total of 9.7 g. (78.3%) in three fractions, b.p. 87–91° (22 mm.), $n^{27°}$D 1.5241–1.5259. This product was a colorless oil, with small amounts of suspended colorless solid. On refrigeration the entire product crystallized in large needles, which reliquefied on warming to room temperature. This was redistilled collecting a total of 7.3 g., b.p. 92–94° (42 mm.), $n^{27°}$D 1.5246–1.5248. Karmas and Spoerri[37] give the boiling point of this compound as 111–112° (70 mm.), $n^{24°}$D 1.5230.[40]

Absorption Spectra.—The ultraviolet absorption spectra were taken either on a Beckman DU spectrophotometer or a Bausch and Lomb Model 505 recording spectrophotometer. These are given in Table I. Infrared absorption spectra were taken on a Perkin-Elmer Model 21 recording specctrophotometer calibrated with a polystyrene film.

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(40) After this manuscript was completed, the present authors were informed by Dr. Robert I. Meltzer, Warner Lambert Research Institute, Morris Plains, N. J., that the second product resulting from the direct chlorination of 2-methylpyrazine (ref. 23 and 24) had been identified as 2-chloro-6-methylpyrazine. On the basis of this and other work contained in a paper submitted for publication by Dr. Meltzer and his associates, it is now believed that the 51–52° monochloromethylpyrazine N-oxide (ref. 38) is probably 2-chloro-3-methylpyrazine 1-oxide. The present authors are grateful to Drs. Meltzer and Wilson B. Lutz and their co-workers for the opportunity to read their paper prior to publication.

Carbonium Ion Intermediates in the Deamination of 3-Methyl-2-butylamine and Isopentylamine[1]

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The products from the solvolysis of 3-methyl-2-butyl tosylate and the deamination of 3-methyl-2-butylamine and isopentylamine in aqueous acetic acid have been determined. Comparison of the tosylate solvolysis with the deamination of 3-methyl-2-butylamine leads to the conclusion that an open 3-methyl-2-butyl carbonium ion is an important intermediate in the latter reaction. The *t*-pentyl carbonium ion from deamination of 3-methyl-2-butylamine and the *t*-pentyl and 3-methyl-2-butyl carbonium ions from deamination of isopentylamine do not behave as normal solvolytic carbonium ions. Formation of 1,2-dimethylcyclopropane in the deamination reactions is considered in relation to the general question of cyclopropane formation, 1,3-hydride shifts, and 1,2-alkyl migrations in simple carbonium ion systems.

Our general interest in exploring the relationship between the mode of formation and the behavior of carbonium ions has led to an investigation of carbonium ions generated in halide solvolyses and amine deaminations. Figure 1 diagrams the system chosen for our initial research; an earlier report has considered[2] reactions of *t*-pentyl and neopentyl starting materials in terms of the intermediates in the upper part of Fig. 1. The present paper analyzes carbonium ion reactions of 3-methyl-2-butyl and isopentyl compounds using an approach whose merits and limitations were evaluated previously[2] (*cf.* Fig. 1).

