A simplified form of the relationship discussed in the previous paragraph is that the ratio of D values for the triplet and the corresponding quintets should be approximately constant for a series of *meta* quintets. We find $D_{Va}/D_{IIIa} = 5.8$, $D_{Vb}/D_{IIIb} = 6.1$, and $D_{VI}/D_{IV} = 6.4$.

The theoretical value of the D/E ratio should be ~ 5 for IV or for IIIa,b if the bonds to the divalent carbon are colinear.[9,10] With IIIb, the one case in which E was determined directly, the ratio is 3.6. A possible explanation for this lower value lies in the potentiality for isomers in the methylenes as these are known to be bent about the divalent carbon atom.[4,13] Simple theoretical arguments[9] indicate that $D/E < 5$, ~ 5, > 5 for IIIb, VII, and VIII, respectively. Thus the absorptions used for the assignment of parameters may arise from the particular isomer IIIb.

The possibility exists that some of the epr lines are due to the quartet states such as IX which could be formally produced from IIIb. Arguments analogous to those used above to relate the parameters of the quintet to those of the corresponding triplet may be used to relate the quartet to those of a triplet and doublet.[9,10] The predicted values for the quartet state should not allow lines at as high or low magnetic fields as we observe experimentally. While quartet states may be present in the observed systems, the assignments we are making are most probably based on quintet resonances.

Acknowledgments. We wish to thank Mr. R. M. R. Cramer for his aid in determining the spectra and Dr. J. Higuchi for interesting discussions.

(13) A. M. Trozzolo, E. Wasserman, and W. A. Yager, *J. Am. Chem. Soc.*, 87, 129 (1965).

E. Wasserman, R. W. Murray, W. A. Yager
A. M. Trozzolo, G. Smolinsky
Bell Telephone Laboratories, Inc.
Murray Hill, New Jersey
Received July 27, 1967

Electrochemical Oxidation of $B_{12}H_{12}^{2-}$[1]

Sir:

Recent work[2] has shown that the electrochemical oxidation of the $B_{10}H_{10}^{2-}$ ion in acetonitrile parallels the aqueous chemical oxidation,[3-5] and that controlled-potential electrolysis is a useful method of carrying out the oxidative coupling of $B_{10}H_{10}^{2-}$ and its derivatives.[6] Previous attempts to oxidize $B_{12}H_{12}^{2-}$ in aqueous solution have been unsuccessful or have yielded only borates as products.[7,8] We now report the controlled-potential oxidation of $B_{12}H_{12}^{2-}$ in acetonitrile.

Voltammetry of $[(C_2H_5)_4N]_2B_{12}H_{12}$ at a rotating platinum electrode in acetonitrile (0.1 M tetraethylammonium perchlorate as supporting electrolyte) shows an anodic wave with $E_{1/2} = +1.5$ v (*vs.* sce). At a stationary platinum electrode, an anodic peak is observed at $+1.5$ v, with a shoulder at $+1.85$ v on a large anodic wave. In a typical run, 30 mmoles of $Na_2B_{12}H_{12}$ in 150 ml of acetonitrile was exhaustively electrolyzed under nitrogen at $+1.45$ v, using a graphite cloth anode, with no supporting electrolyte. The current was monitored using a strip chart recorder; the value $n = 0.91$ equiv/mole of $Na_2B_{12}H_{12}$ was found. The yellow solution was evaporated to dryness at room temperature, and the residue was dissolved in H_2O. Addition of CsF to the aqueous solution gave white crystals of $Cs_3B_{24}H_{23} \cdot 3H_2O$ (I) which were recrystallized from an acetonitrile–water mixture.

Anal. Calcd for $Cs_3B_{24}H_{23} \cdot 3H_2O$: B, 35.29. Found: B, 35.10. The compound does not melt below 300°.

In a similar experiment, addition of $(C_2H_5)_4NCl$ to the aqueous solution gave the corresponding tetraethylammonium salt of $B_{24}H_{23}^{3-}$.

Anal. Calcd for $[(C_2H_5)_4N]_3B_{24}H_{23}$: C, 42.82; H, 12.42; N, 6.24; B, 38.52. Found: C, 42.93; H, 12.72; N, 6.18; B, 38.66.

