pectedly rapid radical addition to the double bond be postulated in order to explain the formation of acetate by a route competitive with decarboxylation of the acetoxy radical. The rate expected[44] for $\pi$-complex formation might well be rapid enough to compete with decarboxylation of the acetoxy radical,[7,34] a process which is competitive with diffusion from the solvent cage (including secondary recombination[36] as a cage reaction).

### Conclusions

These observations seem consistent with the postulate that acetyl peroxide decomposes in solution to give caged acetoxy radicals which can, in reactions competitive in rate with diffusion from the solvent cage, either decarboxylate, react with each other to yield cage products, or react with solvent olefin to form a $\pi$ complex. The $\pi$ complex can react with the cage partner radical to give addition products III or IV, collapse to V, or diffuse from the cage and react with hydrogen donors to give II, as outlined in mechanism D.

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# Carbonium Ions. I. The Ethylenephenonium Ion

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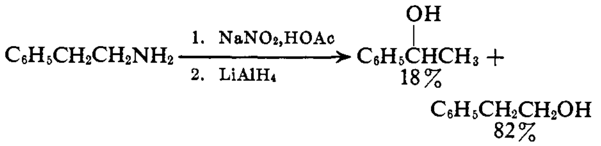
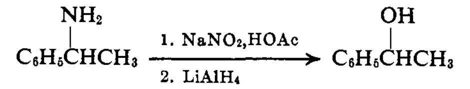
**Abstract:** The reaction of 2-phenylethylamine with nitrous acid in acetic acid has been reinvestigated. It has been found that both 1-phenylethyl acetate and 2-phenylethyl acetate are produced in this reaction in a ratio of about 1:4. The same reaction with 2-phenylethylamine-1-$^{14}$C gives 1-phenylethyl acetate in which 0.23% of the $^{14}$C has migrated and 2-phenylethyl acetate in which 27% of the $^{14}$C has migrated. These results are interpreted as support for an ethylenephenonium ion which does not open back up to a 2-phenylethyl cation.

A number of workers[1] have investigated the reaction of 2-phenylethylamine with nitrous acid both in acetic acid and in water. None of these workers reported the formation of 1-phenylethanol or its acetate. Roberts and Regan[1c] commented on this rather surprising result. As they pointed out one would expect the 2-phenylethyl cation, produced by decomposition of the diazonium cation, to partially rearrange the more stable 1-phenylethyl cation by hydride migration. This kind of rearrangement has been observed in similar systems.[2] It is unfortunate that all the studies on 2-phenylethylamine were carried out before the advent of vapor phase chromatography.

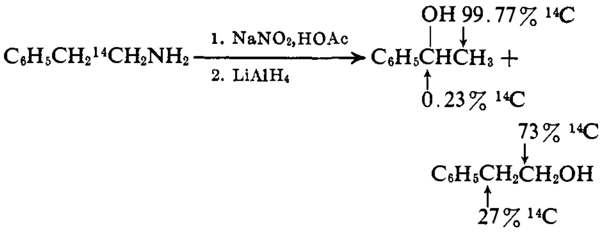
In view of other work we have carried out on rearrangements encountered when primary amines are treated with nitrous acid, we have reinvestigated this reaction on 2-phenylethylamine. Contrary to the observations of earlier workers we have found that rearrangement to give 1-phenylethyl acetate does occur in acetic acid. Evidence for this comes from the following experiment (eq 1). When 2-phenylethylamine was treated with sodium nitrite in acetic acid and the products of this reaction were reduced with lithium aluminum hydride, the alcohol fraction of the product was found to consist of 18% 1-phenylethanol and 82% 2-phenylethanol. The formation of 1-phenylethanol in this reaction has more significance than is apparent since, as will be shown below, it allows one to investigate the nature of an unsubstituted ethylenephenonium ion. When 1-phenylethylamine was treated as above the only product was 1-phenylethanol (eq 2).



