5-Allyl-5-*t*-butylbarbituric acid was obtained in 1–2% yield (crude "disubstituted barbituric acid fraction") from batches of 2–3 g. of the ester. Most of the ester was recovered. The pure product was obtained by several crystallizations from methanol; yield 0.5%, m.p. 221–222°. This product was identical with that prepared several times in this Laboratory twelve years ago from 5-*t*-butylbarbituric acid and allyl bromide by modification of the method of Volwiler.[15] This method was modified by using an isolation procedure similar to that described above. From 1.84 g. of 5-*t*-butylbarbituric acid (m.p. 235–236°) there was obtained 193 mg. (10% yield) of product thrice crystallized from ethanol, to constant m.p. 221–222°.

Anal.[11] Calcd. for $C_{11}H_{16}N_2O_3$: C, 58.90; H, 7.19; N, 12.49. Found: C, 59.02, 59.29; H, 7.10, 7.23; N (Dumas), 12.69, 12.78.

The anesthetic activity of 5-*t*-butyl-5-allyl-barbituric acid was compared with that of amytal in mice, by intraperitoneal injection of aqueous solutions of the sodium salts (5 mg./ml.). The dose required to produce "surgical anesthesia" in 50% of the animals was about 15% higher for the new compound, and the duration of this anesthesia was about twice as long, as for amytal. The quality of the anesthesias was essentially the same.

Acknowledgment.—The authors are indebted to Professor A. W. Ingersoll for his advice during the course of this work.

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[15] E. H. Volwiler, THIS JOURNAL, **47**, 2236 (1925).

[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF THE OAK RIDGE NATIONAL LABORATORY]

Evidence for a Cyclic Intermediate in the Reaction of Diarylethylamines with Nitrous Acid[1]

BY PHILIP S. BAILEY[2] AND JOHN G. BURR, JR.

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The rearrangement at 70° of 2-phenyl-2-(*p*-tolyl)-ethylammonium-1-C^{14} nitrite in either dry ligroin or in water has been found to give a mixture of carbinols. The same rearrangement in dry butanol at 70° has been found to give a mixture consisting of *55% carbinols*, about 35–40% of the corresponding butyl ethers and 5–10% 4-methylstilbene. The per cent. migration of the *p*-tolyl group in this nitrite has been found to be independent of the acidity or the nitrite ion concentration in water. The reaction of 2-phenyl-2-(*p*-tolyl)-ethylamine hydrochloride with nitrous acid has been found to be an over-all second-order reaction at 74°, corresponding to the reaction of other aliphatic amines with nitrous acid. The rearrangement of 2-phenyl-2-(*o*-tolyl)-ethylamine-1-C^{14} with nitrous acid proceeded with 42% *o*-tolyl migration. The facts are discussed in terms of a concerted process for rearrangement step of the conventional mechanism for amine–nitrous acid reactions.

Introduction

Aliphatic amines react with nitrous acid by a presumed mechanism which can be summarized in the steps

$$RNH_2 + HNO_2 \longrightarrow RN_2^+ + OH^- + H_2O \quad (1)$$

$$RN_2^+ \begin{cases} \longrightarrow R^+ + N_2 \\ \xrightarrow{X^-} R\text{—}X + N_2 \end{cases} \quad (2)$$

Investigation of the reaction kinetics of this system[3] has shown that it is over-all second order in very weak acid. It has been usually assumed that the rearrangement step is fast and not rate-determining and that the final products of the reaction are those resulting from the known modes of reaction and rearrangement of carbonium ions, such as R^+; or from nucleophilic displacement of the diazonium ion by a base, X^-, as shown.[4]

It has been shown recently[5] that the migration ratios observed in the reactions of 2,2-diarylethylamines with nitrous acid are not the same as those observed in the acid-catalyzed rearrangement of the corresponding 2,2-diarylethanols. In fact, very little selectivity between phenyl and substituted phenyl was observed in the amine–nitrous acid rearrangement, although the reaction is usually written as proceeding through the same carbonium ion intermediate as does the carbinol rearrangement. It is thus evident that, at least in the case of these amines, the second step of the reaction cannot be set down so assuredly as a simple displacement or rearrangement reaction. It is shown in this paper that not only the migration ratios but also the reaction products are not those which would be expected from such a simple picture.

