

1390 (s), 810, 740, 695, 630  $\text{cm}^{-1}$ ; NMR ( $\text{D}_2\text{SO}_4$ )  $\delta$  9.50 (s).

Anal. Calcd for  $\text{C}_{15}\text{H}_6\text{O}_3\text{S}_6$ : C, 42.23; H, 1.42; S, 45.09. Found: C, 42.23; H, 1.62; S, 45.20.

**2,4,6-Tris(1,3-dithiolan-2-ylidene)-1,3,5-cyclohexanetrione (8).** A mixture of 4.29 g (30 mmol) of ethylene trithiocarbonate and 3.0 mL of dimethyl sulfate was heated at 100 °C for 0.5 h and cooled to room temperature, and then 30 mL of acetic acid, 1.62 g (10 mmol) of 1,3,5-trihydroxybenzene dihydrate, and 3.0 mL of pyridine were added. The mixture was refluxed for 1 h and cooled. The resulting crystalline precipitate was collected and washed with acetic acid and then with benzene to give 1.83 g (42%) of 8. Recrystallization from  $\text{Me}_2\text{SO}$  yielded orange needles: mp >400 °C; IR (KBr) 1565 (s), 1540 (sh), 1400 (sh), 1275, 1150, 950, 890, 840, 815, 620  $\text{cm}^{-1}$ ; UV ( $\text{CH}_3\text{CN}$ ) 4.04 (log  $\epsilon$ , 4.65), 322 (4.67), 262 (4.21) nm; NMR ( $\text{Me}_2\text{SO}-d_6$ )  $\delta$  3.32; NMR ( $\text{D}_2\text{SO}_4$ )  $\delta$  4.90 (2).

Anal. Calcd for  $\text{C}_{15}\text{H}_{12}\text{O}_3\text{S}_6$ : C, 41.64; H, 2.80; S, 44.46. Found: C, 41.61; H, 2.76; S, 44.22.

**Acknowledgment.** We acknowledge the support of the Robert A. Welch Foundation (P-074). This is FASTBIOS contribution number 69.

**Registry No.** 7, 74356-07-3; 8, 2957-46-2; 1,3,5-trihydroxybenzene, 108-73-6; 1,3-dithiolium iodide, 1863-66-7; ethylene trithiocarbonate, 822-38-8.

**Supplementary Material Available:** Tables of atomic positional parameters, thermal parameters, bond lengths, valence angles, and torsion angles and ORTEP diagram of 8 (8 pages). Ordering information is given on any current masthead page.

## Electroreduction of Allyl Quaternary Ammonium and Phosphonium Salts

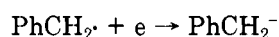
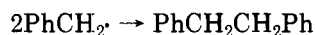
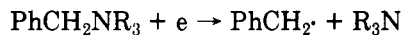
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The electroreduction of quaternary ammonium and phosphonium salts containing the benzyl group has been the subject of a number of papers by Finkelstein et al.<sup>1</sup> The principal products of these electrolyses at an aluminum cathode in nonaqueous solvents have been shown to be bibenzyl and toluene.

Mechanistic studies by Finkelstein et al.<sup>1</sup> and by Mayell and Bard<sup>2</sup> indicate that bibenzyl is formed by the coupling of benzyl radicals and that toluene is formed by the reaction of the benzyl anion with the solvent.

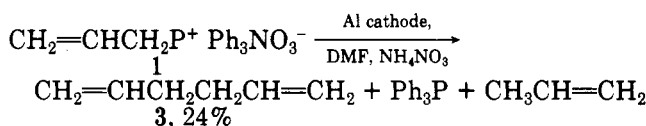
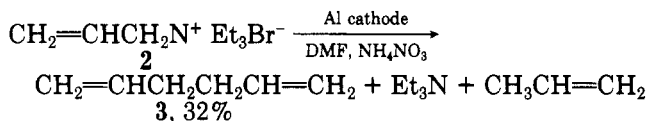


Recent evidence, however, suggests that in the electrochemical reduction of allylic and benzhydryl halides<sup>3,4</sup> dimer formation is more likely to be due to a nucleophilic attack of the carbanion intermediate on the starting halide

rather than to radical coupling.

The electroreduction of allyl quaternary ammonium salts in aqueous solution at aluminum and platinum cathodes has been reported to give propene as the only hydrocarbon product,<sup>5</sup> and Finkelstein<sup>6</sup> found that no dimer was obtained from the electrolysis of allyltriphenylphosphonium nitrate 1 in dimethylformamide (DMF).

