mixture was diluted with water to a total volume of 100 ml. The solution was internally irradiated with a low-pressure mercury lamp (*ca.* 10 W) of Vycor housing, under bubbling nitrogen, at 0° for 5 hr. An aliquot (10 ml) was subjected to analysis for hydrogen peroxide and the remaining portion was treated with 6 g of sodium bisulfite under ice cooling. The reduced mixture was extracted with ether (total volume, 350 ml). The ethereal layer was washed with a small volume of water, dried over anhydrous sodium sulfate, and evaporated to dryness. The residue was analyzed by vpc. The products were identified by a comparison with authentic samples.

**Analysis.**—Hydrogen peroxide was analyzed by iodometry. For vpc analysis, the residue from the above ether extract was mixed with 50 mg of diphenyl (internal standard) and then the mixture was treated with an excess of *N*,*O*-bis(trimethylsilyl)-acetamide in a small volume of absolute benzene. The silylated mixture was analyzed by vpc using a 25% silicone DC 550-on-celite column (1100 × 3 mm).

**Registry No.**—1, 500-81-2; hydroxyl radical, 3352-57-6.

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# Electrochemical Preparation of Highly Strained Hydrocarbons. IV. Controlled Potential Electrolysis

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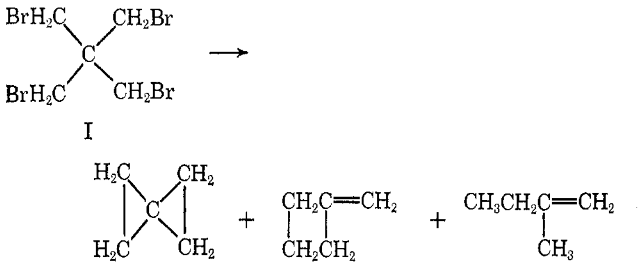
Previous papers in this series[1-3] reported the use of electrolysis as a tool for the preparation of small-ring compounds such as cyclopropane, cyclobutane, bicyclobutane, and spiropentane from the reduction of appropriate α,ω-dihalides. We would now like to describe an important advantage that this technique has, particularly under controlled potential electrolysis (CPE), over conventional reducing agents in organic synthesis.

The reduction of 1,3-dibromobis(bromomethyl)propane (I) by conventional reducing agents has been described[4-6] as forming a variety of products which included the compounds shown below. Under uncontrolled potential electrolysis, however, compound I was reduced to give spiropentane in high yield.[7]


I II III IV

The formation of compounds II–IV from I under uncontrolled potential electrolysis or by conventional reducing agents presumably takes place through a common intermediate, namely 1,1-bromomethylcyclopropane (V). Subsequent reduction of this intermediate under the above reaction conditions has not allowed its isolation. Thus, the electrolysis of I under controlled potential was investigated to isolate the presumed intermediate V and to compare the utility of CPE with conventional reduction methods in organic synthesis.

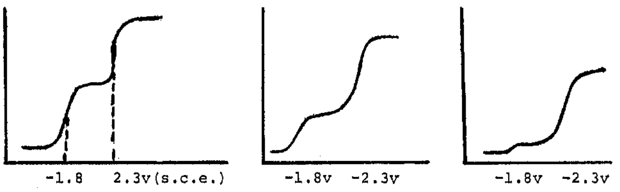
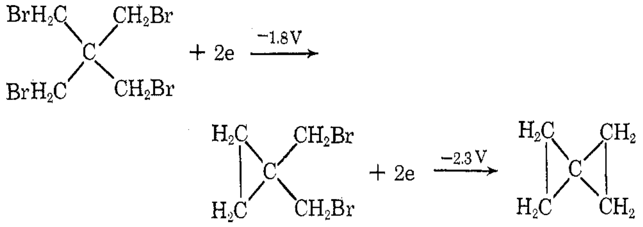


Figure 1.—Polarographic behavior of the cathode solution during electrolysis at a cathode potential of −1.2 to −1.4 V (sce).