Here are reported the results of a more detailed examination of the reaction of several of these amines with nitrous acid. Three aspects of the reaction have been investigated: (1) the effect upon the migration ratio of the acidity, nitrite ion concentration and the nature of the reaction medium; (2) the nature of the reaction products in several different types of reaction medium (3) the over-all kinetic order observed in the reaction of these amines with nitrous acid.

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[2] Member of the Research Participation program sponsored jointly by the Oak Ridge National Laboratory and the Oak Ridge Institute of Nuclear Studies; permanent address, University of Texas, Austin, Texas.

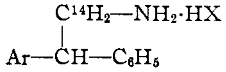
[3] Recent conclusions regarding these kinetics are well summarized in two papers by C. K. Ingold, E. D. Hughes and their co-workers, THIS JOURNAL, **74**, 555 (1952); *Nature*, **166**, 642 (1950). The reactions of amines with nitrous acid are over-all second order in very weak acid, and over-all third order in stronger acid. A good survey of earlier work is found in L. P. Hammett, "Physical Organic Chemistry," 1st Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 294–296.

[4] There has been relatively little systematic examination, such as D. W. Adamson and J. Kenner, *J. Chem. Soc.*, 838 (1934), of the reaction products of aliphatic amines and nitrous acid. This lack of information of the reaction products sometimes brings a certain element of doubt into otherwise excellent work. For example, F. C. Whitmore and R. S. Thorpe reported (THIS JOURNAL, **63**, 1118 (1941)) that the reaction of methylamine with nitrous acid did not give any methanol (nor anything else that they could isolate except recovered methylamine). Nevertheless, a number of investigators have studied the kinetics of this reaction on the assumption that the reaction product is methanol; *cf.*, Taylor, *J. Chem. Soc.*, 1099 (1928); Euler, *Ann.*, **330**, 280 (1903), and more recently Dusenbury and Powell, THIS JOURNAL, **73**, 3269 (1951).

[5] J. G. Burr, Jr., and L. S. Ciereszko, *ibid.*, **74**, 4526 (1952); L. S. Ciereszko and J. G. Burr, Jr., *ibid.*, **74**, 5431 (1952).

The materials employed in this study have been for the most part the crystalline amine nitrites[6] principally that of 2-phenyl-2-(*p*-tolyl)-ethylamine-1-C^{14}. Migration ratios have been determined in this study by the use of carbon-14 labeling as described in the earlier papers[5]; the degradative and counting procedures have been the same as in those papers. The results obtained are shown in Table I.

TABLE I



$$\begin{array}{l} \quad\ \ C^{14}H_2\text{—}NH_2\cdot HX \\ \quad\ \ | \\ Ar\text{—}CH\text{—}C_6H_5 \end{array}$$

Ar	Conditions	Ar migrating, %
p-Tolyl[a]	Nitrite stirred in dry ligroin at 70° with Drierite	48
p-Tolyl	Solution of nitrite in dry butanol stirred at 70° with Drierite	47
p-Tolyl	Solution of nitrite in water stirred at 70°	47
p-Tolyl	Nitrite stirred in water with 1 mole excess sodium nitrite at 70°	48
p-Tolyl	Amine–HCl stirred in excess 0.5 *N* HCl with 1 mole of sodium nitrite at 70°	48
3,4-Dimethylphenyl[b]	Amine–HCl with excess sodium nitrite at 70°	49
3,4-Dimethylphenyl	Amine–nitrite with either an equivalent or an excess of 1 *N* HCl at 70°	48

[a] The carbinol gave 66% Ar migration. [b] The corresponding carbinol gave 66% Ar migration.

The migration ratios in both of these nitrites are apparently insensitive to these changes in solvent acidity and nitrite ion concentration. It is thus probable that the factors which determine the migration selectivity in this reaction occur not in the rate-controlling step, but in the subsequent fast reactions.

