Anal. Calcd. for C$_{24}$H$_{29}$NO: C, 82.9; H, 8.4; N, 4.0. Found: C, 83.0; H, 8.0; N, 4.3.

The same base was obtained by similar oxidation of the lower-melting form of the amino alcohol. The hydrochloride was crystallized from acetone-ether, m.p. 212–213°.

Anal. Calcd. for C$_{24}$H$_{25}$NO·HCl·1/2 H$_2$O: C, 73.4; H, 7.9. Found: C, 73.3; H, 8.2.

1-Phenyl-1-cyclohexyl-2-piperidinomethyl-3-cis-hydroxymethylcyclopropane hydrochloride. One and two-tenths grams (3.3 mmoles) of 1,1-diphenyl-2-piperidinomethyl-3-*cis*-hydroxymethylcyclopropane hydrochloride (compound 51) was dissolved in 50 ml. of glacial acetic acid and shaken with Adams' catalyst under 2–3 atm. of hydrogen over pressure at 40° for 4 hr. Approximately 10 mmoles of hydrogen was absorbed at a moderate rate with no further absorption in the last hour of shaking. The solution was removed from the catalyst, and evaporated to dryness *in vacuo.* The residue was dissolved in acetone, filtered, and diluted with ether and ethereal hydrogen chloride solution was added to incipient turbidity. There was obtained 1.1 g. of a crystalline product, melting at 205–206°.

Anal. Calcd. for C$_{22}$H$_{33}$NO·HCl: C, 72.6; H, 9.4. Found: C, 72.6; H, 9.6.

1-Phenyl-1-cyclohexyl-2-morpholinomethyl-3-cis-hydroxymethylcyclopropane hydrochloride. The hydrogenation of 1,1-diphenyl - 2 - morpholinomethyl - 3 - *cis* - hydroxymethylcyclopropane hydrochloride monohydrate (compound 54) (2.5 g., 0.0065 mole) was carried out by the same procedure as that above. On crystallization from acetone-ether, 2.2 g. of the product, m.p. 219°, was obtained.

Anal. Calcd. for C$_{21}$H$_{31}$NO$_2$·HCl·1/2 H$_2$O: C, 67.3; H, 8.8. Found: C, 67.2; H, 8.9.

2,2-Diphenylcyclopropane carboxylic acid pyrrolidide. Four grams of 2,2-diphenylcyclopropane carboxylic acid,[29,30] m.p. 172°, obtained by the hydrolysis of the reaction product of the diphenyldiazomethane and methyl acrylate, was refluxed in 25 ml. of thionyl chloride for 2 hr. After removal of

excess thionyl chloride, 2.4 g. of pyrrolidine in 10 ml. of benzene was added dropwise. The reaction mixture was left overnight on the steam bath. The benzene layer was washed with dilute hydrochloric acid, with saturated sodium carbonate solution and finally with water. On evaporation of the solvent an oily residue was obtained. It crystallized from benzene-pentane mixture. Four grams of colorless prisms, m.p. 129–130°, was obtained.

Anal. Calcd. for C$_{20}$H$_{21}$NO: C, 82.4; H, 7.1. Found: C, 82.5; H, 7.2.

1,1-Diphenyl-2-pyrrolidinomethylcyclopropane hydrochloride. The above amide (2.9 g.) was reduced with 0.8 g. of lithium aluminum hydride in 150 ml.of anhydrous ether. The ether extract was acidified with alcoholic hydrochloric acid and the solid product was recrystallized from methanol-ether as fine needles, m.p. 220°.

Anal. Calcd. for C$_{20}$H$_{24}$N·HCl: C, 76.6; H, 7.7. Found: C, 76.4; H, 7.8.

1,1-Diphenyl-2-methylcyclopropane-2-carboxylic acid pyrrolidide. The method of Walborsky and Hornyak[30] afforded 1,1-diphenyl-2-methylcyclopropane-2-carboxylic acid which was converted to its methyl ester, m.p. 95°, by diazomethane. This ester survived for 10 hr. of refluxing with pyrrolidine substantially unchanged. Accordingly the acid was converted to the acid chloride (with thionyl chloride in hexane) and the latter was warmed with pyrrolidine in benzene. The amide melted at 101° after recrystallization from ether-pentane mixture.

Anal. Calcd. for C$_{21}$H$_{23}$NO: C, 82.6; H, 7.5. Found: C, 82.7; H, 7.7.

