rium experiments, the deuterated sulfuric acid was made from 99.95% D_2O[12] and 97% sulfuric acid. To about 5 ml. of this deuterated acid was added one drop of an acetic acid solution of the triarylmethanol. The deuterated acid was successively diluted with water–sulfuric acid containing the same mole % H_2SO_4. The optical density was measured after the addition of each increment. All measurements were conducted at 25 ± 0.2°. In correcting for the change in stoichiometric concentration of triarylmethanol due to the dilution, it was assumed that the volumes were additive.

Acknowledgment.—This problem was called to our attention by Dr. R. W. Taft, Jr., and Dr. Lee Purlee, both of whom contributed in discussions of the derivation.

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[12] The D_2O was obtained from the Stuart Oxygen Company with authorization from the Atomic Energy Commission.

[CONTRIBUTION NO. 1996 FROM THE GATES AND CRELLIN LABORATORIES, CALIFORNIA INSTITUTE OF TECHNOLOGY, AND THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Reactions of 3-Phenyl-1-propylamine-1-^{14}C and 3-(p-Methoxyphenyl)-1-propylamine-1-^{14}C with Nitrous Acid[1]

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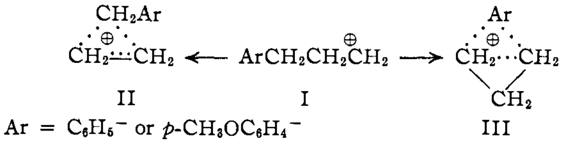
3-Phenyl-1-propylamine-1-^{14}C reacts with nitrous acid in aqueous solution to give hydrocinnamyl alcohol, benzylmethylcarbinol and allylbenzene. Under similar conditions, 3-(p-methoxyphenyl)-1-propylamine-1-^{14}C gives p-methoxyhydrocinnamyl alcohol, p-methoxybenzylmethylcarbinol and p-methoxyallylbenzene. A negligible amount of isotope-position rearrangement attends the formation of the above products. The course of the reactions of 3-aryl-1-propylamines with nitrous acid is discussed.

The tendency of the 3-aryl-1-propyl cations (I) to be converted into the bridged-carbonium ions II and III has been investigated as part of research[3] directed to the elucidation of the factors which determine the degree of rearrangement in carbonium ion-type reactions.



Ar = $C_6H_5^-$ or p-$CH_3OC_6H_4^-$

The isotopic tracer technique was used to detect carbon-skeleton rearrangements and the primary amine–nitrous acid reaction was used for the irreversible generation of I.

The products of the reaction of 3-phenyl-1-propylamine with excess nitrous acid in aqueous solution were hydrocinnamyl alcohol (IV), benzylmethylcarbinol (V) and allylbenzene (VI), along with smaller amounts of organic nitrites and nitro compounds and a considerable amount of higher boiling material, which was probably nitroso secondary amine as found in similar reactions.[4] The absence of other isomeric phenylpropanols and phenylpropenes was demonstrated by comparison of infrared spectra with those of authentic samples of possible contaminants.

β-Phenylpropionitrile-1-^{14}C was prepared by the reaction of 2-phenylethyl bromide with sodium cyanide-^{14}C and was reduced with lithium aluminum hydride to 3-phenyl-1-propylamine-1-^{14}C. A solution of the active amine in dilute aqueous perchloric acid was treated with sodium nitrite at 50–55°. Inactive IV, V and VI were added to act as carriers; the products were separated by fractionation and yields calculated from the extent of isotopic dilution (*cf.* Table I).

TABLE I

PRODUCTS FROM THE REACTIONS OF 3-ARYL-1-PROPYLAMINES WITH AQUEOUS NITROUS ACID

	3-Phenyl-1-propylamine, 50–55°	3-(p-Methoxyphenyl)-1-propylamine, 60°
3-Aryl-1-propanol, %	30[a]	27[a]
1-Aryl-2-propanol, %	19[a]	18[a]
3-Arylpropene, %	12[a]	13[a]
Recovered amine, %	9	7.5

[a] Obtained by isotope-dilution analysis.

