captide ions, than for low polarizability, high basicity nucleophiles such as methoxide ion. The third is a "return" factor: the energy released by (partial) bond formation between the nucleophile and the electrophilic center. The magnitude of the "return" will depend on the strength of the bond being formed and on the extent of its formation in the transition state.

Inasmuch as the bond dissociation energy of the O–H is considerably greater than that of the S–H bond,[41] the third factor favors alkoxide over mercaptide ions when there is a large degree of bonding of base to hydrogen in the transition state. However, this is much less significant when there is but a small degree of bonding of base to hydrogen. In such cases, the smaller energetic cost of desolvating mercaptide ions and of partially removing electrons from outer-shell orbitals should be relatively more important and perhaps predominant. Evidently these factors are predominant in the reactions of *t*-alkyl halides with mercaptide and alkoxide ions in alcoholic solvents.

Table II provides experimental evidence that more desolvation of methoxide than of thioethoxide ion occurs in forming the E2 transition state. Although the experimental uncertainty in the entropies of activation is rather high,[35] it is nevertheless clear that this parameter is more positive for the methoxide than for the thioethoxide reactions. Release of solvent molecules in forming the transition state tends to raise the entropy of activation.

Recently, England and McLennan[42,43] have conducted an independent series of investigations of the variation of the mercaptide/alkoxide reactivity ratio as the character of the transition state varies in E2 eliminations. Their conclusions are in excellent agreement with those drawn in the present discussion.

(41) H. A. Skinner and G. Pilcher, *Quart. Rev.* (London), **17**, 287 (1963)

(42) B. D. England and D. J. McLennan, *J. Chem. Soc.*, (B), 696 (1966).

(43) D. J. McLennan, *ibid.*, (B), 705, 709 (1966).

The Electrochemical Oxidation of Cyclooctatetraene in Acetic Acid Containing Acetate Ion

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The electrochemical oxidation of cyclooctatetraene in acetic acid containing acetate ion has been studied at both constant anode potential and constant current. With a platinum anode two product fractions were obtained. The first was shown to be a mixture of *cis*- and *trans*-7-methyl-8-acetoxybicyclo[4.2.0]octa-2,4-diene. The larger second fraction was shown to be a mixture of *cis*- and *trans*-bicyclo[4.2.0]octa-2,4-diene-7,8-diol diacetate and cycloheptatrienecarboxaldehyde diacetate. With a carbon anode only the latter of the above two product mixtures was obtained. The mechanisms of these reactions have been discussed. The cation radical, resulting from a one-electron transfer, and the planar cyclooctatriene dication are possible intermediates.

Previous studies of the anodic acetoxylation of organic compounds in acetic acid containing acetate ion[1-4] have demonstrated that this reaction commonly occurs *via* an initial two-electron transfer from the organic substrate to form an electrophilic species. The acetoxylated products are formed from ionic intermediates and are not the result of a homolytic reaction between an anodically generated acetoxy radical and the substrate. This interpretation is supported by polarographic measurements,[1,2] by the products formed by electrolysis at controlled potential (cpe),[1,2] and by studies of the rates of gas formation at the anode.[3,4] This mechanism has also been proposed by Salzberg and co-workers,[5,6] by Bonner and Mango,[7] and by Steuber and Dimroth[8] for anodic acetoxylation, by Parker and Burgert[9] for anodic cyanation, and by Schmidt and Meinert[10] for anodic fluorination.

The electrochemical behavior of cyclooctatetraene (COT) is of particular interest, since either a two-electron reduction or a two-electron oxidation offers the possibility of converting COT from its stable, "tub" conformation into a molecule having a planar, regular, octagonal conformation, $4n + 2$ π electrons, and aromatic character.[11] This possibility on reduction has been fully realized.[12,13] Polarography in anhydrous dimethyl sulfoxide or N,N-dimethylformamide (DMF) shows that COT is reduced in two one-electron steps, the intermediate monoanion radical being identified by its esr spectrum during controlled-potential electrolysis in DMF. With proton donors present the two cathodic waves coalesce into a single two-electron wave. Preparative experiments[13]

(1) L. Eberson and K. Nyberg, *Acta Chem. Scand.*, **18**, 1568 (1964).

(2) L. Eberson and K. Nyberg, *J. Am. Chem. Soc.*, **88**, 1686 (1966).

(3) S. D. Ross, M. Finkelstein, and R. C. Petersen, *ibid.*, **86**, 4139 (1964).

(4) S. D. Ross, M. Finkelstein, and R. C. Petersen, *J. Org. Chem.*, **31**, 128 (1966).

(5) M. Leung, J. Herz, and H. W. Salzberg, *ibid.*, **30**, 310 (1965).

(6) H. W. Salzberg and M. Leung, *ibid.*, **30**, 2873 (1965).

(7) F. D. Mango and W. H. Bonner, *ibid.*, **29**, 1367 (1964).

(8) F. W. Steuber and K. Dimroth, *Chem. Ber.*, **99**, 258 (1966).

(9) V. D. Parker and B. E. Burgert, *Tetrahedron Letters*, 4065 (1965).

(10) H. Schmidt and H. Meinert, *Angew. Chem.*, **72**, 109 (1960).

