The Behavior of the *t*-Pentyl Cation as Produced in Deaminations and Halide Solvolyses[1]

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The products from the reactions of some *t*-pentyl and neopentyl derivatives in aqueous acetic acid solutions have been determined. Both neopentyl tosylate and *t*-pentyl halides give the same olefin fraction, consisting of approximately 75% trimethylethylene and 25% 2-methyl-1-butene. Deamination of neopentylamine and *t*-pentylamine gives olefin with a higher content of 2-methyl-1-butene than is encountered in the halide solvolyses. The composition of the olefin fraction from both the deaminations and the halide solvolyses is rather insensitive to changes in the reaction conditions. The possibility that some capacity for unusual reaction in deaminations can be retained in a carbonium ion formed *via* rearrangement is examined and the origin of the products in deaminations and the effect of solvent changes on these products are discussed.

The amine-nitrous acid reaction has been widely used as a means of apparently generating carbonium ions in an irreversible manner. Despite extensive investigation, considerable doubt exists on the nature of this reaction,[2,3] particularly with respect to the origin of the "unusual" products that often accompany a deamination. These products are termed unusual in that they either are not formed[4] or are formed in different amounts in the comparable solvolysis.[5,6] The unusual occurrences in amine-nitrous acid reactions are generally considered to be closely associated with the dissociation of the postulated intermediate alkyldiazonium ion to nitrogen and a carbonium ion (I), a process presumably having an activation energy lower than that for the analogous step in

$$RN_2^+ \longrightarrow R^+ + N_2 \qquad ROC^+ \longrightarrow R^+ + CO$$
$$\text{I} \hspace{4cm} \text{II}$$

halide solvolyses.[2,3] However, a difference of opinion exists as to whether unusual reactions are best visualized as proceeding simultaneously with[2] or subsequent to[3] the loss of nitrogen from the alkyldiazonium ion. Recently, Skell and Starer[4b,7] proposed a similarity between alcohol deoxideations (II) and amine deaminations, based on the resemblance between the products from the two reactions.

The experiments reported herein were undertaken with several purposes in mind. First, it seemed desirable to determine the products of a series of related deaminations and halide solvolyses under similar reaction conditions. Observations on the effect of solvent changes upon these products might prove interesting. In addition, the system chosen (*vide infra*) seemed suitable for comparing β-deuterium isotope effects on E1 elimination in halide solvolysis and deamination reaction.[8] Lastly,

we wished to determine whether a capacity for unusual behavior in deaminations is associated exclusively with the cation derived without rearrangement from alkyldiazonium ion, or a cation derived by methide or hydride rearrangement might also exhibit unusual behavior — is $R_2'-\overset{+}{C}-CRR_2''$ of III necessarily the same regardless of whether it is formed from the chloride or the alkyldiazonium ion?[6]

The system chosen for this study was a family of related pentyl cations, schematically diagrammed

$$(CH_3)_3CCH_2^+ \longrightarrow (CH_3)_2\overset{+}{C}CH_2CH_3 \longleftarrow$$
$$(CH_3)_2CH\overset{+}{C}HCH_3 \longleftarrow (CH_3)_2CHCH_2CH_2^+$$
$$\text{IV}$$

in IV, which appeared to offer many opportunities for exploring the reactions of carbonium ions of the same gross structure, formed by different routes. This system has the advantage that the solvolyses of *t*-pentyl,[9] neopentyl,[10] and 3-methyl-2-butyl[11] halides have been the subject of careful investigation and many of the aspects of these reactions are rather well understood. Our results of the deamination of neopentyl and *t*-pentylamines and the solvolysis of neopentyl and *t*-pentyl halides form the substance of this communication.

Results and Discussion

Table I records the composition of the products from the solvolysis of some *t*-pentyl and neopentyl compounds as taken from the present work (vapor phase chromatographic and infrared analyses) and from the literature. Only substitution products with the *t*-pentyl skeleton have been detected in these reactions.[9,12]

(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) A. Streitwieser, Jr., *J. Org. Chem.*, **22**, 861 (1957).

(3) D. J. Cram and J. E. McCarty, *J. Am. Chem. Soc.*, **79**, 2866 (1957).

(4) A recent example is the formation of cyclopropanes in the deamination of some simple aliphatic amines; (a) M. S. Silver, *ibid.*, **82**, 2971 (1960); (b) P. S. Skell and I. Starer, *ibid.*, **82**, 2971 (1960).

