cerns the fundamental stability of alcohols and alkenes in sulfuric acid toward polymerization.

We wish to thank Drs. R. R. Brattain and D. Stevenson of the Shell Development Laboratories for their coöperation.

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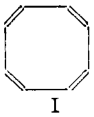
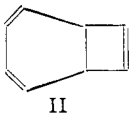
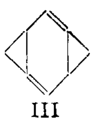
Some Observations on Certain Cycloöctatetraene Derivatives

BY S. L. FRIESS AND V. BOEKELHEIDE

In a recent publication, Reppe and his co-workers[1] have described the preparation of cycloöctatetraene (C.O.T.) and its conversion to many different derivatives. In attempting to explain the formation of the various reaction products of C.O.T., Reppe, *et al.*, have considered that C.O.T. may react as though it were present as any one of three different forms, I, II and III.


I

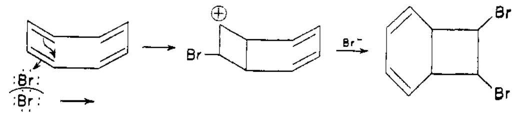

II


III

However, since I, II and III cannot very well be considered to be contributing forms to a resonance hybrid, it would appear desirable that the formation of unusual products from C.O.T. should be explicable on some other basis.

One possible explanation for the formation of certain of these products would be to consider that under attack by a reagent C.O.T. may undergo molecular rearrangement. The reaction of C.O.T. with bromine and with perbenzoic acid has been considered from this viewpoint and the results obtained in the present study are in support of such a postulation.

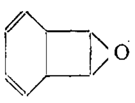
If the assumption is made that the strongest case yet presented for the structure of C.O.T. is the X-ray study[2] pointing to the "tub" or all-*cis* form, then it seems possible to explain certain of the reactions of the compound, and in particular those involving transitions from an initial eight-membered ring to a six–four bicyclic system, by a direct participation of a suitably situated neighboring double bond[3] in these reactions. The bromination process, for example, could be represented by the following scheme, involving the participation of a neighboring double bond in the reaction form presented by the molecule to the attack of a reagent;



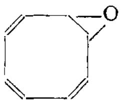
IV

This formulation of the bromination of C.O.T. is in accord with the chemical evidence which Reppe, *et al.*,[1] have presented in support of structure IV.

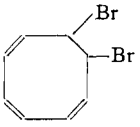
A similar formulation could be postulated for epoxidation, using the electrophilic entity $:\ddot{O}:H^+$ from the perbenzoic acid. The result of participation of the neighboring double bond during epoxidation would be that C.O.T. oxide should be represented by formula V.



V



VI



VII

In this case, however, Reppe, *et al.*,[1] have assigned structure VI to C.O.T. oxide. A reinvestigation of the oxide has been made and evidence supporting structure V has been found.

The ultraviolet absorption spectrum of C.O.T. oxide in ethanol is shown in Fig. 1. It is seen that the position of the absorption peak for the oxide ($\lambda_{max} = 241$ mμ, log $\epsilon = 3.60$) is compatible with a cyclic diene structure, V, as inferred by comparison with the peak of cyclopentadiene[4] in isoöctane ($\lambda_{max} = 241$, log $\epsilon = 3.50$). The maximum of the dibromide ($\lambda_{max} = 260$, log $\epsilon = 3.70$) is somewhat displaced to longer wave lengths, but is not quite as high as would be expected for the conjugated triene form VII.

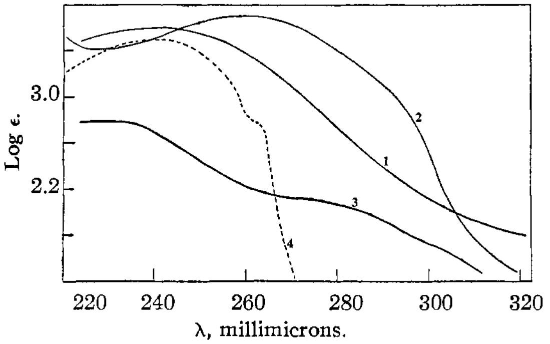


Fig. 1.—Ultraviolet absorption spectra in 95% ethanol of: 1, C. O. T. oxide; 2, C. O. T. dibromide; and 3, C. O. T. oxide hydrogenation product. Curve 4 is for cyclopentadiene in isoöctane.[5]

Further evidence for the diene character of the oxide was obtained from its maleic anhydride adduct. It would be expected that V would yield VIII, whereas structure VI should give IX. When the Diels–Alder reaction was carried out in benzene under anhydrous conditions, an exothermic

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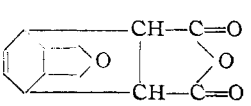
[1] Reppe, Schlichting, Klager and Toepel, *Ann.*, **560**, 1 (1948).