(11) E. Hückel, *Z. Physik*, **70**, 204 (1931).

(12) T. J. Katz, W. H. Reinmuth, and D. E. Smith, *J. Am. Chem. Soc.*, **84**, 802 (1962).

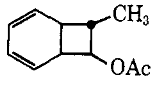
(13) R. D. Allendoerfer and P. H. Rieger, *ibid.*, **87**, 2336 (1965).

demonstrated that 1,3,5-cyclooctatriene was the principal product in the former case, whereas in 80% DMF–water[13] or in 50% ethanol–water[14] a mixture of 1,3,5- and 1,3,6-cyclooctatriene was obtained.[15]

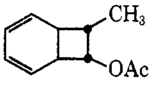
The electrochemical oxidation of COT has not been studied in a comparable manner. The low ionization potential of COT (8.63 ev)[16] suggests that it should be readily oxidized at an anode, and, in fact, polarograms of COT in glacial acetic acid–sodium acetate display a single, two-electron wave at 1.42 v *vs.* the saturated calomel electrode (sce).[2] By analogy with the two-electron reduction of COT which results in the planar 10π-electron COT dianion, a two-electron oxidation would possibly lead to a 6π-electron dication, and it was, therefore, of considerable interest to examine the reaction products from the anodic oxidation of cyclooctatetraene. The system chosen for this study was acetic acid containing acetate ion, since a number of other compounds have been investigated by the cpe technique in this medium.[2] The principal aim was to determine the reaction products, and no attempt was made to carry out the electrolyses under conditions which would allow a direct study of the dication. This latter objective would require a system completely free of nucleophilic reagents. Although possible in principle,[17] the lack of suitable solvents and the possibility that unreacted COT might act as a nucleophile toward any dication formed makes such an experiment of doubtful feasibility.[18]

Results[19]

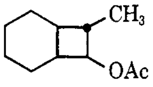
Controlled potential electrolysis of COT at +1.50 v (*vs.* sce) gave a product which on distillation could be separated into a low-boiling fraction [bp 60–80° (0.7 mm)], a high-boiling fraction [bp 105–110° (0.7 mm)], and a nondistillable, resinous residue. The low-boiling fraction was redistilled and it then analyzed correctly for $C_{11}H_{14}O_2$, a monoacetate resulting from the addition of the elements of methyl acetate to COT. This fraction was not separated by vpc into components, although its nmr spectrum clearly indicated two major ones in the approximate proportions 30:70. Catalytic reduction gave a new monoacetate, $C_{11}H_{18}O_2$ [bp 65–70° (0.4 mm)], and nmr data again demonstrated the presence of two components in the proportions 30:70. On the basis of nmr data, described and discussed in the Experimental Section, the structures assigned to the compounds in the monoacetate fraction and its reduction product are **1a** and **1b** and **2a** and **2b**, respectively.



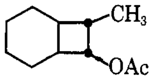
1a



1b

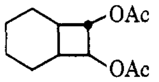


2a

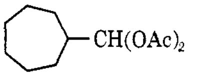


2b

Redistillation of the high-boiling fraction gave a product corresponding to the addition of two acetoxy groups to COT, $C_{12}H_{14}O_2$. Vpc on 5% neopentyl glycol succinate on Chromosorb P revealed the presence of three major components, two of which had retention times very close to each other. Reduction of this product gave a saturated diacetate, $C_{12}H_{18}O_4$, which on vpc analysis showed three well-resolved peaks, corresponding to compounds **3**, **4**, and **5** (arranged in order of increasing retention times) comprising 27, 29, and 44% of the mixture.



3



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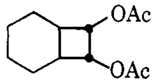
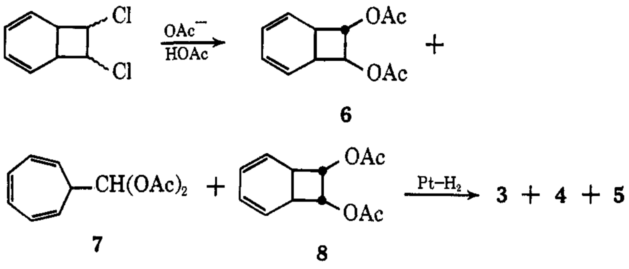


5

Compounds **3** and **4** were identified by comparison with authentic samples, prepared by oxidation of COT with mercuric acetate in glacial acetic acid[20] and with lead tetraacetate–boron trifluoride in glacial acetic acid,[21] respectively, followed by catalytic reduction of the products. Comparison was based on nmr spectral data and vpc retention times. Compound **5** was prepared by the following reaction sequence. COT dichloride can be obtained as a mixture of *cis* and *trans* isomers;[22] on solvolysis in glacial acetic acid in the presence of sodium acetate it is converted into a mixture of **6**, **7**, and **8**, which on reduction give **3**, **4**, and **5**. Vpc and nmr cross checks on the compounds or mixtures obtained from the electrolysis experiments, the chemical oxidations, and the solvolysis experiment, as well as the mixture obtained by catalytic reduction, gave a wholly consistent picture of the high-boiling diacetate fraction obtained on anodic oxidation of COT.