(5) For the sake of brevity, substrates with a halide or (substituted) benzenesulfonate leaving group will often be referred to collectively as halides.

(6) This is how unusual behavior is defined for the purposes of this paper. Deaminations and halide solvolyses will be compared only where the latter reasonably can be expected to have appreciable SN1 character.

(7) P. S. Skell and I. Starer, *J. Am. Chem. Soc.*, **81**, 4117 (1959).

(8) M. S. Silver, *ibid.*, **83**, 3487 (1961).

(9) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, chapters 5-7.

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

(11) S. Winstein and J. Takahaski, *Tetrahedron*, **2**, 316 (1958).

(12) (a) F. C. Whitmore and G. H. Fleming, *J. Chem. Soc.*, 1269 (1934), reported that the reaction of neopentyl iodide with silver acetate in acetic acid at 60° gave no neopentyl acetate, some *t*-pentyl acetate and mainly trimethylethylene; (b) M. Freud and F. Lenze, *Ber.*, **24**, 2150 (1891), reported the formation of *t*-pentyl alcohol in the deamination of neopentylamine.

Effect of Structure and Leaving Group on Products.—The compositions of the olefins from the solvolysis of the *t*-pentyl and neopentyl halides are essentially identical and relatively independent of the reaction conditions (Table I). This observation suggests a precursor for olefin production which is common to both reactions and rules out any bridged methylcarbonium ion (V) which may be

$$CH_3$$
$$(CH_3)_2C \xrightarrow{\;+\;} CH_2$$
$$V$$
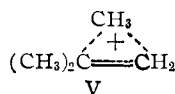
implicated[10] in neopentyl tosylate solvolysis as an important immediate precursor for olefin formation.[13,14] The classical *t*-pentyl carbonium ion

TABLE I

COMPOSITION OF THE PRODUCTS FROM THE REACTION OF SOME *t*-PENTYL AND NEOPENTYL DERIVATIVES[a]

Compound[b]	Conditions[g]	% (CH₃)₂C= CHCH₃[h]	% Olefin[i]	% Substitution[j,k]
t-Br	HOAc	74	68	22
t-Br	94% HOAc	77	45	33
t-Br[c]	EtOH (25°)	82	..	..
t-Cl[d]	HOAc (75°)	69	..	..
t-Cl	75% HOAc	80	..	..
t-Cl	50% HOAc (78°)	79	..	..
neo-OTs	50% HOAc (78°)	76	7	52
t-SMe₂[e]	97% EtOH (50°)	87	..	..
t-SMe₂OEt[e]	97% EtOH, NaOEt (24°)	14	..	..
t-NH₂	HOAc	37[i]	23	29
t-NH₂	75% HOAc	36[i]	..	..
t-NH₂	50% HOAc	42[i]	19	48
t-NH₂	H₂O	39	5	80
t-NH₂	H₂O + NaSCN	45	..	..
neo-NH₂	HOAc	60[i]	18	40
neo-NH₂	50% HOAc	64[i]	..	..
t-OH[f]	*t*-OH (reflux)	20	..	..
neo-OH[f]	*neo*-OH (reflux)	32	..	..

[a] This work unless otherwise noted. [b] *t* = *t*-pentyl, *neo* = neopentyl. [c] M. L. Dhar, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2065 (1948). [d] Ref. 11. [e] E. D. Hughes, C. K. Ingold and L. I. Woolf, *J. Chem. Soc.*, 2084 (1948). [f] Ref. 7. [g] Temperature is 57° unless specified; mixed solvents all contain H₂O as other constituent. [h] % of olefin that was trimethylethylene; other component 2-methyl-1-butene. [i] Corrected for selective destruction of trimethylethylene. [j] % of theoretical yield isolated, based on unrecovered starting material. [k] Depending on conditions, this was *t*-OAc and/or *t*-OH; it should be noted that H₂O is formed during the course of deaminations in HOAc.

is a reasonable formulation for the common precursor. Such a cation, which characteristically gives a three to one ratio of trimethylethylene to 2-methyl-1-butene, will be described here as a "normal" *t*-pentyl cation. A *t*-pentyl cation which affords a different olefin ratio under comparable conditions (our experiments only) will be termed "unusual."

