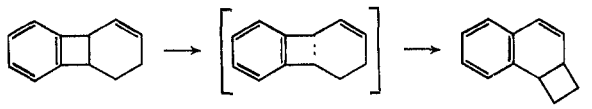
signed to olefinic protons (δ 6.35 and 5.84) were saturated without noticeable effect on the methylene signals. However, decoupling by saturation of the frequency of one of the bridgehead protons (δ 3.2, *cf.* Figures 2 and 3) led to simplification of the signals in the olefinic region. The combined results point strongly to **5** as the structure of the new product.

We speculate that 4,5-benzobicyclo[4.2.0]octa-2,4-diene (**5**) is produced by thermal rearrangement from **4**, which may be unstable under the conditions of vapor chromatographic work-up.



4 5

Registry No.—**3**, 21473-05-2; **5**, 21367-71-5; benzyne, 462-80-6; 1,3-cyclohexadiene, 592-57-4.

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A New Electrochemical Method for the Selective Reduction of Aliphatic Amides to Aldehydes or Alcohols

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Although the reduction of aliphatic amides to alcohols and aldehydes has been reported, the reaction has been limited to rather specific compounds. Thus aldehydes were obtained from amides using sodium in liquid ammonia,[1] but reaction occurred only with compounds possessing a phenyl group attached either to the nitrogen atom or to the carbonyl carbon.

The reduction of amides has also been accomplished electrolytically, but, here again, the substrates were quite specific, *e.g.*, N-aryl amides,[2] amides of isonicotinic acid,[3] and 2-carboxythiazole.[4] It was our purpose to develop a general and selective method, if possible, for the electrolytic reduction of primary, secondary, and tertiary amides to either the corresponding alcohol or aldehyde.

The reductions were carried out in an undivided electrolytic cell[5] consisting simply of a three-neck, round-bottom flask fitted with a Dry Ice condenser and two platinum electrodes. Lithium chloride dissolved in monomethylamine was used as electrolyte.

As can be seen (Table I), alcohols were obtained as major product when the reductions were carried out in the absence of an added proton source like ethanol. Further, it can be seen that the yield of alcohol product was generally good and not adversely affected by the length of the carbon chain of the starting amide or by substitution of one or two alkyl groups on the amide nitrogen.

TABLE I[a]

ELECTROREDUCTION OF VARIOUS ALIPHATIC AMIDES TO THE CORRESPONDING ALDEHYDE OR ALCOHOL

Entry	Amide[b]	Alcohol, %	Aldehyde, %	Coulombs
1	$CH_3(CH_2)_4CONH_2$ (0.05, 700)	58[c]	...	50,400
2	$CH_3(CH_2)_6CONH_2$ (0.01, 350)[d]	...	22	14,400
3	$CH_3(CH_2)_8CONH_2$ (0.05, 700)	59[c]	...	50,400
4	$CH_3(CH_2)_8CONH_2$ (0.005, 350)[e]	...	28	14,400
5	$CH_3(CH_2)_{12}CONH_2$ (0.02, 450)	92	...	50,400
6	$CH_3(CH_2)_{14}CONH_2$ (0.01, 450)	86	...	50,400
7	$CH_3(CH_2)_{16}CONH_2$ (0.01, 450)	79	...	50,400
8	$CH_3(CH_2)_4CONHCH_3$ (0.05, 600)[e]	4	50	12,960
9	$CH_3(CH_2)_4CONHCH_3$ (0.05, 600)	51	...	50,400
10	$CH_3(CH_2)_8CONHCH_3$ (0.02, 300)	81	...	46,800
11	$CH_3(CH_2)_8CONHCH_3$ (0.01, 300)[e]	24	58	14,400
12	$CH_3(CH_2)_5CON(CH_3)_2$ (0.008, 350)	93	...	14,400
13	$CH_3(CH_2)_5CON(CH_3)_2$ (0.01, 350)[e]	...	45	14,400
14	$CH_3(CH_2)_{14}CON(CH_3)_2$ (0.02, 450)	97	...	50,400
15	$CH_3(CH_2)_8CONH_2$ (0.005, 350)[e]	50	4	57,600

[a] The products reported in this table were identified by a combination of physical (ir and nmr spectra) and chemical methods (*e.g.*, melting points of compounds and derivatives such as 2,4-dinitrophenylhydrazones of aldehydes and 3,5-dinitrobenzoates of alcohols. [b] The first value in parentheses represents the number of moles of amide used; the second value represents the number of milliliters of methylamine employed as solvent. [c] A minor product observed in this case was the N-methylimine of the corresponding aldehyde. [d] Seven grams of ethanol present during reduction. [e] Five grams of ethanol present during reduction.

Reduction to aldehydes was achieved in the same cell and under the same reaction conditions as were used to produce alcohols, except that absolute ethanol was added to serve as a proton source. The yield of aldehydes (Table I) was not affected by the length of the carbon chain of the starting amide, but was influenced by alkyl substitution on the amide nitrogen. Reduction of secondary and tertiary amides resulted in better yields of aldehydes than reduction of primary amides.

The mechanistic scheme shown in Scheme I has been proposed[1] to explain such reaction products.

