about 2 hours at room temperature, had precipitated (ordinary) ester, which gave acid–base titers very markedly less than those of similar aliquots titrated at once. With 2-chloro-5-nitrobenzonitrile, on the other hand, there was no difference, even when allowed to stand overnight, thus demonstrating the presence of imido ester in the former reaction mixture only.

Duplicate kinetic runs using equimolar concentrations (0.0509 *M*) of 4-chloro-3-nitrobenzonitrile and OMe^- in MeOH were carried out at 44.9°. In one the progress of the run was followed by a standard procedure involving "quenching" aliquots with standard HOAc and back-titrating against baryta to *p*H 7.75 with the automatic titrimeter. In the other the procedure involved "quenching" aliquots with standard chloride-free HNO_3 and estimating Cl^- by titration against $AgNO_3$ with the automatic titrimeter. Both runs, followed to about 60% completion for calculation of k_2, gave identical results: $k_2 = 3.14 \times 10^{-3}$ l. mole^{-1} sec.$^{-1}$. The amount of OMe^- consumed and Cl^- liberated for 100% reaction is that calculated for replacement of Cl^- by OMe^- without any irreversible side-reaction.

Finally it was shown that the nitriles did not form imido ester with MeOH alone, nor was there any reaction of the CN group with MeOH/HCl aq., which could conceivably occur as side-reactions in procedure 4.

Acknowledgments.—The authors thank Dr. A. R. H. Cole for helpful advice and discussion of the infrared measurements and the Nuffield Foundation for the grant of the infrared spectrometer.

NEDLANDS, WESTERN AUSTRALIA

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Some Secondary Amines in the Sommelet Reaction

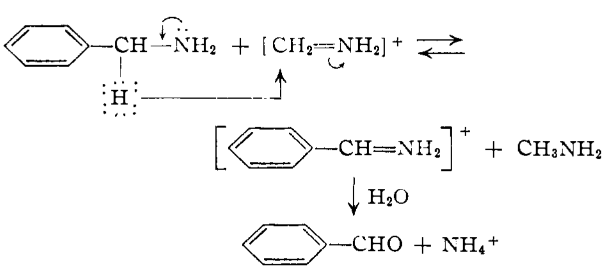
BY H. R. SNYDER AND JOHN R. DEMUTH

RECEIVED SEPTEMBER 7, 1955

A number of secondary amines have been subjected to the Sommelet reaction, and the amounts of aromatic aldehydes produced from them have been determined. Most of the observations are better correlated on the assumption that the first step in the Angyal mechanism of reaction is the loss of a hydride ion from the nitrogen atom rather than from an adjacent carbon atom.

In the course of their investigation of the Sommelet reaction, Angyal and Rassack[1] found that in the hydrolysis of a hexaminium salt *via* the Sommelet procedure a primary amine is formed and converted to an aldehyde. Angyal and Rassack obtained a 79% yield of benzaldehyde by the hydrolysis of benzylhexaminium chloride in aqueous solution, and Graymore and Davies[2] reported a 66% yield of the aldehyde by allowing benzylamine, formaldehyde and hexamine to react in the same solvent. In this Laboratory, yields of benzaldehyde as high as 84% have been obtained from benzylamine when 50% acetic acid was used as the solvent.

The conversion of an amine to the aldehyde by the Sommelet procedure is visualized by Angyal and his associates[3] as being an oxidation–reduction process in which the amine is dehydrogenated by the conjugate acid of methyleneamine ($CH_2{=}NH$), a hydrolysis fragment of hexamine, to the corresponding benzylideneamine, which in turn is hydrolyzed to the aldehyde. The reaction scheme postulated by these investigators is shown as



The use of primary amines as precursors of aldehydes in the Sommelet reaction has not been thoroughly investigated, although Angyal and his associates have prepared a number of aldehydes from primary amines. The behavior of secondary amines, which are generally not as reactive as primary ones in the Sommelet reaction, has received even less attention; N-methylbenzylamine and dibenzylamine have been used in the reaction,[1] and one study of the behavior of a series of symmetrical, phenolic dibenzylamines has been made.[4] The present investigation was undertaken to study the fate of a number of other secondary amines in the Sommelet reaction.

