tion of un-ionized catalyst is essentially constant, and becomes pH independent after ionization because the linear increase in OH^- concentration is balanced by a linear decrease in catalyst concentration. Thus, the rate reaches a plateau because of catalyst saturation by the first mechanism and because of catalyst exhaustion by the second. The log k_{OBS}–pH profiles are identical for both mechanisms.

The second mechanism is preferred because it is analogous to the most acceptable mechanism for the uncatalyzed hydrolysis. In addition, since the same nucleophile is involved in the catalyzed and uncatalyzed reaction, no difference in solvent deuterium isotope is expected for the two reaction paths.

Experimental

Materials.—The preparation of the quaternary aldehyde salt was described previously.[6] *p*-Trimethylammoniumaniline chloride was prepared by refluxing *p*-dimethylaminoacetanilide with methpl iodide, hydrolyzing and exchanging the iodide ion of the quaternary salt for chloride on Amberlite IRA-400 ion-exchange resin. Chloride salts of the Schiff bases were generally more soluble than the iodides. The Schiff bases were prepared by warming together the aldehyde and amine in an appropriate solvent. The reaction solvents and times, melting points, and elemental analyses are given in Table IV.

Kinetics.—For most of the runs, a weighed sample of Schiff base, sufficient to give a 1×10^{-4} *M* solution after dilution, was dissolved in 1 ml. of ethanol in a volumetric flask and thermostated at 25.0°. This sample was diluted to 100 ml. with aqueous phosphate or carbonate buffer having an ionic strength of 0.05. The disappearance of Schiff base was followed on a Beckman DU spectrophotometer at a wave length that gave the greatest difference in absorbance between the Schiff base and aldehyde. The first-order rate constants were calculated by the Guggenheim method. For those runs that were too rapid to be followed conveniently by this method, 40 μl. of the ethanolic solution of Schiff base was injected into 4 ml. of buffer in a quartz cuvette, and the absorbance change monitored continuously at the appropriate wave length with a Cary Model 14 recording spectrophotometer.

The pH values were measured at the temperature of the kinetic runs with a glass electrode that had been standardized with 0.01 *M* sodium tetraborate reference buffer at the same temperature. The runs in deuterium oxide were buffered with 1% sodium carbonate. The carbonate was dried several hours at 130°. Identical runs were made in water. The pH of the solutions was 11.2, so that the hydroxyl groups of **6** and **12** were completely ionized. Under these conditions, the differences between pK_a (H_2O) and pK_a (D_2O) and between pH and pD were not important.

Acid Dissociation Constants.—The pK_a's for the ionizable hydroxyl groups were obtained from the absorption curves determined in buffers of different pH. In those cases where the hydrolysis was rapid enough to give trouble, the absorbance at the analytical wave length was measured as a function of time at each pH and was then extrapolated at zero time. All measurements were made at 25° and an ionic strength of 0.05.

Acknowledgment.—The help of Dr. Wendell F. Smith, Jr., in preparing many of the compounds, and of Mr. Richard W. Andrus, for technical assistance, is gratefully acknowledged. We are indebted to Dr. E. H. Cordes for helpful discussion of this work.

Rearrangement of Some Piperidine N-Oxides to Hexahydro-1,2-oxazepines[1]

LOUIS D. QUIN AND FRANK A. SHELBURNE

Department of Chemistry, Duke University, Durham, North Carolina

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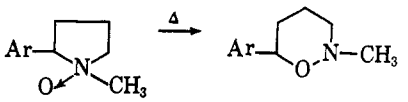
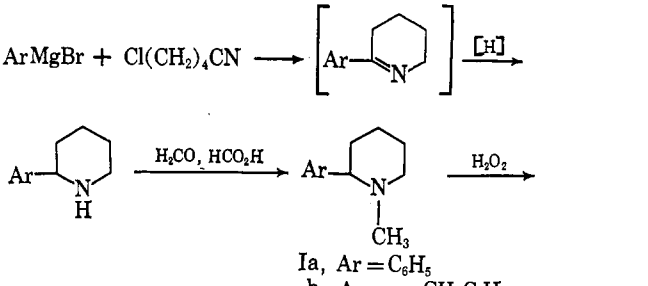
Pyrrolidine N-oxides bearing a 2-aryl substituent are known to rearrange with ring expansion to form tetrahydro-2H-1,2-oxazines. Similar piperidine N-oxides have now been found to follow the same course, and for the first time compounds with the hexahydro-1,2-oxazepine ring system have been made available. The reactions were performed at 170° in dimethylacetamide and were accompanied by some loss of oxygen from the N-oxides. The infrared, n.m.r., and mass spectra of the products support the assigned ring structure.