1,1-Diphenyl-2-methyl-2-pyrrolidinomethylcyclopropane hydrochloride. The above amide (3.1 g.) was reduced with 0.8 g. of lithium aluminum hydride. The ethereal solution of the base was acidified with methanolic hydrogen chloride solution and the resultant hydrochloride was recrystallized from methanol-ether mixture. There was obtained 1.5 g. of colorless prisms melting at 203°.

Anal. Calcd. for C$_{21}$H$_{25}$N·HCl: C, 77.1; H, 8.0. Found: C, 77.0; H, 8.3.

TUCKAHOE, N. Y.

(29) H. Wieland and O. Probst, *Ann.*, **530**, 274 (1937).

(30) H. M. Walborsky and F. M. Hornyak, *J. Am. Chem. Soc.*, **77**, 6026 (1955).

Hydrogenolysis by Metal Hydrides. III. Hydrogenolysis of Alkylallylarylamines by Lithium Aluminum Hydride[1]

VIRGIL L. TWEEDIE AND JOHN C. ALLABASHI[2]

Certain alkylallylarylamines readily undergo hydrogenolysis with lithium aluminum hydride in the presence of nickel(II) chloride to yield alkylarylamines and a mixture of propene and propane. The extent of hydrogenolysis showed a marked dependence on the solvent, the reaction temperature, the amount of nickel chloride, the mole ratio of lithium aluminum hydride to amine, and the structure of the tertiary amine. *N*-Allyl-*N*-methylaniline was 75% hydrogenolyzed after thirty hours in refluxing tetrahydrofuran with two moles of lithium aluminum hydride and 0.003 mole of nickel chloride. Hydrogenolysis was decreased by *o*-, *m*-, or *p*-methyl and *o*-chloro ring substituents but was increased by *m*- and *p*-chloro groups. A mechanism is proposed.

Among the numerous applications of lithium aluminum hydride there are relatively few reports of hydrogenolysis of the C—O or C—N single bond of the simple ether or amine functional groups. The alkyl-oxygen bond of allyl aryl ethers has been hydrogenolyzed by lithium aluminum hydride catalyzed with nickel or cobalt salts.[3,4] Under similar conditions aryl vinyl ethers have been

(1) Presented at the 135th Meeting of the American Chemical Society, Boston, Mass., April 1959, Abstracts of Papers, p. 102-0.

(2) Taken from the Ph.D. dissertation of J.C.A., Baylor University, 1959. Present address: Hercules Powder Co., Cumberland, Md.

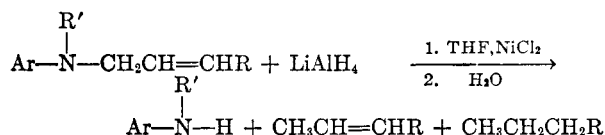(3) P. Karrer and O. Ruttner, *Helv. Chim. Acta*, **33**, 812 (1950).

(4) V. L. Tweedie and M. Cuscurida, *J. Am. Chem. Soc.*, **79**, 5463 (1957). (Paper I in this series.)

cleaved to give good yields of phenols and hydrocarbons.[5] Soffer and Parrotta[6] have reported considerable hydrogenolysis of the ether linkage of the β-alkoxy- and β-aryloxypropionitriles during their reduction by lithium aluminum hydride.

Mustafa[7] reported the lithium aluminum hydride hydrogenolysis of a benzoyl group from N-benzoylcarbazole and N,N-dibenzoylaniline. Likewise one or both benzoyl groups have been cleaved from 1,1-dibenzoyl-2,2-dimethylhydrazine.[8] The oxazolidine ring has been opened by lithium aluminum hydride with hydrogenolysis of the carbon-oxygen rather than the carbon-nitrogen bond.[9] The hydrogenolysis of the carbon-nitrogen bond of a tertiary amine has been reported[10] to occur to some extent during the lithium aluminum hydride reduction of 2-diethylamino-1-methylethyl phenyl ketone. Diethylamine and 1-phenyl-2-methyl-1-propanol were isolated in addition to the expected alcohol. There appears to have been no report of a reaction between lithium aluminum hydride and simple dialkylarylamines which have no other functional group. However, aluminum hydride forms stable coordination complexes with tertiary alkylamines.[11,12]

The purpose of this investigation was to determine the applicability of lithium aluminum hydride for hydrogenolysis of tertiary amines, particularly those that are structurally analogous to the allylaryl ethers, and further to examine systematically the effect of reaction variables such as time, temperature, catalysis, solvent, ratio of reactants, and amine structure.