$$C_6H_5CH_2CH_2NH_2 \xrightarrow[\text{2. LiAlH}_4]{\text{1. NaNO}_2\text{,HOAc}} \underset{18\%}{C_6H_5\overset{\overset{\displaystyle OH}{|}}{C}HCH_3} + \underset{82\%}{C_6H_5CH_2CH_2OH} \quad (1)$$



$$\overset{\overset{\displaystyle NH_2}{|}}{C_6H_5CHCH_3} \xrightarrow[\text{2. LiAlH}_4]{\text{1. NaNO}_2\text{,HOAc}} \overset{\overset{\displaystyle OH}{|}}{C_6H_5CHCH_3} \quad (2)$$



$$C_6H_5CH_2{}^{14}CH_2NH_2 \xrightarrow[\text{2. LiAlH}_4]{\text{1. NaNO}_2\text{,HOAc}} \underset{0.23\%\ ^{14}C}{\overset{\text{OH }99.77\%\ ^{14}C}{C_6H_5CHCH_3}} + \underset{27\%\ ^{14}C}{\overset{73\%\ ^{14}C}{C_6H_5CH_2CH_2OH}} \quad (3)$$

We have repeated earlier work on the deamination of 2-phenylethylamine-1-$^{14}$C and have separated the products in order to check the location of $^{14}$C in each product formed (eq 3). The method used was to carry out the deamination by addition of sodium nitrite to an acetic acid solution of the amine. The mixture of crude esters and alcohols isolated from this reaction was then reduced with lithium aluminum hydride and separated by gas chromatography. The alcohols were converted to their phenylurethans in order to purify them rigorously. The exact per cent $^{14}$C at each position was determined by oxidation of each compound to benzoic acid. The radioactivity data are

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[1] (a) D. W. Adamson and J. Kenner, *J. Chem. Soc.*, 838 (1934); (b) C. C. Lee and J. W. T. Spinks, *Can. J. Chem.*, 31, 761 (1953); (c) J. D. Roberts and C. M. Regan, *J. Am. Chem. Soc.*, 75, 2069 (1953).

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

**Table I.** Radioactive Analyses

| Compound | Source | Activity, dpm/mmole | % rearrangement[a] |
|---|---|---|---|
| $C_6H_5CH_2CH_2NH_2$ | $LiAlH_4$ on nitrile | 272,000 | 0.00 |
| $C_6H_5COOH$ | $KMnO_4$ on amine | 0 | |
| $C_6H_5\overset{\overset{OH}{\vert}}{C}HCH_3$ | $HNO_2$ and $LiAlH_4$ on amine | 122,000[b] | 0.53[c] |
| $C_6H_5COOH$ | $KMnO_4$ on secondary alcohol | 644 | |
| $C_6H_5NHCOO\overset{\overset{CH_3}{\vert}}{C}HC_6H_5$ | From secondary alcohol | 112,000 | 0.23 |
| $C_6H_5COOH$ | $KMnO_4$ on secondary alcohol urethan | 254 | |
| $C_6H_5CH_2CH_2OH$ | $HNO_2$ and $LiAlH_4$ on amine | 265,000 | 26 |
| $C_6H_5COOH$ | $KMnO_4$ on primary alcohol | 68,300 | |
| $C_6H_5NHCOOCH_2CH_2C_6H_5$ | From primary alcohol | 259,000 | 27 |
| $C_6H_5COOH$ | $KMnO_4$ on primary alcohol urethan | 70,200 | |

[a] This was calculated by the formula (activity of the benzoic acid)(100)/(activity of the compound oxidized). [b] This activity is lower than that of the other alcohol because the crude reaction product was diluted with 200 mg of inactive 1-phenylethanol to facilitate separation and purification. [c] This per cent rearrangement is too high because vpc analysis of the 1-phenylethanol indicates it still contains about 0.5% of 2-phenylethanol.

