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A NEW SYNTHESIS OF *CIS*-BICYCLO(4.2.0)OCTANE-7,8-DIOL

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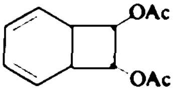
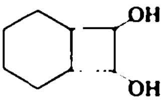
Abstract—A convenient electrochemical preparation of *cis*-bicyclo(4.2.0)octane-7,8-diol from cycloöctatetraene is described. When the reduced electrolysis product from cycloöctatetraene is hydrolysed with methanol and hydrochloric acid the *cis*-diol is not isolated because of the intermediate formation of the acetal from cycloheptanecarboxaldehyde and the *cis*-diol.

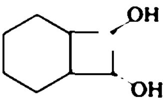
The formation of *cis*-bicyclo(4.2.0)octa-2,4-diene-7,8-diol diacetate (I) as one of the major products in the electrochemical oxidation of cycloöctatetraene in acetic acid has recently been demonstrated.[1] VPC and NMR analysis of the material obtained from the reduction of the electrolysis product indicated that 24–28% of it consisted of the compound with the *cis* configuration. Hydrolysis of the reduced electrolysis product using the method which Cope[2] used for the *trans* isomer gave a yield of 31% of *trans*-bicyclo(4.2.0)octane-7,8-diol (II). The corresponding *cis*-diol III could not be isolated.



I



II



III

Cope[2] obtained II in 71% yield on hydrolysis of the *trans*-diacetate and it was somewhat surprising that the same procedure applied to the reduced electrolysis product (which consisted of a mixture of the diacetates of II, III and cycloheptanecarboxaldehyde) did not yield III.

Since there are two possible *cis* isomers of bicyclo(4.2.0)octane-7,8-diol with *cis* ring juncture it was of considerable interest to isolate this material and compare it

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[1] L. Eberson, K. Nyberg, M. Finkelstein, R. C. Petersen, S. D. Ross and J. J. Uebel, *J. Org. Chem.* **32**, 16 (1967).

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

with the *cis*-bicyclo(4.2.0)octane-7,8-diols obtained by Cope and Herrick[3] and Vogel.[4] The former workers used a laborious and involved method to obtain a very small amount of *cis*-diol, while in the latter case (yield not reported) the use of osmium tetroxide was required. Because of the difficulties in the Cope procedure and because of the inherent disadvantages of osmium tetroxide[5] it was decided to investigate the possibility of devising a suitable electrochemical method for the synthesis and isolation of III.

For the purpose of the present work the most satisfactory procedure for the electrolysis of cycloöctatetraene consisted of the constant current process at a carbon anode with acetic acid as the solvent.[1] A slight excess over two equivalents of charge per mole of hydrocarbon was used. The crude product was reduced over platinum oxide, and a procedure was developed in which the reduction product was saponified with aqueous methanolic potassium hydroxide. This hydrolysis permitted the separation of both the *trans*-diol, II and the *cis*-diol, III in yields of 29% and 20%, respectively.

The structure of III was established by analysis, mixed m.p. with material obtained from Professor R. Criegee (prepared by the method of Vogel[4]) and identity of the IR spectra of these substances in carbon tetrachloride solution.[6] The IR spectrum indicates clearly that the compound obtained has its OH groups in a *cis* relationship to each other since both a free OH and an intramolecularly bonded interaction can be detected. The *trans* compound has its OH groups disposed such that only absorption due to free OH is observed.

In various photochemical reactions[7,8] the bicyclo(4.2.0)octane system with a *trans* ring juncture has been reported. Since Allinger[9] has shown that the bicyclo(4.2.0)-octene-7 which was used in the preparation of the *cis*-diol by Vogel[4] has a *cis* ring juncture it seems unlikely that the *trans* ring juncture need be considered here.

A sample of III prepared in this work was treated with *p*-phenylazobenzoyl chloride in pyridine to give a bis-*p*-phenylazobenzoate which had the correct analysis and which melted at 167–168°. Cope and Herrick[3] reported a m.p. of 165–166° for the bis-*p*-phenylazobenzoate prepared from their sample of III which had a m.p. of 71·5 73·5°.

The reaction of III with acetic anhydride in pyridine afforded a compound, m.p. 42–44° which had the correct analysis for a diacetate and had the same NMR absorptions previously[1] assigned to the *cis*-diacetate. This diacetate was hydrolysed[2] to give a 95% yield of III.

The reduced electrolysis product was refluxed with hydrochloric acid in methanol

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[3] A. C. Cope and E. C. Herrick, *J. Am. Chem. Soc.* **72**, 983 (1950).

[4] E. Vogel, *Angew. Chem.* **65**, 346 (1953).

[5] F. D. Gunstone in *Advances in Organic Chemistry. Methods and Results*-Vol. 1, p. 103. Interscience, New York, N.Y.