The hydrogenolysis of a series of eighteen alkylallylarylamines was effected with lithium aluminum hydride under conditions similar to those used for the allyl aryl ethers.

$$
\begin{array}{c}
\text{R}' \\
|\ \ \ \ \\
\text{Ar—N—CH}_2\text{CH=CHR + LiAlH}_4 \xrightarrow[\ \ 2.\ \ \text{H}_2\text{O}\ \ ]{1.\ \text{THF,NiCl}_2} \\
\text{R}' \\
|\ \ \ \ \\
\text{Ar—N—H + CH}_3\text{CH=CHR + CH}_3\text{CH}_2\text{CH}_2\text{R}
\end{array}
$$

For several of these amines, the cleavage of the allylic carbon-nitrogen linkage was demonstrated by the isolation of an alkylarylamine and a mixture of hydrocarbons. For example, the hydrogenolysis of N-allyl-N-methylaniline gave N-methylaniline and a mixture of propane and propene. No trace of primary amine was detected. Neither the secondary

amine nor the hydrocarbon was released from the reaction complex prior to the hydrolysis step. This was evidenced by the fact that the small amount of gas collected during the course of the hydrogenolysis reaction contained no hydrocarbon, and that only tertiary amine and no secondary amine could be extracted from the reaction mixture before the hydrolysis.

Nickel(II) chloride was used as a catalyst on the basis of earlier work.[4,5] The results of several runs showing the effect of the catalyst are summarized in Table I. No detectable amount of hydrogenolysis occurred without catalyst, even in the presence of excess solid lithium aluminum hydride. The hydrogenolysis of N-allyl-N-methylaniline increased as the amount of catalyst was increased up to 0.3 mole % of the amine. As described earlier[5] the nickel(II) chloride reacted with the homogeneous solution of lithium aluminum hydride to yield a very fine black solid which constituted a heterogeneous system even with the minimum amount of catalyst. The nonmetallic surface, powdered glass wool, failed to catalyze the hydrogenolysis.

TABLE I

EFFECT OF CATALYST ON THE CLEAVAGE OF N-ALLYL-N-METHYLANILINE[a]

Molar Ratio LiAlH₄: Amine	Catalyst Moles/Moles Amine	Cleavage, %
0:1	0.0031	None
2:1[b]	None	None
2:1[b]	0.0008	18
2:1[b]	0.0016	35
2:1[b]	0.0031	75
2:1[c]	None	None
2:1[c]	0.0008	20
2:1[c]	Glass wool	None

[a] Solvent: tetrahydrofuran. Temp.: 65°. Time: 30 hr. [b] Heterogeneous system containing solid lithium aluminum hydride. [c] Homogeneous solution of lithium aluminum hydride.

Since hydrogen was released slowly from the hydrogenolysis reaction during reflux, it seemed important to determine the effect of suspended solids on the production of hydrogen from lithium aluminum hydride solutions. The evolution of hydrogen was measured during four and one-half hours of reflux of a homogeneous solution of lithium aluminum hydride in tetrahydrofuran and from similar solutions with nickel(II) chloride and with powdered glass added. The solution containing the nickel salt yielded 32% more hydrogen than the others which gave identical amounts of hydrogen. The catalytic effect of the nickel(II) chloride reduction product on the evolution of hydrogen suggests this black solid is finely divided nickel. Wiberg[13] has reported the instability of lithium aluminum hydride in ether solutions, and that its decomposition to

(5) V. L. Tweedie and B. G. Barron, J. Org. Chem., in press. (Paper II in this series.)

(6) L. M. Soffer and E. W. Parrotta, J. Am. Chem. Soc., 76, 3580 (1954).

(7) A. Mustafa, et al., J. Am. Chem. Soc., 76, 5447 (1954).

(8) R. L. Hinman, J. Org. Chem., 21, 1177 (1956).

(9) E. D. Bergmann, D. Lavie, and S. Pinchas, J. Am. Chem. Soc., 73, 5662 (1951).

(10) H. Riviere-Larramona, Compt. rend., 244, 1653 (1957).

(11) O. Stecher and E. Wiberg, Ber., 75B, 2003 (1942).

(12) J. K. Ruff and M. F. Hawthorne, J. Am. Chem. Soc., 82, 2141 (1960).

(13) E. Wiberg, R. Bauer, M. Schmidt, and R. Uson, Z. Naturforsch., 6b, 393 (1951).

lithium hydride, aluminum, and hydrogen is catalyzed in ether at room temperature by finely divided metals.