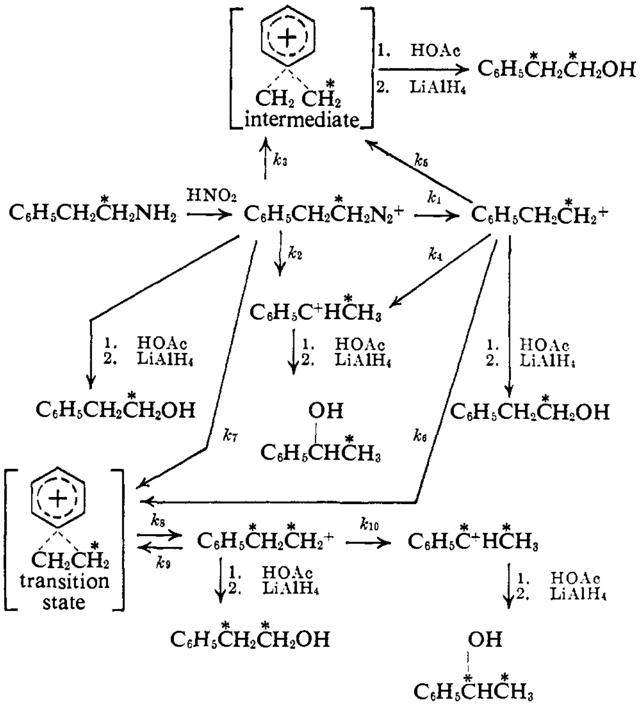
summarized in Table I. We find that in the case of 2-phenylethanol our results agree almost exactly with those of Roberts and Regan,[1c] 73% of the $^{14}C$ being found in position 1 and 27% of the $^{14}C$ being found in position 2. The only way the $^{14}C$ can become scrambled between the two positions is for a phenyl-bridged species of some kind to intervene. In the 1-phenylethanol we find that position 2 contains 99.77% of the $^{14}C$ while position 1 contains 0.23% of the $^{14}C$.

In order to interpret these results completely the mechanism of nitrous acid deamination of primary amines must be understood. Although some of the details of this reaction are still obscure, we feel there is enough known[3] to make a reasonable interpretation of our results. In deaminations there is apparently little disagreement as to the mechanism up to the formation of the diazonium cation. Most chemists have argued that the diazonium cation can react by several alternate routes to give various products. One reaction path is by direct displacement by a solvent molecule to give inversion. Another reaction path is the loss of nitrogen to form a carbonium ion. The diazonium cation and the carbonium ion may each react by alkyl, aryl, or hydride shifts to give other carbonium ions which give rise to various products. The work of Streitwieser and Schaeffer[4] on the deamination of optically active 1-deuterio-1-butylamine strongly suggests that although direct displacement of nitrogen may be the major reaction path a reasonable amount of product (in the order of 30% of the 1-butyl acetate) is formed by way of a carbonium ion.

In light of Streitwieser and Schaeffer's work we can propose a plausible mechanistic scheme for the nitrous acid deamination of 2-phenylethylamine-1-$^{14}C$ in acetic acid (Chart I; an asterisk will be used to denote possible locations of $^{14}C$).[5]

The reactions shown in Chart I outline the most likely modes of rearrangement of the diazonium cation and carbonium ions and the labeling patterns that would be expected from each of these rearrangements. We have included the final reaction of each species with

**Chart I**[6]



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(3) A. Streitwieser, Jr., *J. Org. Chem.*, **22**, 861 (1957); J. A. Berson and A. Remanick, *J. Am. Chem. Soc.*, **86**, 1749 (1964); E. H. White and C. A. Aufdermarsh, Jr., *ibid.*, **83**, 1179 (1961); K. L. Servis and J. D. Roberts, *ibid.*, **86**, 3773 (1964).

(4) A. Streitwieser, Jr., and W. D. Schaeffer, *ibid.*, **79**, 2888 (1957).