The reaction of 3-(p-methoxyphenyl)-1-propylamine with excess nitrous acid in aqueous solution at 55° gave p-methoxyhydrocinnamyl alcohol (VII), p-methoxybenzylmethylcarbinol (VIII) and p-methoxyallylbenzene (IX), along with side products of the types mentioned earlier. The infrared spectra of the reaction products were essentially identical in all major respects with those of the corresponding authentic samples except for a strong absorption band at 6.4 μ in the spectrum of VII.

β-(p-Methoxyphenyl)-propionitrile-1-^{14}C was prepared by the reaction of 2-(p-methoxyphenyl)-ethyl p-toluenesulfonate with sodium cyanide-^{14}C, and was reduced to 3-(p-methoxyphenyl)-1-propylamine-1-^{14}C with lithium aluminum hydride. A solution of the active amine in excess dilute aqueous perchloric acid was treated with sodium nitrite

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[1] Supported in part by the program of research of the U. S. Atomic Energy Commission and the Petroleum Research Fund of the American Chemical Society.

[2] (a) National Science Foundation Predoctoral Fellow, 1952-1954; (b) Gates and Crellin Laboratories, California Institute of Technology.

[3] (a) J. D. Roberts, R. E. McMahon and J. S. Hine, THIS JOURNAL, **72**, 4237 (1950); (b) J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 2509, 3542 (1951); (c) J. D. Roberts and C. C. Lee, *ibid.*, **73**, 5009 (1951); (d) J. D. Roberts, W. Bennett, R. E. McMahon and E. W. Holroyd, Jr., *ibid.*, **74**, 4283 (1952); (e) J. D. Roberts and G. R. Coraor, *ibid.*, **74**, 3586 (1952); (f) J. D. Roberts and J. A. Yancey, *ibid.*, **74**, 5943 (1952); (g) J. D. Roberts and C. M. Regan, *ibid.*, **75**, 2069 (1953); (h) J. D. Roberts and J. A. Yancey, *ibid.*, **75**, 3165 (1953); (i) J. D. Roberts and M. Halmann, *ibid.*, **75**, 5759 (1953); (j) J. D. Roberts, C. C. Lee and W. H. Saunders, Jr., *ibid.*, **76**, 4501 (1954).

[4] (a) D. W. Adamson and J. Kenner, *J. Chem. Soc.*, 838 (1934); (b) E. Linnemann, *Ann.*, **161**, 43 (1872).

at 60°. Inactive VII, VIII and IX were added to the reaction mixture and the products were isolated and yields calculated as before (*cf.* Table I).

Degradative Procedures

The degradative procedures used for hydrocinnamyl-x-^{14}C alcohol (IV), benzylmethylcarbinol-x-^{14}C (V) and allylbenzene-x-^{14}C (VI) are outlined in Fig. 1a, b and c, respectively. The data for the corresponding ^{14}C-activity measurements are given in Table II.