Stationary-electrode voltammetry of I in acetonitrile showed only the $+1.85$-v shoulder found in the voltammetry of $B_{12}H_{12}^{2-}$. The conductivity of I in H_2O gave $\Lambda_m = 462$ ohm^{-1} cm^{-1}, typical of a 3:1 electrolyte.

A solution of compound I was passed through a strong acid ion-exchange column, and the liberated acid was neutralized with sodium hydroxide (equivalent weight: calcd, 245.1; found, 246 ± 1). The infrared spectrum of I in KBr showed bands at 2500, 1050, and 940 and multiple bands from 750 to 710 cm^{-1}.

The ^{11}B nmr spectrum of aqueous I at 32.0 Mc consisted of an unsymmetrical doublet at $+15.4$ ppm relative to external $BF_3 \cdot O(C_2H_5)_2$, with $J = 130$ cps. The 100-Mc ^1H spectrum irradiated at 32.0 Mc consisted of two peaks of approximately equal intensities at $+3.02$ and $+3.21$ ppm from H_2O. The optimum decoupling frequencies for the two peaks differed by about 30 cps, which implies that the ^{11}B unsymmetrical doublet includes two doublets separated by less than 1 ppm. The low-field ^1H peak was considerably broader under optimum decoupling conditions than was the high-field peak.

The controlled-potential electrolysis of $B_{12}H_{12}^{2-}$ apparently parallels that of $B_{10}H_{10}^{2-}$, a one-electron oxidation followed by a dimerization reaction with the B_{12} cage left intact.

R. J. Wiersema, R. L. Middaugh
Department of Chemistry, University of Kansas
Lawrence, Kansas 66044
Received July 31, 1967

(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the University of Kansas General Research Fund for partial support of this research.
(2) R. L. Middaugh and F. Farha, Jr., *J. Am. Chem. Soc.*, 88, 4147 (1966).
(3) A. Kaczmarczyk, R. D. Dobrott, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, 48, 729 (1962).
(4) B. L. Chamberland and E. L. Muetterties, *Inorg. Chem.*, 3, 1450 (1964).
(5) M. F. Hawthorne, R. L. Pilling, and P. F. Stokeley, *J. Am. Chem. Soc.*, 87, 1893 (1965).
(6) R. L. Middaugh and A. P. Schmitt, unpublished work.
(7) D. Kaczmarczyk, G. B. Kolski, and W. P. Townsend, *J. Am. Chem. Soc.*, 87, 1413 (1965).
(8) M. F. Hawthorne, "The Chemistry of Boron and Its Compounds," E. L. Muetterties, Ed., John Wiley and Sons, Inc., New York, N. Y., 1967, Chapter 5.

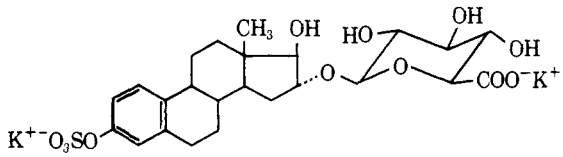
Steroid Conjugates. III.[1] The Synthesis of a Sulfoglucuronide Derivative of Estriol

Sir:

We wish to describe the first chemical synthesis of estriol 3-sulfate 16-glucuronide (3-sulfooxy-17β-hydroxyestra-1,3,5(10)-trien-16α-yl-β-D-glucopyranosidur-

(1) Paper II: E. W. Cantrall, M. G. McGrath, and S. Bernstein, *Steroids*, 8, 967 (1966).

onic acid) in the form of its dipotassium salt I.[2] Increasing reference to this double conjugate, and related



I

conjugates, in significant amounts in human fluids suggests an important role for such species in estrogen endocrinology and metabolism.[3]

