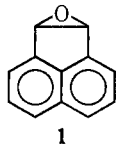
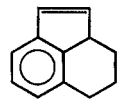
necessary to synthesize 1,2-epoxyacenaphthene (**1**). Several attempted preparations of **1** or its substituted derivatives are described in the literature, but none of these were successful.[4,5] The very recent report of Richter and Silver[6] describes several additional un-



1



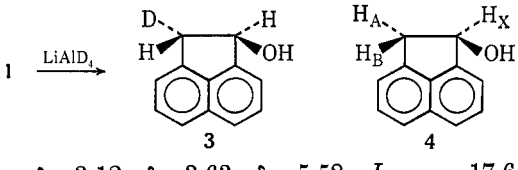
2

successful attempts to isolate **1** or the epoxide of 2,3,4,5-tetrahydroacenaphthylene (**2**). We wish to describe now a simple preparation and some of the chemical properties of **1**.

Acenaphthylene, when treated with an equimolar amount of *m*-chloroperbenzoic acid in chloroform solution at 0° for 24 hr, is converted in >90% yield to **1**. This is apparent from an nmr spectrum of the crude reaction mixture, which shows the complete absence of the olefinic acenaphthylene resonance at 6.85 ppm and the appearance of a two-proton singlet at 4.77 ppm due to the epoxide methine protons. Impurities of acenaphthenone (*ca.* 5%, methylene resonance at 3.75 ppm) and another minor, as yet unidentified component were evident in the reaction mixture.

Solutions of **1** are labile to heat and protonic media. Attempts to purify **1** by chromatography on neutral alumina or silica gel resulted in nearly quantitative conversion to acenaphthenone. This facile rearrangement is not unexpected and probably accounts for the problems previously encountered in isolation of **1** and related substances. Careful work-up followed by recrystallization gives **1** as colorless plates in 35% yield. Crystalline **1** is quite stable and exhibited no change in physical properties after 18 months.

Compound **1** undergoes several reactions characteristic of epoxides. Reaction with alkyl Grignard reagents yields 2-alkyl-1-acenaphthenols, which can be dehydrated to 1-alkylacenaphthylenes free from the isomeric alkylidenes.[7] Reaction of **1** with lithium aluminum deuteride produces *trans*-2-*d*-acenaphthenol (**3**) in quantitative yield. The stereochemical assignment in **3** follows from a comparison of its nmr spectrum with that of **4**, which shows a pattern analyzed as



3 **4**

ABX: δ_B 3.12, δ_A 3.63, δ_X 5.58, J_{AB} = 17.6 Hz, J_{AX} = ±7.3 Hz, and J_{BX} = +2.9 Hz. This assignment of H_A and H_B is consistent with the known relationship of dihedral angle and coupling constants,[9] and is in excellent agreement with the coupling constants reported for 1-bromoacenaphthene.[10]

(4) G. Wittig and K. Henkel, *Ann.*, **542**, 130 (1939).
(5) P. D. Bartlett and R. F. Brown, *J. Amer. Chem. Soc.*, **62**, 2927 (1940).
(6) H. J. Richter and S. F. Silver, *J. Org. Chem.*, **33**, 3283 (1968).
(7) Dehydration of 1-alkyl-1-acenaphthenols yields mixtures of isomers which are inseparable and which result in the loss of isotopic label in deuterio alkyl derivatives.[8]
(8) Unpublished results from the Ph.D thesis of P. J. Ihrig, Iowa State University, 1968.
(9) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961).
(10) M. J. S. Dewar and R. C. Fahay, *J. Amer. Chem. Soc.*, **85**, 2245, 2704 (1963).

The nmr spectrum of **3** exhibits a doublet (J = 2.9 Hz, δ_X 5.58) and a broad resonance (δ_B 3.13, broadened and unresolved due to deuterium coupling) in addition to the typical aromatic proton multiplet.

Finally, compound **1** is deoxygenated by triphenylphosphine with added hydroquinone under standard reaction conditions[11] to produce acenaphthylene in 68% yield. The results of the reactions described above demonstrate that, once purified, **1** undergoes typical epoxide reactions without complications caused by prior rearrangement to acenaphthenone.