The influences of reaction conditions were investigated using *N*-allyl-*N*-methylaniline in order to establish conditions suitable for a study of the relationship of amine structure to amine cleavage. The results of several runs with a variety of combinations of solvent, time, temperature, and mole ratio of reactants are given in Table II.

TABLE II

EFFECT OF REACTION CONDITIONS ON THE CLEAVAGE OF *N*-ALLYL-*N*-METHYLANILINE[a]

Solvent	Time, Hr.	Temp.	Molar Ratio LiAlH₄:Amine	Cleavage, %
THF[b]	7	65	1:1	18
THF	7	65	2:1	34
THF	7	65	3:1	54
THF	30	65	2:1	75
THF	30	35	2:1	7
THF	30	65	3:1	93
THF	30	65	4:1	99
Dioxane	30	101	2:1	49
Dioxane	30	35	2:1	4
Ethyl ether	30	35	2:1	0

[a] Catalyst: NiCl₂ (0.0031 mole/mole amine). [b] Tetrahydrofuran.

The nature of the solvent has been shown to influence markedly lithium aluminum hydride reactions. Especially in hydrogenolyses,[4-6] the use of tetrahydrofuran or dioxane as solvent instead of ethyl ether greatly increased the extent of reaction even though the temperature remained constant. Likewise, for the hydrogenolysis of *N*-allyl-*N*-methylaniline, tetrahydrofuran was superior to dioxane at a given temperature, and no reaction was obtained in ethyl ether. Further, the effect of the solvent was indicated by the larger increase in cleavage per degree of temperature rise in tetrahydrofuran compared with that in dioxane.

As the ratio of lithium aluminum hydride to amine was increased, hydrogenolysis increased roughly linearly. Essentially complete hydrogenolysis of the amine was obtained with a fourfold molar excess of hydride after thirty hours of reflux in tetrahydrofuran.

The reaction conditions selected as suitable for determining the effects of amine structure were a 2:1 molar ratio of lithium aluminum hydride to amine, nickel(II) chloride catalyst, and thirty hours of reflux in tetrahydrofuran. Using the 75% hydrogenolysis of *N*-allyl-*N*-methylaniline under these conditions as a reference value, the effect of structural changes in the amine and the general applicability of this reaction to tertiary amines are shown in Table III.

Among the tertiary amines investigated only those having an allylic, an alkyl, and an aryl group were found susceptible to hydrogenolysis under these

TABLE III

EFFECT OF AMINE STRUCTURE ON HYDROGENOLYSIS[a]

Amine	Hydrogenolysis, %
N-Allyl-*N*-methylaniline	75
N-Benzyl-*N*-methylaniline	None
N-Propyl-*N*-methylaniline	None
N,*N*-Dimethylaniline	None
N-Allyl-*N*-methylcyclohexylamine	None
N-Allylaniline	None
N-Methylaniline	None
N-Allyl-*N*-ethylaniline	67
N-Allyl-*N*-isopropylaniline	16
N-Allyl-*N*-methyl-*o*-toluidine	24
N-Allyl-*N*-methyl-*m*-toluidine	59
N-Allyl-*N*-methyl-*p*-toluidine	32
N-Allyl-*N*-methyl-2,6-dimethylaniline	29
N-Allyl-*N*-methyl-*o*-chloroaniline	54
N-Allyl-*N*-methyl-*m*-chloroaniline	88
N-Allyl-*N*-methyl-*p*-chloroaniline	91
N-Crotyl-*N*-methylaniline	6
N-Cinnamyl-*N*-methylaniline	35
N-γ-Chloroallyl-*N*-methylaniline	None

[a] Reaction time: 30 hr. Temperature: 65° Catalyst: NiCl₂ Solvent: tetrahydrofuran. Molar ratio: LiAlH₄ to amine, 2:1.

conditions. The difference in behavior between the allyl and the benzyl compounds was surprising and in contrast to the cleavages observed with both the allyl and benzyl aryl ethers.[4] The secondary amines, *N*-methylaniline and *N*-allylaniline, which were possible products from the hydrogenolysis of several of the tertiary amines, were recovered without cleavage from the reaction mixture.

As the size of the alkyl group was increased in the series from methyl to ethyl to isopropyl, the hydrogenolysis decreased sharply. While this order is the expected order of increasing basicity of these amines,[14,15] it is also the expected order of decreasing stability of the initial coordination complex with the aluminohydride ion.[16] The relative importance of these effects in explaining the decreased cleavage with increasing size of alkyl group was not determined.