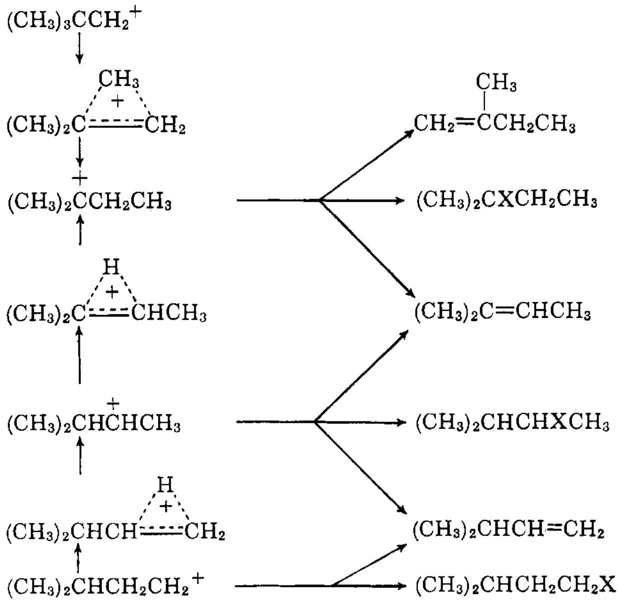

Figure 1

Results

Table I records the observed composition of the products from the deamination of 3-methyl-2-butylamine and isopentylamine, as determined by gas–liquid partition chromatography (g.l.p.c.) and infrared analysis. Reproducibility in duplicate runs is seen to be good. Control runs established the stability of the acetates and *t*-pentyl alcohol, the instability of 3-methyl-2-butanol and isopentyl alcohol and the selective destruction of 2-methyl-2-butene under the deamination conditions. The Experimental discusses determination of corrections for product instability and Table II summarizes product compositions after such corrections. Comparison of lines 7 and 11 to lines 13 and 14 (Table I) and of Table I to Table II demonstrates that corrections for the instability of the two alcohols alter the composition of the substitution product detectably but not significantly. The same comparisons reveal that corrections for olefin fractionation are more important. Since the fact that relatively little 2-methyl-2-butene is formed in the deaminations will play a prominent part in our discussion, we have applied maximum corrections for 2-methyl-2-butene destruction. The observation that the uncorrected olefin compositions for runs 9 and 12 agree with the corrected values for runs 7 and 11 (Table I), respectively, confirms the validity of these corrections. The first two reactions produced large quantities of olefin, and in such instances olefin fractionation becomes insignificant. The degree of olefin fractionation also diminishes as the water content of the solvent increases, as may be seen by comparing the data in Tables I and II for different solvent compositions.

Discussion

The 3-Methyl-2-butyl System.—Winstein and Takahashi[3] established neighboring group rate enhancement

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(1) Supported by a grant from The Petroleum Research Fund, administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

(2) M. S. Silver, *J. Am. Chem. Soc.*, **83**, 3482 (1961).

(3) S. Winstein and J. Takahashi, *Tetrahedron*, **2**, 316 (1958).

TABLE I

COMPOSITION OF THE PRODUCT MIXTURE ISOLATED FROM THE DEAMINATION OF 3-METHYL-2-BUTYLAMINE AND ISOPENTYLAMINE IN AQUEOUS ACETIC ACID[a–c] AT 55°

Run	Compd.	HOAc, %	Amine, g.	$NaNO_2$, g.	RX g. (%)[d]	Olefin, g. (%)[d]	t-X,[e] %	s-X,[e] %	p-X,[e] %	2-Me-1-butene,[f] %	2-Me-2-butene,[f] %	3-Me-1-butene,[f] %	1,2-Me$_2$-cyclopropane,[f,g] %
1	p-NH$_2$	25	20	30	11(51)	2.3(14)	41	20	39	4	11	85	—
2		25	20	30	14(61)	—	42	19	39	—	—	—	—
3		50	20	30	14(59)	2.9(18)	33	20	47	8	16	77	—
4		75	20	30	15(59)	—	22	19	59	—	—	—	—
5		100	25	30	19(58)	3.7(19)	19	16	65	15	17	68	—
6		100	25	29	21(66)	—	19	15	66	—	—	—	—
7		100	27	50	21(54)	3.6(17)	20	16	64	15	19	64	1.5
8		100	20	30	—	—	—	—	—	18	17	66	—
9		100[h]	66	100	—	12	—	—	—	17	22	60	1.9
10	s-NH$_2$	50	20	30	12(52)	4(25)	39	61		19	34	34	13
11		100	20	30	8(38)	3.7(28)	27	73		20	24	38	18
12		100[h]	24	45	10(33)	8(41)	27	73		18	32	35	15
13	p-NH$_2$	100[i]					18	20	63	14	25	59	1.5
14	s-NH$_2$	100[j]					24	76		18	33	31	18

[a] Abbreviations are as follows: p = isopentyl; s = 3-methyl-2-butyl; t = t-pentyl; R = $p + s + t$; X = alcohol + acetate. [b] Mole % used throughout. [c] A dash (—) indicates quantity not measured. [d] % Yield based on unrecovered amine. [e] Total RX = 100%. [f] Total C_5H_{10} fraction = 100%. [g] *Trans–cis* was about 2:1; no attempt was made to determine relative stability of these compounds under reaction conditions. [h] No correction was applied to olefin from this run because of the high yield of olefin. [i] Corrected composition of run 7. [j] Corrected composition of run 11.

