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SYNTHESIS OF OLEFINS BY ANODIC OXIDATION OF VICINAL DICARBOXYLIC ACIDS

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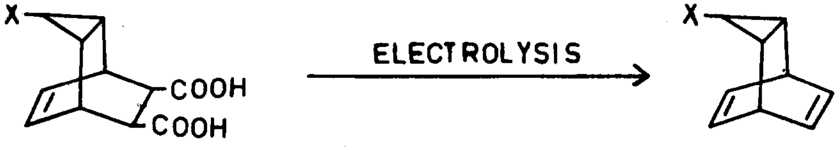
Recent studies in these laboratories concerned with the chemistry of homobarrelene derivatives necessitated finding a practical synthetic route to tricyclic compounds of type I (1). The study described herein has shown that anodic oxidation of the vicinal dicarboxylic acids provides an easy method for introduction of the second double bond.



I

The ready availability of these diacids either from Diels-Alder or photochemical cyclo-additions makes this synthesis especially attractive. Although the yields in the electrolysis step are generally less than 50%, this is compensated for by the simplicity of the procedure as well as by the small number of steps involved overall.

The apparatus used is easily constructed from a 200 ml. tall form beaker, two electrodes of platinum gauze and a stirring apparatus. A Sargent synchronous rotator is used to turn a cylindrical platinum gauze anode inside a cylindrical cathode, both of which are within the 200 ml. beaker. In a typical reaction, 3-carboethoxytricyclo[3.2.2.0^{2,4}]non-8-ene-6,7-dicarboxylic acid (1.25 g.) was dissolved in water (10 ml.) to which had been added triethylamine

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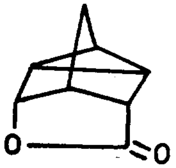
*Deceased, April, 1968.

(1.25 ml.).[*] This was then placed in the electrolysis cell which already contained pyridine (95 ml.). The cell was cooled externally with an ice-bath to maintain an internal temperature of about 20°C. An initial current (D.C.) of 0.8A was allowed to pass through the solution. After eight hours the current had dropped to less than 0.2A and the electrolysis was discontinued. The 3-carboethoxytricyclo[3.2.2.0^{2,4}]nona-6,8-diene was obtained in very pure form simply by dilution of the reaction solution with water (250 ml.) followed by pentane extraction. Washing the pentane extract with dilute acid, drying over anhydrous sodium sulfate and distillation gave 0.33 g. (40%) of the diene (3).

Our investigation, together with that of the accompanying communication (4), extends the earlier work of others (5-7) with this reaction and allows a comparison with the closely related lead tetraacetate bis-decarboxylations. Recognition of the potential synthetic usefulness of this reaction prompted us to extend it beyond our original preparative needs. Thus the series of compounds shown in Table I has been studied.

In all cases shown in Table I, except norbornadiene, the Kolbe synthesis provides a rapid means of obtaining the desired diene systems. It should be noted that cis-endo isomers give lower yields than the corresponding trans- or cis-exo diacids. We have found this to be a result of a competing internal lactonization similar to that encountered in lead tetraacetate oxidative bis-decarboxylations. Isolation of the nonhydrocarbon adducts from electrolysis of cis-endo-norborn-5-ene-2,3-dicarboxylic acid showed that nearly 70% of the original diacid had been converted to a lactone assigned structure II.[**]



II

In the cis-exo case this lactone was not found and the yield of norbornadiene was higher.