Cyclooctatetraene was also electrolyzed in acetic acid containing 1.67% water and potassium acetate at constant current (2 amp) both with platinum electrodes (two pieces of platinum, 0.025 cm thick, 2.5 cm wide immersed to a depth of 5 cm and at a separation of 2 cm) and with a platinum cathode and a carbon anode (the above platinum electrodes interconnected to form the cathode and a carbon rod, 0.6 cm in diameter immersed to a depth of 5 cm and centered between the two cathodes, as the anode).

As in the cpe experiment, the electrolysis with platinum electrodes resulted in two product fractions—a small monoacetate fraction (7.7% yield) and a larger diacetate fraction (34.7% yield). The mono-

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[14] L. E. Craig, R. M. Elofsen, and I. J. Ressa, *J. Am. Chem. Soc.*, **75**, 480 (1953).

[15] The 1,3,6 isomer is probably not a primary product and may result from alkali-catalyzed isomerization of the 1,3,5-triene.

[16] I. Omura, H. Baba, and K. Higashi, *J. Phys. Soc. Japan*, **10**, 317 (1955); *Chem. Abstr.*, **50**, 11*h* (1956).

[17] G. J. Hoijtink, *Chem. Ing. Tech.*, **35**, 333 (1963).

[18] For an unsuccessful attempt to prepare the COT dication by a chemical method (the reaction of COT dibromide with stannic chloride), see D. Bryce-Smith and N. A. Perkins, *J. Chem. Soc.*, 1339 (1962).

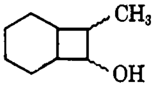
[19] The products formed by the electrochemical oxidation of COT in acetic acid containing acetate ion were investigated simultaneously and independently in two laboratories, the University of Lund and the Sprague Electric Co. In spite of differences in reaction conditions, similar if not identical results were obtained, and similar conclusions were reached. It was, therefore, mutually agreed to publish these results jointly.

[20] A. C. Cope, N. A. Nelson, and D. S. Smith, *J. Am. Chem. Soc.*, **76**, 1100 (1954).

[21] M. Finkelstein, *Chem. Ber.*, **90**, 2097 (1957).

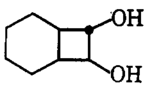
[22] M. Avram, I. Dinulescu, M. Elian, M. Farcasin, E. Marica, G. Mateescu, and C. D. Nenitzescu, *ibid.*, **97**, 372 (1964).

acetate composition was, within experimental error, the same as that obtained in the cpe experiment. This conclusion is based on nmr data described in the Experimental Section and supported by catalytic reduction of the monoacetate ($C_{11}H_{14}O_2$) to the saturated product ($C_{11}H_{18}O_2$), its hydrolysis to the alcohol ($C_9H_{16}O$, **9**), and preparation of a phenylurethan from this alcohol.



9

The higher boiling diacetate fraction contained the same three compounds formed by cpe, in altered but not significantly different proportions. Analysis by nmr indicated the presence of 40% **6**, 25–35% **7**, and 25–35% **8**. The structural assignments were confirmed by catalytic reduction of the mixture to the saturated compounds and nmr analysis of the reduced mixture as well as by hydrolysis of this latter mixture and isolation of cycloheptanecarboxaldehyde as the known semicarbazone and of the known *trans* glycol (**10**).



10

The electrolysis with a carbon anode gave a single product in 61% yield. This proved to be almost identical with the higher boiling diacetate fraction obtained with the platinum anode, and no trace of the lower boiling monoacetate fraction was found. Analysis by the methods described above indicated the presence of 34–44% **6**, 28–33% **7**, and 28–33% **8**.

Finally, confirmatory evidence for the presence of the *cis* diacetate (**8**) in the electrolysis product and of **5** in the reduction product was obtained by isomerizing *trans*-bicyclo[4.2.0]octane-7,8-diol with aluminum triisopropoxide in isopropyl alcohol containing acetone and converting the isomerized product into a mixture of diacetates. Analysis by vpc indicated that the mixed diacetates contained 99% **3** and 1% **5**, with the *cis* diacetate (**5**) showing exactly the same retention time as the compound in the reduced electrolysis product to which structure **5** had been assigned.

Experimental Section

Blank Run on COT.—COT, sodium acetate, and acetic acid in the same proportions as used in the electrolysis experiments were kept at 35–40° for 40 hr without passing any electric current. After the usual work-up, 78% of the COT was recovered. On vpc of the distillation residue no mono- or diacetate was detectable.

Cpe Oxidation of COT in Glacial Acetic Acid–Sodium Acetate.—A solution of freshly distilled COT (27.5 g) and anhydrous sodium acetate (12.0 g) in glacial acetic acid (220 ml) was electrolyzed at an anode potential of 1.5 v in an apparatus which has been described previously.[2] This potential allowed a current of approximately 0.4 amp to pass through the electrolyte. The temperature was maintained at approximately 30° by external cooling. A total of 57,000 coulombs was passed through the solution (calculated for a two-electron oxidation, 52,000 coulombs). The reaction mixture was poured into water (1000 ml), and the organic material was extracted with two 250-ml portions of ether. The ether extracts were washed with water, sodium bicarbonate solution, and water and dried over anhydrous magnesium sulfate. After removal of the ether, the residue was distilled *in vacuo* giving the following fractions: (1) bp 60–80° (0.7 mm), 1.4 g; (2) bp 80–105° (0.9 mm), 1.0 g; and (3) bp 105–110° (0.9 mm), 19.1 g. Slight decomposition was noted toward the end of the distillation. The resinous residue, soluble in chloroform, contained acetate groups and probably methyl groups and may be a polymeric product resulting from intermolecular carbonium ion reactions.