The rate-determining step in these reactions is the same as in other amine–nitrous acid reactions as shown by a study of the kinetics of the reaction of phenyl-(*p*-tolyl)-ethylamine hydrochloride with sodium nitrite in water at 74°. The data are shown in Table II.

It is evident from these data that the reaction is over-all second order, as would be expected[3] in the nearly neutral solution employed and thus that it has the normal rate-controlling step. Corresponding data on the decomposition of the amine nitrite could not be obtained owing to the impurity of this material. However, the approximate first-order constants observed in its decomposition showed a dependency upon nitrite ion concentration, (see Table III). The reaction is thus actually not first order and probably follows the same rate law as mixtures of amine hydrochloride and sodium nitrite.

TABLE II

REACTION OF PHENYL-(*p*-TOLYL)-ETHYLAMINE WITH NITROUS ACID IN WATER AT 74.0°

Run	Time (min.)	V_{N_2} (ml.)	x[a]	$[NO_2^-]$ (initial), mole/l.	$[RNH_2]$ (initial), mole/l.	k (l. mole^{-1} min.$^{-1}$)
1	10	10.0	0.0158	0.100	0.0776	0.254
	20	17.0	.0268			.269
	30	22.6	.0354			.262
	40	26.3	.0414			.265
	50	29.2	.0457			.265
	60	31.3	.0493			.256
2	..	..	....	.150	.0776	.259
3	..	..	....	.200	.0776	.257

[a] The rate expression used was $k = 2.303/t(a - b) \log b(a - x)/a(b - x)$; x = ml. of $N_2/(25.4)(25.0)$ where 25.4 was the observed millimolar gas volume and 25.0 was the volume of solution. This is the same expression that Tassilly (*Bull. soc. chim.*, [4] **27**, 19 (1920)) used, except that since he had equal initial amounts of amine and nitrous acid he employed the form $k = (1/t)\log (a - x)^2$. Hughes, Ingold and Ridd[3] have shown that this second-order reaction is actually zero order in *free amine* and second-order in *unionized nitrous acid*. They worked with buffered solutions containing a large excess of *stoichiometric nitrous acid*. These special conditions were not present in our case and thus we observed the same over-all second-order kinetics as did Tassilly, and also Hantzsch and Schumann (*Ber.*, **32**, 169 (1899)).

TABLE III

DECOMPOSITION OF PHENYL-(*p*-TOLYL)-ETHYLAMMONIUM NITRITE AT 74° IN SODIUM NITRITE SOLUTIONS

Wt. of amine nitrite in 25 ml. of H_2O, g.	$[NO_2^-]$ initial, *M*	k (min.$^{-1}$)
0.500	0.09	0.017
.500	.13	.023
.500	.18	.040

It has been expected, from the work of Hellerman,[6] that the product of the thermal decomposition of phenyl-(*p*-tolyl)-ethylamine nitrite in dry ligroin suspension with added finely divided Drierite would be 4-methylstilbene which is a well characterized solid melting at 120°. However, the product actually obtained was an oil which resisted crystallization, did not absorb bromine from carbon tetrachloride solution and which upon dehydration with phosphorus pentoxide in benzene was converted in excellent yield to 4-methylstilbene. An examination of the infrared spectra (no. 3, Table IV) of the reaction product (after acid-washing, to remove unreacted amine) showed that it consisted mostly of hydroxylic material (compare the absorption of 2.90 with that of benzylphenylcarbinol) along with a relatively small amount of stilbene (compare the absorption at 10.45 μ with that of stilbene). The hydroxylic material is undoubtedly the mixture of carbinols (III and IV); since the dehydration product was, as mentioned, the corresponding stilbene, and since the degradative procedure showed the absence of primary carbinol.[5]

For the purposes of comparison, a similar decomposition was carried out in water solution and the product chromatographed upon alumina with hexane. The first portion of the material eluted