Our studies have shown that the electrolysis of allyltriethylammonium bromide (2) in nonaqueous solvents at an aluminum cathode gives appreciable yields of the coupled product, 1,5-hexadiene (3). Contrary to the report of Finkelstein,<sup>6</sup> coupling also occurs in the electrolysis of allyltriphenylphosphonium nitrate (1) under the above conditions.



It is notable that anhydrous materials are necessary in order to achieve an appreciable yield of dimer in the electroreduction of these compounds. As in the electrolysis of benzyl quaternary ammonium salts,<sup>1</sup> it appears that in the presence of water rapid protonation of the intermediate radical or anion occurs, preventing the coupling reaction. The electrolysis of allyltriethylammonium nitrate failed to give any 1,5-hexadiene, but it was noted that this salt was very hygroscopic. Very low yields of the dimer were formed in the electrolysis of the phosphonium salt 1 unless it was carefully dried before use.

We have also investigated the effect of various factors, such as current, concentration of the quaternary salt, nature of the solvent and supporting electrolyte, and temperature, on the yield of 1,5-hexadiene in the electrolysis of these quaternary salts at constant current. The results of these electrolyses are summarized in Table I.

In their polarographic and coulometric studies on the electrolysis of benzyl quaternary ammonium salts, Mayell and Bard<sup>2</sup> suggested that radical coupling is favored by low temperatures, high concentration of quaternary salt, and relatively high current densities.

Our results show little evidence that changing the current over the range 0.25–1.0 A affects appreciably the yield of the coupled product. It was observed, however, that at the highest current used (1.0 A) the temperature rose considerably as the electrolysis proceeded, possibly causing some loss of the rather volatile product.

In agreement with Mayell and Bard,<sup>2</sup> it can be seen from Table I that there is a tendency for increased yields of 1,5-hexadiene when higher concentrations of the quaternary salt 2 were used.

The yields of dimer were compared with three different solvents: DMF, dimethyl sulfoxide ( $\text{Me}_2\text{SO}$ ), and acetonitrile. Much lower yields were obtained in acetonitrile than in DMF and  $\text{Me}_2\text{SO}$ . It was notable that in acetonitrile, lower temperatures actually decreased the yield of 1,5-hexadiene.

Electrolyses of 2 were carried out in the presence of 0.1 M ammonium nitrate, tetraethylammonium nitrate, and

(1) (a) S. D. Ross, M. Finkelstein, and R. C. Peterson, *J. Am. Chem. Soc.*, **92**, 6003 (1970); (b) M. Finkelstein, R. C. Peterson, and S. D. Ross, *Electrochim. Acta*, **10**, 465 (1965), and references cited therein.

(2) J. S. Mayell and A. J. Bard, *J. Am. Chem. Soc.*, **85**, 421 (1963).

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(5) M. Finkelstein, R. C. Petersen, and S. D. Ross, *J. Am. Chem. Soc.*, **81**, 2361 (1959).

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Table I. Electrolysis of Allyl Quaternary Salts

reactant	concn, M	current, A	no. of Faradays passed	solvent	electrolyte	% yield of dimer 3
2	0.6	0.25	0.014	DMF		26.3
2	0.6	0.5	0.015	DMF		21.1
2	0.6	1.0	0.012	DMF		28.0
2	0.6	0.5	0.019	DMF	NH <sub>4</sub> NO <sub>3</sub>	32.0
2	0.6	0.5	0.028	DMF	Et <sub>4</sub> N <sup>+</sup> NO <sub>3</sub> <sup>-</sup>	11.3
2	0.6	0.5	0.019	Me <sub>2</sub> SO	NH <sub>4</sub> NO <sub>3</sub>	24.3
2	0.6	0.5	0.028	CH <sub>3</sub> CN		6.0 <sup>a</sup>
2	0.6	0.5	0.028	CH <sub>3</sub> CN		trace <sup>b</sup>
2	0.3	0.5	0.009	DMF	NH <sub>4</sub> NO <sub>3</sub>	26.3
2	1.2	0.5	0.040	DMF	NH <sub>4</sub> NO <sub>3</sub>	32.6
1	0.3	0.5	0.026	DMF		3.7 <sup>c</sup>
1	0.3	0.25	0.031	DMF	NH <sub>4</sub> NO <sub>3</sub>	23.8
1	0.3	0.5	0.028	DMF	NH <sub>4</sub> NO <sub>3</sub>	23.0

<sup>a</sup> Temp 15 to 34 °C. <sup>b</sup> Temp -30 to -16 °C. <sup>c</sup> Moisture present.

without added electrolyte in order to investigate the effect of added electrolyte. The presence of ammonium nitrate generally resulted in higher yields of the coupled product. At constant current, the voltage increases considerably as the electrolysis proceeds when no electrolyte is present. In the presence of added electrolyte, however, the voltage remains relatively constant, thus decreasing the possibility of side reactions. The fact that tetraethylammonium nitrate is hygroscopic may account for the lower yield when this electrolyte was used.