(5) The symbol used here to represent the ethylenephenonium ion is merely for convenience and has no special significance. Our work sheds no light on the exact bonding in this ion. We wish only to show it as a bridged entity. We have not included the reactions leading to olefin formation since these have bearing only on the per cent of various products that can be isolated and do not alter the arguments based on the isotopic distribution.

(6) We hesitate to use the conventional symbols $k\Delta$, $k_s$, and $k_c$ of Winstein here since these symbols have special significance in solvolysis reactions. We have simply designated each reaction path by a symbol $k$ and numerical subscript for reference purposes. The terms intermediate and transition state are used here to designate species corresponding to an energy minimum and maximum, respectively, along the reaction coordinate.

acetic acid and lithium aluminum hydride to show the labeling pattern expected in the two possible alcohols produced by all routes. We do not claim to know the relative importance of every reaction shown. The important thing to keep in mind is that the 1-phenylethanol isolated has only 0.23% of the $^{14}C$ rearranged and the 2-phenylethanol has 27% of the $^{14}C$ rearranged. This indicates that 54% of the 2-phenylethanol arose by way of a bridged species which we would presume to be the phenonium ion although we do not know its exact nature as yet.

As shown in Chart I we wish to assume first that the phenonium ion is an intermediate and second that it is a transition state and examine the consequences of each of the assumptions on the labeling pattern of the 1-phenylethanol, for it is uniquely this compound that allows us to examine the nature of the phenonium ion. Assume first that the phenonium ion is an intermediate and that its rate of collapse to product is fast relative to its rate of reversal to 2-phenylethyl cation. This assumption demands that $k_3$ and $k_5$ represent irreversible processes and leads to the conclusion that $k_2$ and $k_4$ are the only routes available to form the 1-phenylethyl cation and hence the 1-phenylethanol. But note that these arguments do not allow the 1-phenylethanol to show any scrambling of $^{14}C$. Now assume that the phenonium ion is a transition state which arises by $k_6$ or $k_7$. This demands that formation of the phenonium ion be a reversible process, but note that this reversibility ($k_8$ and $k_9$) would lead to scrambling of $^{14}C$ between the two possible positions in the 2-phenylethyl cation. This in turn would lead to scrambling of $^{14}C$ in the 1-phenylethyl cation ($k_{10}$) and hence in the 1-phenylethanol.[7] The exact degree of scrambling predicted in the 1-phenylethanol by this last assumption (phenonium ion as transition state) will depend on the degree of phenonium ion formation, which the scrambling in the 2-phenylethanol indicates is extensive, and the relative importance of $k_{10}$ *vs.* $k_2$. We feel that $k_{10}$ would be of reasonble significance relative to $k_2$ and should predict appreciable scrambling of $^{14}C$ in the 1-phenylethanol.

These arguments lead us to conclude that the 0.23% scrambling of $^{14}C$ in the 1-phenylethanol is strong evidence for the ethylenephenonium being an intermediate and not a transition state in this deamination reaction. It is our hypothesis that this work indicates that in the solvolysis of 2-phenylethyl tosylate there is probably no leakage from the $k_\Delta$ route to the $k_s$ route (using Winstein's nomenclature). Since Winstein[8] has already shown that there is no leakage from $k_s$ to $k_\Delta$, this hypothesis has many interesting ramifications. We are attempting to obtain experimental evidence to either support or disprove this hypothesis.

We are currently investigating aryl-substituted 2-phenylethyl systems and the effects of solvent change and will report on these later. We would like to point out that in this paper we are dealing only with the completely unsubstituted 2-phenylethyl system and at this time we are not willing to extrapolate our experimental results nor our conclusions to any other systems.