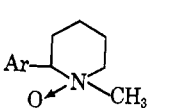
It is known that pyrrolidine N-oxides, if substituted in the α-position by 3-pyridyl[2] or aryl[3a] groups, can be rearranged thermally to tetrahydro-2H-1,2-oxazines. The reaction is a special case of the Meisenheimer N to O rearrangement of allyl- or benzylamine oxides. Application of this reaction to similarly substituted piperidine N-oxides could lead to hexahydro-1,2-oxazepines, an apparently unknown class of compounds.[3b] We describe conditions for the performance of this synthesis in this paper.



Three 1-methyl-2-arylpiperidine N-oxides (II) were prepared for this study by the following reactions.



Ia, Ar = C_6H_5
b, Ar = *p*-$CH_3C_6H_4$
c, Ar = *p*-ClC_6H_4



IIa-c

The oxides, characterized as the picrates, were used without purification in subsequent reactions. Immedi-

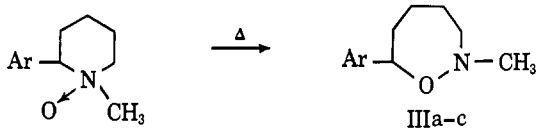
(1) Presented at the Southeastern Regional Meeting of the American Chemical Society, Charleston, W. Va., Oct. 1964.

(2) C. H. Rayburn, W. R. Harlan, and H. R. Hanmer, *J. Am. Chem. Soc.*, **72**, 1721 (1950); T. Kisaki, M. Ihida, and E. Tamaki, *Bull. Agr. Chem. Soc. Japan*, **24**, 719 (1960).

(3) (a) L. D. Quin and G. L. Roof, *J. Org. Chem.*, **27**, 4451 (1962). (b) Hexahydro-2-methyl-7-(3-pyridyl)-1,2-oxazepine has now been reported; it was prepared similarly by thermal rearrangement of N-methylanabasine N-oxide: W. Carruthers and R. A. W. Johnstone, *J. Chem. Soc.*, 1653 (1965).

ately after preparation, the oxides contained small amounts of unchanged I; on standing, however, the amount of I increased. The oxides were therefore used promptly in the rearrangement.

Attempts to cause the desired rearrangement by direct heating of oxide IIa, effective for pyrrolidine N-oxides, were only partly successful. Generally, the only product which could be distilled was the piperidine Ia, although gas chromatography indicated some of the rearranged product IIIa to be present in some preparations. The process was greatly improved by the use



IIIa-c

of a solvent; the amount of deoxygenation accompanying the rearrangement was reduced, and satisfactory yields of the hexahydro-1,2-oxazepine IIIa were obtained. Polar solvents were required to dissolve the starting N-oxide; dimethylacetamide, dimethylformamide, dimethyl sulfoxide, and diglyme were found to provide suitable media, although considerable difference in the rate of the reaction and in the ratio of products existed among these solvents (Table I). It is

TABLE I

SOLVENT EFFECTS ON REARRANGEMENT OF 1-METHYL-2-PHENYLPIPERIDINE N-OXIDE

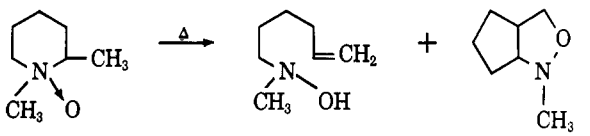
Solvent	Temp., °C.	Time (t), min.[a]	Ratio of IIIa to Ia[b] $\frac{1}{4}t$	$\frac{1}{2}t$	t
Diglyme	130	1400	0.39	0.35	0.25
Diglyme	145	230	0.66	0.56	0.44
Diglyme	161	40	1.50	1.38	1.04
Dimethylformamide	153	135	3.45	2.40	2.25
Dimethyl sulfoxide	163	30	0.40	0.74	0.40
Dimethylacetamide	170	35	6.00	3.94	4.08
Diethylformamide	178	...[c]	...	...	...

