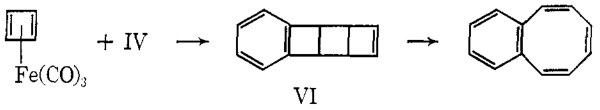
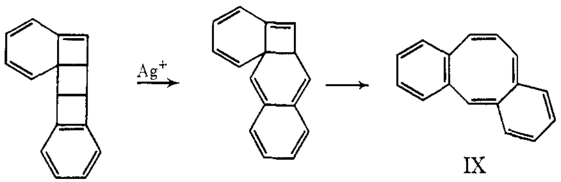
Compound VI undergoes thermal isomerization to benzocyclooctatetraene in almost quantitative yield.[7]



VI

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.



VII VIII IX

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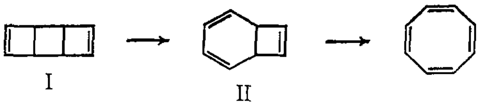
Metal Ion Catalyzed Cyclobutene–Butadiene and Benzocyclobutene–*o*-Xylylene Isomerizations

Sir:

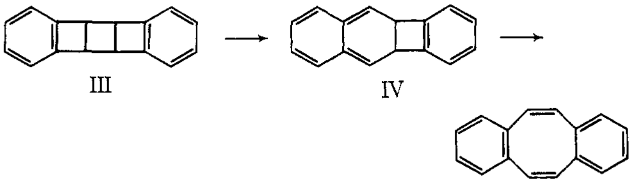
We wish to report examples of facile metal ion (Ag^+ and Cu^+) catalyzed isomerizations of derivatives of cyclobutene to those of butadiene. Of particular interest in these reactions is the fact that if they proceed in a concerted manner they must do so by means of a disrotatory process.

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.



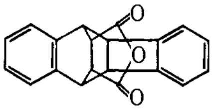
I II

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.



III IV V

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-

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

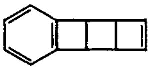
(2) M. Avram, D. Dinu, G. Mateescu, and C. D. Nenitzescu, *ibid.*, **93**, 1789 (1960).

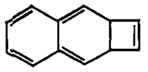
(3) M. Avram, I. G. Dinulescu, D. Dinu, G. Mateescu, and C. D. Nenitzescu, *Tetrahedron*, **19**, 309 (1963).

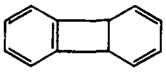
(4) W. Merk and R. Pettit, *J. Am. Chem. Soc.*, **89**, 4787 (1967).

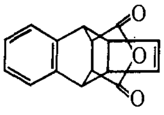
(5) The nmr spectrum of this adduct confirms the structure indicated.

arrangement to give VIII as an intermediate rather than a cyclobutene–butadiene rearrangement involving compound IX. Again, addition at room temperature of maleic anhydride to either benzocyclooctatetraene or to compound VII produces none of the adduct X.

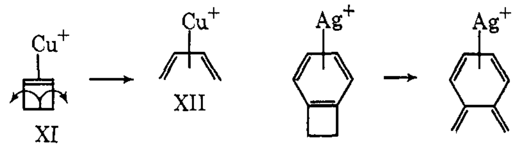

VII


VIII


IX


X

The isomerizations of compounds I, III, and VII would be expected to be exothermic reactions. The compounds owe their stability in part to the fact that the cyclobutene–butadiene transformations and, as can be shown by analogous reasoning, the benzocyclobutene-*o*-xylylene isomerizations are expected by the Woodward–Hoffmann rules to be conrotatory processes.[6] In these instances such rotations cannot occur because of constraints imposed by the nature of the rings to be formed. One possible explanation for the role of the metal ion in the isomerizations is that they allow the concerted disrotatory process to proceed *via* intermediate metal π complexes. Extension of the arguments given by Longuet-Higgins and Abrahamson[7,8] for the cyclobutene ring opening, applied to the isomerization of the cyclobutene–cuprous complex XI to the butadiene–cuprous complex XII, offers support of this.



XI XII XIII XIV

The symmetry of the appropriate orbitals of cyclobutene, butadiene, and the metal ion (Cu^+ or Ag^+), respectively, in the disrotatory process are as indicated: symmetrical, σ,π; ψ_1,ψ_3; s, p_y,p_z,d_{yz},d_{z^2}; antisymmetrical, σ^*,π^*; ψ_2,ψ_4; p_x,d_{xy},d_{xz}.