Estriol (II) in absolute ethanol was refluxed for 2 hr with benzyl chloride in the presence of potassium carbonate to provide 3-benzyloxyestra-1,3,5(10)-triene-16α,17β-diol (III), mp 124–125° (acetone–hexane), [α]D +51°.[4] In benzene, III was coupled selectively at the C-16 position with methyl (tri-O-acetyl-α-D-glucopyranosyl bromide)uronate[5] in the presence of silver carbonate according to the procedure of Meystre and Miescher[6] to give methyl (3-benzyloxy-17β-hydroxyestra-1,3,5(10)-trien-16α-yl-2′,3′,4′-tri-O-acetyl-β-D-glucopyranosid)uronate (IV) (mp 245–246°, [α]D +6°), isolated by direct crystallization in 27% yield.[7]

The important consequence of glucuronide coupling at C-16 was confirmed by oxidation of IV in acetone with chromic acid at 0–5° which gave methyl (3-benzyloxyestra-1,3,5(10)-trien-17-on-16α-yl-2′,3′,4′-tri-O-acetyl-β-D-glucopyranosid)uronate (VI), mp 217–218° (methylene chloride–methanol).[8] Acetylation of IV with acetic anhydride–pyridine afforded the 17-acetate VII, which sinters at 119°, melts at 180° (methanol), [α]D −23°. Methyl (17β-acetoxy-3-hydroxyestra-1,3,5(10)-trien-16α-yl-2′,3′,4′-tri-O-acetyl-β-D-glucopyranosid)uronate (VIII), mp 213–215° (methylene chloride–methanol), [α]D −30°, was obtained on hydrogen–palladium–charcoal debenzylation in glacial acetic acid of recrystallized VII, or from IV without purification of VII. Sulfation of VIII using triethylamine–sulfur trioxide[9] in pyridine at room temperature provided the completely blocked double conjugate, methyl (17β-acetoxy-3-sulfooxyestra-1,3,5(10)-trien-16α-yl-2′,3′,4′-tri-O-acetyl-β-D-glucopyranosid)uronate triethylammonium salt (IX), mp 212–213° (methanol), [α]D −28°. *Anal.* Calcd for $C_{39}H_{57}NO_{16}S$: C, 56.58; H, 6.93; N, 1.69; S, 3.87. Found: C, 56.79; H, 6.76; N, 1.68; S, 3.89. Saponification with 1 *N* potassium hydroxide–methanol at room temperature for 18 hr gave the desired sulfoglucuronide dipotassium salt I as a dihydrate in the form of fine needles (aqueous acetone); mp >250° with slow decomposition; [α]D −5° (water). *Anal.* Calcd for $C_{24}H_{30}O_{12}SK_2 \cdot 2H_2O$: C, 43.88; H, 5.22; S, 4.88; K, 11.87; H_2O, 5.42. Found: C, 43.35, 43.80, 43.50; H, 5.07, 5.83, 5.56; S, 5.12; K, 11.87; H_2O, 6.0. The mixed conjugate I did not exhibit the diagnostic methylene blue test for sulfates;[10] this has also been observed for estradiol 3-sulfate 17-glucuronide.[1] However, the blocked mixed conjugate IX gave the typical positive color test with this reagent.

(2) M. Levitz, J. Katz, and G. H. Twombly, *Steriods*, **6**, 553 (1965), have presented compelling evidence for the successful biosynthesis of estriol 3-sulfate 16-glucuronide by incubation of estriol-16-glucuronide in a 100,000*g* supernatant of homogenized guinea pig liver in the presence of adenosine triphosphate and magnesium sulfate.

(3) (a) R. F. Straw, P. A. Katzman, and E. A. Doisy, *Endocrinology*, **57**, 87 (1955); (b) P. Troen, B. Nilsson, N. Wiqvist, and E. Diczfalusy, *Acta Endocrinol.*, **38**, 361 (1961); (c) J. C. Touchstone, J. W. Greene, Jr., R. C. McElroy, and T. Murawec, *Biochemistry*, **2**, 653 (1963); (d) R. Wilson, G. Ericksson, and E. Diczfalusy, *Acta Endrocrinol.*, **46**, 525 (1964); (e) E. Diczfalusy, M. Barr, and J. Lind, *ibid.*, **46**, 511 (1964); (f) M. Levitz, S. Shotsky, and G. H. Twombley, "Estrogen Assays in Clinical Medicine," C. A. Paulsen, Ed., University of Washington Press, Seattle, Wash., 1965, p 155; (g) O. W. Smith and D. D. Hagerman, *J. Clin. Endocrinol. Metab.*, **25**, 732 (1965); (h) M. Levitz, *ibid.*, **26**, 773 (1966); (i) U. Goebelsmann, G. Eriksson, E. Diczfalusy, M. Levitz, and G. P. Condon, *Acta Endocrinol.*, **53**, 391 (1966); (j) S. Emerman, G. H. Twombly, and M. Levitz, *J. Clin. Endrocrinol. Metab.*, **27**, 539 (1967); (k) E. R. Smith and A. E. Kellie, *Biochem. J.*, **104**, 83 (1967).