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(6) It is not widely known but nevertheless well established that a number of aliphatic amines form stable, and in some cases, isolable nitrite salts. *Cf.*, Hellerman, Cohn and Hoen, THIS JOURNAL, **50**, 1724 (1928); Noyes, *Am. Chem. J.*, **15**, 539 (1893); and Wolfe and Temple, THIS JOURNAL, **70**, 1414 (1948). No way was found to prepare the amine nitrites used here both in good yield and good purity. Therefore we could not obtain good data on the kinetics of the amine nitrite decompositions. The data actually obtained could be represented, *for the purposes of comparison only*, by first-order rate constants and this has been done where the comparison would be useful. These were obtained by plot of the evolved N_2 against time, extrapolation of this curve, and plot of log $(V_\infty - V)$ against time. This plot gave a straight line.

by hexane (7% by weight of the product) was non-hydroxylic but the remaining material eluted by hexane as well as the material stripped from the column with methanol was the carbinol mixture (no. 4 and 5, Table IV), comprising at least 93% by weight of the reaction product.

If the formation of carbinols in this reaction is considered to occur by a nucleophilic displacement of nitrogen by hydroxyl or by attack of a carbonium ion upon a water molecule, then the formation of carbinols in dry ligroin suspension can only arise because the diffusion of water from the reacting particles of amine nitrite into the solvent is very slow (*i.e.*, the reaction happens essentially in a concentrated water solution).

If the carbinols are formed in this manner then the replacement of water as a reactant by another polar substance such as dry butanol should result in the formation of the corresponding butyl ethers; or, if butanol is insufficiently polar to replace water as a reactant, then the product should be 4-methylstilbene. In any case, very little hydroxylic material should be formed.

However, the pyrolysis of the amine nitrite in dry homogeneous butanol solution gave a mixture which was shown by chromatographic analysis and infrared analysis to consist of 55% of a mixture of carbinols (not eluted from alumina with hexane, and having strong absorption at 2.90 μ, no. 7, Table IV) and 45% of a mixture of butyl ethers and 4-methylstilbene (eluted from alumina by hexane). The infrared absorption curves (no. 6, Table IV) indicate that this fraction is about 10% stilbene and about 90% of a mixture of ethers (presumably corresponding to the carbinols, III and IV), since the very strong band at 9.20 μ is probably that assigned to the ether linkage.

This seems to indicate that the carbinols *originate in the intramolecular transfer of a hydroxyl group during the reaction.*

TABLE IV

INFRARED SPECTRA OF PRODUCT FRACTIONS[a]

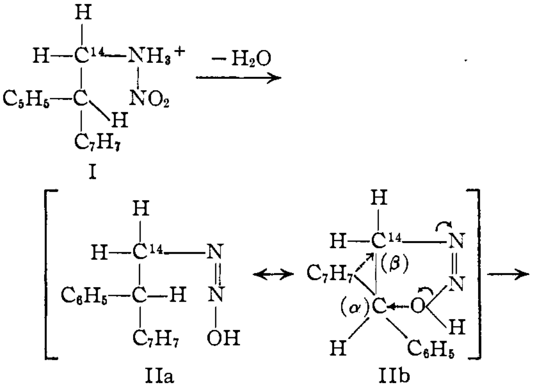
	Fraction	Transmission at indicated wave length (microns), % 2.90	9.20	10.45
1	Benzylphenylcarbinol	20	30	75
2	Stilbene	98	65	5
3	Product of pyrolysis in ligroin	30	30	20
4	Product of pyrolysis in water; fraction *eluted* from alumina by hexane	30	45	65
5	Product of pyrolysis in water; fraction *not eluted* from alumina by hexane	25	20	55
6	Product of pyrolysis in butanol; fraction *eluted* from alumina by hexane	95	0	45
7	Product of pyrolysis in butanol; fraction *not eluted* from alumina by hexane	35	25	60

[a] All solutions (except that for entry 3 in the table) were *ca.* 1.26 *M;* cell thickness was 0.015 mm. The spectra were observed in a Perkin–Elmer Model 21 instrument with sodium chloride optics.

Discussion

In the first paper on this subject[5] mention was made of two hypotheses potentially capable of explaining the lack of selectivity in the rearrangement of these amines with nitrous acid. One of these was the possibility that the diazonium ion lost nitrogen to give a "hot" carbonium ion which attacked the migrating aryl groups without selectivity; the other hypothesis was that the amines proceeded through a diazohydrocarbon intermediate rather than a diazonium ion. Aside from the theoretical difficulty of demonstrating the first hypothesis and the experimental difficulty of demonstrating the second, neither one is capable of explaining the intramolecular hydroxyl group transfer described in this paper.