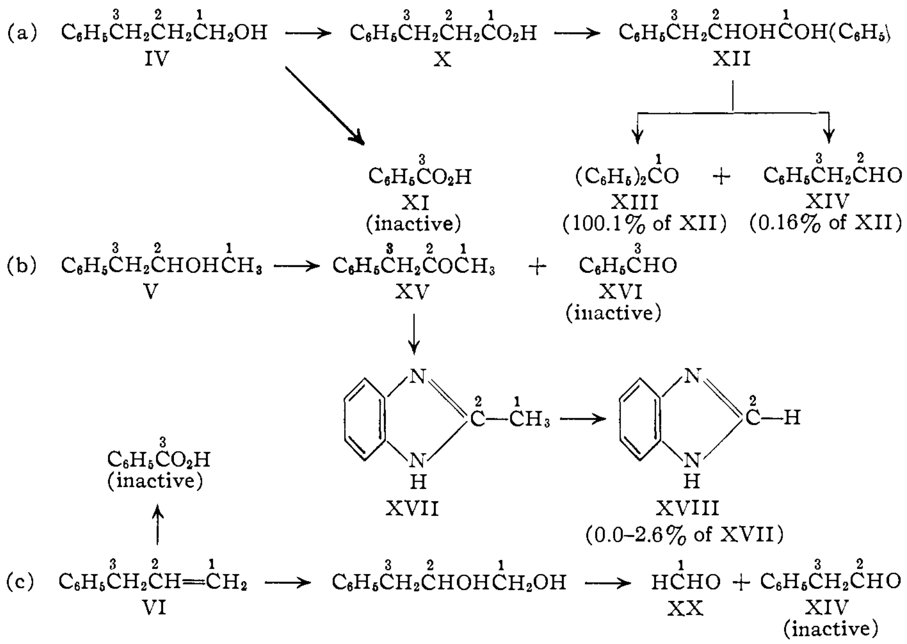


Fig. 1.—Degradation of the products of the reaction of 3-phenyl-1-propylamine-1-^{14}C with nitrous acid. The ^{14}C-distribution is indicated in parentheses under the degradation products.

Both hydrocinnamyl-x-^{14}C alcohol from 3-phenyl-1-propylamine-1-^{14}C and authentic hydrocinnamyl-1-^{14}C alcohol were oxidized to hydrocinnamic-^{14}C acid and the corresponding radioactive acid samples treated with hydrazoic acid to give 2-phenylethylamine and carbon dioxide. The fraction of total ^{14}C-activity appearing in the 2-phenylethylamine fragment from hydrocinnamyl-1-^{14}C alcohol was the same, within experimental error, as that found in the 2-phenylethylamine fragment from the amine–nitrous acid reaction product IV. Thus, the amount of carbon-skeleton rearrangement attending the formation of alcohol IV in the amine–nitrous acid reaction is zero, within experimental error. The data for the ^{14}C-activity measurements in the degradation of hydrocinnamyl-1-^{14}C alcohol are given in Table II.

TABLE II

^{14}C-ACTIVITY MEASUREMENTS ON THE 3-PHENYL-1-PROPYLAMINE-1-^{14}C–NITROUS ACID REACTION PRODUCTS

Compound	µcuries/mmole[a]
Degradation of hydrocinnamyl-x^{14}-C alcohol (IV)	
$C_6H_5CH_2CHOHCOH(C_6H_5)_2$ (XII)	0.950 ± 0.008
$(C_6H_5)_2CO$ (XIII) as 2,4-dinitrophenylhydrazone[c]	0.951 ± 0.017
$C_6H_5CH_2CHO$ (XIV) as dimethone derivative	$(1.5 \pm 0.2) \times 10^{-3}$
$C_6H_5CH_2CH_2CO_2H$ (X)	1.39 ± 0.01[b]
$C_6H_5CO_2H$ (XI)	(0.0–8.6)[b] × 10^{-5}
$C_6H_5CH_2CH_2NH_2$ as benzoyl derivative	(2.8 ± 1.6)[b] × 10^{-3}
Degradation of hydrocinnamyl-1-^{14}C alcohol	
$C_6H_5CH_2CH_2CO_2H$ as anilide	0.785 ± 0.011[b]
$C_6H_5CH_2CH_2NH_2$ as benzoyl derivative	(2.5 ± 0.4)[b] × 10^{-3}
$C_6H_5CO_2H$ (XI)	(0–9)[b] × 10^{-5}
Degradation of benzylmethylcarbinol-x-^{14}C (V)	
$C_6H_5CH_2CHOHCH_3$ (V) as *p*-toluenesulfonate	1.405 ± 0.020
C_6H_5CHO (XVI) as octahydroxanthene derivative	(5.3 ± 1.6)[b] × 10^{-4}
2-Methylbenzimidazole (XVII)[c]	(1.03 ± 0.03)[b] × 10^{-2}
Benzimidazole (XVIII)[c]	(0.0–2.7)[b] × 10^{-4}
Degradation of allylbenzene-x-^{14}C (VI)	
$C_6H_5CH_2CHOHCH_2OH$ as bis-*p*-phenylazobenzoate	1.16 ± 0.02
HCHO (XX) as dimethone derivative	1.223 ± 0.011
$C_6H_5CH_2CHO$ (XIV) as dimethone derivative	(4.4 ± 1.6)[b] × 10^{-4}
$C_6H_5CO_2H$	1 × 10^{-4}