N-Methylbenzylamine was reinvestigated and found to be converted to benzaldehyde in 15% yield, while N-isopropylbenzylamine was even less reactive, only 6% of the aromatic aldehyde being obtained from it. Dibenzylamines proved to be somewhat more reactive. Dibenzylamine itself gave benzaldehyde in yields of from 25–30%, and *p,p'*-dinitrodibenzylamine afforded the corresponding aldehyde in yields of 31–48%, while *p,p'*-dicarbomethoxydibenzylamine furnished *p*-carbomethoxybenzaldehyde in only 12.2% of the theoretical amount. These yields are calculated on the assumption that each molecule of a dibenzylamine would furnish two molecules of aldehyde. The relatively small amount of *p*-carbomethoxybenzaldehyde obtained from the secondary amine is difficult to understand, for *p*-carbomethoxybenzylhexaminium bromide is converted into the aldehyde in 74.7% yield by hydrolysis *via* the Sommelet procedure.

Six unsymmetrical dibenzylamines were subjected to the conditions of the reaction. The results are shown in Table I.

The behavior of some of the secondary amines in

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[1] S. J. Angyal and R. C. Rassack, *J. Chem. Soc.*, 2700 (1949); for an excellent discussion of the Sommelet reaction see S. J. Angyal, "Organic Reactions," Vol. VIII, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 197.

[2] J. Graymore and D. R. Davies, *J. Chem. Soc.*, 293 (1945).

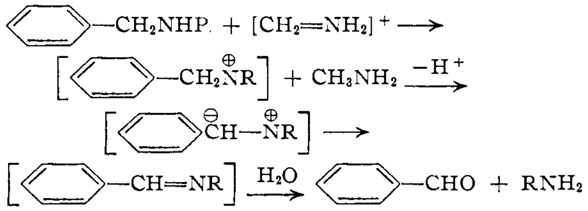
[3] S. J. Angyal, D. R. Penman and G. P. Warwick, *ibid.*, 1742 (1953).

[4] J. C. Duff and V. I. Furness, *ibid.*, 1512 (1951).

TABLE I

Amine	A	Aldehydes, %	B	%	Ratio A/B
$C_6H_5CH_2NHCH_2C_6H_4OCH_3$	C_6H_5CHO	51.1	$CH_3OC_6H_4CHO$	27.6	1.85/1
		46.2		23.1	2.00/1
		57.1		29.9	1.91/1
$C_6H_5CH_2NHCH_2C_6H_4OH$	C_6H_5CHO	53.9	HOC_6H_4CHO	10.8	5.02/1
		59.2		8.6	6.88/1
$O_2NC_6H_4CH_2NHCH_2C_6H_5$	$O_2NC_6H_4CHO$	44.9	C_6H_5CHO	23.9	1.87/1
		46.2		23.2	1.99/1
		30.6		12.7	2.41/1
$H_3COOCC_6H_4CH_2NHCH_2C_6H_5$	$H_3COOCC_6H_4CHO$	36.0	C_6H_5CHO	25.5	1.41/1
		36.0		24.1	1.49/1
$H_3COC_6H_4CH_2NHCH_2C_6H_4NO_2$	$H_3COC_6H_4CHO$	34.6	$O_2NC_6H_4CHO$	26.0	1.33/1
$H_3COC_6H_4CH_2NHCH_2C_6H_4COOCH_3$	$H_3COC_6H_4CHO$	29.8	$H_3COOCC_6H_4CHO$	30.7	0.970/1
		34.0		30.3	1.13/1
		33.7		30.8	1.10/1

this study appears difficult to rationalize on the basis of the Angyal mechanism of the Sommelet reaction. The low yield of benzaldehyde obtained from N-methylbenzylamine is one of these, for if the hydride ion is abstracted from the carbon atom of the benzyl group, benzylidenemethylamine would result. Hydrolysis of this compound, a reaction which should proceed very well under the slightly acidic conditions of the Sommelet process, would produce benzaldehyde. If the hydride ion is lost from the methyl group, methylenebenzylamine would be formed, and Graymore and Davies[2] have shown that this compound reacts with hexamine to give a 60% yield of benzaldehyde. The results obtained from the first four unsymmetrical dibenzylamines shown in the table are also contrary to the predictions which would be made on the basis of the Angyal mechanism, for that α-carbon atom which is the more electron-rich should cede a hydride ion more readily than the one which is relatively electron-poor, and consequently that aldehyde which bears the more strongly electron-donating group in the *para* position should be formed in the larger amount. However, if it were assumed that the hydride ion is abstracted from the nitrogen atom, and that this oxidation is immediately followed by the loss of a proton from one of the α-carbon atoms, then the predictions of effects of substituents would be reversed.