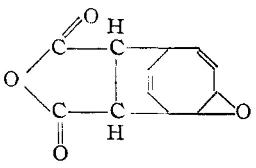
[2] Kaufman, Fankuchen and Mark, *Nature*, **161**, 165 (1948).

[3] For participation of a neighboring double bond in replacement reactions, see Winstein and Adams, THIS JOURNAL, **70**, 838 (1948).

[4] The ultraviolet absorption spectrum for cyclopentadiene in isoöctane solution is given for illustration since it is recorded in the literature,[5] whereas the complete solution spectrum of 1,3-cyclohexadiene was not available to us. A study of the variation of λ_{max} and log ϵ with increasing ring size in the conjugated cyclic dienes is contemplated.

[5] Data for cyclopentadiene were obtained from Ultraviolet Spectrograms, National Bureau of Standards, A.P.I. Research Project 44, serial no. 53.


VIII

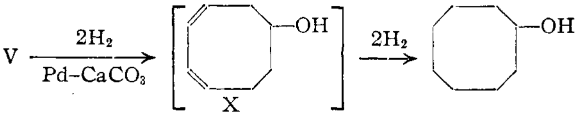

IX

reaction occurred giving an adduct, m. p. 206–207°, which corresponds to that reported by Reppe. Upon catalytic hydrogenation in ethanol with Adams catalyst at one atmosphere pressure, the adduct consumed exactly one mole of hydrogen, would take up no more, and yielded the dihydro compound of m. p. 240–245°, as reported. Upon treatment with perbenzoic acid in chloroform, the adduct consumed exactly one mole of the reagent, indicative again of just one double bond and form VIII as the molecular structure. This affords rather conclusive evidence for V as the structure of the oxide.

Interestingly, when the Diels–Alder reaction on the oxide was carried out under non-anhydrous conditions, a fair proportion of an isomeric adduct of m. p. 147–148° was also obtained. This too consumed exactly one mole of hydrogen, in methanol with platinum catalyst, and also consumed just one mole of perbenzoic acid. In the latter reaction, the product $C_{12}H_{10}O_5$ was isolated as a crystalline material sintering above 300°.

The only important evidence not favoring V as the structure of C.O.T. oxide is the fact that the oxide yields cycloöctanol on hydrogenation. In view of the strain which would be present in a molecule having a fused tricyclic ring system of this type, it seemed possible that cleavage of the fused rings would occur during hydrogenation so that V also would yield cycloöctanol. Evidence for this was obtained as follows.

When C.O.T. oxide in methanol solution was hydrogenated over a palladium-on-calcium carbonate catalyst, and the vigorous hydrogenation process stopped after absorption of just two moles of hydrogen, a colorless liquid fraction was obtained whose ultraviolet absorption spectrum in ethanol (λ_{max} = 230 mμ, log ϵ = 2.79) is also shown in Fig. 1. The position of the peak strongly suggests that a diene structure exists within the molecule. Further, the infrared spectrum of the substance shows a high intensity band at 2.85μ (3509 cm.$^{-1}$), a region characteristic[6] of the OH group vibration. This combination of features makes the formula X for the product most probable, although its homogeneity is not proven, and raises the possibility that in the complete hydrogenation of C.O.T. oxide, an over-all process requiring four moles of hydrogen to cycloöctanol,[1] the ring-fusion and the oxide ring are ruptured first, before the diene system is touched.



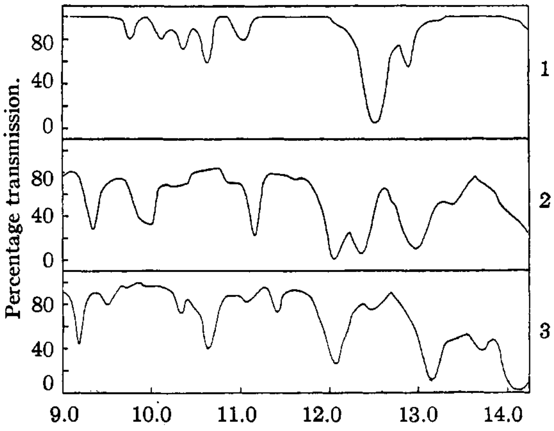


Fig. 2.—Infrared absorption spectra of: cycloöctatetraene (1); C. O. T. oxide (2); and C. O. T. dibromide (3). Data were obtained using 0.025-mm. cell.