Fraction 1 gave a single, large peak with a retention time of 9.8 min on vpc on 5% neopentylglycol succinate on Chromosorb P (2 m × $^1/_8$ in.). The nmr spectrum in deuteriochloroform was as follows: 1.05, doublet (J = 6.8 cps), and 1.10, doublet (J = 6.3 cps), sum of three protons, ratio 1.05/1.10 = 71/29; 1.94, singlet, and 1.89, singlet, sum of three protons, ratio 1.94/1.89 $\sim$ 70/30; 2.86, complex multiplet, one proton; and 6.00 ppm, multiplet, four protons.

This spectrum is that to be expected for a mixture of **1a** and **1b**. The doublets at 1.05 and 1.10 ppm, with integrated band areas in the proportions 70:30, are assignable to the methyl groups. The two acetate methyl signals at 1.94 and 1.89 ppm show the same approximate 70:30 ratio. The broad and complex absorption around 2.86 ppm was assigned to the bridgehead hydrogens and the hydrogen α to the methyl group. The proton α to the acetoxy group gave a multiplet in the region 4.50–5.20 ppm. Finally, the vinyl protons appeared as a complex multiplet centered around 6.0 ppm. The different groups of signals occurred in the proportions 3:3:3:1:4 in agreement with structures **1a** and **1b**.

Fraction 2 was a mixture of the compounds found in fractions 1 and 3, and was discarded.

Fraction 3 was separated by vpc at 165° into three major components with retention times of 16.5, 17.0, and 19.8 min. The first two components appearing were **7** and **6**, respectively. Their presence was also confirmed by the nmr spectrum of the mixture which exhibited the characteristic doublet of authentic **7** at 7.15 ppm, and the vinyl signals typical of authentic **6**.

Reduced Cpe Product.—The electrolysis was carried out as before with acetic acid (160 ml), anhydrous sodium acetate (12.0 g), and freshly distilled COT (16.0 g). The anode potential was +1.5 v, the current was 0.2–0.3 amp, and the electrolysis time was 30 hr. On catalytic hydrogenation over platinum at room temperature and 60 psi, the isolated, crude product in ether (100 ml) absorbed 0.26 mole of hydrogen. Distillation at 0.4 mm gave the following fractions: (1) bp 60–70°, 1.0 g; (2) bp 70–92°, 0.8 g; and (3) bp 92–110°, 10.6 g.

Vpc of fraction 1 at 130° revealed the presence of two compounds with retention times of 7.3 and 7.9 min in the approximate proportions of 3:7. The nmr spectrum had the following signals: 1.00, doublet (J = 6.0 cps), and 1.05, doublet (J = 6.5 cps), sum of three protons, ratio 1.00/1.05 = 3/7; 1.53, broad band, eight protons; 1.95, strong singlet, and 1.98, weak singlet, sum of three protons; 2.00–2.70, broad band, three protons; and 4.2–5.1 ppm, multiplet, one proton.

This spectrum is in good agreement with that expected for a mixture of **2a** and **2b**. The two doublets at 1.00 and 1.05 ppm (areas in the proportions 30:70) correspond to the methyl groups, and the broad signal around 1.53 ppm is due to methylene groups. The acetate methyl groups result in singlets at 1.95 and 1.98 ppm. The broad, poorly defined band in the region 2.0–2.7 ppm is attributable to the bridgehead hydrogens and the hydrogen α to the methyl group, and the complex multiplet from 4.2–5.1 ppm arises from the hydrogen α to the acetoxy group. The proportion between the areas under the signals was approximately 3:8:3:3:1.

Fraction 2 had the same components as fractions 1 and 3, and was discarded.

Fraction 3, after redistillation, was found by vpc at 160° to contain three components, **3**, **4**, and **5**, with retention times of 19.8, 22.1, and 24.8 min, in the proportions 27:29:44. Authentic **3** and **4** had retention times of 19.8 and 22.1 min, respectively. The *cis* diacetate (**5**) prepared by solvolysis of COT–dichloride had a retention time of 24.9 min. The nmr spectrum of this mixture was also used to determine its composition. Use was made of the doublet at 6.55 ppm exhibited by authentic **4**, the eight-line multiplet at 4.6–5.3 ppm shown by authentic **3**, and the doublet at 5.13 ppm (coupling constant to the bridgehead hydrogen = 3.8 cps), which is ascribed to the protons α to the acetoxy group in **5**. From integration of the nmr spectrum the proportions of **3**, **4**, and **5** were 30:25:45 in reasonable agreement with the vpc results.