The existence of this intramolecular transfer of a hydroxyl group limits the kinds of mechanisms which must be considered. The simplest sort of process which will explain this is one postulating a transition state which includes a cyclic intermediate, as shown below.



$N_2 + C_7H_7C^{14}H_2CHOHC_6H_5 + C_6H_5C^{14}H_2CHOHC_7H_7$

III IV

There is nothing in this process which would render unlikely the observed lack of selectivity in the aryl group migrations. In fact, the above process makes this lack of selectivity seem probable. This is so since the coördination of the hydroxyl group is presumably the result only of the net charge on the α-carbon atom, and thus not selective between the two aryl groups; and because this coördination is also presumably backside to the bulkiest of the two aryl groups, and thus when both are of equal bulk, again not selective.

However, when 2-phenyl-2-(*o*-tolyl)-ethylamine-1-C^{14} was rearranged with nitrous acid, the per cent. migration of the *o*-tolyl group was only 42% (the *o*-tolyl migration in the corresponding carbinol was 45%[7]; and the migration in the carbinol with a *p*-tolyl group was 66% *p*-tolyl[5]). Thus in this amine, the *o*-tolyl group, although the bulkiest group still migrated the least. On the above hypothesis, this can only mean the normal "ortho" effect[7] at the β-carbon determines the relative migration of the two groups, rather than the steric effects governing the coördination of the hydroxyl group in IIb.

An effort was made to study the even more interesting 2-phenyl-2-mesitylethylamine-1-C^{14} but somewhat to our surprise, treatment of this amine

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[7] B. M. Benjamin and C. J. Collins, THIS JOURNAL, 75, 402 (1953).

with nitrous acid did not produce any rearrangement; the product was presumably the primary carbinol and/or the unsymmetrical ethylene. The corresponding 2-phenyl-2-mesitylethanol-1-C^{14} could not be induced to rearrange either.

Although the physical nature of the system differs widely in the three media employed (in ligroin, the amine salt was insoluble and the product was soluble; in water, the amine salt was soluble but the product insoluble; while in butanol both the amine salt and the product were soluble), nevertheless, the distribution of products, the migration ratios and the approximate rates of reaction were very similar. It seems probable therefore that the same mechanistic process is occurring in all three solvents.

Experimental[8]

Reaction Rate Measurements.—Measurement of reaction rates was carried out in a jacketed glass cell (of about 75-ml. capacity) attached with a standard taper joint to a gas buret system. Water from a thermostated bath was circulated through the jacket of the cell while the medium or solvent was stirred magnetically. When the medium or solvent had reached equilibrium with the gas buret system, a weighed amount of sample was introduced through a long funnel and an auxiliary joint into the reaction flask. This auxiliary joint was quickly stoppered and measurements begun.

The ligroin used was dried over sodium, and the butanol dried by distillation. The reaction medium used consisted of about 15 ml. of the liquid and 2.0 g. of 20–30 mesh Drierite. The amine nitrites were sandy or crystalline solids and were dried in high vacuum over sodium hydroxide pellets for several days. The data on migration ratios were obtained by oxidizing one half of the pyrolysis product to the proper acid[5] and by dehydrating the other half to the stilbene before oxidizing it.

2-Phenyl-2-(*p*-tolyl)-ethylamine-1-C^{14} Nitrite.—Five grams of the amine hydrochloride[5] was dissolved in 25 ml. of water and a solution of 5 g. of sodium nitrite in 15 ml. of water added. A heavy yellow oil precipitated. This was separated quickly (since it decomposed rather quickly in the presence of such an excess of nitrite) by decantation, sometimes with the help of centrifugation. The oil layer was taken up in alcohol and then diluted with several volumes of ether. It was dried thoroughly over magnesium sulfate, filtered and evaporated at room temperature in a desiccator containing sodium hydroxide. The remaining glassy solid was rubbed with ether until it became sandy solid. It was then filtered, dried again *in vacuo* and stored in the refrigerator; yield 3.8 g. with a melting point of 90–100° (on a hot-stage). When room temperature reached 35–40°, samples of the salt standing in the room decomposed visibly from day to day.