[a] Time required to achieve the maximum concentration of IIIa. [b] Gas chromatographic peak areas. [c] Yield of IIIa was nil after 30 min.

evident that the most favorable ratio of rearrangement to deoxygenation is obtained in refluxing dimethylacetamide; the rate of the reaction is also convenient. Dimethylformamide also provided a satisfactory medium; in diethylformamide, however, only deoxygenation could be detected. The by-product Ia in these reactions does not appear to originate from the oxazepine derivative; the concentration of the latter does not change after reaching its maximum value in a reaction, while the concentration of the piperidine continues to rise slightly. Furthermore, a solution of the oxazepine derivative in dimethylacetamide held at 165° for 45 min., or in diethylformamide at 177° for 60 min., showed no detectable conversion to the piperidine. Deoxygenation was also noted in the rearrangement of pyrrolidine N-oxides[3] and appears to occur commonly in N-oxide pyrolyses.[4]

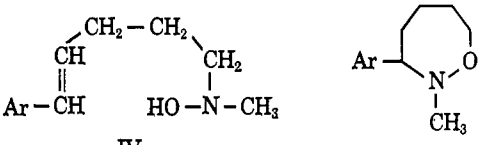
Preparative-scale rearrangements were carried out in refluxing dimethylacetamide. The products IIIa, IIIb, and IIIc were separated from the solvent and the by-product piperidines by fractional distillation. Gas chromatographic analysis of fractions containing I and III permitted determination of the following yield figures: from IIa, 26% Ia and 37% IIIa; from IIb, 21% Ib and 35% IIIb; and from IIc, 36% Ic and 20% IIIc. It is thus seen that the conversion of the piperidine N-oxides to the hexahydro-1,2-oxazepines is characterized by moderate yields, and the process has synthetic value. When allowance is made for the amount of recovered piperidine, the yields of III are: a, 49%; b, 44%; and c, 54%. These yields are still lower than those for pyrrolidine N-oxide rearrangement, and considerably more deoxygenation takes place.

It is noteworthy that N-methylpiperidine N-oxide, as well as its 2-methyl derivative, behave differently on pyrolysis.[5] The former was resistant to thermal decomposition, and gave no elimination or rearrangement products. The latter underwent an elimination in which the 2-methyl group provided a proton, yielding N-methyl-N-(5-hexenyl)hydroxylamine. There was also obtained a bicyclic isoxazolidine. The aryl derivatives used in the present study cannot form either type of product, and with the assistance of benzylic



character at the 2-position the alternative ring-expanding reaction is realized. The situation resembles that in the pyrrolidine N-oxide family, where it was shown that the 2-ethyl derivative rearranged by β-elimination and gave no indication of the ring expansion encountered for the 2-aryl derivatives.[3]

The infrared spectra of the rearrangement products were in accord with the assigned cyclic structures, rather than with the isomeric unsaturated hydroxylamines (IV) which conceivably could result from β-elimination. There was no –OH absorption, and a peak



IV V

of medium to strong intensity at 923–926 cm.$^{-1}$ indicated the O–N bond to be present.[3] The n.m.r. spectra also indicated the correctness of the assigned structures and spoke against another isomeric structure V, an alternative, but unlikely, rearrangement product. Thus, nonaromatic protons of IIIa included: NCH_3 at 2.52, ArCH at 4.82 (triplet, J = 7 c.p.s.), a 2H multiplet at 2.79, and a 6H multiplet centered at 1.77 p.p.m. The spectrum of IIIb was nearly identical, showing additionally $ArCH_3$ at 2.26 p.p.m. The position of the 2H multiplet is suggestive of NCH_2 rather than OCH_2 (in V), which is generally farther downfield.[6] Furthermore, the spectrum of IIIa resembles closely that of tetrahydro-1-methyl-6-phenyl-2H-1,2-oxazine, whose ring structure was confirmed by degradation.[3] This compound showed a 2H multiplet at 2.80 p.p.m., again

(4) A. C. Cope and E. R. Trumbull, *Org. Reactions*, **11**, 317 (1960).