This modified mechanism may offer several advantages over the proposal by Angyal. When R = alkyl, the low yield of aromatic aldehyde can be attributed to steric hindrance about the nitrogen atom. Such steric effects should be more pronounced than if the attack of the oxidizing agent is at the benzyl carbon atom. In addition, the second hydrogen should be more difficult to remove from the nitrogen than the first. This effect, however, will be counterbalanced to some extent by the effectiveness of the alkyl group in donating electrons to the nitrogen through hyperconjugation. Thus, as has been stated previously, N-methylbenzylamine gave a 15% yield of benzaldehyde, while N-isopropylbenzylamine, a compound in which the steric effect is greater and the degree of hyperconjugation is smaller, gave only 6% of the aromatic aldehyde. When the unsymmetrical dibenzylamines are considered (R = $CH_2C_6H_4Y$), the predictions made on the basis of the modified Angyal mechanism are somewhat more accurate, for after the hydride ion has been removed from the nitrogen atom, the α-carbon atom which is the more depleted of electrons should lose a proton more readily than the other α-carbon, and consequently that aldehyde which bears the more strongly electron-attracting group in the *para* position should be formed in the larger amount. This prediction is borne out by the results obtained from four of the six unsymmetrical dibenzylamines which were employed. The inversion of the predicted aldehyde ratio obtained when *p*-methoxy-*p*′-carbomethoxydibenzylamine was employed may be related to the low reactivity shown by *p,p*′-dicarbomethoxydibenzylamine in the Sommelet reaction.

Four of the amines shown in the table are new. One of them, *p*-hydroxydibenzylamine, was prepared by reduction of the Schiff base formed from *p*-hydroxybenzaldehyde and benzylamine, while the other three, *p*-carbomethoxydibenzylamine, *p*-methoxy-*p*′-carbomethoxydibenzylamine and *p*-methoxy-*p*′-nitrodibenzylamine, were made by allowing a substituted benzyl halide to react with an excess of a benzylamine. Since, with the exception of *p*-methoxydibenzylamine, none of the unsymmetrical dibenzylamines could be distilled, they were isolated and stored as the hydrochlorides. One compound, *p*-hydroxydibenzylamine, was particularly sensitive toward heat; even concentration of an ethanolic solution of the amine led to extensive polymerization, so this compound had to be prepared by a procedure which avoided elevated temperatures.

Experimental

Sommelet Reactions.—Sommelet reactions were carried out by dissolving 0.005–0.02 mole of the amine, or its hydrochloride, and 0.01–0.04 mole of hexamine in 20 ml. of 50% acetic acid. The solutions were refluxed for one hour at which time a second quantity of hexamine equal to the first was added and refluxing was continued for an additional hour. The solutions were made strongly acidic, boiled for a few minutes, cooled and extracted with three 50-ml. portions of ether. The ether extracts were neutralized with 20% sodium carbonate solution,[5] washed with water and dried over anhydrous sodium sulfate. Removal of the ether by distillation left the aldehyde as a residue.

Determination of Aldehydes.—The aldehydes left as residues after the evaporation of the ether were diluted with water or ethanol to give solutions having theoretical aldehyde concentrations of 10.0×10^{-5} mole per liter. The optical densities of these solutions, which were contained in 1.00-cm. quartz cuvettes, were read on a Beckman DU spectrophotometer.

Solutions of a single aldehyde were determined at the wave length of maximum absorption by locating the optical densities of experimental solutions on a graph of optical density *versus* concentration of the aldehyde.