If the basicity of the amine is important in the hydrogenolysis reaction, then ring substituents which alter the electron density of the nitrogen would be expected to have a significant effect on the amount of cleavage. The methyl and chloro groups were used as ring-activating and ring-deactivating substituents since these groups are comparable in steric requirements[17] and are not attacked by lithium aluminum hydride. Hydrogenolysis was markedly decreased by methyl substituents on the ring, especially in the *ortho*- and *para*- positions, and was increased by chloro substituents in the *para*-

(14) N. F. Hall and M. R. Sprinkle, *J. Am. Chem. Soc.*, **54**, 3469 (1932).

(15) G. Vexlearschi and R. Rumpf, *Compt. rend.*, **228**, 1655 (1949).

(16) H. C. Brown and M. D. Taylor, *J. Am. Chem. Soc.*, **69**, 1332 (1947).

(17) R. Adams and H. C. Yuan, *Chem. Revs.*, **12**, 284 (1933).

and *meta-* but not in the *ortho-* positions. Similar effects were found in the hydrogenolysis of analogously substituted allyl phenyl ethers.[4] Thus it appears that an increase in basicity either as the result of changes in the alkyl group or in ring substituents causes a decrease in hydrogenolysis. The steric considerations of ortho substituents and of bulky alkyl groups are undoubtedly important also in decreasing hydrogenolysis.

Structural changes in the allylic chain by substitution of either a phenyl or a methyl group in the γ-position greatly decreased the cleavage; with chloro substitution no cleavage at all was observed. These results are in contrast to the increased hydrogenolysis of analogously substituted allyl aryl ethers.[4] However, in both the amines and the ethers an allylic shift in the cinnamyl group was shown to accompany the hydrogenolysis by the isolation of allylbenzene instead of propenylbenzene.

A mechanism which provides reasonable explanation of the experimental observations is shown in Fig. 1. The dissociation of the aluminohydride ion as proposed by Paddock[18] would be enhanced by coordination of the aluminum hydride with the nucleophilic solvent and/or by formation of complex I. The hydride addition to α-olefins has been shown by Ziegler[19] to proceed readily with aluminum hydride at temperatures above 50° to form aluminum alkyls. The proximity of the reacting groups in I should facilitate the closure of the five-membered ring in II. The decrease in cleavage when R is not hydrogen may be explained by the much slower addition of hydride to nonterminal olefinic groups.[19] The cyclic intermediate may be a spiro complex, IIa, similar to those proposed by Hochstein and Brown[20] and by Attenburrow[21] in explaining the reduction of the double bonds of cinnamyl and propargyl alcohols. The hydride ion or the aluminohydride ion in solution would attack the *alpha* carbon leading to cleavage by nucleophilic displacement. A decrease in the electron density of the nitrogen, as in the chloro substituted amines, would be expected to favor the attack at the α carbon. A competitive process would be the hydride attack on the β hydrogen with elimination of the amine and formation of the olefinic complex, VI, in which an allylic shift has occurred. Since neither the hydrocarbons nor the secondary amine could be detected prior to decomposition with water, the product complexes V and VI must be stable in solution.

The removal of a methyl group from a quaternary ammonium ion by lithium aluminum hydride has been reported.[22] Complexes I and II are hardly analogous to substituted ammonium ions since the

(18) N. L. Paddock, *Nature*, **167**, 1070 (1951).

(19) K. Ziegler, *Angew. Chem.*, **64**, 323 (1952).

(20) F. A. Hochstein and W. G. Brown, *J. Am. Chem. Soc.*, **70**, 3484 (1948).