TABLE II

PRODUCTS FROM THE SOLVOLYSIS OF SOME RELATED C_5 COMPOUNDS AT 55° IN AQUEOUS ACETIC ACID[a,b]

Compd.	HOAc, %	t-X, %	s-X, %	p-X, %	2-Me-1-butene	2-Me-2-butene	3-Me-1-butene	1,2-Me$_2$-cyclopropane
p-NH$_2$	25	35	24	41	4	11	85	
	50	28	24	48	7	18	76	
	75	19	23	58	—	—	—	
	100	17	20	64	15	23	60	2
s-NH$_2$	50	36	64		19	38	31	13
	100	24	76		18	33	33	17
s-OTs	94	96	4		13	86	1	
	100	92	8		13	86	1	
	100[c]	90	10		21	77	2	
t-NH$_2$[d]	0				61	39		
	50				58	42		
	75				64	36		
	100				63	37		
t-Cl[d]	50[e]				20	80		
	75				21	79		
t-Br[d]	94				23	77		
	100				26	74		

[a] The footnotes of Table I pertain where applicable. [b] This work unless otherwise noted. [c] Ref. 3, 75°. [d] Ref. 2. [e] 78°.

by the tertiary hydrogen in the acetolysis of 3-methyl-2-butyl tosylate. This hydrogen participation reinforces the natural tendency[4] of a tosylate or halide to undergo E 1 elimination in the Saytzeff sense, and nearly all the acetolysis product from 3-methyl-2-butyl tosylate is derived from loss or rearrangement of the tertiary hydrogen (Table II).[3] Only a trace of 3-methyl-1-butene and a few per cent of 3-methyl-2-butyl acetate are formed. The immediate precursors of the products cannot be assigned, but the difference between the products from acetolysis of t-pentyl halides and 3-methyl-2-butyl tosylate establishes that the t-pentyl carbonium ion is not the sole precursor in reactions of the latter.[3]

The neighboring tertiary hydrogen plays a considerably smaller role in the acetic acid deamination of 3-methyl-2-butylamine than in the acetolysis of 3-methyl-2-butyl tosylate. The amine yields about 75% unrearranged substitution product, where the tosylate gives less than 10% (Table II). A direct displacement mechanism does not explain the large amount of 3-methyl-2-butyl substitution product in the deamination, since 2-butylamine gives only 28% inversion in acetic acid and 22% inversion in water.[5] Involvement of the tertiary hydrogen in the tosylate reaction also magnifies the usual[2] difference in olefin composition from halide solvolyses and deaminations, and 3-methyl-2-butylamine affords far more 3-methyl-1-butene than does the tosylate. Postulation of an open 3-methyl-2-butyl carbonium ion as an intermediate in the deamination provides the most economical rationalization for the above results (we ignore methyl-bridged intermediates for now). The open carbonium ion presumably undergoes rearrangement and directly forms 3-methyl-1-butene, 2-methyl-2-butene, and 3-methyl-2-butyl product (Fig. 1).

An estimate of the lower limit to the amount of 2-methyl-2-butene arising from this open 3-methyl-2-butyl carbonium ion is useful for subsequent discussion. The estimate can be made by comparing the deamination of 3-methyl-2-butylamine and 2-butylamine,[6,7] and by employing the following facts: (1) statistically, internal elimination[8] is favored in the 2-butyl system by a factor of two; (2) thermodynamically, internal elimination is favored in the 3-methyl-2-butyl system, where a trisubstituted ethylene is formed; (3) the effect of relative conformational considerations[5] for the two amines on the amounts of internal and external elimination is difficult to predict; (4) 2-butylamine in water gives[6,7] about 3 for the ratio 2-butene/1-butene. On the basis of these considerations, a prediction that the open 3-

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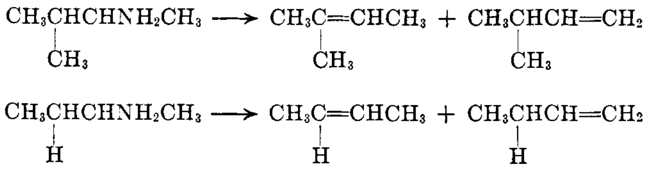
(4) A. Streitwieser, Jr., *Chem. Rev.*, **56**, 571 (1956).

(5) A. Streitwieser, Jr., *J. Org. Chem.*, **22**, 861 (1957), and citations therein.

(6) A. Streitwieser, Jr., and W. D. Schaeffer, *J. Am. Chem. Soc.*, **79**, 2888 (1957).

(7) W. B. Smith and W. H. Watson, Jr., *ibid.*, **84**, 3174 (1962).