When electrolysis is conducted in the absence of ethanol, the equilibrium between I and II (path b)

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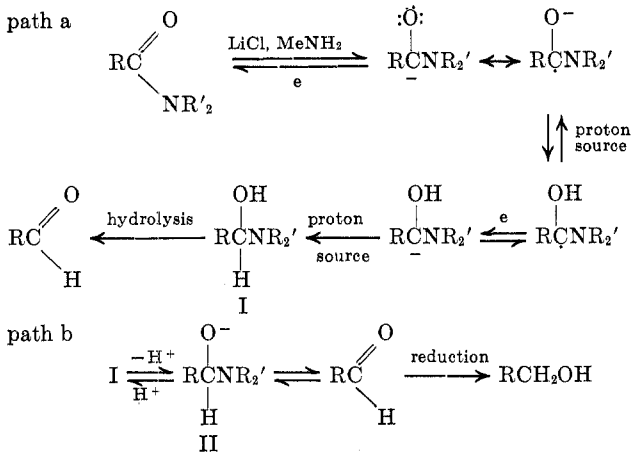
SCHEME I



would likely favor II because of the relative acid–base strengths involved. Hence the alcohol products observed would arise from II *via* path b as shown. It is necessary to assume that the aldehyde formed by path b undergoes rapid reduction to alcohol in the immediate vicinity of the cathode; otherwise it may well have sufficient opportunity to react with solvent to form the N-methylimine, which upon further reduction would yield amine.[6] The fact that amines were not obtained as reaction products excludes the formation of such N-methylimines, since we have shown that imines are converted into amines under the reaction conditions employed.

Electrolysis in the presence of a proton donor such as ethanol causes the reaction to proceed by path a, the equilibrium between I and II now favoring I. Since in the presence of ethanol the yields of alcohols were greatly reduced and amine products were not observed, one might conjecture that intermediate I effectively resists further reduction. Hydrolysis of I with aqueous acid yields the corresponding aldehyde.

To determine the effect of increased reaction times, a fiftyfold excess of current was passed through a solution of decanamide containing ethanol. It was found (entry 15, Table I) that decanol was the major product, with the yield of aldehyde being significantly decreased. This would be the predicted result if intermediates I and II were in equilibrium as depicted in Scheme I. Longer reaction times would increase the opportunity for intermediate II to follow path b, leading to aldehyde and ultimately alcohol.

Experimental Section

Preparation of Amides.—All amides were prepared by bubbling ammonia, methylamine, or dimethylamine through the corresponding carboxylic acids at reflux temperature followed by vacuum distillation of the product.

Electrolytic Reduction of Amides to Alcohols.—Primary, secondary, and tertiary amides were reduced to alcohols in an undivided electrolytic cell[5] consisting of a three-neck flask fitted with a Dry Ice condenser and two platinum electrodes. The flask was charged with lithium chloride (34 g, 0.8 mol), anhydrous monomethylamine (350–700 cc) and the amide (0.008–0.05 mol). A current of 2 A was passed through the solution, after which solvent was allowed to evaporate through a condenser maintained at −5°. The resulting residue was hydrolyzed with water (30–200 cc) and the aqueous solution was extracted with ether. The latter was dried with $MgSO_4$. Table I summarizes the results.

Electrolytic Reduction of Amides to Aldehydes.—Primary, secondary, and tertiary aliphatic amides were reduced to aliphatic aldehydes as described above except that the flask was charged with lithium chloride (17 g, 0.4 mol), anhydrous monomethylamine (300–600 cc), absolute ethanol (5 g, 0.1 mol), and the amide (0.005–0.05 mol). A current of 2 A was passed through the solution for *ca.* 2 hr (*ca.* 14,400 C). At the end of this time, solvent was allowed to evaporate through a condenser which was maintained at −5°. The resulting residue was hydrolyzed with water (20–30 cc) and the aqueous solution was extracted with ether. After removal of ether at room temperature under reduced pressure, the residue was acidified with 10% HCl at 0° and extracted with ether. Drying of the ether layer and removal of solvent at room temperature yielded products which were identified by their 2,4-dinitrophenylhydrazones, glpc, and ir. Table I summarizes the results.

Electrolytic Reduction of the N-Methylimine of Hexanal.—The reduction was carried out in a three-neck flask fitted with a Dry Ice condenser and two platinum electrodes. A current of 0.6 A was passed through a solution of anhydrous monomethylamine containing lithium chloride (4 g, 0.1 mol) and the N-methylimine of hexanal (1.1 g, 0.01 mol) for a period of 2 hr. The usual work-up gave 0.8 g of residue following hydrolysis with water (10 cc). Analysis by glpc showed the residue to consist of starting imine (56%) and N-hexylmethylamine (44%). The yield of amine was 32%.

Registry No.—$CH_3(CH_2)_4CONH_2$, 628-02-4; $CH_3(CH_2)_6CONH_2$, 629-01-6; $CH_3(CH_2)_8CONH_2$, 2319-29-1; $CH_3(CH_2)_{12}CONH_2$, 638-58-4; $CH_3(CH_2)_{14}CONH_2$, 629-54-9; $CH_3(CH_2)_{16}CONH_2$, 124-26-5; $CH_3(CH_2)_4CONHCH_3$, 3418-05-1; $CH_3(CH_2)_8CONHCH_3$, 23220-25-9; $CH_3(CH_2)_8CON(CH_3)_2$, 14433-76-2; $CH_3(CH_2)_{14}CON(CH_3)_2$, 3886-91-7.

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Reactions of α-Dichloromethylene Ketones[1a]

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β-Chlorovinyl ketones are readily prepared and their high reactivity has led to their use as intermediates in the synthesis of a variety of aliphatic, aromatic, and heterocyclic compounds.[2] Techniques for the preparation of β-β-dichlorovinyl ketones are rather limited and studies of their reactions have been restricted to acyclic analogs.[2-4] We recently described a convenient route to β,β-dichlorovinyl ketones involving the reaction of enamines and carbon tetrachloride[5] which makes available a variety of acyclic and cyclic derivatives. With the ready accessibility of the

(1) (a) Abstracted from part of the thesis submitted by R. V. K. in partial fulfillment of the requirements for the Ph.D. degree, Purdue University, August 1966; (b) David Ross Research Fellow, Purdue University, 1964–1966.

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