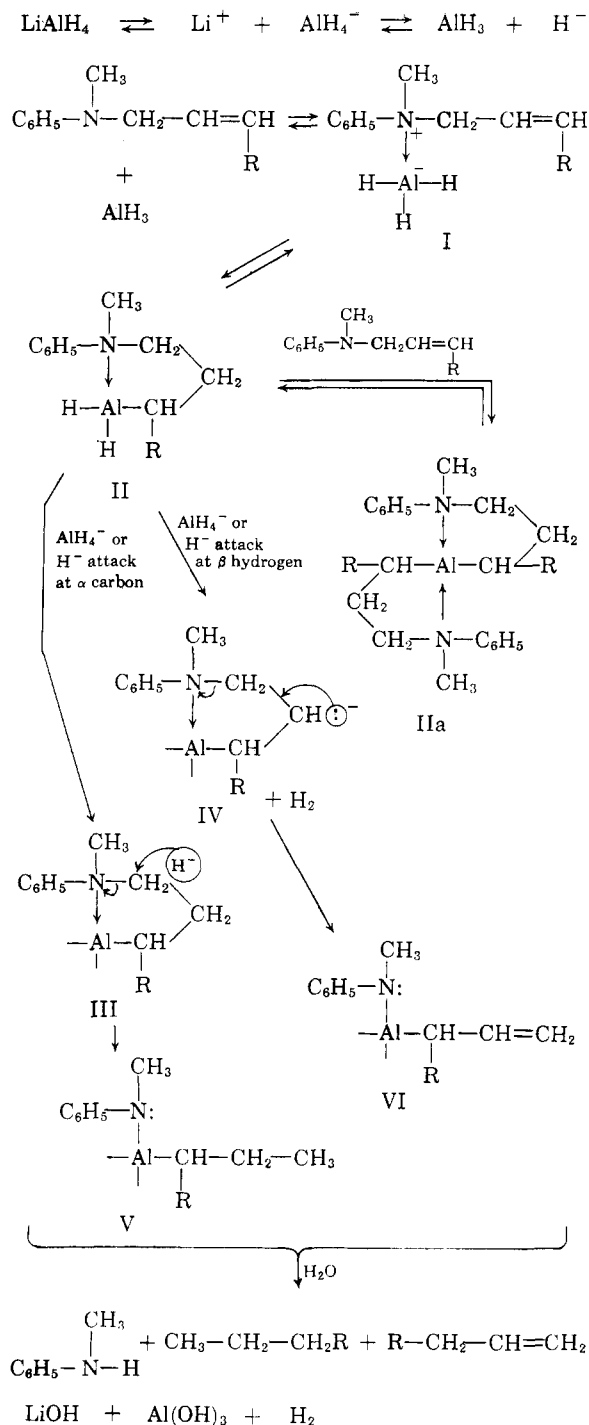(21) A. F. B. Attenburrow *et al.*, *J. Chem. Soc.*, 1094 (1952).

Fig. 1. Proposed mechanism of hydrogenolysis

nitrogen-aluminum coordination involves the partial charge separation of a semipolar bond and the complex as a whole is without ionic charge. Further, there was no indication of N-allylaniline or N-propylaniline contamination of the N-methylaniline isolated.

(22) A. C. Cope and C. L. Bumgardner, *J. Am. Chem. Soc.*, **79**, 960 (1957).

TABLE IV

PREPARATION AND PHYSICAL PROPERTIES OF TERTIARY AMINES

Amine	B.P., °/1 mm.	$n_D^{20.5}$	Formula	Carbon, %		Hydrogen, %	
				Calcd.	Found	Calcd.	Found
N-Allyl-N-methyl-o-chloroaniline	76–78	1.5551	$C_{10}H_{12}NCl$	66.11	65.90	6.61	6.47
N-Allyl-N-methyl-m-chloroaniline	103–104	1.5692	$C_{10}H_{12}NCl$	66.11	65.92	6.61	6.48
N-Allyl-N-methyl-p-chloroaniline	104–105	1.5687	$C_{10}H_{12}NCl$	66.11	65.89	6.61	6.51
N-γ-Chloroallyl-N-methylaniline	106–107	1.5709	$C_{10}H_{12}NCl$	66.11	65.85	6.61	6.38
N-Allyl-N-methyl-m-toluidine	90–91	1.5472	$C_{11}H_{15}N$	81.99	81.76	9.32	9.08
N-Allyl-N-methyl-2,6-dimethyl-aniline	75.6	1.5210	$C_{12}H_{17}N$	82.34	82.08	9.71	9.58
N-Allyl-N-methylcyclohexylamine	202–204 (760 mm.)	1.4674	$C_{10}H_{19}N$	78.49	78.25	12.41	12.26

	B.P. °/760 mm.			B.P., °/760 mm.	n_D		
N-Allyl-N-methylaniline	216–217	1.5519	$C_{10}H_{13}N$	213 (755 mm.)[a]			
N-Allyl-N-ethylaniline	223–225	1.5460	$C_{11}H_{15}N$	227–229,[b] 220–225			
N-Allyl-N-propylaniline	224–225	1.5368	$C_{12}H_{17}N$	225[c]			
N-Allyl-N-isopropylaniline	224–226	1.5321	$C_{12}H_{17}N$	223–227[d]			
N-Allyl-N-methyl-o-toluidine	218–220	1.5260	$C_{11}H_{15}N$	215–220[e]			
N-Allyl-N-methyl-p-toluidine	232–234	1.5461	$C_{11}H_{15}N$	230–232[f]			
N-Cinnamyl-N-methylaniline	149–150 (1 mm.)	1.6229	$C_{16}H_{17}N$	153 (0.33 mm.)[g]	1.6231 (25°)		
N-Crotyl-N-methylaniline	119–120 (14 mm.)	1.5492	$C_{11}H_{15}N$	119 (14 mm.)[g]	1.5503 (25°)		
N-Methyl-N-benzylaniline	158–160 (8 mm.)	1.6060	$C_{14}H_{15}N$	161–162 (8 mm.)[h]	1.6071 (15°) 1.6007 (29.5°)		