(5) A. C. Cope and N. A. LeBel, *J. Am. Chem. Soc.*, **82**, 4656 (1960).

(6) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p. 84.

indicative of NCH_2. In this ring system, the ArCH proton appeared as two doublets (4.75 p.p.m., J = 3 c.p.s.; 4.92 p.p.m., J = 3 c.p.s.), rather than a triplet as observed for the seven-membered ring. A similar effect was noted for the *p*-tolyl derivatives of both ring systems.

Some mass spectral data for two of the hexahydro-1,2-oxazepines (IIIa and IIIb) are recorded in Table II.

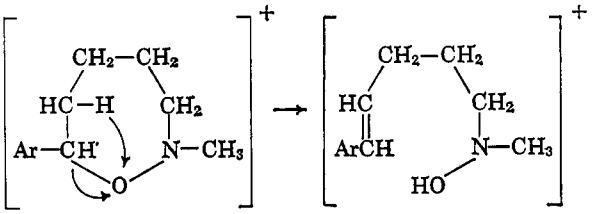
TABLE II

INTENSITIES OF SOME MASS SPECTRAL PEAKS

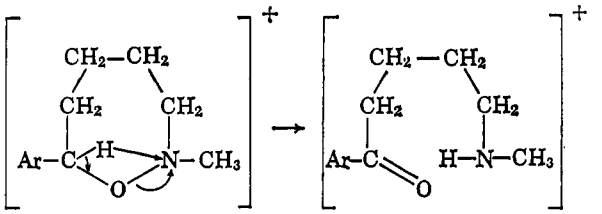
	IIIa	IIIb	VIII[a]	IX[b]
m/e 44	71.60	100.00	3.00	19.80
m/e 60	100.00	96.90	100.00	100.00
$ArC_3H_4^+$	5.76	13.40	4.10	...
$ArCO^+$ (or $ArC_2H_4^+$)	4.29	11.60	4.50	...
$(M - OH)^+$	6.06	17.00	0.71	0.69
M^+	30.20	35.10	14.60	8.29

[a] Tetrahydro-2-methyl-6-(*p*-tolyl)-2H-1,2-oxazine. [b] Methyl-(4-hexenyl)hydroxylamine.

Two peaks of low *m/e*, 44 and 60, dominate the spectra. The latter seems properly assigned as $C_2H_6NO^+$; the former may be $C_2H_6N^+$ or CH_2NO^+. The origin of these peaks cannot be determined without a more refined study, employing deuterated compounds. A simple explanation for each, however, may be found in a preliminary rearrangement of the molecular ion. From



VI



VII

VI or VII, the *m/e* 60 and 44 peaks, respectively, may then be accounted for by cleavage at the position α, β to N, a well-known process.[7] In support of the intermediacy of VI is the appearance of a peak from loss of OH, and of a peak attributable to $ArCH{=}CHCH_2^+$ (or $Ar\triangleleft^+$). Furthermore, a model hydroxylamine, methyl(4-hexenyl)hydroxylamine, also showed a strong *m/e* peak, as well as loss of OH. The other rearrangement, to VII, is indicated by a peak attributable to $ArCO^+$, since aryl ketones are known to lose the alkyl fragment.[8] However, an alternative ion $ArC_2H_4^+$ has not been ruled out for this peak. Also, the *m/e* 44 peak in the spectrum of the model hydroxylamine cannot be accounted for on the same basis, making it appear that other processes are operative to provide this peak.

(7) J. H. Beynon, "Mass Spectrometry and its Application to Organic Chemistry," Elsevier Publishing Co., New York, N. Y., 1960, p. 388.

(8) Reference 7, p. 354.

The mass spectra of IIIa and b from one standpoint are useful in showing the presence of a 7-aryl rather than a 3-aryl substituent (V). If VII is a real rearrangement product, then an explanation is, as mentioned, at hand for the large *m/e* 44 peak and for the presumed $ArCO^+$. No process is obvious whereby V can provide these fragments.