By these definitions, the *t*-pentyl carbonium ion produced by deamination of *t*-pentylamine and neopentylamine is unusual, since both reactions

(13) Cram and McCarty[8] have discussed bridged methylcarbonium ions as intermediates and transition states.

(14) D. J. Cram, *J. Am. Chem. Soc.*, **74**, 2137 (1952), has developed some evidence against concerted (non-bridged) proton loss and opening of a phenyl- or hydrogen-bridged carbonium ion in the 3-phenyl-2-butyl system.

yield olefin containing appreciably less than 75% trimethylethylene. In general, where a particular carbocation can give two alternative olefins, formation of the cation by deamination will produce less of the more highly substituted olefin than formation by halide solvolysis. Table II shows that the 2-butyl cation from 2-butylamine or isobutylamine[15] gives a smaller ratio of 2-butene/1-butene than does that from 2-butyl tosylate. Deoxideations appear to have an even greater tendency to favor formation of the less highly substituted olefin (Table I), the loss of protons approaching statistical distribution. A detailed discussion of deoxideations has not yet been published by Skell and Starer.[7]

TABLE II

OLEFIN COMPOSITION FROM THE REACTION OF SOME BUTYL DERIVATIVES

Reactant	Conditions	2-Butene / 1-Butene	trans-2-Butene / cis-2-Butene
2-BuOTs[a]	HOAc, 118°	9.0	1.1
2-BuNH₂[b]	H₂O, 25°	3.0	2.9
1-BuNH₂[b]	HOAc, 25°	0.4	2.2
i-BuNH₂[c]	H₂O, 38°	2.7	1.3

[a] H. C. Brown and I. Moritani, *J. Am. Chem. Soc.*, **77**, 3607 (1955). [b] A. Streitwieser, Jr., and W. D. Schaeffer. *ibid.*, **79**, 2888 (1957). [c] Ref. 31; isobutylene also was formed.

Transference of Unusual Behavior.—The idea that cations formed by rearrangement in deaminations may manifest unusual behavior is mildly supported by the following observations: (a) isobutylamine[15] and neopentylamine produce proportions of 2-butene and trimethylethylene, respectively, that are possibly indicative of unusual 2-butyl and *t*-pentyl cations (*vide supra*); (b) 1- and isobutylamine give relatively high ratios of *trans*- to *cis*-2-butene, again suggesting an unusual 2-butyl cation[15] (Table II); (c) the olefin from isopentylamine (hydride shift to the 3-methyl-2-butyl cation) contains 1.5% 1,2-dimethylcyclopropane, indicating an unusual 3-methyl-2-butyl cation.[4a,16]

Whether it is better to represent formation of these potentially unusual rearranged carbonium ions as a two-step or a concerted one-step process from the alkyldiazonium ion (see III) is unclear; one can imagine even more complex processes.
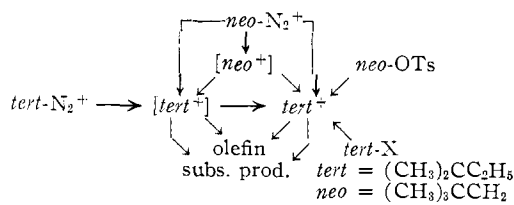
Comparison of the *t*-pentyl cation from neopentylamine to that from *t*-pentylamine suggests that the carbocation produced by rearrangement is not so unusual as structurally the same cation formed without rearrangement. The value of this generalization is limited by the report[7] that deoxideation of 1-, 2- and isobutanols gives essentially the same ratio of *cis*- to *trans*-2-butene. A normal or an equally unusual 2-butyl cation apparently is formed

(15) The 2-butyl cation can be formed directly (2-aminobutane), by hydride shift (1-aminobutane) and by methide shift (isobutylamine). The comparison ignores effects of different reaction conditions and the fact that in several instances the stabilities of the products under the reaction conditions were apparently not established.

(16) The olefin from the deamination of 3-methyl-2-butylamine contains 15%, and that from acetolysis of 3-methyl-2-butyl tosylate, 0%, 1,2-dimethylcyclopropane.[4a] In the tosylate solvolysis, only a small fraction goes *via* the classical 3-methyl-2-butyl cation[11] and a slight amount of methyl participation occurs [A. J. Finlayson and C. C. Lee, *Can. J. Chem.*, **37**, 940 (1959)].

both directly and by rearrangement in the last deoxideations.

