hydroxy-6-methylacetophenone (9), mp and mmp with authentic 9, 158–159°. The aqueous layer from the ether extract was basified (to pH 8) with 30% sodium hydroxide solution and then extracted with chloroform. Evaporation of the dried ($MgSO_4$) chloroform extract afforded a yellow oil which was dissolved in ether. The ether solution was treated with charcoal and then evaporated to give 200 mg (58%) of 2-acetonyl-6-methyl-4-pyrone as a yellow oil: ir (film) 3.26 (=CH), 3.37 and 3.4 (CH_3 and CH_2), 5.82 (strong, acetyl C=O), 6.02 (strong, conjugated C=O), 6.17 and 6.45 (C=C), 7.19, 7.4, 7.49, and 7.62 (CH_3 and CH_2), 8.45, 8 6, and 8.72 (CO), and 10.86 and 11.55 μ (ring =CH); nmr ($CDCl_3$) δ 2.27 (s, 6, CH_3 at position 6 and $COCH_3$), 3.72 (s, 2, $COCH_2$), 6.03–6.14 (m, 1, vinyl hydrogen at position 5), and 6.17 (d, $J_{3,5} = 2.5$ Hz, 1, vinyl hydrogen at position 3). The mass spectrum of this material possessed a parent molecular ion at m/e 166.0637 (calcd for $C_9H_{10}O_3$: 166.0630).

Registry No.—**4**, 22058-73-7; **8**, 22058-74-8; **10**, 22058-75-9; **11**, 22058-76-0.

An Electrochemical Method for the Selective Reduction of Ketones to Alcohols or N-Methylamines

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Received February 20, 1969

The electrolytic reduction of ketones has received extensive coverage in the literature.[1-4] The type of product obtained (pinacol, secondary alcohol, or alkane) has been found to be dependent upon the electrolytic conditions employed (*e.g.*, pH of electrolyte, type of electrode, and applied voltage).

Controlled potential electrolysis of cyclohexanone in methylamine, hydrochloric acid, and water is reported,[5] yielding N-methylcyclohexylamine. This product was rationalized as resulting from reduction of a ketimine intermediate formed by cyclohexanone and methylamine.

Previously,[6,7] we have shown that an ordinary flask fitted with a Dry Ice condenser and two platinum electrodes along with lithium chloride in methylamine as electrolyte could be used to reduce preparatively many types of organic compounds.

Thus, selective reduction of ketones to alcohols or to N-methylamines might be feasible in our electrochemical system by simply varying the length of time the ketone is in contact with the methylamine solvent before electrolysis.

This objective was achieved and a series of cyclic and acyclic aliphatic ketones were selectively reduced electrochemically to either alcohols or N-methylamines.

As can be seen (Table I), when 2-heptanone, cyclohexanone, cyclopentanone, diethyl ketone, and diisopropyl ketone were reduced by a procedure that involved addition of the ketone to a solution of lithium chloride in refluxing methylamine (−7°)[8] followed by immediate electrolysis, excellent yields of alcohol were obtained. Under these conditions interaction of ketone with amine solvent to form a methylimine followed by reduction to an N-methylalkylamine does not occur to any appreciable extent.

TABLE I

ELECTROREDUCTION OF ALIPHATIC KETONES WITH ZERO TIME STANDING BEFORE ELECTROLYSIS

Entry	Ketone	Yield,[a] % Alcohol[b]	Yield,[a] % N-Methylalkylamine
1[c]	2-Heptanone	61	18
2[d]	Cyclohexanone	57	12
3[e]	Cyclopentanone	70	4
4[f]	Diethyl ketone	79	3
5[f]	Diisopropyl ketone	85	0

[a] Yields are based upon starting ketone. [b] The ir spectra of these compounds were identical with the published spectra ("Sadtler Standard Spectra," Sadtler Research Laboratories, Inc., Philadelphia, Pa., 1968). [c] The product was analyzed on a F & M Model 500 gas chromatograph using a 10 ft, 20% Carbowax 20 M–5% KOH column at 125°. [d] The product was analyzed on a F & M Model 500 gas chromatograph using a 10 ft, 20% Carbowax 20 M–5% KOH column at 140°. [e] The product was analyzed on a F & M Model 500 gas chromatograph using a 10 ft, 20% Carbowax 20 M–5% KOH column. [f] The product was analyzed on an Aerograph gas chromatograph using a 10 ft, 24% silicone oil 200 column at 140°.

Greater selectivity in the reduction of 2-heptanone to alcohol was achieved when the electrolysis was carried out by a procedure incorporating dropwise addition of the ketone (dissolved in ether) to a solution of lithium chloride in methylamine that was being electrolyzed by passage of a 2-A current. The products obtained were 2-heptanol (60%) and N-methyl-2-heptylamine (2%).

On the other hand, if the same ketones were reduced by adding the methylamine to a three-neck flask containing lithium chloride and the ketone, followed by a 6-hr standing period[8] before electrolysis, N-methylalkylamines were obtained as major products (except in the case of diisopropyl ketone). The results obtained are listed in Table II.