The mass spectrum of tetrahydro-2-methyl-6-(*p*-tolyl)-2H-1,2-oxazine (Table II) was also taken for comparison. The occurrence of rearrangement to produce the lower homolog of ion VI, and possibly of VII, is suggested by the spectrum. For example, ions of *m/e* 60 and 44 were present, the former greatly predominating in this case. The suspected $ArC_3H_4^+$ and $ArCO^+$ peaks were also present.

Experimental

General.—Melting points were taken on a Mel-Temp apparatus and are corrected. Boiling points are uncorrected. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn., or Triangle Chemical Laboratories, Chapel Hill, N. C. Infrared spectra were taken on liquid films with a Perkin-Elmer Model 21 spectrophotometer. N.m.r. spectra were taken on deuteriochloroform solutions with tetramethylsilane as internal standard, using the Varian A-60 spectrometer. Mass spectra were obtained with a Bendix Model 14-101 spectrometer.

2-Arylpiperidines.—The procedure of Salathiel, Burch, and Hixon[9] was followed. **2-(*p*-Tolyl)piperidine** was obtained in 40% yield, b.p. 122.5–124° at 5 mm. (lit.[9] b.p. 135° at 8 mm.); **2-(*p*-chlorophenyl)piperidine** was formed in 15% yield, b.p. 129–130° at 4 mm. (lit.[9] b.p. 145° at 8 mm.). **2-Phenylpiperidine** was obtained as a damp solid hydrate[9] and was used without purification in the next step.

1-Methyl-2-arylpiperidines.—Following the Clarke procedure,[10] the arylpiperidine (about 20 g.) in a mixture of 30 g. of 90% formic acid and 25 g. of 35% formaldehyde was heated for 12 hr. on a steam bath. Heating was continued for 5 hr. after addition of 15 ml. of concentrated hydrochloric acid. The mixture was made strongly basic and extracted with benzene. After drying over sodium hydroxide, the extract was distilled. **1-Methyl-2-(*p*-tolyl)piperidine**, not previously reported, was obtained in 94% yield, b.p. 117–118° (6 mm.). Its picrate had m.p. 191.5–192.5° (from 95% ethanol).

Anal. Calcd. for $C_{19}H_{22}N_4O_7$: C, 54.54; H, 5.30; N, 13.39. Found: C, 54.42; H, 5.29; N, 13.50.

The new **1-methyl-2-(*p*-chlorophenyl)piperidine** was produced in 93% yield, b.p. 116–117° (4 mm.).

Anal. Calcd. for $C_{12}H_{16}ClN$: C, 68.73; H, 7.64; N, 6.68. Found: C, 68.71; H, 7.71; N, 7.05.

Its picrate had m.p. 201–202° (from 95% ethanol).

Anal. Calcd. for $C_{18}H_{15}ClN_4O_7$: C, 49.25; H, 4.33; N, 12.77. Found: C, 49.37; H, 4.62; N, 12.79.

The yield of **1-methyl-2-phenylpiperidine**, b.p. 90° at 3 mm. (lit.[11] b.p. 58–60° at 0.05 mm.), was 37% over-all from δ-chlorovaleronitrile; its picrate had m.p. 172° (lit.[11] m.p. 171–172°).

1-Methyl-2-arylpiperidine N-Oxides.—1-Methyl-2-phenylpiperidine (5 g.) was placed in 45 ml. of 10% hydrogen peroxide, to which was added 10 ml. of acetone to bring some of the amine into solution. After stirring for 2 days at room temperature, complete solution resulted. Excess hydrogen peroxide was destroyed with platinum black. The mixture was filtered, and the filtrate was stripped of solvent. The residual solid was dried in a vacuum oven at 60°. A picrate was prepared in, and recrystallized from, absolute ethanol, m.p 201–202°.

Anal. Calcd. for $C_{18}H_{20}N_4O_8$: C, 51.42; H, 4.80; N, 13.33. Found: C, 51.57; H, 4.65; N, 12.94.

In a similar manner was prepared **1-methyl-2-(*p*-tolyl)piperidine N-oxide**; the melting point of the picrate derivative was 191.5–192.5°.

(9) R. Salathiel, J. M. Burch, and R. M. Hixon, *J. Am. Chem. Soc.*, **59**, 984 (1937).