Origin of Products. Assumptions.—Diagram VI has been constructed to serve as a basis for discussion of the origin of the products in the amine–nitrous acid reaction.

$$
\begin{array}{c}
\text{neo-N}_2{}^+ \\
\downarrow \\
[neo^+] \quad\quad neo\text{-OTs} \\
tert\text{-N}_2{}^+ \longrightarrow [tert^+] \longrightarrow tert^+ \\
\text{olefin} \quad tert\text{-X} \\
\text{subs. prod.} \quad tert = (CH_3)_2CC_2H_5 \\
neo = (CH_3)_3CCH_2
\end{array}
$$

VI

This highly schematic representation of the reaction system employs hot carbonium ion ($=$ bracketed ion) terminology for convenience. Discussion in terms of alkyldiazonium ions would do about as well, subject to the observations on rearranged cations made previously. Various optional paths are given to the neopentyldiazonium ion since it cannot afford either $[tert^+]$ or $tert^+$ exclusively.

Olefin production from any unusual discrete methyl-bridged carbonium ion involved in the deamination of neopentylamine has been assumed to be insignificant. Our present inability to formulate precise paths for the course of solvolytic reactions (cf. ref. 11) makes it difficult either to prove or disprove this assumption. The failure to detect 1,1-dimethylcyclopropane in the deamination of neopentylamine or the deoxideation of neopentyl alcohol might be offered as a weak argument against V as an immediate precursor of olefin in the unusual reactions. Certainly, the argument against such a process in the neopentyl tosylate solvolysis cannot validly be applied to the neopentylamine deamination. Production of olefin from bridged ion V should greatly disfavor formation of trimethylethylene, since the two methylene hydrogens of V are in a geometrically unfavorable position for elimination.[14] The small deficiency in trimethylethylene from neopentylamine could thus be attributed to elimination from V. The (relatively) high ratio of 1-butene to 2-butene in the olefin from the deamination of isobutylamine (Table II) could likewise be ascribed to elimination from a methyl-bridged ion similar to V, geometrical factors again intervening.

The difference between the olefins from deamination of t-pentylamine and from the solvolysis of t-pentyl halides is not unlike the difference between the olefins from E2, Hofmann-rule, and E1, Saytzeff-rule, elimination with t-C$_5$H$_{11}$SMe$_2$ (Table I).[17] However, the general nature of the amine–nitrous acid reaction,[2,3] the conditions under which these deaminations have been performed, and the small size of the β-deuterium isotope effect upon elimination in the deamination of t-pentylamine justify omitting E2 contributions to VI.

Scheme VI ignores the fact that the halide solvolyses proceed to an ion-pair while the deaminations probably primarily do not, under our conditions.[18] Possible justification for this simplification

is the fact that the E1 reactions of t-pentyl chloride and dimethylsulfonium iodide give olefin of about the same composition (Table I).

Origin of Products. Discussion.—In terms of VI, four extreme pathways for the formation of products in deaminations can be visualized: (a) substitution products arise from a normal cation, e.g., $tert^+$; (b) substitution products arise from an unusual cation, e.g., $[tert^+]$; (c) olefins arise from a normal cation; (d) olefins arise from an unusual cation. Examination reveals that a combination of these interpretations generally is required to explain the experimental data, although a single extreme may be approached under suitable circumstances.

Young and co-workers[19] have compared the substitution products from the deamination and solvolysis of several related allylic amines and halides. On reaction in acetic acid XI and XII yield the same acetate mixture, which is 60% primary acetate, while XIII gives 80% and XIV 33% primary acetate.[19a] The deaminations involve much substitution on a hot cation with localized positive charge, favoring non-rearranged product (path b).[19a] On reaction in water, VII–X provide the same mixture of product alcohols. Presumably the majority of the substitution product from the deaminations now arises from a normal cation (path a), with its delocalized positive charge providing the same mixture of rearranged and non-rearranged product encountered in the halide solvolyses. A further example of reaction predominantly by path a is the report[20] that the aqueous deamination of isobutylamine and t-butylamine and the hydrolysis of t-butyl chloride in the presence of thiocyanate give nearly the same ratio of t-BuSCN/t-BuNCS.