From these data, it can be seen that the degree of crowding at the carbonyl carbon atom had a large influence upon the extent to which the conversion of ketone to Schiff base occurred before electrolysis (as evidenced by the relative proportions of secondary amine and alcohol obtained as reduction product). Thus, methyl and cyclic ketones are reduced in excellent yield to N-methylalkylamines under these conditions, while diisopropyl ketone yielded only diisopropylcarbinol.

It was established that N-methylimines can form and subsequently be reduced under the electrolysis conditions used in our system. The N-methylimine of 2-heptanone, when prepared separately and reduced

(1) See F. D. Popp and H. P. Schultz, *Chem. Rev.*, **62**, 19 (1962), for a comprehensive review of the subject.

(2) (a) S. Swann, Jr., *Bull. Central Electrochem. Res. Inst., Karaikudi* (India), **2**, 6 (1955); (b) S. Swann, Jr., D. K. Eads, and L. H. Krone, Jr., *J. Electrochem. Soc.*, **113**, 274 (1966).

(3) X. de Hemptinne and K. Schunck, *Ann. Soc. Sci. Bruxelles, Ser. I*, **80**, 289 (1966).

(4) D. H. Evans and E. C. Woodbury, *J. Org. Chem.*, **32**, 2158 (1967).

(5) H. Lund, *Acta Chem. Scand.*, **13**, 249 (1959).

(6) R. A. Benkeser, E. M. Kaiser, and R. F. Lambert, *J. Amer. Chem. Soc.*, **86**, 5272 (1964).

(7) R. A. Benkeser and C. Tincher, *J. Org. Chem.*, **33**, 2727 (1968).

(8) When gaseous methylamine is passed into a three-neck flask fitted with a Dry Ice condenser and containing lithium chloride, there is heat generated (solvation of lithium chloride) until enough methylamine has been condensed to the liquid state to hold the system constant at the temperature of refluxing methylamine (−7°). It has been determined that this short period of heat generation, if ketone is present, greatly accelerates the rate of Schiff base formation. Therefore, in the reduction to alcohols the ketone was added after the solvent, while in the reduction to secondary amines the ketone was added before the solvent.

TABLE II
ELECTROREDUCTION OF ALIPHATIC KETONES WITH A 6-HR STANDING PERIOD BEFORE ELECTROLYSIS

Entry	Ketone	Yield,[a] % N-Methylalkylamine	Yield,[a] % Alcohol
1[b]	2-Heptanone	73[c]	5
2[b]	Cyclohexanone	70[d]	9
3[e]	Cyclopentanone	70[d]	10
4[f]	Diethyl ketone	52[g]	27
5[f]	Diisopropyl ketone	0	83

[a] Yields are based upon starting ketone. [b] The product was analyzed on an Aerograph gas chromatograph using a 10 ft, 24% silicone oil 200 column at 150°. [c] The nmr spectrum of this compound was identical with its published spectrum (see footnote *b*, Table I). [d] The ir spectrum of this compound was identical with its published spectrum (see footnote *b*, Table I). [e] The product was analyzed on a F & M Model 500 gas chromatograph using a 10 ft, 20% Carbowax 20 M–5% KOH column at 110°. [f] The product was analyzed on a F & M Model 500 gas chromatograph uing a 10 ft, 20% Carbowax 20 M–5% KOH column at 100°. [g] n^{25}D 1.4066 [lit. n^{25}D 1.4060; A. C. Cope, N. A. Le Bel, H. H. Lee, and W. R. Moore, *J. Amer. Chem. Soc.*, **79**, 4720 (1957)].

electrolytically in the normal manner, produced a material which contained 77% of N-methyl-2-heptylamine.

Experimental Section

General Procedure for the Electroreduction of Cyclic and Acyclic Aliphatic Ketones (Ketone Added after the Addition of Solvent, Zero Standing Time before Electrolysis).—Lithium chloride (17 g, 0.4 mol) and anhydrous methylamine (300 ml) were placed in a three-neck, 0.5-l. flask fitted with a Dry Ice condenser and two (2 × 5 cm) platinum electrodes. Immediately after addition of ketone (0.05 mol), the solution wss electrolyzed by passing a current of 2 A through the system for 2 hr and 41 min (19,300 C).[9] Ether was added, and the solvent was allowed to evaporate through a condenser that was kept at −5°. The residue was hydrolyzed with water, and the aqueous solution was extracted with ether. The ether extracts were combined, dried ($MgSO_4$), concentrated, and distilled to give the product. The results obtained for 2-heptanone, cyclohexanone, cyclopentanone, diethyl ketone, and diisopropyl ketone are summarized in Table I.

Electroreduction of 2-Heptanone (Dropwise Addition of Ketone to Cell during Electrolysis).—Into a four-neck, 100 × 170 mm electrolysis cell[10] fitted with a Dry Ice condenser, addition funnel, and two platinum electrodes were placed lithium chloride (34 g, 0.8 mol) and methylamine (600 ml). Current (2 A) was passed through the cell, and 2-heptanone (5.85 g, 0.05 mol dissolved in 150 ml of ether) was added dropwise over a period of 2 hr and 20 min. Solvent was then allowed to evaporate through a water condenser and the resulting residue was hydrolyzed (water). The organic material was worked up in the usual manner. Distillation afforded 3.6 g (62%) of product, bp 83–92° (*ca.* 40 mm). Analysis by glpc (10 ft, 24% silicone oil 200 column, 155°), showed the product to consist of 2-heptanol (97%) and N-methyl-2-heptylamine (3%). The yields based upon starting ketone were: 2-heptanol, 60%; N-methyl-2-heptylamine, 2%.