A satisfactory description[9] of the ground state of complex XI will be $\sigma^2,(\pi,s\text{–}d_{z^2})^4,(\pi^*,p_x\text{–}d_{xz})^2,(p_y\text{–}d_{yz})^2,d_{xy}{}^2$. From the orbital classification listed, it is seen that the disrotatory process leading to an electron configuration $(\psi_1,s\text{–}d_{z^2})^4,(\psi_2,p_x\text{–}d_{xz})^2,(\psi_3,p_y\text{–}d_{yz})^4,(\psi_4,d_{xy})^2$ is an allowed process and, according to qualitative concepts, this latter should represent a stable configuration of the complex XII.[10] Analogous arguments can be derived for the disrotatory process of the benzocyclobutene complex XIII, giving the *o*-xylylene complex XIV.

We then propose that the role of the metal ion is to form an organometallic complex in which the sterically preferred disrotatory isomerization process is now allowed, the driving force for the reaction being relief of internal strain. Further investigation of these types of isomerizations are in progress.

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Received June 19, 1967

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(6) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).

(7) H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, **87**, 2045 (1965).

(8) Similar applications of these concepts have recently been applied by F. D. Mango and J. H. Schachtschneider [*ibid.*, **89**, 2484 (1967)] in consideration of metal-catalyzed intermolecular cyclization reactions.

(9) M. J. S. Dewar, *Bull. Soc. Chem. France*, **18**, C79 (1951).

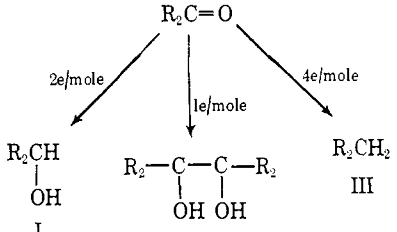
(10) It is to be noted that the over-all change in symmetry involved in the cyclobutene–butadiene conversion, namely $\sigma^2\pi^2$ (SS) to $\psi_1{}^2\psi_2{}^2$ (SA), which is forbidden in the absence of metal ion, becomes compensated through a similar change in the metal ion configuration $(p_x\text{–}d_{xy})^2$ (A) to $(p_y\text{–}d_y)_z{}^2$ (S).

(11) We thank the National Science Foundation, the U. S. Army Research Office (Durham), and the Robert A. Welch Foundation for financial assistance. We also thank Badische Anilin und Soda Fabrik for a generous gift of cyclooctatetraene.

Steroids. CCCXIII. Electrochemical Reactions. I. Reduction of Carbonyl Functions to Methylene or Deuteriomethylene Analogs

Sir:

The cathodic reduction of carbonyl compounds has been studied extensively and several review articles are available in the literature concerning this process.[1] Depending mainly on the electrode potential, the nature of the electrode, and the pH of the electrolyte, the reduction products can be alcohols (I), pinacols (II) and their subsequent rearrangement products, or hydrocarbons (III).



I II III

The synthetic scale electrochemical reduction of nonconjugated steroidal ketones and α-ketols at a stirred mercury cathode was found to yield the thermodynamically more stable equatorial alcohols with a high degree of stereospecificity and in very good yields.[2] We now wish to report an electrochemical method which provides an easy and efficient way of converting steroidal carbonyl compounds to the corresponding hydrocarbons in acidic medium. Furthermore, by using the appropriate solvent system during the electrolysis, deuterium atoms can be inserted into the molecule in place of the carbonyl group, a labeling technique which is indispensable in modern reaction mechanistic and spectroscopic studies.[3]

These reductions were carried out on samples varying in size from 10 mg to 3 g. The required reduction time was usually from 2 to 8 hr. Generally a 100–200-mg sample was dissolved in 30 ml of reagent grade dioxane; then 30 ml of 10% sulfuric acid was added and the resulting solution was placed into the cathode compart-

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(1) M. J. Allen, "Organic Electrode Processes," Reinhold Publishing Corp., New York, N. Y., 1958, Chapter 6; F. D. Popp and H. P. Schultz, *Chem. Rev.*, **62**, 19 (1962); N. Ya. Fioshin, *Usp. Khim.*, **32**, 60 (1963); S. Wawzonek, *Science*, **155**, 39 (1967).

(2) P. Kabasakalian, J. McGlotten, A. Basch, and M. D. Yudis, *J. Org. Chem.*, **26**, 1738 (1961).

(3) For a brief summary of deuterium-labeling techniques see H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Structure Elucidation of Natural Products by Mass Spectrometry," Vol. 1, Holden-Day, Inc., San Francisco, Calif., 1964, Chapter 2.