(8) Internal elimination equals formation of the more highly substituted olefin; external elimination, the opposite.



$$CH_3\underset{CH_3}{C}HCHNH_2CH_3 \longrightarrow CH_3\underset{CH_3}{C}{=}CHCH_3 + CH_3\underset{CH_3}{C}HCH{=}CH_2$$

$$CH_3\underset{H}{C}HCHNH_2CH_3 \longrightarrow CH_3\underset{H}{C}{=}CHCH_3 + CH_3\underset{H}{C}HCH{=}CH_2$$

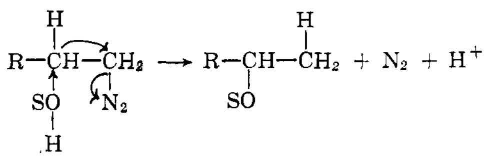
methyl-2-butyl carbonium ion from deamination of 3-methyl-2-butylamine yields approximately equal amounts of 2-methyl-2-butene and 3-methyl-1-butene appears reasonable. Because the reaction produces the two olefins in nearly a 1:1 ratio (Table II) *most* of the 2-methyl-2-butene certainly must come from the open 3-methyl-2-butyl carbonium ion.

The *t*-pentyl carbonium ion generated in the deamination of 3-methyl-2-butylamine, therefore, gives rise to very little 2-methyl-2-butene, but considerable quantities of 2-methyl-1-butene and *t*-pentyl substitution product (Table II). Since the *t*-pentyl carbonium ion from *t*-pentylamine shows the same behavior (Table II), we conclude that *t*-pentyl carbonium ions from the two deaminations are similar. The observation that the ratio of *t*-pentyl substitution product to 2-methyl-1-butene is about 2.0 for the acetic acid deamination of 3-methyl-2-butylamine (Table I) and *t*-pentylamine,[2] but 5.9 for the solvolyis of 3-methyl-2-butyl tosylate (Table II) and 3.2 for the solvolysis of *t*-pentyl bromide[2] in 94% acetic acid[9] supports this conclusion.

The possible role of a hydrogen-bridged intermediate in the deamination of 3-methyl-2-butylamine is unclear.[10] Such a species should favor formation of *t*-pentyl substitution product and 2-methyl-2-butene. Since the intermediates already invoked adequately account for the former and more than account for the latter, no benefit derives from introducing further complications.

Isopentylamine.—Acetic acid deaminations of isopentylamine (Table II), 3-phenyl-1-butylamine,[11] and 1-butylamine[6] yield 60, 62, and 65% nonrearranged substitution product, respectively. The degree of rearrangement is remarkably constant for these deaminations where an initial primary carbonium ion, or precursor thereof, can rearrange to a secondary carbonium ion by hydride shift.[12] The products of this rearrangement are relevant to our argument.

Since isopentylamine furnishes about equal amounts of secondary and tertiary substitution products (Table II), relatively more secondary product is formed than in the acetolysis of 3-methyl-2-butyl tosylate but less than in the deamination of 3-methyl-2-butylamine. One possible explanation is that a hydrogen-bridged intermediate, which produces considerable amounts of secondary substitution product and 3-methyl-1-butene, intervenes between the primary and secondary carbonium ions (Fig. 1). Any carbonium ions formed thereafter are then "normal." Concerted displacement–rearrangement reactions, akin to SN2′ reactions, can also be visualized as leading to 3-methyl-2-butyl product (II).



II

Although arguments such as these, with suitable modifications, will explain all data, we prefer simply postulating open carbonium ions as the prime intermediates. The ratio of secondary to tertiary product suggests that the 3-methyl-2-butyl carbonium ion from isopentylamine is identical to the 3-methyl-2-butyl carbonium ion from neither 3-methyl-2-butyl tosylate nor 3-methyl-2-butylamine, but partakes of some of the properties of each.[13] Such a hybrid 3-methyl-2-butyl species can also rationalize the trace of 1,2-dimethylcyclopropane from the deamination of isopentylamine.

Examination of olefin compositions (Table II) further illuminates the nature of the intermediates in the deamination of isopentylamine. A solvolytic *t*-pentyl carbonium ion produces about three times as much 2-methyl-2-butene as 2-methyl-1-butene (Table II). If a solvolytic *t*-pentyl carbonium ion were formed in the acetic acid deamination of isopentylamine, about 45% 2-methyl-2-butene should be produced from this intermediate (Table II), together with 2-methyl-2-butene from the 3-methyl-2-butyl carbonium ion. Because the 23% 2-methyl-2-butene actually found is not enough to satisfy these conditions, the *t*-pentyl carbonium ion from isopentylamine *cannot* be a normal solvolytic one.[15] This nonsolvolytic *t*-pentyl carbonium ion can be formulated as arising from isopentylamine by successive 1,2-shifts[16] or a single 1,3-shift.[17-19] The absence[11] of 2-phenyl-2-butanol from the deamination of 3-phenyl-1-butylamine implies that the 1,3-shift is unlikely, although it transforms a primary carbonium ion into a tertiary one.