General Procedure for the Electroreduction of Cyclic and Acyclic Aliphatic Ketones (Ketone Added before the Addition of Solvent, 6-Hr Standing Period before Electrolysis).—Lithium chloride (17 g, 0.4 mol) and ketone (0.05 mol) were placed in a three-neck, 500-ml flask fitted with a Dry Ice condenser and two platinum electrodes. Then 300 ml of methylamine was added, and the resulting solution was allowed to stand (6 hr) before a current (2 A) was passed through the system for 2 hr and 41 min (19,300 C).[11] At the end of this time, ether was added and the solvent was evaporated.[12] The usual work-up, followed by distillation, yielded the product. The results for the reduction of 2-heptanone, cyclohexanone, cyclopentanone, diethyl ketone, and diisopropyl ketone are shown in Table II.

N-Methylimine of 2-Heptanone.—2-Heptanone (24 g, 0.2 mol) and methylamine (600 ml) were placed in a 1-l., three-neck flask fitted with a Dry Ice condenser and a magnetic stirrer. After the solution was allowed to stir for 1 hr, solvent was evaporated through a water condenser. The resulting residue was taken up in ether, dried ($CaSO_4$), and stripped of solvent to give 27 g of product. Analysis by glpc (10 ft, 24% silicone oil 200 column), showed the product to consist of 2-heptanone (34%) and the N-methylimine of 2-heptanone (66%).[13]

Electroreduction of the N-Methylimine of 2-Heptanone.—In a three-neck flask (300 ml) fitted with a Dry Ice condenser and two platinum electrodes were placed lithium chloride (8 g, 0.2 mol), 3 g of material (80% N-methylimine of 2-heptanone and 20% 2-heptanone) obtained by preparative gas chromatography[14] of the above reaction product, and 200 ml of methylamine. Current (1 A) was passed through the system for 1 hr and 15 min (4500 C). The solvent was allowed to evaporate, and the resulting residue was worked up as in the previous experiment to give 2.3 g of residue, which (analysis by glpc[14]) was shown to consist of N-methyl-2-heptylamine (77%), 2-heptanone (13%), and the N-methylimine of 2-heptanone (10%).

Registry No.—2-Heptanone, 110-43-0; N-methylimine of 2-heptanone, 22058-71-5; cyclohexanone, 108-94-1; cyclopentanone, 120-92-3; diethyl ketone, 96-22-0; diisopropyl ketone, 565-80-0.

Acknowledgment.—This research was sponsored by the Air Force Office of Scientific Research, Office of Aerospace Research, U. S. Air Force, under AFOSR Grant 822-67.

(9) In the reduction of cyclohexanone, current (2 A) was passed for 4 hr (28,800 C) rather than for 2 hr and 41 min.

(10) R. A. Benkeser and E. M. Kaiser, *J. Amer. Chem. Soc.*, **85**, 2858 (1963).

(11) In the reduction of cyclohexanone, current (2 A) was passed for 6 hr (43,200 C) rather than for 2 hr and 41 min.

(12) In the reduction of 2-heptanone and cyclohexanone, a water condenser was used. In the reduction of cyclopentanone, diethyl ketone, and diisopropyl ketone, a condenser that was kept at −5° was used.

(13) The ir spectrum showed imine absorption at 6.1 μ (L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, N. Y., 1958, p 267) and its nmr spectrum (CCl_4) showed a 2.5 H singlet at τ 7.0, a 2 H multiplet at 7.5–8.0, a 3 H multiplet at 8.0–8.3, a 6 H multiplet at 8.3–8.9, and a 3 H multiplet at 9.0–9.2.

(14) An Aerograph Autoprep gas chromatograph with a 10 ft 24% silicone oil 200 column was used. Although the imine could be collected pure, it undergoes rapid hydrolysis in air.

α Anions of Carboxylic Acids. I. Effect of Hexamethylphosphoramide on Metalation and Alkylation

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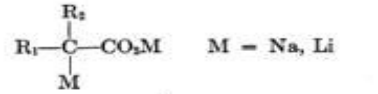
Received May 22, 1969

α anions of carboxylic acids (I) offer unique oppor-



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tunities in synthesis. Unfortunately, their utility has not been investigated with acids other than acetic acid[2] and methyl-branched acids of chain lengths no greater than C_4.[3] Typically, disodio derivatives con-

(1) Agricultural Research Service, U. S. Department of Agriculture.

(2) D. O. DePree and R. D. Closson, *J. Amer. Chem. Soc.*, **80**, 2311 (1958).

(3) P. L. Creger, *ibid.*, **89**, 2500 (1967), and references cited therein.