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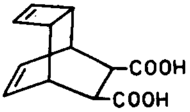
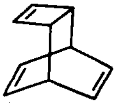
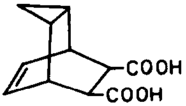
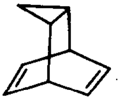
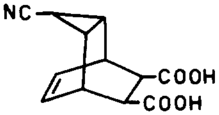
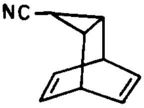
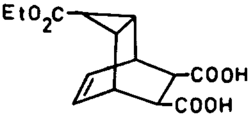
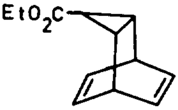
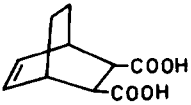
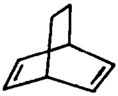
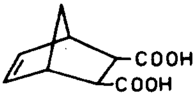
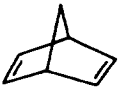
[*] When 3-carboethoxytricyclo[3.2.2.0^{2,4}]non-8-ene-6,7-dicarboxylic anhydride was substituted for the diacid, identical results were obtained. Generally, some heating was necessary to dissolve the anhydride in the aqueous amine solution.

[**] Elemental analysis was correct for this structure. The physical and spectral properties agreed with those reported by Alder and Roth (8).

With [2.2.2] bridged compounds this lactonization apparently still occurs when lead tetraacetate is employed as the oxidant; however, it is sufficiently diminished under electrolytic conditions to allow considerably higher yields of completely decarboxylated product. For a comparable case, Nenitzescu (9) reported a 10% yield of tricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene on treatment of the maleic acid-cyclooctatetrene adduct with lead tetraacetate. As shown in Table I, anodic oxidation gives a yield of 53% in the same reaction. A similar result is observed with maleic acid-cycloheptatriene Diels-Alder adduct. In our laboratory, hydrocarbon I (X=H) could be obtained at best in 3% yield with lead tetraacetate.

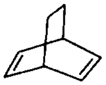
TABLE I

Reactant	Stereochemistry of Acid Groups	Product	Per Cent Yield
	cis-endo trans		37 53
	cis-endo trans		36 45
	cis-endo		48
	cis-endo		40
	cis-endo		40
	cis-endo trans cis-exo		<1 7 15

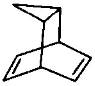
It is not yet possible to present a clear description of the mechanism of the Kolbe bisdecarboxylation sequence; however, a few observations can be made. Most of the results can be explained as follows: At the anode a stepwise loss of carbon dioxide occurs to produce a β-carboxyalkyl radical by the usual mechanism. This intermediate yields products by either of two paths: 1) It loses a second carbon dixoide molecule to give the new olefinic bond; 2) It undergoes cyclopropane ring formation together with internal lactonization to give products such as II. Pathway 2 is favored with *cis-endo* diacids compared to *trans* diacids and accordingly electrolysis of the former provides lower yields of alkene. This is based on the assumption that expulsion of an *exo* and *endo* carboxyl group occurs with equal facility. The experimentally observed product ratio from the three norborn-5-ene-2,3-dicarboxylic acids appears to justify this assumption. Preferential loss of the *exo* carboxyl group in the *trans* diacid should provide a yield of norbornadiene nearly the same as that from the *cis-endo* diacid. The observed value which is intermediate between *cis-endo* and *cis-exo* implies that the loss of carbon dioxide is random.

REFERENCES

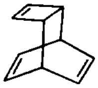
1. Hine's (2) unsuccessful attempts to synthesize III from various bicyclo[2.2.2]octene derivatives demonstrate that normal olefin forming reactions are unsatisfactory in these cases. Preparations of III, IV and V (10) have been realized; however, practical yields are obtained only through multi-step processes.



III



IV



V

2. J. Hine, J. A. Brown, L. H. Zalkow, W. E. Gardner and M. Hine, *J. Amer. Chem. Soc.*, **77**, 595 (1955).

3. The spectral properties are consistent with the structure of this compound. N.M.R. (τ value, shape and relative area): 3.2, t, 2; 4.0, t, 2; 6.05, q, 2; 6.25, m, 2; 8.25, q, 2; 8.4, t, 1; 8.9, t, 3.

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10. Compound III was prepared by C. A. Grob, H. Kny, and A. Gagneux, *Helv. Chim. Acta.*, **40**, 130 (1957). Compounds IV and V were prepared by G. Schröder, *Technical Report, Union Carbide* (ERA), Brussels, Belgium, May, 1964.