Constant-Current Electrolysis. Rate of Gas Generation at the Anode.—Using the technique and cell previously described,[3] a solution of freshly distilled COT (9.2 g, 0.088 mole) and potassium acetate (5 g) in acetic acid (50 ml) was electrolyzed at 0.4 amp for a total of 23.7 hr. After 2 hr the rate of gas generated at the anode was 13.5% of that calculated for Kolbe electrolysis of acetic acid, and after 23.5 hr the rate was 53.7% of that calculated.

Constant-Current Electrolysis. Preparative Experiments.—The electrolysis cell was a water-jacketed, 200-cc beaker fitted with a magnetic stirring bar, a thermometer, and a Teflon cover to which was attached the appropriate electrode assembly. In the experiment with a platinum anode the electrodes were two pieces of platinum, 0.025 cm thick and 2.5 cm wide immersed to a depth of 5 cm and at a separation of 2 cm. When a carbon anode was used, the above platinum electrodes were interconnected to form a dual cathode, and a carbon rod, 0.6 cm in diameter and immersed to a depth of 5 cm, was placed between them as the anode. Current was provided by a variable-voltage power supply.

In the electrolysis at the platinum anode, a solution of freshly distilled COT (27.6 g, 0.265 mole) and potassium acetate (20 g) in acetic acid (120 ml) and water (2 ml) was electrolyzed at a current of 2 amp until 0.53 equiv of charge was passed. The temperature was kept between 40 and 60°. The electrolysis mixture was poured into water (1 l.) and extracted with ether. The ether extract was neutralized by stirring with a suspension of sodium bicarbonate in water, and the bicarbonate suspension was extracted with ether. The combined ether extracts were dried over magnesium sulfate, and the ether was removed by distillation through a Vigreux column at atmospheric pressure. Distillation of the residue at the oil pump under nitrogen gave 3.4 g of recovered COT and then a first fraction of 3.2 g (7.7%), bp 75° (0.05 mm), $n^{23.5}$D 1.4897. A sample redistilled for analysis had $n^{23.5}$D 1.4890.

Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.06; H, 7.88.

An intermediate fraction (0.8 g) was discarded, and then a higher boiling fraction, 17.9 g (34.7%), was collected at 93–96° (0.04 mm), $n^{23.5}$D 1.4919. A sample redistilled for analysis had n^{25}D 1.4907.

Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 65.05; H, 6.66.

The same starting mixture was also electrolyzed using a carbon anode. The time of electrolysis and the work-up were the same as that described above. Midway during the electrolysis the anode was replaced with a fresh carbon rod to maintain the current. With the carbon anode 1.9 g of unreacted COT was recovered. None of the lower boiling product found with the platinum anode was obtained. The only product obtained had bp 80–90° (0.015 mm) and n^{25}D 1.4931. The yield was 33.4 g (61% based on the unrecovered COT). The infrared spectrum of this product was identical with that of the higher boiling product produced at the platinum electrode. There is no separation of the components of this product during distillation. When the product from a separate electrolysis was distilled into arbitrary fractions, the infrared spectra of the first and last fractions were identical.

Reduction of the Lower Boiling Product (Pt Anode).—A solution of the lower boiling product (5 g, 0.0028 mole) in acetic acid (100 ml) was hydrogenated over platinum oxide (100 mg). After the solution was filtered through Celite, the acetic acid was removed with the water pump. The residue was dissolved in ether and washed several times with saturated sodium bicarbonate solution. The ether solution was dried over magnesium sulfate, the ether was separated by distillation through a Vigreux column, and the residue was distilled at the oil pump yielding 4 g (78%) of a liquid, bp 34–40° (0.01–0.02 mm), n^{24}D 1.4610.

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found: C, 72.76; H, 9.55.

Reduction of Higher Boiling Product (Pt Anode).—A solution of the higher boiling product (22.4 g) in glacial acetic acid (150 ml) was hydrogenated over platinum oxide (0.5 g) and worked up as above. The yield was 21 g (92.1%) of water-white liquid, bp 64–74° (0.02 mm), n^{25}D 1.4608.

Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 64.02; H, 8.26.

Reduction of Electrolysis Product (C Anode).—Reduction of this product gave results indistinguishable in all respects from those obtained on reduction of the higher boiling product above.

Nmr Analyses of Products Obtained by Constant-Current Electrolysis.—All spectra were taken at 60 Mc in carbon tetrachloride solution. The lower boiling fraction (Pt anode) showed two doublets at 1.12 (J = 6.4 cps) and 1.17 (J = 6.8 cps) and two sharp singlets at 1.95 and 2.0 ppm. Their relative areas were 62:38:44:66, respectively. Assigning the peaks near 1 ppm to the C-7 methyl groups of **1a** and **1b** and the peaks near 2 ppm to the C-8 acetoxymethyl groups, the isomer ratio is approximately 64:36.

Reduction of this material gave a sample which showed two doublets at 1.00 and a broad singlet at 1.95 ppm, which on higher resolution proved to be a doublet. The area ratio of these two peaks was about 30:70, in fair agreement with the isomer ratio found in the unreduced material.