Portions of the infrared curves of C.O.T., the oxide and the dibromide are shown in Fig. 2. The oxide and dibromide curves are both quite different from that of C.O.T.

Experimental[7]

C.O.T. Oxide.—This compound was prepared essentially according to Reppe's procedure,[1] but in considerably higher yields. In the best run, 5.5 g. of C.O.T. yielded 3.3 g. of oxide; b. p. 68–69° (12 mm.), n^{21}_D 1.5397.

C.O.T. Dibromide.—This too was prepared according to Reppe,[1] in comparable yield. The light yellow liquid had the following constants: b. p. 102–103° (5.5 mm.), n^{21}_D >1.7.

C.O.T. Oxide Hydrogenation Product (X).—To 25 ml. of methanol containing 1.1 g. of prereduced palladium–calcium carbonate catalyst was added 2.36 g. of C.O.T. oxide. The solution was allowed to absorb two molar equivalents (994 ml.) of hydrogen at atmospheric pressure, the catalyst was filtered off, the methanol removed under reduced pressure, and the residue fractionally distilled. There was collected a 0.76-g. fraction of colorless oil; b. p. 82–83° (16 mm.), n^{21}_D 1.4967.

Anal. Calcd. for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.27; H, 10.06.

Maleic Anhydride Adducts of the Oxide.—Reppe's procedure was again followed, with strict precautions against moisture. The adduct A crystallized from the benzene solution as white needles, which were filtered, washed with petroleum ether, and air-dried. From 3.3 g. of the oxide there was obtained 4.3 g. of adduct, m. p. 206–207°. In one run, where the drying tube on the reaction flask was eliminated, a benzene-soluble fraction of the adduct was an isomeric product B. This was obtained in 24% yield as white clusters, m. p. 147–148°.

Anal. Calcd. for $C_{12}H_{10}O_4$: C, 66.05; H, 4.62. Found: C, 66.18; H, 4.76.

Per Acid Titration of the Adducts.—A 0.24-g. sample of adduct A was added to a dried standardized chloroform solution of perbenzoic acid, prepared in the customary manner.[8] The per acid was present in excess. Consump-

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(6) Barnes, Gore, Liddel and Williams, "Infrared Spectroscopy," Reinhold Publishing Co., New York, N. Y., 1944, p. 19.

(7) Analyses by Mrs. G. L. Sauvage; melting points are uncorrected.

(8) Braun, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1947, p. 431.

tion of per acid was checked by titration[9] of aliquots at timed intervals. At the end of 111.7 hours at room temperature the adduct had consumed exactly one molar equivalent of per acid, and would take up no more.

Per acid titration of a 0.246-g. sample of B was carried out in the same manner. During the course of the reaction, the product crystallized from solution. Exactly one molar equivalent of per acid had been consumed when the reaction stopped, 125.9 hours after mixing. The crystalline product was filtered, washed, and purified by sublimation under high vacuum. The product sintered above 300°.

Anal. Calcd. for $C_{12}H_{10}O_5$: C, 61.54; H, 4.30. Found: C, 61.68; H, 4.28.

Hydrogenation of the Adducts.—To 0.10 g. of Adams catalyst prereduced in 10 ml. of ethanol was added 0.400 g. of adduct A dissolved in 40 ml. of alcohol. Hydrogenation at atmospheric pressure and room temperature progressed to the absorption of one molar equivalent of hydrogen (45 ml.) in the course of five and one-half hours, and stopped. After removal of catalyst and solvent, the crude dihydro product melted at 240–245° as reported by Reppe.

A similar hydrogenation of 0.30 g. of B in methanol likewise progressed to the extent of exactly one mole up take (37 ml.) of hydrogen in one hour and stopped.

Acknowledgment.—We gratefully acknowledge receipt of several samples of purified cycloöctatetraene from General Aniline and Film Corp., Easton, Pa.

[9] See ref. 7, p. 434.

DEPARTMENT OF CHEMISTRY
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ROCHESTER 3, NEW YORK

RECEIVED APRIL 28, 1949

The Anion-exchange Separation of Zirconium and Hafnium[1]

BY E. H. HUFFMAN AND R. C. LILLY

An effective separation of zirconium and hafnium as negative fluo-ions has been obtained by using one of the strongly basic anion exchange resins recently developed, although earlier attempts using the weakly basic resins first available were unsuccessful.