Mixtures of aldehydes were determined by reading the optical densities of all solutions at wave lengths of maximum absorption of each aldehyde, and by solving simultaneous equations which involved the optical densities of standard solutions of each aldehyde at each wave length.

In the Sommelet reaction on *p*,*p*′-dicarbomethoxydibenzylamine, the spectrophotometric method of determination was not employed, but the solid aldehyde was isolated instead. In the reaction on *p*-carbomethoxydibenzylamine, recourse was had to quantitative infrared analysis since the ultraviolet absorption spectra of benzaldehyde and *p*-carbomethoxybenzaldehyde are nearly identical. The infrared analysis was made by Mr. James Brader who used the "base line" technique described by Heigl, Bell and White[6] and by Wright.[7]

N-Methylbenzylamine.—To 106 g. (1.0 mole) of benzaldehyde there was added with vigorous shaking 110 g. (1.24 moles) of 35% aqueous methylamine. The reaction mixture was refluxed for half an hour and then allowed to cool. The upper layer of benzylidenemethylamine was separated from the aqueous layer, washed with water and dried over anhydrous sodium carbonate. Distillation at atmospheric pressure gave 85.7 g. (72.2%) of the Schiff base as a colorless viscous oil, b.p. 180–181°, n^{20}D 1.5540; Von Auwers and Ottens[8] report a b.p. of 185° and n^{20}D 1.553.

The Schiff base, 60 g. (0.50 mole), in 125 ml. of absolute ethanol was hydrogenated over Raney nickel catalyst at 80° and 100 atmospheres pressure. After the removal of the catalyst, the solution was distilled. That portion of the distillate boiling at 182–188° weighed 37.0 g. (61.2%).

The crude N-methylbenzylamine was dissolved in a solution composed of 27 ml. of concentrated sulfuric acid and 81 ml. of water. The acidic solution was refluxed for half an hour, cooled and extracted with three 75-ml. portions of ether. It was then made strongly alkaline by the addition of potassium hydroxide and the N-methylbenzylamine was extracted with three 75-ml. portions of ether. Two distillations gave the pure amine, b.p. 184–185°, n^{20}D 1.5235.

The N-methylbenzylamine gave a hydrochloride, m.p. 178–180°, and a picrate, m.p. 119–120°. Embde[9] noted the b.p. of N-methylbenzylamine to be 180–181° and the m.p. of the hydrochloride to be 174–178° while Hinsberg[10] recorded the b.p. of the amine at 184°. The picrate is reported to melt at 117–118°.[11]

N-Isopropylbenzylamine.—This compound was prepared by the method described for the preparation of N-methylbenzylamine. From 1.0 mole of benzaldehyde and 1.0 mole of isopropylamine, 0.415 mole of N-isopropylbenzylamine, b.p. 93° at 10 mm., $n^{20.5}$D 1.5020, was obtained. Lutz, *et al.*,[12] observed n^{20}D 1.5029, and Steck, Hallock and Suter[13] reported n^{25}D 1.5010 for this compound, although the boiling points observed by each of these investigators are markedly different. Lutz cited a value of 66–68° at 1 mm., while Steck claimed a b.p. of 45–46° at 1 mm.

***p*,*p*′-Dinitrodibenzylamine Hydrochloride.**—The preparation of this compound has been described by Strakosch[14] and by Holmes and Ingold.[15] To 51.3 g. (0.30 mole) of *p*-nitrobenzyl chloride was added 300 ml. of concentrated ammonium hydroxide. The flask was fitted with a water-cooled condenser filled with glass helices which were kept wet with ammonium hydroxide, and the solution was heated until the oil, which had formed at first, solidified. After the solid material had been filtered from the solution, it was extracted with 1 l. of boiling hydrochloric acid (1:1). When the filtrate was cooled, 8.3 g. (16.9%) of *p*,*p*′-dinitrodibenzylamine hydrochloride precipitated. Crystallization first from water and then from ethanol gave the pure amine hydrochloride, m.p. 217.5–219°. This value is in good agreement with the m.p. value, 217–218°, reported by Holmes and Ingold.[15]

***p*,*p*′-Dicarbomethoxydibenzylamine Hydrochloride.**—When methyl α-bromo-*p*-toluate was substituted for the corresponding chloro compound in the procedure described by Emerson and Heimsch[16] for the preparation of *p*-carbomethoxybenzylamine hydrochloride, the secondary amine, *p*,*p*′-dicarbomethoxydibenzylamine hydrobromide was formed in 85.8% yield. After this compound had been converted into the hydrochloride and recrystallized from boiling water it had m.p. 254.5–255.5° cor.