(4) The structure of all reported compounds was supported by spectral (ultraviolet, infrared, nmr) data and gave satisfactory elemental analyses. All compounds were shown to be homogeneous by tlc and, in the case of I and IX, by paper electrophoresis. All rotations are for chloroform solutions at 25°, unless otherwise indicated.

(5) G. N. Bollenbach, J. W. Long, D. G. Benjamin, and J. A. Lindquist, *J. Am. Chem. Soc.*, 77, 3310 (1955).

(6) Ch. Meystre and K. Miescher, *Helv. Chim. Acta*, **29**, 231 (1944).

(7) The utility of the 3-benzyloxy group in the synthesis of estrogen glucuronides has been demonstrated by J. S. Elce, J. G. D. Carpenter, and A. E. Kellie, *Biochem. J.*, **91**, 30P (1964).

(8) Compound VI was identical with an authentic sample synthesized by Dr. E. W. Cantrall in these laboratories and subsequently reported by J. C. Elce, J. G. D. Carpenter, and A. E. Kellie, *J. Chem. Soc., Sect. C*, 542 (1967).

(9) The use of this complex as a steroid sulfating agent will be discussed fully in forthcoming publications by J. P. Joseph, J. P. Dusza, and S. Bernstein.

(10) O. Crepy, and F. Rulleau-Meslin, *Rev. Franc. Études Clin. Biol.*, **5**, 283 (1960).

J. P. Joseph, J. P. Dusza, S. Bernstein

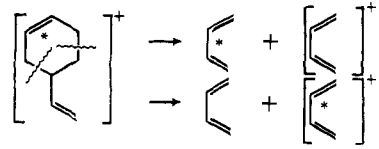
Lederle Laboratories, A Division of American Cyanamid Company
Pearl River, New York 10965

Received June 1, 1967

Mass Spectral Mechanisms. Preferential Association of Positive Charge with the Butadiene Fragment Containing the Vinyl Group of 4-Vinylcyclohexene in Competition with the Butadiene Fragment Arising from the Ring[1,2]

Sir:

The case is well documented that more stable cations are generally formed preferentially in mass spectra. We wish to report an experiment designed to answer the question whether two identical cations (along with two identical neutral species) originating from different environments within the same molecule are formed in equal or unequal abundances. We have found that in the mass spectrum of 4-vinylcyclohexene (dimer of butadiene) the retro-Diels–Alder reaction gives more of the budadiene fragment ion containing the vinyl group of the original molecule than of the butadiene fragment ion originating solely from the ring of the original molecule (eq 1).



(preferential) (1a)

(1b)

Deuterium-labeled 4-vinylcyclohexene,[3] labeled in

(1) Previous paper in this series: S. J. Weininger and E. R. Thornton, *J. Am. Chem. Soc.*, **89**, 2050 (1967).

(2) Supported by Public Health Service Grant 10693 from the National Institute of General Medical Sciences to the University of Pennsylvania.

(3) Prepared by allylic bromination of positions 3 and/or 6 of vinylcyclohexene with N-bromosuccinimide followed by treatment of the bromo derivative with zinc dust, sodium iodide, cupric chloride, and deuterium oxide in dioxane solution.[4] An average of ten nmr integrations showed that 1.00 ± 0.02 proton had shifted from the allylic region of 4-vinylcyclohexene to the region δ 5 in the bromo derivative, confirming that essentially all bromination had occurred at the 3 and/or 6 posi-