(10) H. T. Clarke, H. B. Gillespie, and S. Z. Weisshaus, *ibid.*, **55**, 4571 (1933).

(11) K. H. Buchel and F. Korte, *Ber.*, **95**, 2438 (1962).

Anal. Calcd. for $C_{19}H_{22}N_4O_3$: C, 52.53; H, 5.10; N, 12.90. Found: C, 52.30; H, 5.18; N, 12.63.

Also, **1-methyl-2-(*p*-chlorophenyl)piperidine N-oxide** was synthesized; its picrate had m.p. 186–188° after two recrystallizations from a dilute solution of picric acid in ethanol.

Anal. Calcd. for $C_{18}H_{19}ClN_4O_8$: C, 47.53; H, 4.21; N, 12.32. Found: C, 47.52; H, 4.57; N, 12.12.

Hexahydro-2-methyl-7-phenyl-1,2-oxazepine (IIIa).—1-Methyl-2-phenylpiperidine N-oxide (from 5.0 g. of the piperidine Ia) was placed in 50 ml. of dimethylacetamide, and the solution was heated at 170°. Samples were removed periodically and analyzed by gas chromatography. When no further change in the size of the IIIa peak was detected (50 min.), the reaction was stopped. Comparison of the peak area to that of a standard indicated a yield of IIIa of 59%. Two similar preparations were made, and the three products were combined for removal of solvent by distillation *in vacuo*. The residue was fractionated with a Nester–Faust spinning-band column (Model 115). The material distilling in the range 52–68° (0.3 mm.) was a mixture of Ia and IIIa, and was refractionated: (A) 3.5 g., b.p. 41–45° (0.15 mm.), 100% Ia; (B) 1.0 g., b.p. 45–52° (0.15 mm.), 30% Ia–70% IIIa; (C) 2.5 g., 53° (0.15 mm.), 3% Ia–97% IIIa; and (D) 3.0 g., 53° (0.15 mm.), 100% IIIa. The total yield of Ia was 3.9 g. (26%); of IIIa, 6.1 g. (37%); fraction D was analyzed.

Anal. Calcd. for $C_{12}H_{17}NO$: C, 75.35; H, 8.96; N, 7.32. Found: C, 75.15; H, 8.81; N, 7.28.

The picrate, recrystallized from a dilute solution of picric acid in ethanol, had m.p. 128–129°.

Anal. Calcd. for $C_{18}H_{20}N_4O_8$: C, 51.42; H, 4.80; N, 13.33. Found: C, 51.59; H, 4.91; N, 13.19.

The infrared spectrum of IIIa showed a peak of medium intensity at 923 cm.$^{-1}$, attributed to O–N stretching. The n.m.r. spectrum is described in the Discussion section; mass spectral features appear in Table II.

Hexahydro-2-methyl-7-(*p*-tolyl-1,2-oxazepine) (IIIb).—1-Methyl-2-(*p*-tolyl)piperidine N-oxide (from 8.0 g. of the piperidine Ib) was rearranged in 50 ml. of dimethylacetamide at 170°. The reaction was complete after 40 min. The ratio of IIIb to Ib was 2.2:1. This product was combined with two similar preparations (based on 8.0 g. and 5.0 g. of Ib) and distilled to remove solvent and some Ib. The fraction boiling at 90–99° (0.85 mm.) was refractionated: (A) 3.0 g., b.p. 76–90.5° (0.8 mm.), 67% Ib–33% IIIb: (B) 1.5 g., b.p. 90.5° (0.8 mm.), 2% Ib–98% IIIb; and (C) 5.5 g., b.p. 90.5° (0.8 mm.), 100% IIIb. Total yield of IIIb was 8.0 g. (35%); analysis was performed on fraction C.

Anal. Calcd. for $C_{13}H_{19}NO$: C, 76.05; H, 9.33; N, 6.82. Found: C, 76.40; H, 9.68; N, 6.67.

The picrate as formed from ethanol solution had m.p. 145.5–147°.

Anal. Calcd. for $C_{19}H_{22}N_4O_8$: C, 52.53; H, 5.10; N, 12.90. Found: C, 52.49; H, 4.88; H, 12.87.