Anal. Calcd. for $C_{18}H_{20}NO_4Cl$: C, 61.80; H, 5.78; N, 4.01. Found: C, 62.09; H, 5.92; N, 4.08.

***p*-Methoxydibenzylamine.**—Freshly distilled anisaldehyde, 60 g. (0.44 mole), was dissolved in 100 ml. of toluene and to this solution was added 48.2 g. (0.45 mole) of benzylamine. After the solution had been refluxed for 1.5 hours, the theoretical quantity of water had been collected by means of a modified Dean and Stark tube.

The toluene was removed from the reaction mixture and anisylidenebenzylamine was collected as a pale-yellow oil, b.p. 176–181°, which solidified to a white, waxy solid, m.p. 39.9–40.8°. Grammaticakis[17] reported the m.p. of this compound to be 40°, and Ingold and Shoppee recorded a value of 42°.[18]

Hydrogenation of 88.3 g. (0.393 mole) of anisylidenebenzylamine at 1500 p.s.i. and 100° over Raney nickel catalyst using ethanol as solvent furnished 50.0 g. (56.4%) of *p*-methoxydibenzylamine, b.p. 170–172° at 3 mm. The hydrochloride was prepared and found to melt at 214–215°. Von Braun, May and Michaelis[19] cite a m.p. of 213°.

***p*-Hydroxydibenzylamine Hydrochloride.**—The procedure described for the preparation of anisylidenebenzylamine was used to prepare *p*-hydroxybenzylidenebenzylamine in 95.3% yield from *p*-hydroxybenzaldehyde and benzylamine. After recrystallization from ethanol, the Schiff base had a m.p. of 208–210°. Mason and Winder[20] report a m.p. of 205–206°.

In previous attempts to prepare *p*-hydroxydibenzylamine from the Schiff base, it was found that the amine is extremely sensitive toward heat. Extensive polymerization occurred when an ethanolic solution of the amine was heated to 80°. The following procedure for the preparation of the amine was therefore devised.

A suspension of 23.0 g. (0.109 mole) of *p*-hydroxybenzylidenebenzylamine in 300 ml. of ethanol was hydrogenated at 25° and 1500 p.s.i. over Raney nickel catalyst. After the removal of the spent catalyst, the solution was diluted with five times its volume of water, and the oil which separated was extracted with four 300-ml. portions of ether. Saturation of the dried ethereal solution with gaseous hydrogen chloride promoted the precipitation of 18 g. (69%) of *p*-hydroxydibenzylamine hydrochloride, m.p. 217–219°. The m.p. remained unchanged after recrystallization from an ethanol–ether mixture.

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(5) This step was omitted in the reaction on *p*-hydroxydibenzylamine hydrochloride because of the solubility of *p*-hydroxybenzaldehyde in alkaline solutions.

(6) J. J. Heigl, M. F. Bell and J. U. White, *Anal. Chem.*, **19**, 293 (1947).

(7) N. Wright, *ibid.*, **13**, 1 (1941).

(8) K. Von Auwers and B. Ottens, *Chem. Ber.*, **57B**, 446 (1924).

(9) H. Embde, *Arch. Pharm.*, **247**, 364 (1909).

(10) O. Hinsberg, *Ann. Chem. Justus Liebigs*, **265**, 183 (1891).

(11) W. McMeeking and T. S. Stevens, *J. Chem. Soc.*, 349 (1933).

(12) R. E. Lutz, *et al.*, *J. Org. Chem.*, **12**, 760 (1947).

(13) E. A. Steck, L. L. Hallock and C. M. Suter, THIS JOURNAL, **70**, 4063 (1948).

(14) J. Strakosch, *Ber.*, **6**, 1056 (1873).

(15) E. L. Holmes and C. K. Ingold, *J. Chem. Soc.*, **127**, 1800 (1925).