Since deaminations typically give olefins of composition different from that of olefins produced in halide solvolyses, olefin formation by (c) alone cannot be commonly realized. A modification of (d) should be considered. The relative invariance in the composition of the olefin from the deamination of t-pentylamine and neopentylamine (Table I) over the range of solvents studied[21] suggests that each unusual reaction may yield a characteristic hot carbonium ion, whose presence is indicated by the formation of olefin of a particular composition. This invariance in olefin composition seems to us a mere coincidence, resulting from a fortuitous combination of circumstances. All aspects of the deamination of t-pentylamine are surely not insensitive to solvent changes, since the deamination in

tions is not clear at present. This potential perturbation should be kept in mind, especially in the discussion of the substitution reaction. See (a) R. Huisgen and C. Ruchardt, *Ann.*, **601**, 1 (1956); (b) A. Streitwieser, Jr., and C. E. Coverdale, *J. Am. Chem. Soc.*, **81**, 4275 (1959); (c) H. Felkin, *Bull. soc. chim. France*, 1582 (1960); (d) ref. 19a.

(19) (a) D. A. Semenow, C.-H. Shih and W. G. Young, *J. Am. Chem. Soc.*, **80**, 5472 (1958); (b) R. H. DeWolfe and W. G. Young, *Chem. Revs.*, **56**, 753 (1956).

(20) L. G. Cannell and R. W. Taft, Jr., Abstracts of Papers Presented at the 129th Meeting of the American Chemical Society, Dallas, April, 1956, p. 46-N.

(21) The immunity of certain aspects of deaminations to solvent changes often has been commented upon. See, for instance, the rearrangement in the deamination of p-X-C$_6$H$_4$CH$_2$CH$_2{}^*$NH$_2$ in water and acetic acid; J. D. Roberts and C. M. Regan, *J. Am. Chem. Soc.*, **75**, 2069 (1953).

(17) Reference 9, pp. 173-179.

(18) The role of ion-pairs and frontside displacements in deamina-

water gives an 80% yield, but in acetic acid only a 29% yield of substitution product.

The course of deaminations is probably best interpreted in terms of a variety of cations being initially formed and undergoing varying degrees of solvation to give rise to a whole spectrum of carbonium ions. There are many pathways, some of which may not be available to normal cations, open to these deaminative cations, including routes a through d (*cf.* ref. 2, 18b). Since the favored routes are determined by the interaction of several variables, prediction of the outcome of a deamination is extremely difficult.

		$CH_3CR=CHCH_2Y$	$CH_3CRYCH=CH_2$
R = CH₃,	Y = Cl	VII	VIII
	Y = N₂⁺	IX	X
R = H,	Y = Cl	XI	XII
	Y = N₂⁺	XIII	XIV
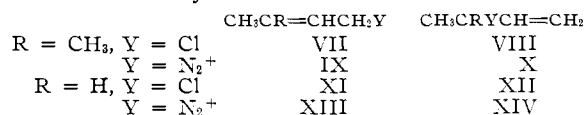
Solvent Effects on Deaminations.—The greater nucleophilicity of water relative to acetic acid leads one to predict, for deaminations, a greater tendency for non-rearrangement in more aqueous solvents, as is indeed observed in normal halide solvolyses.[22] Young has shown that in water, XI and XIII, XII and XIV each give the same product mixture (the products of the primary and secondary reactants differ somewhat).[19a] In acetic acid, chlorides XI and XII give the same products but amines XII and XIV give excessive amounts of *unrearranged* product.[18,19a] The effect of changing the solvent is, if anything, opposite from what is predicted. The observations can be rationalized by postulating that the greater cation-solvating power of water relative to acetic acid (assuming this exists[23]) increases the lifetime of the carbonium ions sufficiently to allow them to achieve their normal planar, resonance-stabilized configurations. In terms of VI, some direct substitution on the hot carbonium ion occurs in acetic acid and the change to water as solvent favors the route hot ion to normal ion more than the route hot ion to substitution product. The report[24] that deamination of optically active 2-butylamine gives a little more net · inversion in acetic acid than in water could also be rationalized along these lines.