Experimental Section

1,2-Epoxyacenaphthene (**1**).—Acenaphthylene (6.08 g, 0.04 mol) was added during 5 min to a solution of *m*-chloroperbenzoic acid (10.3 g, 0.06 mol) in chloroform (100 ml) previously cooled to 0°. The mixture was allowed to stand in the refrigerator for 24 hr, during which the yellow color of acenaphthalene slowly disappeared and a precipitate of *m*-chlorobenzoic acid appeared. The acid was removed by filtration and the filtrate was poured into cold aqueous sodium bicarbonate and quickly extracted with cold chloroform. The organic phase was washed with 5% sodium thiosulfate, saturated sodium bicarbonate, and water, dried, and concentrated to 8.1 g of a yellow oil which slowly crystallized. Three recrystallizations from carbon tetrachloride afforded 1.68 g (35%) of colorless plates, mp 83–84°. The mass spectrum of this material showed an intense molecular ion peak at *m/e* 168 ($C_{12}H_8O$) and a fragmentation pattern essentially identical with that of acenaphthenone. The ir spectrum showed no carbonyl bands but showed bands at 12.34 and 12.84 μ, characteristic of epoxides. The nmr spectrum showed peaks at 4.77 (2 H, singlet) and 7.13–7.75 (6 H, multiplet).

Anal. Calcd for $C_{12}H_8O$: C, 85.69; H, 4.79. Found: C, 85.73; H, 4.83.

trans-**2-Deuterioacenaphthenol** (**3**).—A solution of **1** (0.2 g, 1.2 mmol) in anhydrous ether (6 ml) was added dropwise to a stirred slurry of lithium aluminum deuteride (0.05 g, 1.2 mmol) in ether (5 ml). The addition was complete in 30 min and stirring was continued for 1 hr. Water was added dropwise and the mixture was worked up to afford 0.20 g (100%) of colorless plates, mp 143–145°, mmp with acenaphthenol 143–145°. Low-voltage mass spectral analysis showed that only one deuterium had been incorporated into the alcohol. The nmr spectrum (described in text above) was obtained as a solution in DMSO-d_6 containing a trace of trifluoroacetic acid.

Deoxygenation of 1 with Triphenylphosphine.—Following the procedure of Wittig and Haag,[11] **1** (0.17 g, 1.0 mmol), triphenylphosphine (0.27 g, 1.0 mmol) and hydroquinone (0.03 g, 0.3 mmol) were mixed thoroughly in a small flask equipped with an efficient condenser and heated at 150° for 1 hr. Chromatography on neutral alumina (Woelm) of the crude reaction mixture and elution with hexane afforded 0.104 g (68%) of acenaphthylene, mp 89–90°, mmp 89–90°.

Registry No.—**1**, 22058-69-1.

(11) G. Wittig and W. Haag, *Ber.*, **88**, 1654 (1955).

A Facile Route to a Novel Derivative of 2,4,6,8-Nonanetetraone

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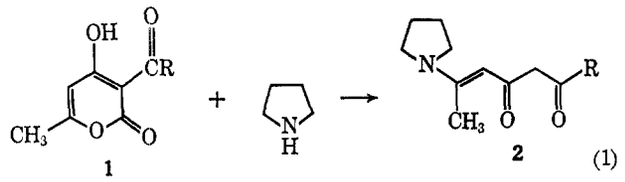
Recent studies in these laboratories[1] have shown that pyrrolidine reacts with 3-acyl-4-hydroxy-6-methyl-2-

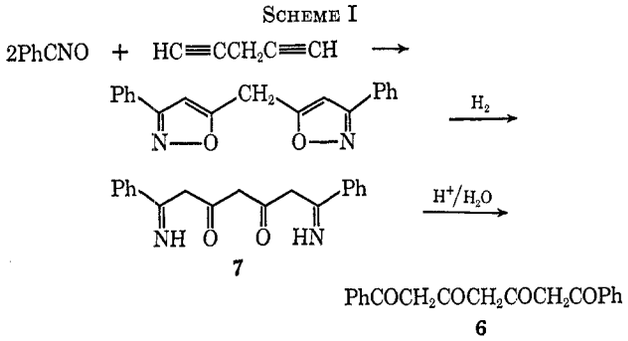
(1) J. F. Stephen and E. Marcus, *J. Org. Chem.*, **34**, 2527 (1969).

pyrones (1), preferentially at the 6 position of the pyrone, to give the corresponding enedione 2 (eq 1).