(16) W. S. Emerson and R. A. Heimsch, THIS JOURNAL, **73**, 1299 (1951).

(17) R. Grammaticakis, *Bull. soc. chim. France*, [5] **8**, 38 (1941).

(18) C. K. Ingold and C. W. Shoppee, *J. Chem. Soc.*, 1199 (1929).

(19) J. Von Braun, W. May and R. Michaelis, *Ann. Chem. Justus Liebigs*, **490**, 189 (1931).

(20) A. T. Mason and G. R. Winder, *J. Chem. Soc.*, **65**, 192 (1894).

Anal.[21] Calcd. for $C_{14}H_{16}NOCl$: C, 67.33; H, 6.46; N, 5.61; Cl, 14.20. Found: C, 66.55; H, 6.62; N, 5.52; Cl, 14.16.

p-**Nitrodibenzylamine Hydrochloride.**—The procedure described by Busch[22] for the preparation of *o*-nitrodibenzylamine was used in this reaction.

A solution of 53.6 g. (0.50 mole) of benzylamine and 42.9 g. (0.25 mole) of *p*-nitrobenzyl chloride in 250 ml. of ethanol was heated under reflux for four hours. It was then diluted with 900 ml. of water and the red oil which separated was extracted with ether. After the ether had been evaporated, the residue was treated with boiling 2% hydrochloric acid solution. The *p*-nitrodibenzylamine hydrochloride which precipitated from this solution was recrystallized first from boiling 2% hydrochloric acid and then three times from absolute ethanol. After the final recrystallization, the compound weighed 29.6 g. (42.4%) and melted at 248° dec.

Anal. Calcd. for $C_{14}H_{15}N_2O_2Cl$: C, 60.32; H, 5.43; N, 10.05. Found: C, 60.43; H, 5.85; N, 10.26.

p-**Carbomethoxydibenzylamine Hydrochloride.**—The method described above for the preparation of *p*-nitrodibenzylamine hydrochloride was used to synthesize this compound. Benzylamine and methyl α-bromo-*p*-toluate furnished a 34.2% yield of *p*-carbomethoxydibenzylamine hydrochloride, m.p. 233–234°

Anal. Calcd. for $C_{16}H_{18}NO_2Cl$: C, 65.86; H, 6.22; N, 4.80. Found: C, 65.95; H, 6.21; N, 4.59.

p-**Nitro-*p*′-methoxydibenzylamine Hydrochloride.**—The method used to prepare *p*-nitrodibenzylamine hydrochloride was used to prepare this compound from *p*-methoxybenzylamine and *p*-nitrobenzyl chloride. The two reactants gave a 31.6% yield of *p*-nitro-*p*′-methoxydibenzylamine hydrochloride, m.p. 222–223°.

Anal. Calcd. for $C_{15}H_{17}N_2O_3Cl$: Cl, 11.48. Found: Cl, 11.55.

p-**Carbomethoxy-*p*′-methoxydibenzylamine Hydrochloride.**—The method described for the preparation of *p*-nitrodibenzylamine hydrochloride was used to prepare *p*-carbomethoxy-*p*′-methoxydibenzylamine hydrochloride in 24.6% yield from *p*-methoxybenzylamine and methyl α-bromo-*p*-toluate. The compound melts at 245–246°.

Anal. Calcd. for $C_{17}H_{20}NO_3Cl$: Cl, 11.02. Found: Cl, 11.12.

p-**Carbomethoxybenzylhexaminium Bromide.**—To a solution of 18.6 g. (0.133 mole) of hexamine dissolved in 175 ml. of chloroform was added 30.6 g. (0.133 mole) of methyl α-bromo-*p*-toluate. Precipitation began after the solution had been heated for about five minutes and within 15 minutes the contents of the flask had become semi-solid. After the reaction mixture had been cooled, the quaternary salt was filtered from the solution, washed with chloroform and dried. The *p*-carbomethoxybenzylhexaminium bromide weighed 45.4 g. (92.3%), m.p. 175° dec.