Anal. Calcd. for $C_{15}H_{18}N_2O_2$: N, 10.82; C, 69.7; H, 7.00. The purest sample obtained had the composition: N, 10.52; C, 69.9; H, 7.11; Cl, 0.13; ash, 0.15. In other samples, the nitrogen content observed was 10.35 (on ash-free basis; the sample had 3% ash as $MgSO_4$), and 9.26%.

2-Phenyl-2-(3,4-dimethylphenyl)-ethylamine-1-C^{14} Hydrochloride.—The nitrile,[5] 13.5 g., was dissolved in 100 ml. of ethanol and reduced on a Parr apparatus with W-7 Raney nickel. The material took up 10 pounds of hydrogen in seven hours. The catalyst was filtered and the filtrate evaporated in an air blast. The residual oil was treated with 20% hydrochloric acid and the solid amine hydrochloride filtered and recrystallized from an alcohol–ether mixture. It melted at 236°.

Anal. Calcd. for $C_{16}H_{20}NCl$: N, 5.35; Cl, 13.54. Found: N, 5.39; Cl, 13.3.

It gave a yellow picrate which after crystallization from dilute ethanol melted at 186°.

Anal. Calcd. for $C_{22}H_{21}N_4O_7$: N, 12.35. Found: N, 12.48.

Treatment of a water solution of the hydrochloride with a solution of sodium nitrite threw down the amine nitrite as an oil which decomposed very rapidly in the presence of excess nitrite. It was worked up as was the phenyl-(*p*-tolyl)-ethylamine nitrite. Ten grams of hydrochloride gave in this manner 3.0 g. of nitrite melting at about 124° with evolution of a gas. The analysis showed that it still contained considerable unreacted hydrochloride.

Anal. Calcd. for $C_{16}H_{20}N_2O_2$: N, 10.28. Found: N, 8.22; Cl, 4.05.

2-Phenyl-2-mesitylacetonitrile-1-C^{14}.—Phenyl mesityl ketone was prepared in 82% yield by a known[9] method and reduced to the benzhydrol with zinc dust and alcoholic alkali as previously described.[5] The benzhydrol (39 g.) dissolved in 200 ml. of dry benzene was converted to the chloride with 35 ml. of thionyl chloride. The product after fractionation boiled at 52° (2 mm.) and weighed 37 g. On long standing, very large prismatic crystals formed which melted below 50°.

Anal. Calcd. for $C_{16}H_{17}Cl$: Cl, 14.5. Found: Cl, 14.6.

Thirty-seven grams of the liquid chloride was heated at 240° with 11.3 g. of CuC^{14}N. The product was extracted with chloroform, concentrated and the residue vacuum distilled to give 21 g. of liquid which quickly crystallized to a solid melting at 82°. Recrystallization of the solid from dilute ethanol raised its melting point to 90° (lit.[10] 91°).

2-Phenyl-2-mesitylacetic-1-C^{14} Acid.—Hydrolysis of the nitrile was accomplished by boiling 3.0 g. of the substance for three hours with 50 ml. of 70% sulfuric acid. Work-up of this mixture gave 1.83 g. of acid, m.p. 175° (lit.[11] 172°). Recrystallization from ligroin gave 1.65 g. of acid melting at 176°. On some samples of the nitrile this hydrolysis gave only tars; in this case the use of 50% H_2SO_4 would occasionally succeed but not always. One attempt at alkaline hydrolysis was unsuccessful.

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.3; H, 7.08. Found: C, 80.1; H, 6.86; C^{14}, 1.69, 1.69, 1.71, μc./mmole.

2-Phenyl-2-mesitylethanol-1-C^{14}.—Reduction with a solution of $LiAlH_4$ in ether of 2.50 g. of the above acid gave 1.6 g. of phenylmesitylethanol as a liquid which crystallized on standing. Trituration of this solid with hexane gave 1.15 g. of yellowish crystals melting at 74°. One further crystallization from hexane gave colorless prisms melting at 76°.