Twenty milligrams of zirconium and 10 mg. of hafnium, as oxides, were added to zirconium and hafnium tracers in a small amount of hydrofluoric and nitric acids, warmed until dissolved, and fumed with 0.5 ml. of sulfuric acid. The residue was dissolved in water and the hydroxides precipitated with ammonium hydroxide. The precipitate was centrifuged, washed with water, dissolved in 5 ml. of 0.64 *M* hydrofluoric acid and diluted to 10 ml. with water. Six hundred milligrams of 200–325 mesh Amberlite IRA-400 resin, in its original chloride form, was added to the sample and the mixture shaken for three hours. The resin was separated from the solution and washed well with 10 ml. of water. Tracer count of the solution and washings indicated that 96% adsorption had taken place. This portion of resin was slurried onto the top of a column of the same resin 30 cm. in length and 0.78 sq. cm. in cross section. Elution with a solution of 0.2 *M* hydrochloric acid and 0.01 *M* hydrofluoric acid at the rate of 6 ml. per hour gave the results shown in Fig. 1. The solid parts of the curve were obtained by counting Zr^{95} and Hf^{181} tracers and the dotted parts by spectrographic analysis. The order of elution of the two elements is the reverse of that obtained by cation-exchange.[2]

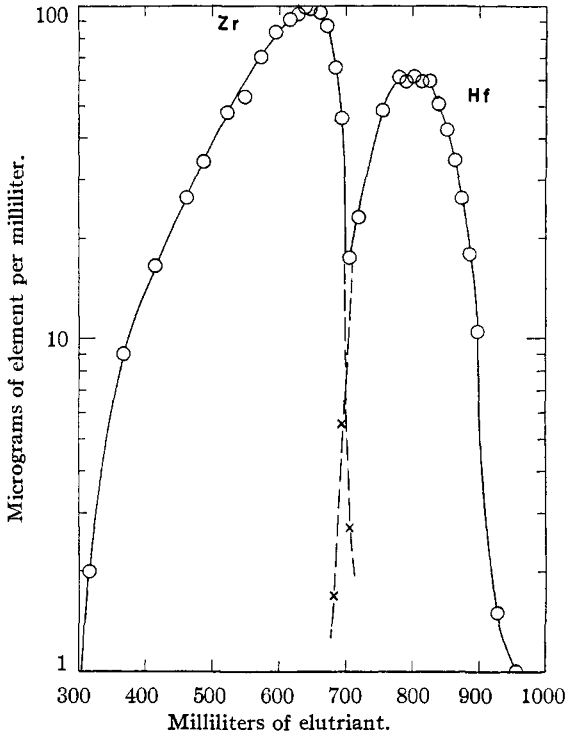

Fig. 1.—Elution of fluozirconate and fluohafniate with 0.2 *M* hydrochloric acid and 0.01 *M* hydrofluoric acid.

Combined fractions of elutriant from 300 ml. to 653 ml., containing 13.8 mg. of zirconium or 69% of the starting material, were found to contain no hafnium detectable by spectrographic analysis. The portion from 300 ml. to 686 ml., containing 17.0 mg. of zirconium or 85% of the starting material, was found to contain 0.04% hafnium. Spectrographic analysis of the 752–1020-ml. portion showed 0.02% zirconium in the 6.9 mg. of hafnium (69% of the starting material). Similarly, 0.03% zirconium was found in the 704–1020-ml. portion containing 8.3 mg. of hafnium (83% of the starting material). The amounts of the major constituents in these portions were determined from the curves.

This work was done under the auspices of the Atomic Energy Commission.

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[1] While official declassification of this paper was being awaited, a communication on a similar separation appeared by Kraus and Moore, THIS JOURNAL, **71**, 3263 (1949). The separation reported here uses a different resin, a much shorter column, a more dilute eluting solution and macro quantities of zirconium and hafnium instead of micro quantities.

[2] Kenneth Street, Jr., and G. T. Seaborg, THIS JOURNAL, **70**, 4268 (1948).

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RECEIVED OCTOBER 7, 1949

Derivatives of 5,6-Dihydrophenanthridine

BY CHARLES P. HUTTRER[1]

In the course of studies concerned with antihistaminic substances a number of derivatives of 5,6-dihydrophenanthridine[2] have been prepared in which the hydrogen in position 5 is

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[1] Present address: National Research Council, Washington, D. C.

[2] Nomenclature according to: "Naming and Indexing of Chemical Compounds," *C. A.*, **39**, 5867 (1945).