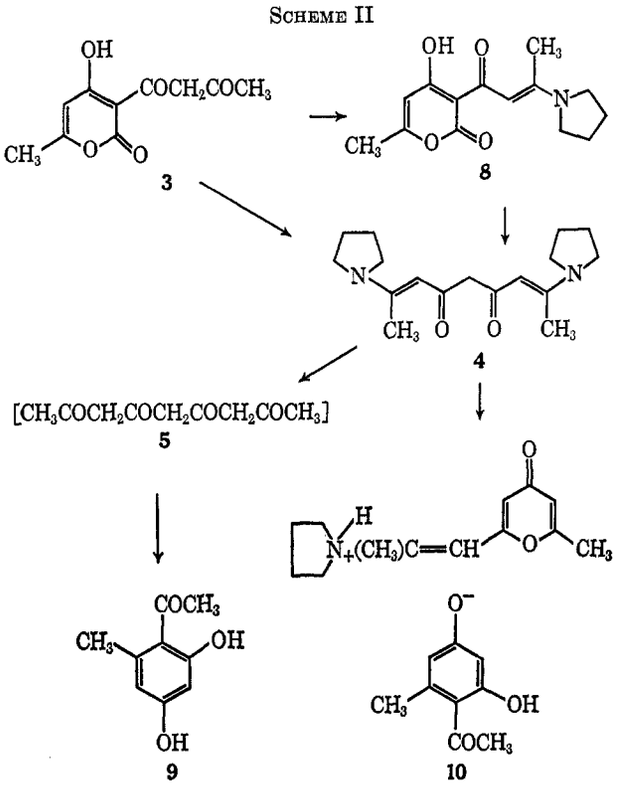
In extension, it occurred to us that reaction of 3-acetoacetyl-4-hydroxy-6-methyl-2-pyrone (3)[2] with pyrrolidine might offer a facile route to the novel derivative 4 (Scheme II), because pyrrolidine would be expected to react with pyrone 3 most likely at the carbonyl of the acetoacetyl side chain remote from the pyrone nucleus and at the 6 position of the pyrone. Dienedione 4 appeared to be a potentially useful precursor of 2,4,6,8-nonanetetraone (5), since Casnati, *et al.*,[3] were able to generate the related tetraketone, 1,7-diphenyl-1,3,5,7-heptanetetraone (6), by acid hydrolysis of the diimino derivative 7, which was obtained *via* a bisisoxazole as outlined in Scheme I. 1,7-Diphenyl-1,3,5,7-heptanetetraone (6) has also been prepared from 1-phenyl-1,3,5-hexanetrione and methyl benzoate in 1,2-dimethoxyethane using sodium hydride as the condensing agent[4] or, more recently, using sodium amide in liquid ammonia.[5]

SCHEME I



3-Acetoacetyl-4-hydroxy-6-methyl-2-pyrone (3) reacted with 1 equiv of pyrrolidine, in toluene at 50°, to afford 3-[3-(N-pyrrolidino)but-2-enoyl]-4-hydroxy-6-methyl-2-pyrone (8) in 80% yield. The structure of 8 was supported by its ir spectrum, which showed broad weak absorption in the 4-μ region, indicating a strongly chelated hydroxyl group, and a strong pyrone carbonyl stretching band at 5.92 μ. The nmr spectrum of 8 provided further support for the assigned structure; the most interesting feature of the spectrum was the low-field position of the enol proton resonance line at 19 ppm, indicating the involvement of this group in strong intramolecular hydrogen bonding. When 8 was treated with an excess of pyrrolidine in refluxing toluene, it was converted into dienedione 4 in 35% yield. Reaction of pyrone 3 with an excess of pyrrolidine in refluxing toluene afforded 4 directly in 71% yield (Scheme II). The structure of 4 was established by elemental analysis as well as by ir and nmr spectra.