[a] ^{14}C-activities with sample standard deviations for more than one combustion determined by vibrating-reed electrometer method as described by O. K. Neville, THIS JOURNAL, **70**, 3499 (1948), corrected for background. [b] Deviations estimated from recorder chart variations for single determinations. [c] To remove oxides of nitrogen, a heated lead peroxide cartridge was placed in the combustion line as recommended by W. A. Bonner and C. J. Collins, *ibid.*, **75**, 3693 (1953).

The wide limits of error in the percentage of ^{14}C-activity found at C-2 of benzylmethylcarbinol-^{14}C (V) are due to excessive isotope dilution in the course of this degradation (Fig. 1b).

The degradations of *p*-methoxyhydrocinnamyl-^{14}C alcohol (VII), *p*-methoxybenzylmethylcarbinol-^{14}C (VIII) and *p*-methoxyallylbenzene-^{14}C (IX) are outlined in Fig. 2a, b and c, respectively. The very low ^{14}C-activity found at C-2 and C-3 in each case shows that essentially no carbon-skeleton rearrangement attends the reaction of 3-(*p*-methoxyphenyl-1-propylamine-1-^{14}C with nitrous acid. The ^{14}C-activity data for the products of the degradation reactions are given in Table III.

Discussion

The failure of benzyl and *p*-methoxybenzyl groups to migrate significantly in the reactions studied in the present work shows that the symmetrical bridged ions, II, were not intermediates.

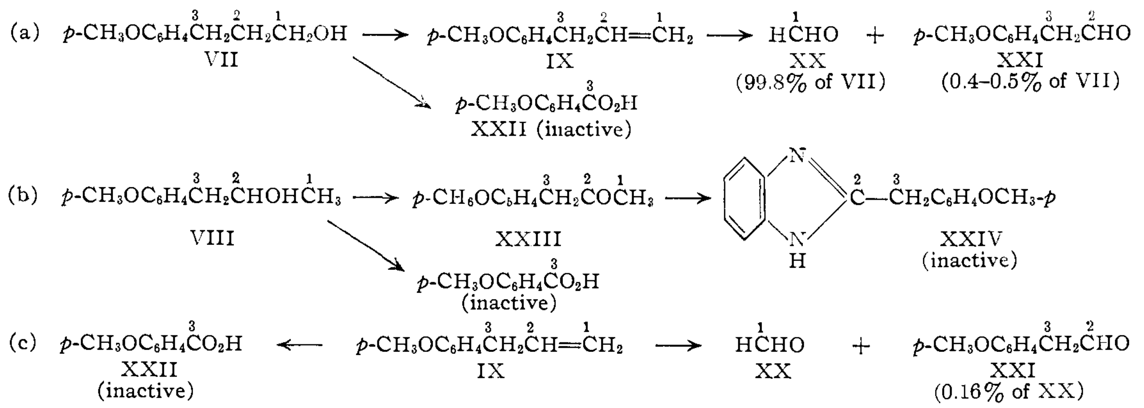
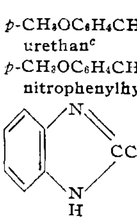


Fig. 2.—Degradation of the products of the reaction of 3-(*p*-methoxyphenyl)-1-propylamine-1-^{14}C with nitrous acid. The ^{14}C-distribution is indicated in parentheses under the degradation products.