Sommelet Reaction on *p*-Carbomethoxybenzylhexaminium Bromide.—A solution of 14.84 g. (0.04 mole) of *p*-carbomethoxybenzylhexaminium bromide in 40 ml. of 50% acetic acid was heated for 2.75 hours, and was then made strongly acidic by the addition of concentrated sulfuric acid. The aldehyde was extracted from the cooled reaction mixture by treatment with three 50-ml. portions of ether and the ether extracts were neutralized with 20% sodium carbonate solution. Evaporation of the ether left a residue of 5.4 g. of *p*-carbomethoxybenzaldehyde, m.p. 60–62°. Recrystallization from low-boiling petroleum ether afforded 4.9 g. (74.7%) of pure aldehyde, m.p. 62–63°. Fuson and Cooke[23] report a m.p. of 61–62° for this compound.

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[21] The values reported for all chlorine analyses are the averages of three individual determinations.

[22] M. Busch, *J. prakt. Chem.*, **159**, 257 (1894).

[23] R. C. Fuson and H. G. Cooke, Jr., THIS JOURNAL, **62**, 1180 (1940).

URBANA, ILLINOIS

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

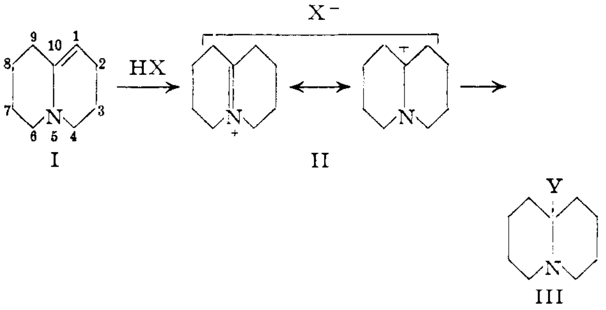
Unsaturated Amines. V. The Attack of Ternary Iminium Compounds by Nucleophilic Reagents[1,2]

BY NELSON J. LEONARD AND ALLAN S. HAY[3]

RECEIVED NOVEMBER 2, 1955

$\Delta^{5(10)}$-Dehydroquinolizidinium perchlorate has been used as a model for the study of the attack of the ternary iminium grouping $(>C{=}\overset{+}{N}< \leftrightarrow >\overset{+}{C}{-}N<)$ by nucleophilic reagents including Grignard reagents, lithium alkyls, metal hydrides, potassium cyanide and RSK and ROK types. Certain reactions of the unconjugated $>C{=}\overset{+}{N}<$ system have been recognized for the first time.

It has been established that the mild dehydrogenation of quinolizidine with mercuric acetate yields $\Delta^{1(10)}$-dehydroquinolizidine (I), the salts of which have been shown to be of the $\Delta^{5(10)}$-dehydroquinolizidinium type (II).[4] $\Delta^{5(10)}$-Dehydroquinolizidinium perchlorate therefore presents, in its cation, an ideal model of a symmetrical, unconjugated ternary iminium grouping $(>C{=}\overset{+}{N}< \leftrightarrow >\overset{+}{C}{-}N<)$,[5] analogous to $>C{=}O \leftrightarrow >\overset{+}{C}{-}O^-$, for the study of attack by nucleophilic reagents.[6] The introduction of a bridgehead substituent at C-10 (III) by attack of the anionic moieties of Grignard reagents, lithium alkyls, metal hydrides, and potassium cyanide, mercaptides and alkoxides on II has now been



I

II

III

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[1] Paper IV in this series: N. J. Leonard, Paul D. Thomas and V. W. Gash, THIS JOURNAL, **77**, 1552 (1955).

[2] Presented at the 128th Meeting of the American Chemical Society, Minneapolis, Minn., September 11–16, 1955; see Abstracts of Papers, p. 9-O.

[3] Monsanto Chemical Co. Fellow, 1953–1954.

[4] N. J. Leonard, A. S. Hay, R. W. Fulmer and V. W. Gash, THIS JOURNAL, **77**, 439 (1955).

[5] We prefer the designation of M. Lamchen, W. Pugh and A. M. Stephen, *J. Chem. Soc.*, 4418 (1954), for the grouping to other suggestions which have been made.

[6] N. J. Leonard and V. W. Gash, THIS JOURNAL, **76**, 2781 (1954).