SCHEME II



In an attempt to generate 2,4,6,8-nonanetetraone (5), dienedione 4 was subjected to hydrolysis with hot 2 *N* sulfuric acid. No tetraketone 5 was obtained. The hydrolysis afforded 2,4-dihydroxy-6-methylacetophenone (9) in 69% yield (presumably *via* tetraketone 5), together with a compound, $C_{22}H_{27}NO_5$, in 8% yield. The acetophenone 9 was identified by a mixture melting point determination and by comparison of its ir spectrum with that of authentic material prepared by acetylating orcinol.[6] The acetophenone 9 was also obtained by Stetter and Vestner[7] from the acid hydrolysis of the 2,8-ethylene diketal of 2,4,6,8-nonanetetraone.

The compound, $C_{22}H_{27}NO_5$, was assigned structure 10 on the basis of spectral evidence. The 100-MHz nmr spectrum of 10 in $CDCl_3$ showed, in addition to multiplets for the pyrrolidino group at δ 1.75–2.10 and 3.20–3.48, four different methyl resonance lines occurring at δ 2.22, 2.27, 2.50, and 2.57; absorption for three different vinyl hydrogens at δ 4.67, 5.85, and 5.96–6.04; and peaks at δ 6.29 and 11.10–11.80, each of relative area two. The downfield pair of methyl resonance lines at δ 2.50 and 2.57, the peak at 6.29, and one half of the signal at 11.10–11.80 (the other half of this signal is due to the proton on the quaternized nitrogen) are readily assigned to the acetophenone moiety in 10. The remaining lines in the spectrum can be accommodated by the pyrone group in 10.

Structure 10 was confirmed by hydrolysis. Treatment of 10 with 2 *N* sulfuric acid at reflux for 1 hr furnished a mixture of 2,4-dihydroxy-6-methylacetophenone (9) and a compound, $C_9H_{10}O_3$, isomeric with 9.

(2) (a) P. F. G. Praill and A. L. Whitear, *Proc. Chem. Soc.*, 112 (1961); (b) E. Marcus, J. F. Stephen, and J. K. Chan, *J. Heterocycl. Chem.*, **6**, 13 (1969).

(3) G. Casnati, A. Quilico, A. Ricca, and P. VitaFinzi, *Tetrahedron Lett.* 233 (1966).

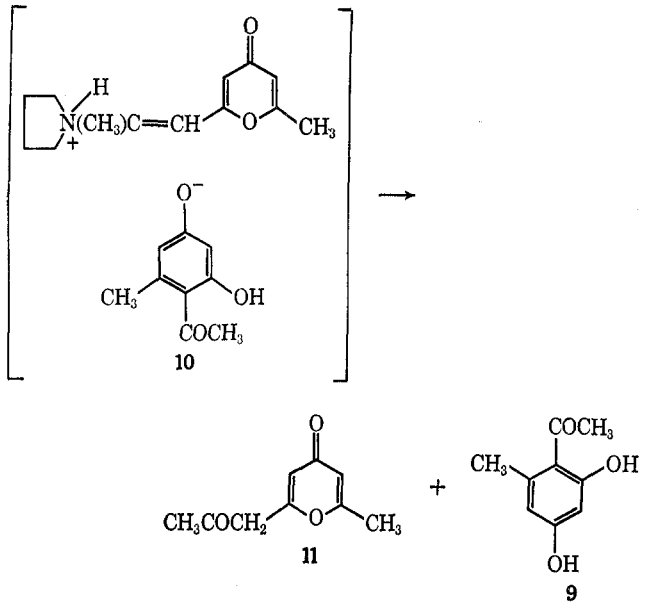
(4) M. L. Miles, T. M. Harris, and C. R. Hauser, *J. Amer. Chem. Soc.*, **85**, 3884 (1963).

(5) K. G. Hampton, T. M. Harris, C. M. Harris, and C. R. Hauser, *J. Org. Chem.*, **30**, 4263 (1965).

(6) K. Hoesch, *Chem. Ber.*, **48**, 1122 (1915).

(7) H. Stetter and S. Vestner, *ibid.*, **97**, 169 (1964).

Based on spectral evidence, this isomer is apparently 2-acetonyl-6-methyl-4-pyrone (**11**). The ir spectrum



of pyrone **11** showed carbonyl absorptions at 5.82 μ, assigned to the acetyl carbonyl, and 6.02 μ, assigned to the ring carbonyl.