If the transition from acetic acid to water favors the formation of normal, solvolytic cations, we might expect the composition of the olefin from deaminations in more aqueous systems to approach the composition of the olefin from halide solvolyses. This is not observed in the deamination of neopentyl-amine and *t*-pentylamine. The realization that the more highly solvated cations produced in such profusion by deamination in highly aqueous media are greatly predisposed to give substitution product provides a possible rationalization. It is conceivable that the proportion of the total olefin formed from the different categories of carbonium ions might hold relatively constant during these solvent changes with the result that the increased importance of the reaction pathway *via* solvolytic cation in

(22) L. de Vries and S. Winstein, *J. Am. Chem. Soc.*, **82**, 5363 (1960), and references therein.

(23) E. Grunwald, G. Baughman and G. Kohnstam, *ibid.*, **82**, 5801 (1960), have concluded that "small cations are *not* solvated preferentially by water molecules" in 50% aqueous dioxane.

(24) K. B. Wiberg, Ph.D. Thesis, Columbia University, July, 1950 (cited in ref. 2).

water would not be reflected by a change in olefin composition.

Experimental[25]

Materials.—The *t*-pentylamine was prepared by alkaline hydrolysis of *t*-pentyl urea,[26] and had b.p. 77–78° (lit.[26] b.p. 78°). Neopentylamine was prepared by conversion of trimethylacetamide to pivalonitrile and reduction of the nitrile with lithium aluminum hydride.[27] The amine had b.p. 79–82°, $n^{20}D$ 1.4031, picrate m.p. 203–205° from benzene (lit.[27] b.p. 80°, $n^{25}D$ 1.4000, picrate m.p. 204–205° from benzene). The *t*-pentyl halides were prepared in the conventional manner from *t*-pentyl alcohol and a concentrated aqueous solution of the appropriate hypohalous acid.[28] The bromide had b.p. 68–71° (about 160 mm.) and the chloride had b.p. 84–86° (lit.[29] b.p. 86°). The purity of the halides was checked with v.p.c. The bromide may have had as much as 2% olefin in it, primarily trimethylethylene. Different preparations of the chloride all had less than 1% olefin. The detection of small amounts of olefin with v.p.c. may have been at least partially caused by decomposition of the halide during the chromatogram, especially with the bromide. Neopentyl tosylate[30] had m.p. 47–48° (lit.[30] m.p. 48–49°). Dry acetic acid was prepared by heating glacial acetic acid and acetic anhydride under reflux and then distilling. Reagent grade acetic acid was used in many runs. Other chemicals were commercial samples.

Analysis of Reaction Mixtures.—Product compositions were determined by v.p.c. and many were checked by comparing infrared spectra of synthetic mixtures and reaction samples. It was shown by preparing samples of known composition that the peak areas recorded by v.p.c. accurately reflected the weight % composition.

Solvolysis of *t*-Pentyl Bromide.—A 1-liter two-necked round-bottomed flask, equipped with magnetic stirrer, glass stopper and outlet tube attached to two Dry Ice-cooled traps, was immersed in a small heated oil-bath. The magnetic stirrer could agitate the contents of the flask through the oil-bath and this setup, with modifications, was used in all studies. In the flask were placed 20 g. (0.20 mole) of potassium acetate and 150 ml. of dry acetic acid. Stirring was started and the bath temperature raised to 57° (± 1). The *t*-pentyl bromide (26 g., 0.17 mole) was introduced into the reaction flask and heating maintained for 8 hours. The heating bath was replaced by an ice-bath and the stopper by a dropping funnel, and a solution of 110 g. of sodium hydroxide in 500 ml. of water was added slowly. The dropping funnel was replaced by a gas inlet tube which reached below the surface of the solution and nitrogen was bubbled through the system. The traps contained 10.0 g. of material, some of which was olefin. The v.p.c. showed that 76% of the olefin was trimethylethylene and 24% 2-methyl-1-butene. The aqueous solution in the reaction flask was separated from the organic layer (3.3 g., primarily *t*-pentyl acetate) and was extracted with ether. The ether extracts yielded perhaps 0.3 g. more of *t*-pentyl acetate. Distillation of the material that had been isolated from the Dry Ice traps gave 8.5 g. of olefin and a residue of 1.5 g., primarily *t*-pentyl acetate but containing about 17% olefin (total olefin, 8.75 g.). Correction for possible olefin in the starting bromide was made. The assumption that 0.5 g. of olefin was initially present and that it was about 90% trimethylethylene reduces the yield of olefin from the solvolysis to 8.25 g. (68%) of which 73.5% is trimethylethylene. This is the maximal correction and the composition of the olefin fraction was taken as 74% trimethylethylene. The yield of *t*-pentyl acetate was 5 g. (22%).

