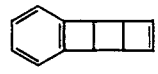
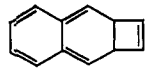
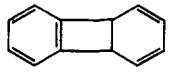
arrangement to give VIII as an intermediate rather than a cyclobutene–butadiene rearrangement involving compound IX. Again, addition at room temperature of maleic anhydride to either benzocyclooctatetraene or to compound VII produces none of the adduct X.



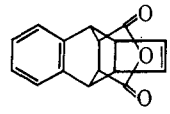
VII



VIII

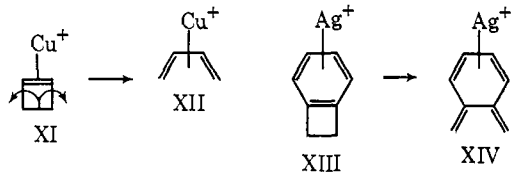


IX



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.

(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).

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.

(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.

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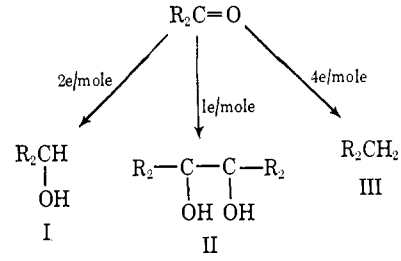
Steroids. CCCXIII. Electrochemical Reactions. I. Reduction of Carbonyl Functions to Methylene or Deuteriomethylene Analogs

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).



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-

(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.

Table I. Electrochemical Reduction of Carbonyl Compounds in Strongly Acidic Medium

Starting material	Product	Mp, °C	Yield, %	Electrolysis time, hr
17β-Hydroxy-5α-androstan-3-one	5α-Androstan-17β-ol	162–164	97	3.5
3-Methoxy-1,3,5(10)-estratrien-17-one	3-Methoxy-1,3,5(10)-estratriene	77.5–78.5	94	20
17α,20:20,21-Bismethylenedioxy-3β-acetoxypregn-5-en-19-one	17α,20:20,21-Bismethylenedioxy-3β-hydroxypregn-5-ene[a]	242–245	90	4
3β-Hydroxypregn-5-en-20-one	3β-Hydroxypregn-5-ene	133–134	96	5.5
3β,17α-Dihydroxypregn-5-en-20-one	3β-Hydroxypregn-5-ene	133–134	85	6

[a] The product was hydrolyzed by heating it with sodium hydroxide in methanol to yield the free alcohol.

Table II. Deuterium Incorporation by Electrochemical Reduction of Carbonyl Compounds

Starting material	Product	Mp, °C	Isotope composition,[a] % d_0	d_1	d_2	d_3	d_4	d_5
Estrone	Estra-1,3,5(10)-trien-3-ol-17,17-d_2	133–135		6	89	5		
Estrone-16,16-d_2 methyl ether[b]	3-Methoxy-1,3,5(10)-estratriene-16,16-d_2	76–78		6	94			
3β-Hydroxypregn-5-en-20-one	Pregn-5-en-3β-ol-20,20-d_2	134–136		4	84	11	1	
17β-Hydroxy-5α-androstan-3-one	5α-Androstan-17β-ol-3,3-d_2 acetate[c]	80–81.5		1	33	34	25	7
17α,20:20,21-Bismethylenedioxy-3β-acetoxypregn-5-en-19-one	17α,20:20,21-Bismethylenedioxy-3β-acetoxypregn-5-ene-19,19-d_2	170–172	1	6	93			
5α-Cholest-22-en-16-one[d]	5α-Cholest-22-ene-16,16-d_2	96.5–97.5		7	90	3		

[a] The isotope composition was determined mass spectrometrically. [b] The deuterium exchange was carried out by heating under reflux for 48 hr a solution of estrone methyl ether in 90% tetrahydrofuran and 10% deuterium oxide containing a drop of 10% sodium deuterioxide in deuterium oxide. Isotope composition: 5% d_1 and 95% d_2. The reduction was carried out in a protic medium. [c] The reduction product was acetylated with acetic anhydride in pyridine to facilitate purification. [d] This reaction was carried out by Dr. S. G. Wyllie at the Chemistry Department, Stanford University.

ment of the cell.[4] The same electrolyte was used in the anode compartment. The cell was kept at room temperature, the cathode compartment was magnetically stirred, and the current was kept constant at 200 ma. The progress of the reduction was followed by spot testing the reaction mixture directly on thin layer chromatographic plates.