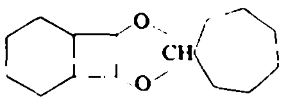
[6] A more detailed investigation of the IR spectrum of III was performed by Dr. L. P. Kuhn of the Ballistic Research Laboratories, Aberdeen Proving Grounds, Maryland. It was found that III has two OH bands: 3630 cm^{-1} (free) and 3577 cm^{-1} (intramolecular hydrogen bonded). The *trans* compound has only one OH band: 3630 cm^{-1} (free). The $\Delta\nu$ of 53 cm^{-1} is intermediate between that of *cis*-1,2-dihydroxycyclopentane, 61 cm^{-1} and *cis*-1,2-dihydroxycyclohexane, 39 cm^{-1}.

[7] J. A. Barltrop and R. Robson, *Tetrahedron Letters* 597 (1963).

[8] P. de Mayo, R. W. Yip and S. T. Reid, *Proc. Chem. Soc.* 54 (1963).

[9] N. L. Allinger, M. A. Miller and L. A. Tushaus, *J. Org. Chem.* **28**, 2555 (1963).

and worked up as previously reported.[1] A yield of 30% of II was obtained. After removal of II the reaction mixture was neutralized and a short path distillation gave an additional 62% yield of IV, the acetal of cycloheptanecarboxaldehyde and III.



IV

This structure was confirmed by the identity of the IR spectrum of this substance with that of the product obtained when the dimethylacetal of cycloheptanecarboxaldehyde and III were reacted in benzene containing hydrochloric acid. Further proof of structure was afforded by the aqueous acid hydrolysis of IV which gave cycloheptanecarboxaldehyde and III.

The failure to isolate III, when Cope's hydrolysis procedure[2] is used, is due to the fact that III and cycloheptanecarboxaldehyde are present in the reaction mixture in nearly equivalent quantities and readily interact to form IV. The *trans*-diol does not form an acetal and is isolated. When the Cope procedure is modified by the addition of water, some of the acetal, IV is hydrolysed and it becomes possible to isolate III as well as II. The preferred procedure is to hydrolyse under basic conditions where neither glycol forms an acetal and all three components of the mixture can be satisfactorily separated.

It is probable that the diol obtained in this work and the *cis*-diol of Cope and Herrick are the same compound since the same bis-*p*-phenylazobenzoate is found. Identity with the material reported by Vogel was shown by direct comparison. Although the m.ps of the compounds prepared by the three different methods vary by as much as ten degrees it appears that in each case the same compound was formed. Apparently the other *cis* isomer has not yet been synthesized.

EXPERIMENTAL

The electrolysis of cycloöctatetraene in acetic acid at constant current using a carbon anode, and the subsequent reduction of this product were performed as previously described.[1] This is the material referred to as reduced electrolysis product.

The dimethylacetal of cycloheptatrienecarboxaldehyde was prepared[2] and reduction to the dimethylacetal of cycloheptanecarboxaldehyde was accomplished with PtO_2 in MeOH, and the free aldehyde was obtained by the method of Finkelstein.[10]

cis-*Bicyclo*(4.2.0)*octane*-7,8-*diol* (III)

A soln of 22·6 g (0·1 mole) reduced electrolysis product in 30 ml MeOH was heated under reflux for 7 hr with a soln of 20 g KOH in 30 ml water. The MeOH was distilled at the aspirator and the residue was poured into salt water and extracted 4 times with ether. The ether extract was dried over $MgSO_4$ and distilled at the aspirator. Crystallization of the residue from benzene gave 4·15 g of II, m.p. 137–139° (29·2%). The mother liquor was evaporated, hexane was added, and on cooling in the freezer for several days, 2·87 g (20%) of III crystallized. Crystallization from hexane followed by sublimation and recrystallization from hexane gave the analytical sample, m.p. 60–62°. (Found: C, 67·66; H, 10·04. Calc. for $C_8H_{14}O_2$: C, 67·57; H, 9·92%.)

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

A mixed m.p. with a sample[11] of III prepared by the method of Vogel[4] was undepressed. IR spectra of 10% solns of the two materials in CCl_4 were identical.

The bis-*p*-phenylazobenzoate of the isolated material was prepared by the standard method.[12] A sample crystallized for analysis from benzene–hexane had m.p. 167–168° (m.p. reported[3] 165–166°). (Found: C, 72·81; H, 4·96; N, 10·00. Calc. for $C_{34}H_{30}N_4O_4$: C, 73·10; H, 5·41; N, 10·03%.)

Stability of III *to acid hydrolysis conditions*

A soln of 0·101 g of III in 5 ml MeOH was heated under reflux with 3 drops conc HCl for 3 hr. The solvent was distilled at the aspirator and the residue crystallized from benzene–hexane to give 0·072 g (72%) of III m.p. 55–60°.