The procedure was repeated, using as solvent 150 ml. of dry acetic acid and 10 ml. of water and starting with 25 g. of bromide. The purpose of this run was to determine if the presence of water (produced during deaminations) in acetic acid could affect the olefin to be expected from the normal

(25) All melting points and boiling points are uncorrected. Typical procedures are given.

(26) D. E. Pearson, J. F. Baxter and K. N. Carter, *Org. Syntheses*, **29**, 21 (1949).

(27) D. Y. Curtin and S. M. Gerber, *J. Am. Chem. Soc.*, **74**, 4052 (1952).

(28) J. F. Norris and A. W. Olmstead in "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 144.

(29) A. Wischnegradsky, *Ann.*, **190**, 328 (1877).

(30) S. Winstein, *et al.*, *J. Am. Chem. Soc.*, **74**, 1113 (1952).

reaction. The bromide used contained less than 1% olefin, which was about 90% trimethylethylene. There were isolated from the reaction 5.2 g. (45%) of olefin which was 77% trimethylethylene and about 6.5 g. of a mixture of t-pentyl acetate and t-pentyl alcohol; yield of acetate 23%, of alcohol 10% by v.p.c.

Solvolysis of t-Pentyl Chloride.—The usual apparatus was modified by interposing a reflux condenser between the reaction flask and the gas outlet tube. For 50% acetic acid, 200 ml. of water and 200 ml. of glacial acetic acid were used; for 75% acetic acid, 300 ml. of glacial acetic acid and 100 ml. of water were used. The solvent contained 1 g. of potassium acetate per gram of chloride to be solvolyzed. No attempt was made to isolate substitution products. The workup procedure was to add 400 ml. of water, sweep with nitrogen and analyze the crude olefin from the Dry Ice traps by v.p.c. This was far from a quantitative isolation, but it gave an accurate value for the composition of the olefin fraction (*vide infra*).

Solvolysis of Neopentyl Tosylate.—An inhomogeneous mixture of 35 g. of the ester, 18 g. of potassium acetate, 200 ml. of water and 200 ml. of dry acetic acid was stirred in the usual apparatus at 78° for 90 hours. Neutralization of the acid and sweeping with nitrogen gave 0.4 g. (4%) of olefin (75.8% 2-methyl-2-butene). There were also isolated 14.9 g. (42.5%) of recovered ester and 3.8 g. (30%) of t-pentyl alcohol. No t-pentyl acetate was detected.

Deamination Reactions.—The setup described for the solvolysis of t-pentyl bromide was modified by replacing the stopper with a piece of wide rubber tubing attached to a flask containing sodium nitrite. The gas outlet tube from the reaction flask was connected to a trap containing potassium carbonate, then successively to two Dry Ice–cooled traps, an alkaline permanganate trap and a calibrated flask for measuring gas volume (gas collected over dilute sodium hydroxide). Starting with 23.6 g. (0.27 mole) of t-pentylamine, 34 g. (0.49 mole) of sodium nitrite slowly was added. At the end of this addition, the actic acid was a very thick slurry and 6 liters of gas (83%) had been collected. The work-up procedure was similar to that described for the solvolysis of t-pentyl bromide. The ester and alcohol product mixture was distilled and 3.5 g. of high boiling residue was encountered. Shaking the crude ester–alcohol mixture with dilute hydrochloric acid before distillation and neutralization of the acid extract afforded unreacted amine. This run gave 12.2% recovered amine, 13.6% t-pentyl acetate, 7.1% t-pentyl alcohol and 26.9% olefin (69.5% 2-methyl-1-butene). A similar run with 25 g. of amine and 30 g. of sodium nitrite yielded values of 25, 10.3, 6.6 and 21.2% (69.7% 2-methyl-1-butene), respectively.

Several deaminations were carried out in which only the olefin was isolated, by a procedure analogous to that described for the solvolysis of t-pentyl chloride. These include (Table I) t-pentylamine in glacial acetic acid (twice, 2-methyl-1-butene 70.1% and 68.9%), in 75% acetic acid (70.8% 2-methyl-1-butene) and in 50% acetic acid (59.5% 2-methyl-1-butene), and neopentylamine in 50% acetic acid (38.0% 2-methyl-1-butene). A deamination of t-pentylamine was carried out[31] in aqueous perchloric acid and the t-pentyl alcohol formed was isolated. A deamination of t-pentylamine in water plus sodium thiocyanate was performed[20] and only the olefin was isolated.