It was the polarographic behavior of the tetrabromide I (two 2-electron waves at −1.8 and −2.3 V) which led us to believe that its reduction proceeds in a stepwise manner to yield spiropentane through the intermediate V. It was thus concluded that if the reduction of I is carried out at a controlled potential the isolation of V would be possible. This was indeed verified experimentally as the reduction of I at a cathode potential of −1.2 to −1.4 V (sce) yielded compound V and the reduction of V at a potential of −2.2 V (sce) yielded spiropentane. Furthermore, the course of the reduction was easily followed by examining the polarographic behavior of the cathode solution in the macroscale reduction. Thus, in the formation of compound V, the intensity of the polarographic wave with $E_{1/2}$ = −1.8 V (sce) decreased with time while that of the wave with $E_{1/2}$ = −2.3 V did not change (Figure 1). Compound V exhibits one 2-electron polarographic wave with $E_{1/2}$ at −1.8 V (sce). Thus, its reduction was easily followed by observing the decrease of the intensity of this wave with time.



The isolation of the previously undetected intermediate V from the reduction of I demonstrates the merit of CPE in conjunction with polarography. It is believed that CPE represents a powerful tool for the elucidation of certain organic reactions as well as the synthesis of organic compounds. The synthesis of V by conventional methods[8] involves four steps while the current method requires only one.

## Experimental Section

**Polarographic Studies.**—All polarograms were measured on a Beckman electroscan-30. A saturated calomel electrode (sce) was used as the reference. A solution of 0.05 *N* $n$-Bu$_4$NClO$_4$

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[1] M. R. Rifi, *J. Amer. Chem. Soc.*, **89**, 4442 (1967).
[2] M. R. Rifi, *Tetrahedron Lett.*, 1043 (1969).
[3] M. R. Rifi, *Collect. Czech. Chem. Commun.*, **36**, 932 (1971).
[4] D. E. Applequist, *J. Org. Chem.*, **23**, 1715 (1958).
[5] H. O. House, R. C. Lord, and H. S. Rao, *ibid.*, **21**, 1487 (1956).
[6] V. A. Slabey, *J. Amer. Chem. Soc.*, **68**, 1335 (1946).
[7] F. Covitz, unpublished results.
[8] M. Slobodin and I. N. Shokhar, *J. Gen. Chem. USSR*, **21**, 2231 (1951).

(polarographic grade, Matheson Coleman and Bell) in dimethylformamide (reagent grade) was used for all measurements. The tetrabromide I exhibited two 2-electron waves at −1.8 and −2.33 V (sce), while compound V exhibited one 2-electron wave at −2.33 V (sce).

**Macroscale Electrolysis. Preparation of Compound V.**—The electrolysis cell used for controlled potential electrolysis was described in a previous article.[1] Compound I (25 g, 0.06 mol) in 200 ml of 0.05 *N* $n$-$Bu_4NClO_4$ in DMF was electrolyzed at a mercury cathode at room temperature. The potential of the cathode varied between −1.2 and −1.4 V (sce). The overall voltage was 80 V and allowed the passage of 0.3 A through the cell.[9] The course of the reaction was followed polarographically (see Figure 1). At the conclusion of electrolysis, as indicated by the near disappearance of the first wave,[10] no product had collected in the trap. Distillation at atmospheric pressure did not afford any low-boiling material. The product was hydrolyzed with 200 ml of water and extracted into 500 ml of pentane. The pentane layer was distilled at atmospheric pressure to give 7.8 g of a slightly yellowish liquid which was distilled at reduced pressure 63° (7 mm) [reported[8] for V, bp 83–87° (22 mm)] to give 6.9 g of V. The identity of V was arrived at from its nmr spectrum ($CCl_4$) which exhibited two singlets of equal areas at 0.92 and 3.45 ppm (spiropentane and compound I exhibit one singlet each at 0.75 and 3.52 ppm, respectively) and from its elemental analysis. *Anal.* Calcd for $C_5H_8Br_2$: C, 26.34; H, 3.54; Br, 70.17. Found: C, 26.6; H, 3.63; Br, 70.10.

**Preparation of Spiropentane from Compound V.**—The reduction of the dibromide V (11.0 g) was carried out under the same conditions described for I. The potential of the cathode was kept at −2.2 V (sce). This afforded spiropentane (1.3 g) which was identified from its nmr spectrum ($CCl_4$) which exhibited a singlet at 0.75 ppm.

**Registry No.**—I, 3229-00-3; V, 29086-41-7.

[9] Under these conditions enough heat is generated to boil spiropentane and similar products; hence, a Dry Ice–acetone trap was connected to the cathode compartment.

[10] Further electrolysis may cause the formation of spiropentane.