The nmr spectrum of the higher boiling fraction (Pt anode) showed four peaks at 1.98, 2.00, 2.02, and 2.05 ppm with relative areas of 20:35:20:25, respectively. By comparison with authentic **6** and **7**, these peaks were assigned as 1.9 and 2.02 ppm to **6**, 2.0 ppm to **7**, and 2.05 ppm to **8**. This permits an estimate of the composition as 40% **6**, 35% **7**, and 25% **8**. An estimate of the amount of **7** present may also be made by comparing the area of the doublet at 7.05 ppm ($J \sim 6$ cps) to the total area of the acetoxy methyl peaks. This suggests the presence of 27% **7**, in only fair agreement with the above result.

The nmr spectrum of the reduced material was analyzed using the absorption peaks due to those protons α to the acetoxy groups. From this it was estimated that the mixture contained 40% **3**, 24% **4**, and 36% **5**.

Analysis of the nmr spectrum of the product obtained using a carbon anode, in the manner described above, indicated the composition to be approximately 34% **6**, 33% **7**, and 33% **8**.

Analysis of the nmr spectrum of the reduced product, again as above, permitted an estimate of the composition as 44% **3**, 28% **4**, and 28% **5**.[23]

Hydrolysis of Reduced, Lower Boiling Product.—A solution of the reduced, lower boiling product (1.5 g) and potassium hydroxide (2 g) in methanol and water was refluxed 3 hr. The reaction mixture was poured into water (100 ml) and extracted with ether. The ether extract was dried over magnesium sulfate, and the ether was removed through a Vigreux column. Distillation of the residue at 0.005 mm yielded a middle fraction of 0.86 g, bp 40–42°, n^{24}D 1.4827.

Anal. Calcd for $C_9H_{16}O$: C, 77.08; H, 11.50. Found: C, 76.39; H, 11.39.

The phenylurethan was prepared and crystallized from hexane, mp 109–110°.

Anal. Calcd for $C_{16}H_{21}NO_2$: C, 74.10; H, 8.16; N, 5.40. Found: C, 74.75; H, 8.30; N, 5.23.

Acid Hydrolysis of the Reduced Higher Boiling Product.—A solution of the reduced higher boiling product (5.08 g) in methanol (15 ml) was treated with concentrated hydrochloric acid (20 drops) and refluxed for 3 hr. The solvent was removed with the water pump, and the residue was crystallized from benzene to give white crystals, mp 139–140° (with authentic *trans*-bicyclo[4.2.0]octane-7,8-diol, mmp 138–140°). A second crop was obtained on concentration of the mother liquor to yield a total of 1.0 g (31%) of **10**.

Isolation of Cycloheptanecarboxaldehyde as the Semicarbazone.—A solution of the reduced, higher boiling product (1.621 g) in methanol was treated with potassium hydroxide in aqueous methanol. After 10 min the reaction mixture was poured into water. Extraction with ether and work-up gave a mixture containing the aldehyde from which a semicarbazone was prepared following the procedure of Shriner, Fuson, and Curtin.[14] The total crude product (0.141 g) was twice crystallized from benzene–hexane; with authentic semicarbazone of cycloheptanecarboxaldehyde (mp 151–152°),[20] mmp 149–151°.

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(23) As a check and comparison of the somewhat different analytical methods used here and in Sweden, these last two samples were analyzed at the University of Lund, using both vpc and nmr. For the reduced sample the results were 40% **3** by vpc, 32% **4** by vpc, 28% **5** by vpc, and 46% **3** by nmr, 30% **4** by nmr, 24% **5** by nmr. The results from the nmr spectrum of the unreduced mixture were consistent with the above.

(24) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 5th ed, John Wiley and Sons, Inc., New York, N. Y., 1964, p 253.

***trans*-Bicyclo[4.2.0]octa-2,4-diene-7,8-diol Diacetate (6).**—This *trans* diacetate was prepared by the method of Cope, *et al.*,[20] mp 62–63°. The nmr spectrum in deuteriochloroform was as follows: 2.06, sharp singlet, and 2.11, sharp singlet, sum of six protons (CH_3COO); 2.3–2.9, undefined, two protons (CH bridgehead); 5.2–5.5, complex multiplet, and 5.8–6.1 ppm, complex multiplet, sum of six protons (H α to acetoxy and vinylic hydrogens).

***trans*-Bicyclo[4.2.0]octane-7,8-diol Diacetate (3).**—Compound 3 was obtained by hydrogenation of 6.[20] It had the following nmr spectrum in deuteriochloroform: 1.53, broad band, eight protons (CH_2); 2.02, doublet split ($J \sim 1$ cps), six protons (CH_3COO); 2.50, broad multiplet, two protons (CH bridgehead); and 4.6–5.3 ppm, eight lines, two protons (H α to acetoxy).

Oxidation of COT with Lead Tetraacetate–Boron Trifluoride.—The procedure used was that of Finkelstein.[21] The product (11.0 g from 10.0 g of COT) boiled at 80–88° (0.3 mm). Vpc at 160° gave two overlapping peaks. The nmr spectrum was complicated but clearly showed the characteristic doublet at 7.15 ppm to be expected for a proton α to two geminal acetoxy groups in **7**. The presence of **6** was indicated and this was readily demonstrated after catalytic hydrogenation at room temperature in ether solution. Vpc on the reduced product demonstrated the presence of **3** and **4** in the proportion 1:2; the same ratio was found by integration of the α-H peaks in the nmr spectrum. The spectrum above 3.0 ppm was complicated except for the acetate signals at 2.00, 2.04, and 2.10 ppm. Below this region the following signals were observed: 3.76, multiplet [$>CHCH(OAc)_2$]; 4.6–5.3, eight lines, on high resolution, identical with those of **3**; and 6.55 ppm, doublet ($J \sim 4$ cps) [$CH(OAc)_2$].