In conclusion, this investigation has shown that a coupling reaction does in fact occur in the electrolysis of allyl quaternary ammonium and phosphonium salts at an aluminum cathode in nonaqueous solvents to form 1,5-hexadiene. The coupling reaction is favored by the use of relatively high concentrations of the allyl quaternary salt with ammonium nitrate as the added electrolyte and DMF as the solvent.

### Experimental Section

Gas-liquid chromatography (GLC) was carried out with a Varian Aerograph Model 90-P with a CDS 111 integrator and a 6-ft column of Carbowax 1500 on Chromosorb W. NMR spectra were obtained with a Varian Model A-60 and IR spectra were recorded on a Beckman Acculab 1 spectrophotometer. A Hewlett-Packard 0-60V DC power supply, Model 6274B, was used in the electrolyses.

**Materials.** Allyltriphenylphosphonium nitrate (1), mp 164-165 °C, was prepared by the reaction of allyl bromide with triphenylphosphine in acetone followed by treatment of the resulting allyltriphenylphosphonium bromide with aqueous AgNO<sub>3</sub>. The product was recrystallized from methyl ethyl ketone/DMF. 1 and 2 (Eastman) were dried in vacuo over P<sub>2</sub>O<sub>5</sub>. DMF and Me<sub>2</sub>SO were dried by refluxing over calcium hydride followed by distillation in vacuo and final drying over molecular sieves. Acetonitrile was dried by distillation from P<sub>2</sub>O<sub>5</sub>.

**Electrolysis Procedure.** A water-jacketed polarographic cell of 60-mL capacity was used which was fitted with a rubber stopper through which a capillary tube for the passage of nitrogen, a platinum wire anode, and two aluminum cathodes were inserted. The Pt wire was centered between the two Al cathodes which were placed 1.5 cm apart. The immersed area of the each cathode was 3 cm<sup>2</sup> (2 cm high and 1.5 cm wide) and the anode was also immersed to a depth of 2 cm.

The allyl quaternary ammonium or phosphonium salt was dissolved in 40 mL of the solvent and cold water was circulated through the jacket of the cell throughout the electrolyses. The electrolyses were conducted at constant current which was provided by the variable voltage power supply. When an added electrolyte was used, its concentration was 0.1 M. Samples were withdrawn at regular intervals from the electrolysis solution and analysed by GLC at 75 °C. When 2 was electrolyzed three peaks, other than that of the solvent, were observed. They were found to be due to propene, 1,5-hexadiene, and triethylamine, in order of increasing retention time. When 1 was electrolyzed propene

and 1,5-hexadiene were detected. The concentration of 1,5-hexadiene in each sample was found by integration and comparison with a standard containing a known concentration of 1,5-hexadiene in the solvent. Electrolyses were discontinued when no further increase in concentration occurred (generally after 1-3 h).

The identity of the product was confirmed by fractional distillation of the combined products of several electrolyses of 2. A colorless liquid, bp 60-65 °C, was obtained, shown by NMR and IR to consist of 1,5-hexadiene together with a small amount of triethylamine.

The results of the electrolyses are summarized in Table I.

**Registry No.** 1, 35171-86-9; 2, 29443-23-0; 3, 592-42-7; allyl bromide, 106-95-6; triphenylphosphine, 603-35-0.

## Anti-Bredt Molecules. 2.<sup>1</sup> 1-Azabicyclo[3.3.1]nonan-2-one, a New Bicyclic Lactam Containing Bridgehead Nitrogen

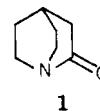
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### Introduction

Until recently, bicyclic lactams containing bridgehead nitrogen had been very difficult, if not impossible, to synthesize. In 1938, Lukes<sup>3</sup> attributed these difficulties to the lack of resonance stabilization of the N-C=O moiety in the same manner that Bredt's Rule<sup>4</sup> forbids bridgehead olefins. However, this did not deter synthesis chemists from attempting to synthesize these compounds. In 1957, Yakhontov and Rubstov<sup>5</sup> reported the synthesis of 1-azabicyclo[2.2.2]octan-2-one (1).



More conclusive was the synthesis of 2,2-dimethyl-1-azabicyclo[2.2.2]octan-2-one and 2,2,6-trimethyl-1-azabi-

(1) Paper 1: H. K. Hall, Jr., and R. C. Johnson, *J. Org. Chem.*, **37**, 697 (1972).

(2) Department of Nutrition and Food Sciences, College of Agriculture, University of Arizona.

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