[a] E. Wedekind, *Ber.*, **32**, 524 (1899). [b] *Ann.*, **318**, 97 (1901). [c] S. Komatsu, *Chem. Z.*, **1913** I, 801. [d] J. V. Braun, *Ber.*, **33**, 2734 (1900). [e] E. Wedekind and F. Oberheide, *Ber.*, **37**, 3896 (1904). [f] *Ber.*, **37**, 2720 (1904). [g] R. F. Kleinschmidt and A. C. Cope, *J. Am. Chem. Soc.*, **66**, 1932 (1944). [h] E. Wedekind, *Ber.*, **32**, 519 (1899).

EXPERIMENTAL

All melting points and boiling points are uncorrected.

Preparation and purification of tertiary amines. A mixture of 1.0 mole of the mono alkyl- or allylaniline, 1.1 moles of the alkyl or allyl halide, 0.6 mole of sodium carbonate or 1.2 moles of sodium bicarbonate, 400 ml. of 95% ethyl alcohol, and 100 ml. of water was refluxed for 12 hr. The alcohol was practically removed under reduced pressure, and the residue was diluted with 400 ml. of water. The amine product was separated by decantation and extraction with 250 ml. of ether. The solution of crude amine was washed with water and dried over sodium sulfate. After removal of the solvent and reactants, the tertiary amine was distilled under reduced pressure. Whenever analysis indicated the presence of any secondary amine, enough acetic anhydride was added to acetylate completely the secondary amine and the tertiary amine was recovered by extraction and redistillation under reduced pressure. The tertiary amines thus prepared are listed in Table IV. The yields ranged from 50 to 85% of theory.

The aniline derivatives used in these syntheses were those available commercially, namely: N-methylaniline, N-ethylaniline, N-methyltoluidines (o,m,p), N-methylcyclohexylamine, 2,6-dimethylaniline, and chloroanilines (o,m,p) (all Fisher), and N-allylaniline (Aldrich Chem. Co.). The N-methylchloroanilines (o,m,p) and N-methyl-2,6-dimethylaniline were prepared by the lithium aluminum hydride reduction of the corresponding formanilides according to the method of Kelly *et al.*[23] The alkyl and allyl halides used were the following: allyl bromide, allyl chloride, propyl bromide, isopropyl bromide (all Fisher), crotyl bromide (K & K Laboratories), and 1,3-dichloropropene (Shell Chemical Co.). Cinnamyl chloride was prepared from cinnamyl alcohol (Fisher) by treatment with thionyl chloride in pyridine.[24]

Hydrogenolysis of tertiary amines. The apparatus consisted of a three necked, 250-ml. flask equipped with a dropping funnel and a reflux condenser, and protected from atmospheric moisture. In a typical reaction, lithium aluminum hydride (0.1 mole) and nickel(II) chloride (0.0031 mole) were placed in the dry flask which was immersed in ice water. To these solids the amine (0.05 mole) and the solvent were added from the funnel. After the initial reaction subsided, the mixture was heated under reflux for 30 hr. The reaction flask was again cooled with ice water and the excess hydride was decomposed by addition of aqueous base. The organic layer was decanted, the aqueous suspension of solids was filtered by suction, and the cake was washed with ether. The organic layer and washings were combined and dried, the volatile solvents were evaporated, and the residual mixture of amines was submitted for quantitative analysis. When the hydrogenolysis reaction was attempted under homogeneous conditions, the catalyst was omitted and the amine was added to a saturated homogeneous solution of lithium aluminum hydride in the solvent.

The solvents, ethyl ether (Merck, U.S.P.), tetrahydrofuran (Eastman, White Label) and dioxane (Fisher, Purified) were refluxed over and distilled from either metallic sodium or lithium aluminum hydride. Anhydrous nickel (II) chloride was prepared by heating its hexahydrate (Baker & Adamson, Reagent Grade).