Solvolysis of COT–Dichloride.—The dichloride was obtained as a mixture of *cis* and *trans* isomers.[22] After catalytic reduction, the *cis/trans* ratio could be estimated at 1:1. The protons α to chlorine in the reduced mixture consisted of a sharp doublet, assigned to the *cis* isomer (J = 4.3 cps) and a complex pattern of at least seven lines for the *trans* isomer.

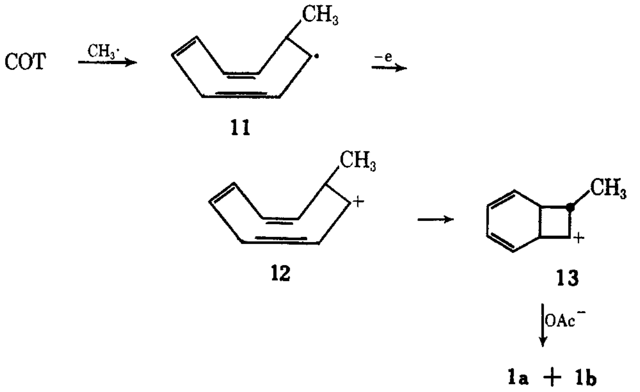
The above unreduced COT–dichloride (5.0 g) was added dropwise to a solution of potassium acetate (6.0 g) in acetic acid (25 ml) at 70°. The mixture was then kept at 100° for 2.5 hr. After work-up the product was hydrogenated. Distillation at 0.2 mm gave 3.7 g, bp 82–90°. This product, on vpc, was found to contain **3**, **4** (retention times identical with those of authentic specimens), and **5** in the proportion 69:33:6. Integration of the nmr spectrum gave the same ratio.

The nmr spectrum had a doublet at 6.55 ppm exhibited by authentic **4**, the characteristic eight-line pattern of the hydrogens α to CH_3COO in **3**, and also a weak doublet at 5.13 ppm ascribed to the α hydrogens of **5** (J (bridgehead hydrogens) = 3.8 cps).

Isomerization of *trans*-Bicyclo[4.2.0]octane-7,8-diol.—The *trans* diol (1.18 g), prepared from very pure diacetate which had been prepared *via* the mercuric acetate oxidation of COT and subsequent hydrogenation, was refluxed for 72 hr with aluminum isopropoxide (0.85 g), anhydrous 2-propanol (80 ml), and acetone (1.5 ml). The solvent was removed in a rotating film evaporator, and the residue was treated with 10% hydrochloric acid (15 ml). The organic material was extracted with ether (four 75-ml portions) and the ether solution was dried over magnesium sulfate. After evaporating the ether, the residual solid was boiled for 2 hr with acetic anhydride (9 ml) and a few drops of pyridine. The solution was then allowed to stand overnight. After the usual work-up the residue was analyzed by vpc at 160°. A new peak, not present in the starting *trans* diacetate, was observed. Its retention time was identical with that of the *cis* diacetate obtained from the electrolysis and also from acetolysis and hydrogenation of the COT–dichloride. Vpc indicated that the mixture contained ~99% *trans* diacetate and 1% *cis* diacetate. The nmr spectrum of the mixture had the characteristic eight-line pattern for the protons α to the acetoxy groups in the *trans* diacetate, but also the doublet assigned to the *cis* diacetate.

Discussion

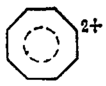
The formation of monoacetates **1a** and **1b** must involve a methyl radical at some stage of the reaction. At the higher anode potential of the constant-current electrolysis the proportion of the low-boiling methylated monoacetate fraction increased at the expense of the diacetate fraction. It is highly probable that the formation of **1a** and **1b** is actually initiated by a methyl radical and that there is a competition between the direct anodic oxidation of COT, giving rise to the diacetate fraction, and attack on COT by methyl radicals from the normal Kolbe electrolysis of acetate ion. Such an attack of methyl radicals might lead to the monoacetate by the following route. This interpretation is supported by the results obtained in the electrolysis using a carbon anode, which is known to strongly suppress the formation of methyl radicals in the Kolbe oxidation of acetic acid.[25] The product in this case was a mixture of diacetates and did not contain any monoacetate.[26]



The stereochemistry of **1a** and **1b** is not deducible from the nmr spectra, but it is tentatively considered that the two monoacetates have the methyl group situated *trans* to the ring junction. This assignment is based on the assumption that ring contraction of **12** proceeds stereospecifically so as to avoid a *cis* interaction between the six-membered ring and the methyl group.[27]

The electrochemical reaction to form the diacetates must involve in its over-all process the transfer of two electrons to the anode, a valency tautomerism to give either the cycloheptatriene ring system or the bicyclo[4.2.0]octadiene ring system and the addition of two acetate residues. The problem of mechanism for this reaction is one of determining the timing of these various steps. Our experiments do not permit a clear designation of this timing. Nevertheless, some possibilities warrant discussion.