The reduction of some typical steroidal ketones to their methylene analogs proceeded in high yield (see Table I). The thermodynamically more stable alcohol epimer[2] is usually observed as a minor side product (*ca.* 5%). These alcohols resisted further reduction under the same reaction conditions and, therefore, are not reaction intermediates. The observed reductive cleavage of the hydroxyl function α to the carbonyl group in 3β,17α-dihydroxypregn-5-en-20-one (see Table I) is in agreement with the observations of Kabasakalian, *et al.*[2] Other hydroxyl groups are unaffected.

Incorporation of two deuterium atoms in place of the carbonyl group can be achieved with a high degree of isotopic purity (see Table II). This method[5] provides an easy means of labeling certain positions on the steroid nucleus, such as the C-17,[6,7] C-19,[8] and C-20[6] positions, which have proven difficult to attain by the application of the usual chemical reaction sequences. Deuterium exchange of the enolizable protons α to the carbonyl groups appears to be the major cause of isotopic impurity and it is more pronounced for ketones such as at C-3, for example, for which the enolization is extremely rapid. This technique can also be employed to introduce deuterium atoms onto the carbon atoms adjacent to the carbonyl group by exchanging the enolizable protons with deuterium atoms, followed by the cathodic reduction of the carbonyl group in a protic medium (see the entry for estrone-16,16-d_2 methyl ether in Table II).

Examination of the scope of this reaction and its extention to α,β-unsaturated ketones and other functionalities is currently in progress.

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(4) The electrolyses were performed in a divided cell equipped with a cellulose dialysis membrane. The electrodes were cut from a 1.5-mm-thick lead sheet.

(5) The deuterium-labeled hydrocarbons were prepared in a microcell by using 6 ml of reagent grade dioxane and 6 ml of 10% deuteriosulfuric acid in deuterium oxide (deuterium content 97%) in both compartments. In order to prevent isotope dilution by atmospheric moisture, the air spaces in the cells were flushed with a slow current of dry nitrogen.

(6) C. Djerassi and L. Tökés, *J. Am. Chem. Soc.*, **88**, 536 (1966).

(7) An improved method for the preparation of androstane-17,17-d_2 *via* the lithium aluminum deuteride reduction of the *p*-toluenesulfonylhydrazone of the 17-ketone was reported by L. Tökés, Ph.D. Dissertation, Stanford University, 1965.

(8) C. Djerassi and M. A. Kielczewski, *Steroids*, **2**, 125 (1963); R. H. Shapiro, D. H. Williams, H. Budzikiewicz, and C. Djerassi, *J. Am. Chem. Soc.*, **86**, 2837 (1964).

The Radiation Cross-Linking of Hydrogenated Polyethylene[1]

Sir:

Cross-linking of linear polyethylene induced by high-energy irradiation has been shown to be dependent on both the sample temperature and level of crystallinity.[2-4] In particular, it was concluded from the

(1) This work was supported by the National Aeronautics and Space Administration under Research Grant NSG 247-62 to Florida State University.

(2) R. Kitamaru, L. Mandelkern, and J. Fatou, *J. Polymer Sci.*, 2B, 511 (1964).

(3) R. Kitamaru and L. Mandelkern, *J. Am. Chem. Soc.*, **86**, 3529 (1964).

(4) T. Okada and L. Mandelkern, Abstracts, International Symposium on Macromolecular Chemistry, Tokyo, 1966; *J. Polymer Sci.*, in press.