions is the fact that if they proceed in a concerted manner they must do so by means of a disrotatory process.

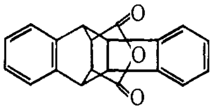
Nenitzescu and co-workers have reported that *anti*-tricyclooctadiene (I) isomerizes to cyclooctatetraene with a half-life of 20 min at 140°.[1] We have found that, in the presence of silver fluoroborate, the half-life is 5 min at 56°. A solution of I with equimolar amounts of $AgBF_4$ in boiling acetone is completely isomerized to cyclooctatetraene within 40 min; under the same conditions, in the absence of the silver salt, there is practically no isomerization after 24 hr. Similar rate enhancements are observed in acidified methanolic solutions containing cuprous chloride. Because of the *trans* nature of the rings in I, a one-step isomerization to cyclooctatetraene seems highly improbable; the initial step more likely involves the triene II.



The effect of silver ion is most dramatic in the case of dibenzotricyclooctadiene (III). This hydrocarbon is reported to undergo thermal isomerization to dibenzocyclooctatetraene (V) upon heating in refluxing *o*-dichlorobenzene (bp 180°) for 4–5 hr.[2] We find that at room temperature, in tetrahydrofuran in the presence of molar quantities of $AgBF_4$, the isomerization is complete within 10 sec. A solution of III in the absence of silver ion reveals no detectable (nmr) isomerization after standing at room temperature for 1 week.



When the hydrocarbon III is slowly added to a solution of $AgBF_4$ and maleic anhydride in ether at room temperature, the Diels–Alder adduct VI[3] is produced in high yield. Compound VI is not produced when maleic anhydride is added at room temperature to V, with or without added $AgBF_4$, or to compound III alone. This strongly suggests that the silver ion catalyzed isomerization of III proceeds *via* the *o*-xylylene derivative IV.



VI

A further interesting case is afforded by benzotricyclooctadiene (VII).[4] Addition of $AgBF_4$ to an ethereal solution of VII at 25° produces an almost instant precipitate of the silver complex of benzocyclooctatetraene; decomposition of the complex with NaCl affords benzocyclooctatetraene in better than 90% over-all yield. Again a solution of VII shows no detectable isomerization upon standing at 25° for several days. Addition of VII to maleic anhydride and $AgBF_4$ in ether at 25° produces the Diels–Alder adduct X.[5] This indicates that the catalyzed rearrangement of VII involves first a benzocyclobutene–*o*-xylylene re-

[1] M. Avram, I. G. Dinulescu, E. Marica, G. Mateescu, E. Sliam, and C. D. Nenitzescu, *Chem. Ber.*, **97**, 382 (1964).

[2] M. Avram, D. Dinu, G. Mateescu, and C. D. Nenitzescu, *ibid.*, **93**, 1789 (1960).

[3] M. Avram, I. G. Dinulescu, D. Dinu, G. Mateescu, and C. D. Nenitzescu, *Tetrahedron*, **19**, 309 (1963).

[4] W. Merk and R. Pettit, *J. Am. Chem. Soc.*, **89**, 4787 (1967).

[5] The nmr spectrum of this adduct confirms the structure indicated.