It is clear from the polarographic data that COT is oxidized at the anode in the primary step. If an initial two-electron transfer is involved, the 6π-electron dication (**14**) is an intermediate. If two consecutive one-electron transfers are involved, cation radical **15** and radical **16** may be intermediates.[28]



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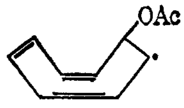

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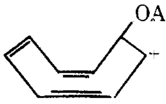
[25] W. J. Koehl, Jr., *J. Am. Chem. Soc.*, **86**, 4686 (1964).

[26] A similar competition between anodic oxidation of the substrate and attack by methyl radicals is observed in the electrolysis of an acetic acid solution of naphthalene and sodium acetate,[2] where the former reaction results in α-acetoxynaphthalene and the latter attack results in α-methylnaphthalene.

[27] G. J. Fonken and S. Shiengthong, *J. Org. Chem.*, **28**, 3435 (1963).

[28] C. L. Perrin, *Progr. Phys. Org. Chem.*, **3**, 220 (1965).

Subsequent steps might then lead to the cations **17**, **18**, and **19** and the final products **6**, **7**, and **8**. An alternate possibility is an acetate ion assisted, two-electron transfer at the electrode to give **17** in the primary step. Cation **17** might be expected to form acetoxonium ion **20** readily, since the driving force for generation of an acetoxonium ion exceeds that for formation of a bromonium ion.[29] Acetoxonium ion **21** is a possible but less likely intermediate because of the steric strain inherent in such a tricyclic form.



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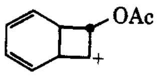

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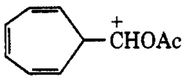

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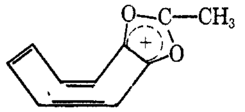

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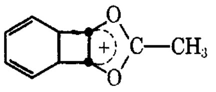

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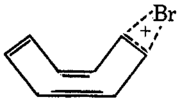
A striking feature of the electrochemical reaction is the absence of stereospecificity in the formation of bicyclo[4.2.0]octa-2,4-diene-7,8-diol diacetates **6** and **8**. This is in sharp contrast to purely chemical transformations of COT to 7,8-disubstituted bicyclo[4.2.0]-octa-2,4-dienes which are invariably highly stereospecific. Examples which can be cited are the mercuric acetate oxidation to give the *trans* diacetate,[20] the boron trifluoride–lead tetraacetate oxidation to give the *trans* diacetate in addition to cycloheptatrienecarboxaldehyde diacetate,[21] chlorine addition to give the *cis* dichloride,[30,31] and bromine addition to give the *trans* dibromide.[30]

The course of the latter two reactions has been convincingly rationalized by Georgian *et al.*[30] In the bromine addition, bromonium ion **22** is the significant intermediate; **22** reacts with bromide ion to give a *trans*-cyclooctatriene dibromide, which then undergoes valency tautomerism to give the final *trans* product. In the chlorination there is no driving force for chloronium ion formation.[29] The significant intermediate is **23**, in which overlap of the cationic center with the p orbitals of the cyclohexadiene system lead to the *cis*-dichloride.



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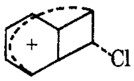
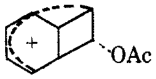


23

In the electrochemical oxidation of COT, not only is the reaction nonstereospecific, but it is also the thermodynamically less stable product (**8**) which predominates. Carbonium ions **20** and **21** cannot be precursors of the *cis* diacetate. Even ion **17** is an unlikely intermediate for **8**, since there is a driving force of almost 5 kcal/mole for the conversion of **17** to **20**.[29] The most probable intermediate is **18**, which may perhaps then be partitioned between **21** and **24**, with **21** leading to *trans* diacetate **6**, and **24** leading to *cis* diacetate, **8**. The formation of **24** is favored over the formation of **21** because of the steric barrier to formation of the tricyclic ring system in **21**.



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A reasonable course for the over-all reaction would involve the generation of **14** or **15** at the electrode and subsequent collapse of these intermediates by concerted reactions to **18** and **19**. The latter ions then go to the final products by paths already discussed. The polarographic results indicate a single two-electron wave, but this may result from the fact that in the highly nucleophilic solvent system two one-electron transfers coalesce to a single wave. Although the present results do not constitute proof, our preference is for **14** as the primary product of the electrode reaction, because of the stabilization gained by formation of the 6π-electron system.

Acknowledgments—Generous gifts of cyclooctatetraene from Badische Anilin und Sodafabrik, Germany are acknowledged. L. E. also gratefully acknowledges a grant from the Swedish Natural Science Research Council.

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[29] S. Winstein E. Grunwald, and L. L. Ingraham, *J. Am. Chem. Soc.*, **70**, 821 (1948). For another example of acetoxonium ion formation during anodic acetoxylation, see ref 7.

[30] V. Georgian, L. Georgian, and A. V. Robertson, *Tetrahedron*, **19**, 1219 (1963).

[31] Mixtures of *cis* and *trans* dichlorides reported by Nenitzescu, *et al.*,[22] very probably result from isomerization of the *cis* dichloride during the work-up.