The infrared spectrum of IIIb showed medium absorption at 924 cm.$^{-1}$. The n.m.r. spectrum contained a broad multiplet of 6H centered at 1.78, a CCH_3 singlet at 2.26, a NCH_3 singlet at 2.51, a 2H multiplet assigned to NCH_2 at 2.75, and a 1H triplet (J = 7 c.p.s.) at 4.74 p.p.m., assigned to the 7-proton. Mass spectral data are given in Table II.

Hexahydro-2-methyl-7-(*p*-chlorophenyl)-1,2-oxazepine.—The N-oxide from 10.0 g. of 1-methyl-2-(*p*-chlorophenyl)piperidine was rearranged as above. The ratio of IIIc to Ic was 0.43:1. The product was fractionated to provide: (A) 2.0 g., b.p. 77° (0.6 mm.), 98% Ic–2% IIIc; (B) 1.0 g., b.p. 77–86° (0.6 mm.), 50% Ic–50% IIIc; (C) 1.0 g., b.p. 86° (0.6 mm.), 10% Ic–90% IIIc; and (D) 0.5 g., b.p. 86° (0.6 mm.), 2% Ic–98% IIIc. The total yield of IIIc was 2 g. (20%). The infrared spectrum showed absorption at 925 cm.$^{-1}$. A picrate prepared from fraction D and recrystallized from a dilute solution of picric acid in ethanol had m.p. 134–135°.

Anal. Calcd. for $C_{18}H_{19}ClN_4O_8$: C, 47.53; H, 4.21; N, 12.32. Found: C, 47.32; H, 4.25; N, 12.34.

Tetrahydro-1-methyl-6-phenyl-2H-1,2-oxazine.—This compound was prepared by the reported method.[3] The boiling point was erroneously recorded[3] as 93° (0.30 mm.); the value is 78° (0.53 mm.).

Methyl(4-hexenyl)hydroxylamine.—This compound was available from the previous investigation,[3] having been obtained by pyrolysis of 1-methyl-2-ethylpyrrolidine N-oxide. Its structure was not completely established at that time, in that distinction between the presence of a 4-hexenyl or a 3-hexenyl group was not made. The n.m.r. spectrum of a benzene solution has now been prepared. The position of the methyl protons (1.59 p.p.m.) indicates the grouping $CH_3C{=}C$ rather than $CH_3CH_2C{=}C$.[6]

Acknowledgment.—Gratitude is expressed to Dr. John M. Ruth, Liggett and Myers Tobacco Company, for preparing the mass spectra and for assistance in their interpretation. F. A. S. thanks the Liggett and Myers Tobacco Company for financial assistance.

Electrolytic Reductive Coupling. IX.[1] Couplings with Representative Michael Acceptors

MANUEL M. BAIZER AND JAMES D. ANDERSON

Central Research Department, Monsanto Company, St. Louis, Missouri 63166

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As illustrations of the participation in electrolytic reductive coupling of a variety of Michael acceptors, data are presented on the hydrodimerization of benzalacetone, mesityl oxide, diethyl vinylphosphonate, diphenylvinylphosphine oxide, and methyl vinyl sulfone and on the mixed reductive couplings of the pairs diethyl fumarate–methyl vinyl ketone, benzalacetone–acrylonitrile, mesityl oxide–acrylonitrile, and methyl vinyl sulfone–N,N-diethylcinnamamide. The factors governing the success or failure of the method are discussed.

The scope of electrolytic reductive coupling of activated olefins was outlined in 1963.[2] Details have been published of the participation in this reaction of derivatives of α,β-unsaturated acids[3] and of butadiene,[4] of vinylpyridines,[5] and of aromatically substituted ethylenes.[6] This paper, in reporting electrolytic reductive couplings with a variety of other representative Michael acceptors, affords further confirmation of the specified synthetic utility and limitations of this method.

α,β-Unsaturated Ketones.—The electrochemical reduction of α,β-unsaturated aliphatic ketones is reported to yield hydrodimers in acid solutions and saturated monomolecular ketones in alkaline solutions.[7] The corresponding aromatic ketones give bimolecular prod-

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