The nmr spectrum also agreed with that anticipated for structure **11**. Thus, on an over-all basis, sulfuric acid liberated the anion of **10** to give 2,4-dihydroxy-6-methylacetophenone (**9**), and it hydrolyzed the enamine function of the cation moiety in **10** to produce **11**. Compound **10** is presumably formed during the hydrolysis of dienedione **4** by partial hydrolysis of **4** to an enetrione which cyclizes to form a pyrone, which in turn interacts with 2,4-dihydroxy-6-methylacetophenone (**9**) to afford **10**.

Experimental Section[8]

Reaction of 3-Acetoacetyl-4-hydroxy-6-methyl-2-pyrone (3) with 1 Equiv of Pyrrolidine.—A stirred solution of pyrone **3** (21 g, 0.1 mol) in 120 ml of toluene at 50° was treated dropwise during 15 min with pyrrolidine (7.1 g, 0.1 mol). After the addition was complete, the mixture was stirred overnight at room temperature. The precipitated solid of 22.4 g, mp 163–165°, was collected by filtration and recrystallized from ethanol to give 21 g (80%) of 3-[3-(N-pyrrolidino)but-2-enoyl]-4-hydroxy-6-methyl-2-pyrone (**8**), mp 168–170°. A second recrystallization from ethanol afforded an analytical sample: mp 169–170°; compound **8** gave an intense green color with ethanolic ferric chloride; ir (KBr) 3.18 (=CH), 3.35, and 3.46 (CH_3 and CH_2), 4 (weak, broad, chelated OH), 5.92 (strong, conjugated lactone C=O), 6.1 and 6.2 (C=C and chelated C=O), 6.46 (α,β-unsaturated C=O), 8.06 (lactone CO), and 10.05 and 12.18 μ (RR'C=CHR''); nmr ($CDCl_3$) δ 1.80–2.20 (m) and 2.13 (d) (overlapping, 7, methylenes β,β' to nitrogen in the pyrrolidino ring and CH_3 at position 6), 2.56 [s, 3, $=C(N)CH_3$], 3.28–3.70 (m, 4, methylenes α,α' to nitrogen in the pyrrolidino ring), 5.72 (d, 1, vinyl hydrogen at position 5), 6.71 (s, 1, COCH=) and 19.00 (broad s, 1, intramolecularly chelated OH at position 4).

Anal. Calcd for $C_{14}H_{17}NO_4$: C, 63.86; H, 6.51; N, 5.32. Found: C, 63.59; H, 6.55; N, 5.34.

Reaction of 3-[3-(N-pyrrolidino)but-2-enoyl]-4-hydroxy-6-methyl-2-pyrone (8) with an Excess of Pyrrolidine.—Pyrrolidine (8.52 g, 0.12 mol) was added dropwise during 9 min to a stirred solution of pyrone **8** (15.78 g, 0.06 mol) in 150 ml of boiling toluene. After the addition was complete, the mixture was stirred and refluxed for 5 hr and cooled in ice, and the precipitated dienedione **4**, 6.1 g (35%), mp 194–200° dec, was collected. An analytical sample recrystallized from dimethylformamide had mp 198–200° dec; ir (KBr) 3.28 (=CH), 3.36 (CH_3), and 3.48 (NCH_2), 6.55 (strong, broad, C=O and C=C), 7.3 (CCH_3), 8.55 (CN), and 12.4 μ (RR'C=CHR''); nmr (pyridine-d_5) δ 1.40–1.62 (m, 8, methylenes β,β' to nitrogen in pyrrolidino ring), 2.60 [s, 6, $=C(N)CH_3$], 2.83–3.24 (m, 8, methylenes α,α' to nitrogen in pyrrolidino ring), 3.75 (s, 2, $COCH_2CO$), and 5.39 [s, 2, $=C-(CO)H$].

Anal. Calcd for $C_{17}H_{25}N_2O_2$: C, 70.31; H, 9.02; N, 9.65. Found: C, 70.34; H, 9.00; N, 9.59.

Reaction of Pyrone 3 with an Excess of Pyrrolidine.—Pyrrolidine (80 g, 1.13 mol) was added dropwise during 15 min to a stirred solution of pyrone **3** (60 g, 0.286 mol) in 400 ml of boiling toluene contained in a flask equipped with a water separator. During the addition the heat source was removed and the temperature fell to 72°. After the addition was completed, the mixture was heated to reflux and a yellow solid began to precipitate from solution. After 1 hr, the mixture was cooled in ice and the precipitated dienedione **4**, 58.7 g (71%), mp 196–199° dec, was collected by filtration and washed with toluene and ether. This material was identical in all respects with **4** obtained from the reaction of **8** with pyrrolidine.