The hydrocarbon products from some runs were separated and collected by passing the large volume of hydrogen evolved during the decomposition through a series of three traps attached to the reflux condenser and cooled in a mixture of acetone and Dry Ice. The condensed hydrocarbons were vaporized from the cold traps and exhausted into a gas measuring system and sampling tubes for chromatographic

(23) R. B. Kelly, W. I. Taylor, and K. Wiesner, *J. Chem. Soc.*, 2095 (1953).

(24) G. Gilman and S. A. Harris, *Rec. trav. chim.*, **50**, 1052 (1931).

analysis.[25] The small amount of hydrogen evolved prior to decomposition contained no hydrocarbon material.

The hydrocarbon fraction isolated from the hydrogenolysis of N-cinnamyl-N-methylaniline apparently was a mixture of allylbenzene and propylbenzene and did not contain propenylbenzene. Its boiling range was 157–159° (lit.[26] allylbenzene, b.p. 156.3°; propylbenzene, b.p. 159.2°; trans-propenylbenzene, b.p. 179°). This fraction readily decolorized solutions of bromine and of permanganate, but it was only partially soluble in concentrated sulfuric acid. The ultraviolet spectra showed a broad maximum about 2625 Å but no absorption at 2830 or 2945 Å. The reported maxima for allylbenzene and propylbenzene are 2620 and

(25) The chromatographic analyses, obtained through the courtesy of L. F. Hatch, The University of Texas, were made on an instrument of proprietary design used regularly for analysis of mixtures of gaseous hydrocarbons. Only qualitative identification of the gases was made because collecting, sampling, and transportation techniques precluded reliable quantitative measurements.

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2600 Å respectively, and for propenylbenzene are 2830 and 2945 Å.[27]

In two runs the isolation of the secondary amine was attempted before decomposition of the reaction mixture. The solvent was removed under reduced pressure, and the residual semisolid mass was continuously extracted with hexane. The extract contained no secondary amine and only small amounts of the original tertiary amine.

Analytical methods. The amine mixtures were analyzed by the nonaqueous titration method of Siggia[28] using perchloric acid in glacial acetic acid as the titrant. To perchloric acid (72%) (8.5 ml.) in glacial acetic acid (200 ml.) acetic anhydride (20 ml.) was added as a drying agent. The mixture, after standing 15 hr., was diluted to 1 l. with glacial acetic acid and was standardized several hours later against potassium acid phthalate. A glass-calomel electrode system was used with a Beckman Zeromatic pH meter.

On known mixtures of primary, secondary, and tertiary amines the average accuracy of the perchloric acid titration was ±0.25%. The titration method was also used to determine the purity of the tertiary amines from preparative procedures.

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Ammonolysis of Vicinal Acetoxy Chlorides

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Ammonolyses of vicinal acetoxy chlorides proceed more readily than the related vicinal dichlorides. Surprisingly, in anhydrous ammonia at 220°, the principal product is vicinal diol; trans-2-acetoxycyclohexyl chloride giving a 77% yield of cis-1,2-cyclohexanediol. A reversal occurs with aqueous ammonia; an 81% yield of trans-2-aminocyclohexanol was isolated. The distribution of products is attributed to a competition between ester ammonolysis and intramolecular chloride displacement by the carbonyl-ammonia intermediate.

The role of neighboring acetoxy groups has been shown in the hydrolysis,[1,2] ethanolysis,[2] and acetolysis[2] of 2-acetoxycyclohexyl arylsulfonates. While the individual steps of ester ammonolysis[3–6] and halide displacement by ammonia and amines[7] are well known, the course of ammonolysis of neighboring acetoxy halide systems has not yet been established. Systems such as these were studied in this work.

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RESULTS

The acetates derived from the chlorohydrins of 2-dodecene, 1-hexene, and cyclohexene, as well as 1,2-dichlorododecane, were subjected to ammonolysis at 220° under autogenous pressure with both aqueous ammonia and anhydrous ammonia in hydrocarbon solvents. Studies in the acyclic series were somewhat complicated by the fact that the starting esters are mixtures of the 1-chloro-2-acetoxy and 1-acetoxy-2-chloro compounds. With the acetoxy chlorides from 1-hexene, for example, vapor phase chromatography indicated a 50/50 mixture of the two isomers. These isomers need not react at the same rate or even by the same mechanism; however, neither the results nor the conclusions appear to be altered by this complication.

The products and yields for the acyclic systems are given in Table I. The acetoxy chlorides from 1-dodecene undergo a 62% conversion to products under conditions where 1,2-dichlorododecane is inert, showing neighboring acetoxy is much more rate enhancing than chloro. The acetoxy group is