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# A Facile Reduction of Unsaturated Compounds Containing Oxygen[1]

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During the syntheses of some sesquiterpenoid natural products, we had the necessity of reducing an allylic diol to the corresponding saturated diol. We subsequently found that nickel boride catalyzed the addition of gaseous hydrogen to the $\pi$ bond quantitatively in 0.5 hr with no accompanying hydrogenolysis of the alcohol functions.

The catalyst, nickel boride, has been described previously.[2] The Browns[3,4] have reported two types of nickel boride catalyst (P-1, prepared in water, and P-2, prepared in ethanol) and the results of hydrogenations of many hydrocarbons over these catalysts in their own hydrogenation apparatus.

We have hydrogenated many oxygen-containing compounds employing nickel boride in a Parr hydrogenator. All compounds, with three exceptions, gave quantitative yields of single compounds from reduction of the carbon–carbon $\pi$ bond(s) only. A representative selection of the olefinic compounds hydrogenated is listed in Table I. Table II lists some acetylenic compounds that were hydrogenated and some olefin derivatives that did not undergo hydrogenation.

Table I

Times of Hydrogenations Over Nickel Boride

| Compd | Time[a] |
|---|---|
| Diallyl ether | 20 min[b] |
| Allyl alcohol | 30 min |
| 2-Butene-1,4-diol (cis) | 1 hr |
| Cinnamyl alcohol (trans) | 3 hr |
| 2-Cyclopentene-1,4-diol | 30 min |
| 1-Phenyl-2-propenol | 8 min |
| Cinnamaldehyde (trans) | 24 hr[c] |
| 5-Hexen-2-one | 12 min |
| Mesityl oxide | 6.75 hr |
| Allyl acetate | 16 min |
| Ethyl cinnamate | 2 hr |
| Cinnamic acid (trans) | *d* |
| Maleic acid | 1 hr |

[a] Time required for the uptake of 1 equiv of hydrogen. [b] Time required for the uptake of 2 equiv of hydrogen. [c] Half reaction. [d] No hydrogen uptake after 37 hr.

Table II

Other Compounds Treated with Nickel Boride

| Compd | Reaction time, hr |
|---|---|
| 2-Butyne-1,4-diol | 7.25[a] |
| 2-Methyl-3-butyn-2-ol | 1[a] |
| 1-Ethynylcyclohexanol | *b* |
| Propargyl acetate | *b* |
| 1,2-Epoxybutane | 20[c] |
| 2-Methyl-1,2-epoxypropane | 20[c] |

[a] Time required for the uptake of 2 equiv of hydrogen. [b] Not available: data supplied by Dr. C. A. Brown, private communication. [c] No hydrogen uptake.

The reaction products of the compounds listed were isolated by gas chromatographic techniques and identified by spectral methods. No products resulting from either hydrogenation or hydrogenolysis of the functional groups were detected by gas chromatography. Also, no further uptake of hydrogen was observed for any of the compounds listed following the uptake of the calculated amount.

The results of the hydrogenations of the $\pi$ bonds are similar to results indicated by Polkovnikov, *et al.*,[5] for three other borohydride-reduced metals. They reported times for the uptake of equivalents of hydrogen by cyclopentadiene, cyclohexene, cinnamaldehyde, crotonaldehyde, and dimethyl maleate using platinum, palladium, and rhodium borides. However, they reported no products.

The compounds that did not undergo hydrogenation did not deactivate the catalyst. After attempting to hydrogenate each one, allyl alcohol was added to the

[1] Presented in part at the 50th Anniversary Meeting of the Southwestern Rocky Mountain Division of the American Association for the Advancement of Science, Las Vegas, N. M., April 1970.

[2] (a) H. I. Schlesinger and H. C. Brown, U. S. Patent 2,461,661 (1949); (b) R. Paul, P. Buisson, and N. Joseph, *Ind. Eng. Chem.*, **44**, 1006 (1952).

[3] H. C. Brown and C. A. Brown, *J. Amer. Chem. Soc.*, **85**, 1003, 1005 (1963).

[4] (a) C. A. Brown, *Chem. Commun.*, 952 (1969); (b) C. A. Brown, *J. Org. Chem.*, **35**, 1900 (1970).

[5] B. D. Polkovnikov, A. A. Balandin, and A. M. Taber, *Dokl. Akad. Nauk SSSR*, **145**, 809 (1962).