Hydrolysis of Dienedione 4 with 2 *N* Sulfuric Acid.—A solution of dienedione **4** (28 g, 0.097 mol) in 150 ml of 2 *N* sulfuric acid was heated under reflux for 0.5 hr. The mixture was cooled in ice and the precipitated 2,4-dihydroxy-6-methylacetophenone (6 g, mp 157–159°) was collected by filtration. The pH of the filtrate was adjusted to 7 by addition of 30% aqueous sodium hydroxide, and the solution was extracted with ether. The aqueous layer was saturated with magnesium sulfate and extracted again with ether. The combined ether extracts were evaporated under reduced pressure, and the solid residue was recrystallized from water to afford 5 g of 2,4-dihydroxy-6-methylacetophenone, mp 158–159°. The yield of combined 2,4-dihydroxy-6-methylacetophenone (11.0 g) was 69%. The mixture melting point with an authentic sample of **9**, prepared by the method of Hoesch,[6] was undepressed; the materials were spectrally identical.

The aqueous layer from the ether extract was extracted with chloroform. The dried ($MgSO_4$) chloroform extract was evaporated under reduced pressure. The resulting orange-yellow solid was recrystallized from acetone to give 1.5 g (8.1%) of **10**: mp 161–162° dec; ir (KBr) 3.26 (=CH), 3.35 and 3.45 (CH_3 and CH_2), 3.9 and 5.3 (broad, strongly chelated OH and N^+H, respectively), 6.05 (C=O and C=C), 6.2 (chelated C=O), 6.25 and 6.46 (conjugated C=C), 6.66 (aromatic C=C), 7.2 and 7.27 (CCH_3), 7.9, 8.0, 8.35, and 8.57 (CO), and 11.5 and 11.7 μ (isolated aromatic hydrogens); nmr ($CDCl_3$) δ 1.75–2.10 (m, 4, methylenes β,β' to nitrogen in pyrrolidino ring), 2.22 and 2.27 [d (J <1 Hz) and s, 6, CH_3 at the 6 position of the pyrone and $=C(N^+H)CH_3$, respectively], 2.50 (s, 3, CH_3 at the 6 position of the acetophenone moiety), 2.57 (s, 3, $COCH_3$), 3.20–3.48 (m, 4, methylenes α,α' to nitrogen in pyrrolidino ring), 4.67 [s, 1, $CH=C(N^+H)$], 5.85 [d ($J_{3,5}$ = 2.5 Hz), 1, vinyl hydrogen at the 3 position of the pyrone], 5.96–6.04 (m, 1, vinyl hydrogen at the 5 position of the pyrone], 6.29 (s, 2, aromatic protons of the acetophenone moiety), and 11.10–11.80 (broad s, 2, intramolecularly chelated OH and NH^+).

Anal. Calcd for $C_{22}H_{27}NO_5$: C, 68.55; H, 7.06; N, 3.63. Found: C, 68.30; H, 7.02; N, 3.52.

Hydrolysis of 10 with 2 *N* Sulfuric Acid.—A solution of **10** (0.8 g, 0.002 mol) in 10 ml of 2 *N* sulfuric acid was heated under reflux for 1 hr. The cold mixture was extracted with ether. Evaporation of the ether extract afforded a solid residue which was recrystallized from water to give 300 mg (87%) of 2,4-di-

(8) Melting points are uncorrected. The ir spectra were obtained with a Baird-Atomic Model AB-2 spectrometer using potassium bromide pellets of the compounds. Nmr spectra were determined at either 60 or 100 MHz with Varian Associates A-60 and HA-100 spectrometers. Field position values are recorded in ppm referred to an internal tetramethylsilane standard. Nmr peak multiplicities are abbreviated as follows: s (singlet), d (doublet), and m (multiplet). Mass spectra were recorded on an AE1 Model MS 902b spectrometer. The microanalyses were performed by Union Carbide Corporation, Analytical Department, South Charleston, W. Va.

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).

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(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.