In conclusion, deamination of 1-butyl-,[7] neopentyl-,[2] 3-methyl-2-butyl-, or isopentylamine gives rearranged carbonium ions which differ in behavior from the corresponding solvolytic species. As the water content of the solvent increases in reaction of the last two compounds (Table II), the per cent of rearrangement (at least in substitution product), the ratio of *t*-pentyl to 3-methyl-2-butyl product, and the ratio of 2-methyl-2-butene to 2-methyl-1-butene all increase. Although the first trend presumably arises in part from the diminishing importance of ion-pair reactions,[20] together the three trends may reflect the increasing importance of

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[9] Because of the corrections made in determining the products of the deaminations, we hesitate to put too much reliance on ratios of substitution to elimination.

[10] For an extended discussion of ethylene protonium ions see D. J. Cram and J. Tadanier, *J. Am. Chem. Soc.*, **81**, 2737 (1959).

[11] A. W. Fort and R. E. Leary, *ibid.*, **82**, 2494 (1960).

[12] L. G. Cannell and R. W. Taft, Jr., *ibid.*, **78**, 5812 (1956), report *that i-butylamine in water gives only about 10% nonrearranged substitution product.* The greater amount of rearrangement must at least in part stem from the fact that here a tertiary carbonium ion arises from hydride shift.

[13] A referee has objected to terming this a "warm" 3-methyl-2-butyl carbonium ion.[14]

[14] J. A. Berson and D. A. Ben-Efraim, *J. Am. Chem. Soc.*, **81**, 4094 (1959), considered but discarded "warm" carbonium ions as intermediates in the deamination of *endo*-norbornylamine.

[15] The fact that the ratio of *t*-pentyl substitution product to 2-methyl-1-butene is about 3.1:3.2 in acetic acid somewhat mars the appeal of this argument (see first section of Discussion).

[16] By two migrations concerted with loss of nitrogen from the alkyldiazonium ion [W. H. Saunders, Jr., *J. Am. Chem. Soc.*, **78**, 6127 (1956)], rearrangement from bridged ion to bridged ion,[11] etc.

[17] O. A. Reutov and T. N. Shatkina, *Tetrahedron*, **18**, 237 (1962).

[18] G. J. Karabatsos and C. E. Orzech, Jr., *J. Am. Chem. Soc.*, **84**, 2838 (1962).

[19] P. S. Skell and R. J. Maxwell, *ibid.*, **84**, 3963 (1962).

[20] Two recent reviews of the amine–nitrous acid reaction are (a) J. H. Ridd, *Quart. Rev.*, **15**, 418 (1961) and (b) H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961.

solvolytic carbonium ions in more highly aqueous solvents.

Cyclopropane Formation.[21]—Investigations of cyclopropane formation,[22] 1,3-hydrogen shifts and 1,2-methyl migrations in carbonium ion reactions have undergone a recent renaissance. In the deamination of *n*-propylamine, cyclopropane is formed, 1,3-hydrogen migration occurs and methyl migration is absent.[17,18,23] In the deoxidation of 2-methyl-1-butanol, all three processes take place.[19] A brief study of the deamination of 2-methyl-1-butylamine, which is related to our system of amines, gave results in general agreement with those for the corresponding deoxidation.

Deamination of 3-methyl-2-butylamine affords 15% 1,2-dimethylcyclopropane and less than 1% 2-methyl-1-butyl substitution product, the result of 1,3-hydrogen shift. The hydrogen shift should be insignificant, as it converts a secondary to a primary carbonium ion.[24] 1,2-Methyl migration is undetected, but not unexpected, since the acetolysis of 3-methyl-2-butyl tosylate gives[25] 1–2% methyl migration. Deamination of isopentylamine yields 2% 1,2-dimethylcyclopropane, and no detectable 1,1-dimethylcyclopropane. 1,3-Hydrogen and 1,2-isopropyl shifts have not yet been studied. Table III summarizes the experimental data.

