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ELECTROLYTIC DECARBOXYLATION OF VICINAL DICARBOXYLIC ACIDS TO OLEFINS: PREPARATION OF TRICYCLO[3.2.2.0^{2,4}] NONA-6,8-DIENE, AND TRANS-BICYCLO[6.2.0]-DECA-9-ENE DERIVATIVES

Phillip Radlick, Robert Klem and Steven Spurlock
Department of Chemistry, University of California
Riverside, California

James J. Sims
Department of Plant Pathology, University of California
Riverside, California

Eugene E. van Tamelen and T. Whitesides
Department of Chemistry, Stanford University
Stanford, California

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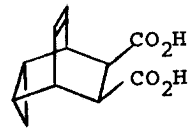
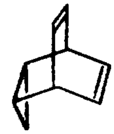
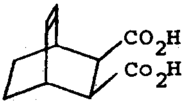
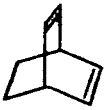
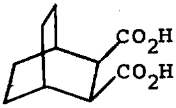
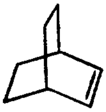
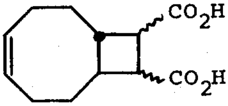
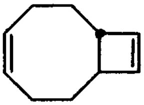
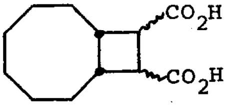
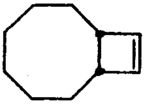
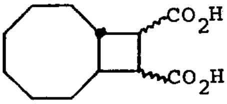
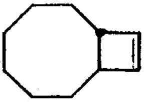
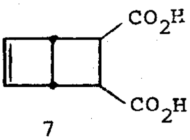
The familiar method for conversion of 1,2-dicarboxylic acids to olefins is treatment with lead tetraacetate. However, this method suffers from low, variable yields and cannot be expected to be useful at all with bicyclic diacids containing a proximal olefinic bond (1,2).

An alternative method in which diacids are smoothly decarboxylated with concomitant introduction of a double bond upon electrolysis was first described by Fichter (3) and has since made its appearance in only a few studies (4-6). We have now discovered that this electrolysis is generally superior to the use of lead tetraacetate. It gives consistently higher yields of olefins and more importantly is much less affected by the presence of a proximate double bond in the starting material. We have found that electrolytic decarboxylation of the acids 1 - 7 produces the corresponding olefins 8 - 14 in the indicated yields, figure 1.

FIGURE 1

ACID	OLEFIN	YIELD (%)
 1	 8	35
 2	 9	48
 3	 10	63
 4	 11	35
 5	 12	24
 6	 13	35
 7	 14	35[18]

The acids 4, 5 and 6 were prepared by aqueous acetone hydrolysis of the anhydrides, which were in turn prepared by benzophenone sensitized photoaddition of maleic anhydride in acetone to cyclooctene and 1,5-cyclooctadiene. The acids 1, 2, 3 and 7 were all prepared by published procedures (7-10).

The electrolysis was conducted by a procedure very similar to that used by Corey (5) and also by Plieninger (6). The diacid (0.005 mole) is dissolved in 10% aqueous pyridine (100 ml), and triethyl amine (1.25 ml) is added. This stirred mixture is then electrolyzed at room temperature between two stationary platinum wire gauze electrodes at 60-100 volts dc with an initial current of 0.5-0.8 amp. The reaction usually requires external cooling with an ice water bath. After 2-10 hours the current drops to 0.1 amp and the reaction is worked up by quenching with water, extraction with pentane, and distillation of the resulting mixture.

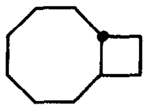
The olefins 9, 10 and 12 have all been prepared previously by different methods and were identified by comparison of their properties with those published (11-13).

The structure for homobarrelene (8) is completely in accord with its nmr spectrum with two vinyl protons at τ 3.42 (double doublet), two vinyl protons at τ 4.03 (double doublet), two bridgehead protons at τ 6.38 (multiplet), two tertiary cyclopropyl protons at τ 8.85 (multiplet) and two secondary cyclopropyl protons at τ 9.45 (multiplet) (14).

The structure for 11 is supported by its infrared spectrum with bands at 3118 cm^{-1} and 1550 cm^{-1} for the cyclobutene ring (17) and its nmr spectrum with two cyclobutene vinyl protons at τ 3.95 (singlet) two cyclooctene vinyl protons at τ 4.3 (multiplet) and a very complex multiplet for the other ten protons at τ 7.2-9.0.

The structure of 13 follows from its infrared spectrum which has bands at 3120 cm^{-1} and 1555 cm^{-1} characteristic of the cyclobutene ring (17) and from its nmr spectrum which has two vinyl protons at τ 4.0 (singlet), two bridgehead protons at τ 7.5 (multiplet) and twelve methylene protons as a very broad multiplet at τ 7.8-8.6.

In addition, 11 and 13 were hydrogenated with platinum in ether to the same hydrocarbon, <u>trans</u>-bicyclo[6.2.0]decane (15). This assignment is made on the basis that thermal decomposition of the tosylhydrazone salt 16 produces 12 as the only bicyclic olefin, which must have a <u>cis</u> ring fusion (13). Catalytic hydrogenation of 12 gives <u>cis</u>-bicyclo[6.2.0]decane (17) which is completely different from 15 as shown by comparison of their gas chromatographic retention times and their infrared and nmr spectra.



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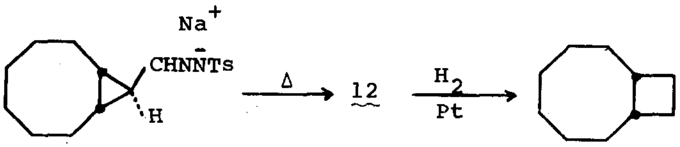

16 17

The olefins 11, 12, 13 and 14 represent the first application of the *bis*-decarboxylation procedure to small ring chemistry. Its success in this respect indicates that this reaction should become an important tool in the study of electrocyclic reactions.

In addition, the great versatility of maleic anhydride in the Diels Alder reaction (19), its facile entry into photosensitized 2π + 2π type cycloaddition reactions (20) and its reaction in the "ene synthesis" (21-22) coupled with this electrolytic decarboxylation reaction, provide powerful synthetic sequences. By means of this method, one can now introduce the equivalent of acetylene in cycloaddition reactions, a previously very difficult accomplishment.

ACKNOWLEDGMENT

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