Anal. Calcd. for $C_{17}H_{20}O$: C, 85.0; H, 8.40. Found: C, 84.8; H, 8.38.

The α-naphthylurethan melted indefinitely at 87°.

Anal. Calcd. for $C_{28}H_{27}O_2N$: N, 3.42. Found: N, 3.72.

Rearrangement of 2-Phenyl-2-mesitylethanol-1-C^{14}.—A sample of the crystalline carbinol (0.74 g.) was refluxed for 20 minutes with a suspension of phosphorus pentoxide in xylene. The solution was decanted from the solid, filtered and evaporated. The residue was a colorless oil. It was dissolved in hexane and passed through an alumina column. Elution of the column with more hexane, and evaporation of the hexane gave 0.74 g. of a colorless oil. The column was stripped with methanol but no appreciable amounts of additional material were thus recovered. These results suggest that the dehydration product was, in fact, olefinic and not unreacted or rearranged carbinol since carbinols are removed but slowly from alumina by a petroleum hydrocarbon solvent.[12]

A portion (0.45 g.) of the eluted hydrocarbon was oxidized in 66% aqueous acetone solution with 0.85 g. of potassium permanganate and 0.9 g. of magnesium chloride. This procedure, as shown below, will oxidize 1-phenyl-2-mesitylethylene to mesitoic acid in good yield. In this case, however, the acidic products of the oxidation were negligible. The only recoverable product was 0.30 g. of a neutral oil, presumably phenyl mesityl ketone.

2-Phenyl-2-mesitylethylamine-1-C^{14}.—Phenylmesitylacetonitrile (17 g.) was reduced in ethanolic (200 ml.) solution with W-7 Raney nickel in a Parr apparatus. The catalyst

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(8) Melting points were taken upon a Kofler Hot Bench. Carbon-14 assays were accomplished by wet combustion of the compounds and ionization chamber counting of the evolved carbon dioxide on a vibrating reed electrometer. Microassays for carbon, hydrogen, nitrogen and halogen were done by Dr. H. W. Galbraith, Knoxville, Tennessee.

(9) K. Elbs, *J. prakt. Chem.*, **35**, 485 (1887).

(10) H. A. Michaël and J. J. Jeanprêtre, *Ber.*, **25**, 1617 (1892).

(11) R. W. Maxwell and R. Adams, THIS JOURNAL, **52**, 2969 (1930).

(12) D. J. Cram, *ibid.*, **74**, 2129 (1952).

was filtered and the filtrate evaporated. Treatment of the residual oil with 20% hydrochloric acid gave a solid amine hydrochloride which after washing with water and ether weighed 13.6 g. It was crystallized from ethanol–ether and then melted at 259°.

Anal. Calcd. for $C_{17}H_{20}NCl$: N, 5.08; Cl, 12.9. Found: N, 5.23; Cl, 12.6.

The picrate, after crystallization from dilute ethanol, melted at 249°.

Anal. Calcd. for $C_{23}H_{24}N_4O_7$: N, 12.0. Found: N, 12.1.

The nitrite separated in excellent yield when solutions of equal weights of the amine hydrochloride and sodium nitrite were mixed. It was purified by thorough washing with water and then melted at about 140°. This salt was stable for several hours at 100°. This is a remarkable stability considering the nature of the salt.

Anal. Calcd. for $C_{17}H_{22}N_2O_2$: N, 9.77. Found: N, 9.71; Cl, 0.11; ash, none.

Rearrangement of this salt, of a mixture of the amine hydrochloride and sodium nitrite, in aqueous solution at 70–90° gave oils which could not be oxidized to mesitoic acid, and which did not absorb bromine—they are presumably unrearranged carbinol or unrearranged olefin or a mixture of these two.