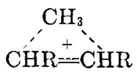
TABLE III

TABULATION OF CYCLOPROPANE FORMATION, 1,3-HYDRIDE SHIFTS AND 1,2-ALKYL MIGRATIONS IN SOME SIMPLE "HOT" CARBONIUM ION REACTIONS[a]

System	Cyclopropanes,[b] %	Shift, % 1,3-H	Shift, % 1,2-R
n-Propyl	10	8–12	0
2-Methyl-1-butyl	4	>1	Much
3-Methyl-2-butyl	15	<1	Probable
Isopentyl	0[c]	?	?
Neopentyl	0	0	100

[a] For references, see text. [b] % of hydrocarbon fraction. [c] No 1,1-dimethylcyclopropane.

Skell[19,22] combines cyclopropane formation and 1,3-hydride shift in, and excludes 1,2-alkyl shifts from, the category of "1,3-interactions." An interplay between 1,2-alkyl shifts and "1,3-interactions" is hinted at in the realization that the greatest cyclopropane formation (Table III) occurs where intermediate III is symmetrical and is expected to have the highest stability relative to its nonbridged isomers.[26] For this and other reasons, we believe that it may be more useful to examine the reasons for the presence or absence of *all three* effects in


R = H, Me

III

any particular reaction. For example, an explanation of why there is no 1,3-hydride shift or cyclopropane formation by the "hot" neopentyl carbonium ion[2,27] should be part of any satisfactory theory. We are unable to offer such a theory at the present.

Comparison to a Similar System.—The 3-methyl-2-butyl, isopentyl series is analogous to the 3-phenyl-2-butyl,[28] 3-phenyl-1-butyl[11] series in many ways. Acetolysis of 3-phenyl-2-butyl tosylate gives almost exclusive phenyl and hydrogen participation, whereas deamination of 3-phenyl-2-butylamine involves phenyl, hydrogen, and methyl participation plus open carbonium ions.[28] These results closely parallel the observation that acetolysis of 3-methyl-2-butyl tosylate proceeds with almost exclusive hydrogen participation,[3,25] while deamination of 3-methyl-2-butylamine gives much more methyl participation (as witnessed by cyclopropane formation) and open carbonium ion reaction. Comparison of Fort and Leary's data[11] for 3-phenyl-1-butylamine with our results with isopentylamine is not so satisfying. Fort and Leary report[11] no 2-phenyl-2-butene, 2-phenyl-2-butanol, or phenylisopropylcarbinol from the deamination of 3-phenyl-1-butylamine. They analyze their data in terms of a 3-phenyl-2-butyl carbonium ion which, surprisingly, shows an even smaller variety of reactions than does the normal solvolytic 3-phenyl-2-butyl carbonium ion. These observations are at variance with those on the isopentyl, 3-methyl-2-butyl, neopentyl[2] and 1-butyl[7] systems, which lack a phenyl group and which yield "hot" rearranged carbonium ions.

Experimental[29]

Materials.—3-Methyl-2-butyl tosylate had m.p. 19–21° (lit.[30] m.p. 20.1–20.8°). Isopentylamine was purchased from Matheson Coleman and Bell. 3-Methyl-2-butylamine, prepared according to Buck and Hjort,[31] had b.p. 85–87° (lit.[32] b.p. 84–87°); the phenyl isocyanate derivative had m.p. 141–143° (lit.[33] m.p. 144°). We attempted to check the purity of the amines with g.l.p.c. The quality of the chromatograms was poor, but each amine appeared to be free of isomeric amines. A mixture of *cis*- and *trans*-1,2-dimethylcyclopropane was prepared[34] and the isomers separated by g.l.p.c. over col. A. The *trans* isomer, b.p.[35] 28.2°, had the lower retention time (*cis*, b.p.[35] 37.0°). The infrared spectrum of the *cis* isomer agreed with the A.P.I. spectrum of the same material. 1,1-Dimethylcyclopropane was prepared according to Shortridge, *et al.*[36]

G.l.p.c.—All chromatograms were run on a Perkin-Elmer 154-C vapor fractometer, utilizing columns A (diisodecyl phthalate), K (Carbowax 1500), and Ag (homemade column containing a saturated solution of silver nitrate in ethylene glycol). Calibration solutions were used throughout to determine retention times and the relative response of the detector to different components.

Acetolysis of 3-Methyl-2-butyl Tosylate.—The procedure was that previously described[2] for the acetolysis of *t*-pentyl bromide. The ester (33.5 g.) was heated at 55° for 4.5 days with 150 ml. of acetic acid and 17.4 g. of potassium acetate. There was obtained 5.7 g. of acetates (30%) and 4.7 g. of olefin (46%). The composition of the acetate was determined on col. A at 100° and the

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[21] A preliminary report of this work has appeared: M. S. Silver, *J. Am. Chem. Soc.*, **82**, 2971 (1960).

