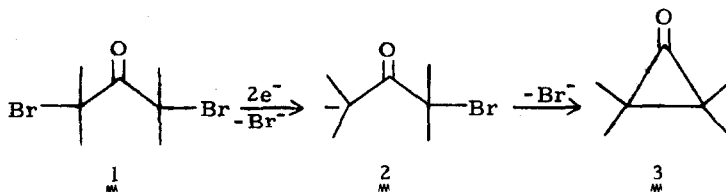


CONCERNING THE INTERMEDIACY OF CYCLOPROPANONES IN THE
ELECTROCHEMICAL REDUCTION OF α, α^1 -DIBROMOKETONES

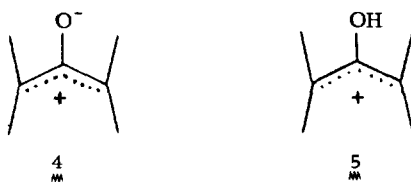
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A recent report by Dirlam, Ebersson, and Casanova¹ described a study of the electrochemical reduction of 2,4-dibromo-2,4-dimethyl-3-pentanone (1). Reasoning by analogy with the electrochemical reduction of a number of other 1,3-dibromides to cyclopropanes,² these investigators hoped that reduction of 1 would afford tetramethylcyclopropanone (3) via anion 2. They were, however, unable to obtain any evidence for 3 as either a product or intermediate,

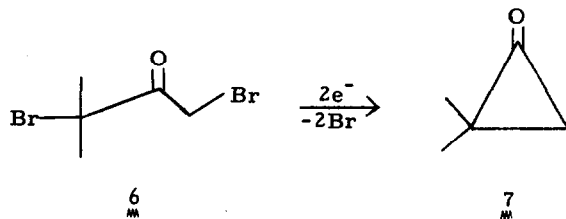


and were in fact inclined to interpret their results in terms of intermediates 4 and 5.¹



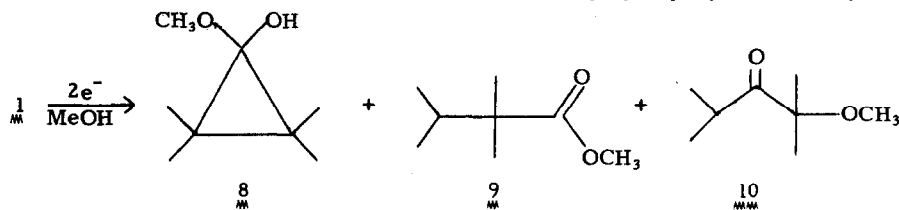
We have also been interested in the electrochemical cyclization of 1,3-dibromides,³ and have independently investigated the electrochemical reduction of several α, α^1 -dibromoketones, including 1. We wish now to report certain results which bear upon the question of possible intermediacy of cyclopropanones in this reaction.

(1) Spectroscopic identification of a cyclopropanone. The infrared spectrum of a solution of 2,4-dibromo-2-methyl-3-pentanone (6) in dimethylformamide (DMF) containing tetraethylammonium bromide (TEAB) was monitored by taking periodic aliquots during a controlled-potential electrolysis of 6 at -1.0V (vs. S. C. E.) at room temperature. Characteristic



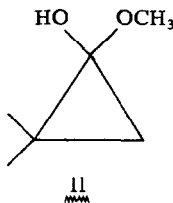
cyclopropanone absorption⁴ appeared at 1825 cm^{-1} , grew to maximum size about halfway through the electrolysis, and then began to decrease in intensity, until it had disappeared by the time electrolysis was complete (ca. 2 hours). We regard this as strong evidence for cyclopropanone **7** as a transient intermediate in the electrolysis. Since coulometry showed that only 2 Faradays were consumed per mole of **6** reduced, we believe that cyclopropanone **7** is disappearing by nonelectrochemical pathways. The product of this reaction was a complex mixture similar to those obtained from **1** by Dirlam, Ebersson, and Casanova under similar conditions.¹

(2) Isolation of cyclopropanone hemiketals. Electrochemical reduction of **1** in methanol at room temperature afforded a mixture of tetramethylcyclopropanone methyl hemiketal **5** (**8**) (90%),



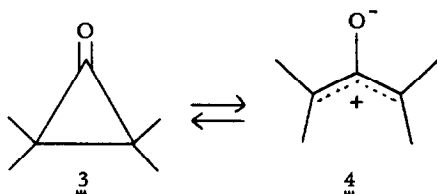
methyl 2,2,3-trimethylbutyrate (**9**) (4%) and α -methoxydiisopropylketone (**10**) (6%). We regard **9** and **10** as secondary products, formed by decomposition of **8**, since (a) hemiketal **8** can be isolated in quantitative yield (homogeneous by i. r. and n. m. r. spectroscopy) when electrolysis and work up are carried out at 0°C or below, and (b) **8** completely disappears (and **9** and **10** increase correspondingly) when the electrolysis mixture is heated for several hours, on the steam bath. Turro has already reported that thermolysis of **8** affords **9** and **10** in the ratio of 1:3.⁶

Electrolysis of **6** at 0° likewise afforded a mixture of hemiketal **11**,⁷ contaminated by

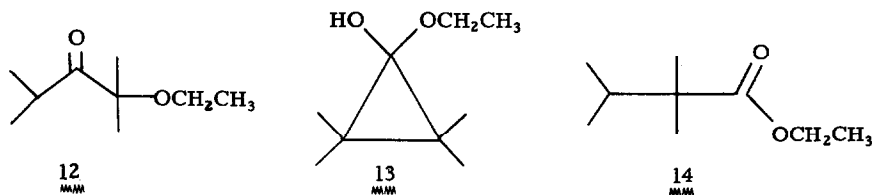


thermolysis products of 11; heating the solution resulted in the disappearance of 11 in a few hours.

We regard these spectroscopic and chemical results as strong evidence for intermediacy of cyclopropanones under certain conditions during the electrochemical reduction of α, α^1 -dibromoketones. At the same time one puzzling feature remains. Dirlam, Ebersson, and Casanova obtained 12, but not 13 or 14, from an electrolysis of 1 carried out in acetonitrile containing ethanol. This may well arise as these investigators suggested, from a solvent-electrolyte effect upon the equilibrium between 3 and 4. It is certainly true, as these investigators have



pointed out, that the strongly ionizing conditions (polar solvents containing added electrolytes) involved in electrolysis should make 4 more favorable relative to 3 than it would be otherwise be in the non-polar solvents often used for studies of cyclopropanone chemistry. (Dipolar ion 4 may also be involved in the reaction leading to gradual disappearance of 2 in DMF-TEAB). Turro has provided evidence for the multiplicity of pathways connecting 2, 3, 4, and 8 and for a dependence of these pathways upon experimental conditions.⁶ Our results suggest that the solvent dependence of these reactions is still incompletely understood.



Acknowledgement

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