Acid hydrolysis of reduced electrolysis product

(A) *In aqueous methanol.* A soln of 5·3 g (0·0235 mole) reduced electrolysis product and 1 ml conc HCl in 20 ml MeOH and 10 ml water was heated under reflux for 21 hr. The MeOH was distilled and the residue was treated with sat $NaHCO_3$aq until neutralized. The aqueous soln was treated with salt and extracted 3 times with ether. The ether was dried over $MgSO_4$ and removed at the aspirator. The residue was taken up in a minimum of hot benzene and II crystallized, 0·866 g (26%), m.p. 139–141°. The benzene was removed and the residue crystallized from hexane to give III, 0·261 g (8%), m.p. 54–59°.

(B) *In methanol.* A soln of 5·29 g (0·0234 mole) reduced electrolysis product and 20 drops conc HCl in 15 ml MeOH was heated under reflux for 5 hr. The solvent was distilled and the residue dissolved in hot benzene. After concentration and addition of hexane, 0·99 g (30%) of II, m.p. 138–140° was obtained. The mother liquor was concentrated to an oil which was taken up in ether and washed twice with sat $NaHCO_3$aq. The bicarbonate soln was extracted with ether and the combined extract was dried over $MgSO_4$ and distilled through a Vigreux column. The residue was distilled in a short path still at 0·01 mm to give a total of 1·81 g (62%), the main portion of which had n_D^{23} 1·5004. The IR spectrum of a 10% soln of this substance in CCl_4 was identical to that of the acetal formed from cycloheptanecarboxaldehyde and III.

Hydrolysis of the liquid product from procedure (B)

A soln of 1·8 g of the liquid product obtained from hydrolytic procedure (B) in 25 ml MeOH was treated with 2 ml conc HCl in 10 ml water. The soln was heated under reflux for 5·25 hr and the MeOH was distilled at atm pressure. The residue was distributed between water and ether and the aqueous layer was extracted 3 times with ether. After washing with $NaHCO_3$aq the ether was dried over $MgSO_4$ and distilled. The residue, which amounted to 1·51 g, was analysed by VPC and found to contain 0·073 g (8%) of cycloheptanecarboxaldehyde and 0·196 g (19%) of III. Hydrolysis of the residue by heating with methanolic HClaq under reflux for 5 days gave, after neutralization, a residue which on VPC analysis accounted for a total yield of 40% of cycloheptanecarboxaldehyde and its dimethylacetal.

cis-*Bicyclo(4.2.0)octane-7,8-diol diacetate*

A soln prepared by boiling a mixture of 2·4 g (0·017 mole) of III, 10 ml pyridine and 20 ml Ac_2O was let stand for 24 hr. Excess reagents were distilled through a Vigreux column at the aspirator. The residue was distilled at 0·03 mm to give 3·1 g (81%), b.p. 75°. The distillate eventually crystallized, m.p. 42–44°. (Found: C, 63·99; H, 8·20. $C_{12}H_{18}O_4$ requires: C, 63·70; H, 8·02%).

Acid hydrolysis of cis *bicyclo(4.2.0)octane-7,8-diol diacetate*

The procedure was that used for acid hydrolysis of the reduced electrolysis product.[1] From 0·537 g diacetate a total of 0·319 g (95%), m.p. 59–60°, of white crystals was obtained. A mixed m.p. with III was undepressed.

Acetal from cycloheptanecarboxaldehyde and III

A soln containing 0·20 g (0·0014 mole) of III, 0·24 g (0·0014 mole) cycloheptanecarboxaldehyde dimethylacetal, 3 drops conc HCl and 10 ml benzene was refluxed for 3 hr. The solvent was distilled, the residue

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[11] We are indebted to Professor R. Criegee, Karlsruhe, Germany, for supplying us with a sample of the authentic *cis*-diol.

[12] E. O. Woolfolk, F-E. Beach and S. P. McPherson, *J. Org. Chem.* **20**, 391 (1955).

poured into water and neutralized by the addition of solid $NaHCO_3$. The mixture was extracted twice with ether and the ether was dried over $MgSO_4$. The solvent was distilled through a Vigreux column and the residue distilled through a short path still at 0·01 mm. A main cut of 0·235 g, n_D^{23} 1·5004 was taken. (Found: C, 75·95; H, 10·47. $C_{16}H_{26}O_2$ requires: C, 76·75; H, 10·47%.)

Acknowledgement—A generous gift of cycloöctatetraene from Badische Anilin-und Sodafabrik, Germany, is acknowledged. The NMR spectra were determined by Professor J. J. Uebel at the University of New Hampshire, Durham, N. H.