## Experimental Section[9]

**2-Phenylethylamine-1-$^{14}C$.** A solution of 7.0 g (0.06 mole) of phenylacetonitrile-1-$^{14}C$ (prepared according to the procedure of Roberts and Regan[1c]) in 100 ml of ether was added slowly to a stirred solution of 3.8 g (0.1 mole) of lithium aluminum hydride in 500 ml of ether. The resulting mixture was stirred and heated at reflux for 7 hr. The reaction was worked up by successive addition of 4 ml of water, 3 ml of 20% sodium hydroxide, and 14 ml of water. The ether layer was decanted, and the solid aluminum hydroxide was washed well with ether. The ether solutions were combined, dried, and evaporated to give an oil which was distilled to give 2.5 g (34%) of 2-phenylethylamine-1-$^{14}C$, bp 128–131° (100 mm) (lit.[1c] bp 72–75° at 8 mm).

**Nitrous Acid Deamination of Amines.** The following procedure is representative of all the deamination reactions except that in the nonradioactive compounds no actual separation of products was carried out, they were simply analyzed by vpc. Solid sodium nitrite, 1.38 g (0.020 mole), was added slowly (15 min) with stirring to a solution of 2.35 g (0.019 mole) of 2-phenylethylamine-1-$^{14}C$ in 50 ml of glacial acetic acid at room temperature. The resulting solution was stirred for 24 hr and then diluted with 350 ml of water and extracted with four 100-ml portions of ether. The combined ether solutions were washed with water several times, and then dilute sodium bicarbonate to remove excess acetic acid, and were then dried over magnesium sulfate. The products were not isolated at this point but were reduced directly with 3.8 g (0.1 mole) of lithium aluminum hydride in the usual way to give 0.80 g of a mixture of alcohols containing 18% 1-phenylethanol and 82% 2-phenylethanol. In order to facilitate isolation of the minor component the reaction product was diluted with 0.20 g of inactive 1-phenylethanol. The resulting mixture was then separated by vapor phase chromatography to give 0.27 g of radioactive 1-phenylethanol and 0.52 g of radioactive 2-phenylethanol.

**Phenylurethans of $^{14}C$ Alcohols.** The phenylurethans were prepared by heating an equal weight of phenyl isocyanate and the alcohol on a steam bath for 10 min and were purified by two crystallizations from petroleum ether (30–60°). The radioactive 1-phenylethanol gave a phenylurethan, mp 89–90.5° (identical with an authentic sample), and the radioactive 2-phenylethanol gave a phenylurethan, mp 76–77° (identical with an authentic sample).

**Oxidation of Compounds to Benzoic Acid.** The procedure of Lee and Spinks[1b] was followed using alkaline potassium permanganate. The samples of benzoic acid were crystallized twice from water.

**Acknowledgment.** The author would like to thank Professor S. Winstein and Professor W. H. Saunders, Jr., for interesting discussions concerning this work.

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(7) We are assuming here that the 2-phenylethyl cation formed by opening of phenonium ion transition state would have the same reactions as and be identical with the 2-phenylethyl cation produced by initial loss of nitrogen from the diazonium cation ($k_1$). We have no way at present to test this assumption, but it seems logical to us to expect any 2-phenylethyl cation produced by reaction $k_8$ to undergo some hydride migration (reaction $k_{10}$).

(8) E. F. Jenny and S. Winstein, *Helv. Chim. Acta*, **41**, 807 (1958); L. Eberson, J. P. Petrovich, R. Baird, D. Dyckes, and S. Winstein, *J. Am. Chem. Soc.*, **87**, 3505 (1965).

(9) All melting points were taken on a calibrated Kofler hot stage. All distillations were done through a 2-ft Podbielniak-type column and the boiling points are corrected. Gas chromatographic separations and analyses were done with an F & M Model 500 gas chromatograph using a 1-m column of 20% potassium hydroxide and 5% Carbowax 6000 on Firebrick at 150° and a flowrate of helium of 60 cc/min. The counting of radioactive samples was done on a Model 314EX Packard Tri-Carb liquid scintillation counter using a solution of 0.5 g of PPO and 0.03 g of POPOP per 100 ml of toluene at an efficiency of 72%. Activities are corrected for background count and efficiency of the counter.