The Oxidation of 1-Phenyl-2-mesitylethylene.—The reaction at room temperature of 48 g. of phenylacetaldehyde dissolved in 100 ml. of ether with the RMgX solution prepared from 80 g. of bromomesitylene and 10 g. of magnesium in 300 ml. of ether gave, after hydrolysis and usual work-up, the carbinol as a thick oil which could not be induced to crystallize. The oil was heated and stirred on the steam-bath overnight with 400 ml. of 50% (by weight) sulfuric acid. The organic material was recovered and distilled to give 29 g. (33% yield from phenylacetaldehyde) of the 1-phenyl-2-mesitylethylene. It crystallized spontaneously, and after crystallization from methanol melted at 53° (lit.[13] 55–56°). The substance reacted slowly with a solution of bromine in carbon tetrachloride to give a tetrabromide of unknown constitution, m.p. 210°, as a white microcrystalline powder from benzene.

Anal. Calcd. for $C_{17}H_{16}Br_4$: Br, 59.2. Found: Br, 59.4.

It was discovered that chromic acid in acetic acid would not oxidize this olefin; and that potassium permanganate in acetone oxidized it to a mixture of benzene polycarboxylic acids. The procedure finally found to be successful employed magnesium chloride as a buffer. A solution of 1.0 g. of the olefin was stirred for 1.5 hours or refluxed for 10 minutes with a solution of 1.90 g. of potassium permanganate and 2.0 g. of magnesium chloride in 60 ml. of 66% aqueous acetone. The MnO_2 was filtered and the filtrate concentrated on a steam-bath in an air blast until the acetone was gone. The residual solution was acidified and heated to boiling. Filtration of the boiling solution gave about 400 mg. of crude mesitoic acid melting at 150°. Crystallization of this from ligroin gave 170 mg. of massive small prisms which melted at the correct temperature, 154°.

2-Phenyl-2-(*o*-tolyl)-ethylamine-1-C^{14}.—The reduction of 3.00 g. of the corresponding nitrile[7] with W-7 Raney nickel resulted in hydrogen absorption of 26.5 mmoles (92%). Evaporation of the filtered solution gave the amine as an oil which upon treatment with 20% hydrochloric acid formed a solid hydrochloride, 2.7 g. This salt melted at 266°.

Anal. Calcd. for $C_{15}H_{18}NCl$: N, 5.66; Cl, 14.2. Found: N, 5.60; Cl, 14.2. Carbon-14, 3.05, 3.05 μc./mmole.

The picrate formed yellow needles melting at 244°.

Anal. Calcd. for $C_{21}H_{24}N_4O_7$: N, 12.7. Found: N, 12.6.

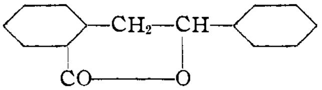
Rearrangement of the hydrochloride (2.7 g.) in water at about 80° with a solution of 2.7 g. of sodium nitrite gave 2.2 g. of oily carbinols. One half of this product (1.1 g.) was oxidized with 50 ml. of 5% sodium hydroxide and 4.0 g. of potassium permanganate. The MnO_2 was filtered off, and the filtrate acidified. Continuous ether extraction of the acidified solution and evaporation of the ether gave a solid acid which was washed with chloroform. It then melted at 228° (on a hot-stage; authentic phthalic acid was also found to melt at 228° on this apparatus).

Assay 1.26, 1.28 μc. of C^{14}/mmole.

This corresponds to 42% *o*-tolyl group migration.

It is of interest to note that if this oxidation of the rearrangement product is carried for a shorter period of time, another product is formed. The oxidation of 1.11 g. of a similar rearrangement product gave 0.87 g. of acids insoluble in dilute hydrochloric acid and soluble in chloroform. Crystallization of this mixture from dilute ethanol gave 210 mg. of a product which melted at 115°. This melting point was not raised by further crystallization; the mixture melting point with benzoic acid was 100°, and the mixture melting point with phthalic anhydride was 100°.

The crystalline product was now neutral to alcoholic sodium hydroxide (indicating lactone formation), and the analysis was satisfactory for the following structure.



Anal. Calcd. for $C_{14}H_{11}O_2$: C, 79.6; H, 5.24. Found: C, 79.6; H, 4.84.

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[13] R. C. Fuson, J. J. Denton and C. E. Best, *J. Org. Chem.*, **8**, 64 (1943). This is the only other preparation of this olefin in the literature.