[22] The work of P. S. Skell and I. Starer, *ibid.*, **84**, 3962 (1962), demonstrates that cyclopropane formation is not the result of a carbene intermediate.

[23] P. S. Skell and I. Starer, *ibid.*, **82**, 2971 (1960).

[24] Because the deamination of 2-methyl-1-butylamine gives primarily rearranged products, a small amount of 1,3-hydride shift cannot be excluded.

[25] A. J. Finlayson and C. C. Lee, *Can. J. Chem.*, **37**, 940 (1959).

[26] III is also helpful in interpreting the ratio of *trans* to *cis* 1,2-dimethylcyclopropane.

[27] P. S. Skell, I. Starer, and A. P. Krapcho, *J. Am. Chem. Soc.*, **82**, 5257 (1960). 1,2-Methyl migration to give the *t*-pentyl carbonium ion may be so favorable that hydride shift cannot compete; III will be highly asymmetric if it is present.

[28] D. J. Cram and J. E. McCarty, *ibid.*, **79**, 2866 (1957).

[29] Typical procedures are given.

[30] S. Winstein and H. Marshall, *J. Am. Chem. Soc.*, **74**, 1120 (1952).

[31] J. S. Buck and A. M. Hjort, *ibid.*, **59**, 2567 (1937).

[32] D. Trasciatti, *Gazz. chim. ital.*, **29**, **II**, 92 (1899) [*Chem. Zentr.*, **70**, **II**, 801 (1899)].

[33] A. Mailhe, *Bull. soc. chim. France*, **29**, 219 (1921).

[34] Procedure of J. D. Bartleson, R. E. Burk, and H. P. Lankelma, *J. Am. Chem. Soc.*, **68**, 2513 (1946).

[35] R. G. Kelso, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *ibid.*, **77**, 1751 (1955).

[36] R. W. Shortridge, *et al.*, *ibid.*, **70**, 946 (1948).

composition of the olefin on col. A at room temperature. Comparison of the infrared spectra of the reaction products and standard solutions confirmed the g.l.p.c. analysis.

Deamination Reactions.—The procedure was that previously described[2] for the deamination of *t*-pentylamine. Realization that some of the reaction products were unstable led us to settle on a standard reaction of 20 g. of C_5-amine and 30 g. of sodium nitrite. This standardization simplified the application of corrections for product instability. Some early runs were not run under standard conditions. Product analysis was primarily by g.l.p.c. Col. A at 100° readily resolved tertiary and secondary products and isopentyl acetate. However, isopentyl alcohol had the same retention time as *t*-pentyl acetate on col. A and was determined with col. K at 70°. For ease in tabulation, we report only the sum alcohol plus ester in Tables I and II. Col. A at room temperature clearly resolved 3-methyl-1-butene, 2-methyl-2-butene, and 2-methyl-1-butene.

Substitution Products from the Deamination Reaction.—A mixture (7 g.), 53% *t*-butyl alcohol and 47% *t*-butyl acetate, was treated with 17 g. of 2-butylamine and 30 g. of sodium nitrite in 200 ml. of 75% acetic acid. The recovered ester–alcohol layer contained these materials in the relative amounts 52.5% and 47.5%, respectively. From this and earlier work[2] we deduce that *t*-pentyl alcohol and acetate are entirely stable under the reaction conditions. However, many control studies indicated that the primary and secondary alcohols are partially destroyed during the course of the deamination (oxidation?) while the corresponding acetates are stable. The destruction amounted to about 0.8–0.9 g. of alcohol, and appeared to be fairly independent of solvent, the nature of the alcohol, or the amount of alcohol initially present. We assumed that 0.9 g. of 3-methyl-2-butanol and isopentyl alcohol were destroyed in each deamination in determining the corrected composition of the alcohol–ester fraction (Table II). Here is an example of controls on the destruction of isopentyl alcohol: 10 g. and 6 g. of a solution which was 26% isopentyl alcohol (E) and 74% isopentyl acetate (F) were treated with 19.5 ml. of isopropylamine and 30 g. of sodium nitrite in 200 ml. of acetic acid. The recovered ester–alcohol layer from the former showed 20% E, 80% F, and from the latter, 17% E, 83% F, corresponding to losses of 0.8 g. and 0.7 g., respectively. In the same way 4.6 g. and 3.3 g. of a solution which was 81% 3-methyl-2-butanol (G) and 19% 3-methyl-2-butyl acetate (H) was treated with 19.5 ml. of isopropylamine and 30 g. of sodium nitrite in 300 ml. of 50% acetic acid. The recovered ester–alcohol layer from the former showed 76% G, 24% H and from the latter, 75% G, 25% H, corresponding to losses of 0.9 g. and 0.8 g., respectively, of 3-methyl-2-butanol. G.l.p.c. analyses of a few of the alcohol–ester fractions were confirmed by infrared analyses.