Control 1.—This control demonstrates that the procedure by which the substitution product is isolated results in a good recovery of t-pentyl acetate and alcohol but a poor re-

covery of olefin. In the general deamination apparatus were placed 150 ml. of acetic acid, 25 g. of potassium acetate, 10 g. of water, 9.8 g. of a solution of t-pentyl acetate (78%) and alcohol (22%) and 6.6 g. of a solution of 2-methyl-1-butene and 2-methyl-2-butene (about equal amounts of each). Sodium nitrite (5 g.) was added and the mixture worked up by neutralization with alkali, nitrogen sweep, etc., to yield 4 g. of olefin (61%) and 9.1 g. of ester plus alcohol (93%) of which 20% was t-pentyl alcohol.

Control 2.—This control establishes that the procedure of isolation used in control 1 results in no fractionation of olefin. The procedure was like control 1, and nitrogen sweep gave an olefin sample that was analyzed. The olefin added to the reaction mixture had been 55.0% and the recovered olefin was 53.5% trimethylethylene. The slight decrease in the percentage of trimethylethylene probably is caused by selective destruction of this olefin (see below).

Control 3.—A faster method was sought for running deaminations and controls in which only the olefin composition was of interest. This control establishes that just adding water to the reaction mixture and sweeping with nitrogen (described for the solvolysis of t-pentyl chloride) provides some olefin from which an accurate estimate of olefin composition can be made. In the usual reaction system were placed 5 g. of potassium acetate, 100 ml. of water and 300 ml. of acetic acid. The bath was heated to 57° and 4 g. of an olefin mixture (76.5% trimethylethylene) was added. Heating was maintained for 1.5 hours, the flask was cooled, 400 ml. of water was added and nitrogen was passed through the system to give 2.15 g. of crude olefin, 76.6% trimethylethylene. This general isolation procedure was used in many deaminations and in the controls described below.

Controls 4 and 5.—These controls establish that neither trimethylethylene nor 2-methyl-1-butene isomerizes and that both t-pentyl alcohol and acetate are stable under the deamination conditions in acetic acid. In controls 4–9, the procedure was to use 200 ml. of acetic acid and 18 g. of t-butylamine and to add 30 g. of sodium nitrite at 57°. The olefin was isolated as in control 3 and a variety of chemicals were introduced into the acetic acid before and sometimes during the sodium nitrite addition. In control 4, there were initially present 15 g. of t-pentyl acetate, 5 g. of t-pentyl alcohol and 5 ml. of 2-methyl-1-butene. The re-isolated olefin contained no detectable amount of trimethylethylene. In control 5, substitution of trimethylethylene for the 2-methyl-1-butene of 4 gave recovered olefin in which no 2-methyl-1-butene could be detected.

Controls 6–9.—The procedures were similar to controls 4–5. These controls reproduce approximately the deamination conditions in glacial acetic acid. The change in the olefin composition observed in control 6 was applied as a correction to deamination runs in acetic acid. This correction is probably a maximum, since the amount of olefin used in the control corresponds approximately to that isolated and thus not to that really formed in the actual deamination (controls 1–3). The amount of the apparent correction increases with decreasing amounts of olefin taken in the controls (control 9). In control 6, 4.5 g. of olefin was taken. Olefin was initially 62.0% and finally 69.3% 2-methyl-1-butene. Control 8 was like 6 except that the olefin was initially 42.0% and finally 49.4% 2-methyl-1-butene. Control 9 was like 6 except 3.3 g. of olefin was used; olefin initially 62.0% and finally 73.1% 2-methyl-1-butene.

Control 10.—This was a control for deaminations in 50% acetic acid. The procedure was that of control 7 except the solvent was 200 ml. of water plus 200 ml. of acetic acid and 3.3 g. of olefin were used. The olefin was initially 62% and finally 64% 2-methyl-1-butene.

(31) L. G. Cannell and R. W. Taft, Jr., *J. Am. Chem. Soc.*, **78**, 5812 (1956).