An effort was made to determine if 2-methyl-1-butyl acetate was formed in the deamination of 3-methyl-2-butylamine in acetic acid. On col. A at 100°, a small peak appeared in the chromatogram of the reaction mixture at the same retention time as this ester. On col. K at 75°, there was a very slight bump in the chromatographic curve of the reaction mixture at the point where this ester should appear. By observing the chromatogram of the reaction mixture to which a known amount of 2-methyl-1-butyl acetate had been added, it was determined that less than 1% of this ester could have been originally present.

Olefins from the Deamination Reaction.—We previously reported[2] that, in the deamination of *t*-pentylamine, some fractionation occurs between 2-methyl-2-butene and 2-methyl-1-butene. Similar effects were encountered in the present work. In 200 ml. of acetic acid were placed 18 g. of 2-butylamine and 3.9 g. of a mixture which was 22% 2-methyl-1-butene (B), 42% 2-methyl-2-butene (C), and 37% 3-methyl-1-butene (D). After the addition of 30 g. of sodium nitrite, the per cents were 24, 32, and 45, respectively. A duplicate run gave values of 24, 34, and 42. These particular controls were used to correct the olefin composition from the deamination of 3-methyl-2-butylamine in acetic acid. In another control run, 18 g. of *n*-butylamine and 3.2 g. of a mixture which was 13% B, 13% C, and 74% D were treated with 30 g. of sodium nitrite. The recovered olefin had per cents 14, 3, and 83, respectively, and a duplicate run gave values of 15, 6, and 79. These controls were applied to the deamination of isopentylamine in acetic acid. In agreement with previous experiments,[2] fractionation of olefin decreased with decreasing acetic acid content of the solvent. For example, a mixture (3.2 g.) which was initially 15% B, 14% C, and 72% D was 16% B, 12% C, and 72% D after treatment with 18 g. of *n*-butylamine and 30 g. of sodium nitrite in 300 ml. of 50% acetic acid. No controls were run for olefin destruction in 25% acetic acid or for runs 9 and 12 of Table I (see Results). Infrared analysis of some reaction mixtures confirmed the correctness of the g.l.p.c. analysis.

1,2-Dimethylcyclopropane from the Deamination of 3-Methyl-2-butylamine.—With col. K and Ag in series, g.l.p.c. cleanly separated *cis*- and *trans*-1,2-dimethylcyclopropane from the other C_5H_{10} hydrocarbons present and from each other. The C_5H_{10} fraction from the deamination showed peaks with retention times corresponding to those of the cyclopropanes. In operations with other g.l.p.c. columns, these peaks behaved entirely in accord with this assignment. When the C_5H_{10} fraction was stirred with aqueous permanganate for 23 hr. at 25°, the band assigned to the *trans* isomer increased to 61% from 10%. At the time of this experiment, we had not yet found a way to separate the *cis* isomer from 2-methyl-2-butene. After permanganate treatment, this composite band had also increased in size, in agreement with the supposition that *cis*-1,2-dimethylcyclopropane was present. The infrared spectrum of the hydrocarbon recovered from the permanganate treatment was nearly identical to that of a mixture of 66% *trans*- and 34% *cis*-1,2-dimethylcyclopropane. The slight differences in the two spectra were readily accounted for by the small amounts of C_5H_{10} olefin that had survived the permanganate treatment.

1,2-Dimethylcyclopropanes from the Deamination of Isopentylamine.—Consideration of the C_5H_{10} fraction from this reaction, in the manner outlined, indicated the possibility of the presence of traces of 1,2-dimethylcyclopropanes. Many passes of small samples of the hydrocarbon fraction from one deamination through col. Ag enabled us to collect a dilute solution of the cyclopropanes in carbon tetrachloride. The infrared spectrum of this solution confirmed the formation of 1,2-dimethylcyclopropanes. We were unable to detect with g.l.p.c. any 1,1-dimethylcyclopropane in the C_5H_{10} fraction.