TABLE III

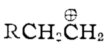
^{14}C-ACTIVITY MEASUREMENTS ON THE 3-(*p*-METHOXYPHENYL)-1-PROPYLAMINE-1-^{14}C–NITROUS ACID REACTION PRODUCTS

Compound	μcuries/mmole[a]
Degradation of *p*-methoxyhydrocinnamyl-*x*-^{14}C alcohol (VII)	
p-$CH_3OC_6H_4CH_2CH_2CH_2OH$ (VII) as phenylurethan[c]	0.719 ± 0.010
HCHO (XX) as dimethone derivative	0.718 ± 0.010
p-$CH_3OC_6H_4CH_2CHO$ (XXI) as dimethone derivative	$(3.4 \pm 0.3)^b \times 10^{-3}$
p-$CH_3OC_6H_4CO_2H$ (XXII)	$(1.6 \pm 0.6)^b \times 10^{-4}$
Degradation of *p*-methoxybenzylmethylcarbinol-*x*-^{14}C (VIII)	
p-$CH_3OC_6H_4CH_2CHOHCH_3$ (VIII) as phenylurethan[c]	0.528 ± 0.010
p-$CH_3OC_6H_4CH_2COCH_3$ (XXIII) as 2,4-dinitrophenylhydrazone[c]	0.0542 ± 0.0007
 $CCH_2C_6H_4OCH_3$-*p* (XXIV)[c]	$(0.0\text{-}2.1)^b \times 10^{-5}$
p-$CH_3OC_6H_6CO_2H$	$(0\text{-}0) \times 10^{-5}$
Degradation of *p*-methoxyallylbenzene-*x*-^{14}C (IX)	
HCHO (XX) as dimethone derivative	1.072 ± 0.015
p-$CH_3OC_6H_4CH_2CHO$ (XXI) as dimethone derivative	$(1.7 \pm 0.2)^b \times 10^{-3}$
p-$CH_3OC_6H_4CO_2H$	$(0.0\text{–}2.6)^b \times 10^{-4}$

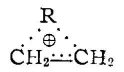
[a,b,c] See corresponding footnotes to Table II.

The present results, taken with data from similar work on 2-(*p*-methoxyphenyl)-ethylamine-1-^{14}C,[3g] 2-phenylethylamine-1-^{14}C,[3g] *n*-propylamine-1-^{14}C,[3i] and ethylamine-1-^{14}C,[3f] indicate the following decreasing order of stability of the symmetrical "ethyleneonium" ions (XXVI) relative to the corresponding classical carbonium ions (XXV)

$$R = p\text{-}CH_3OC_6H_4\text{–} > C_6H_5\text{–} > CH_3\text{–} > H\text{–} > C_6H_5CH_2\text{–} \simeq p\text{-}CH_3OC_6H_4CH_2\text{–}$$


$RCH_2\overset{\oplus}{C}H_2$

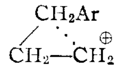
XXV



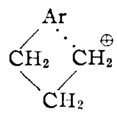
XXVI

This order can be correlated with Kharasch's "electronegativity series,"[5] which was established by the direction of cleavage of unsymmetrical organomercury compounds with hydrogen chloride. The following decreasing order of "electronegativity" (decreasing ease of cleavage of the R–Hg bond) was established: *p*-$CH_3OC_6H_4$– > C_6H_5– > CH_3– > $C_6H_5CH_2$–. The parallelism between ease of cleavage of R–Hg bonds and ease of rearrangement of R– could be anticipated on the basis that in each reaction the R– group is transferred to an electrophilic center; in one case, a proton, and, in the other, an adjacent cationic carbon.

The failure of either phenyl or *p*-methoxyphenyl groups to migrate in the reactions studied shows that the *symmetrical* bridged-ions III were also not important intermediates. However, the *unsymmetrical* bridged ions, XXVII and XXVIII, cannot be eliminated as intermediates by the results of the present work. If XXVII or XXVIII were intermediates in the 3-arylpropylamine–nitrous acid reactions and led to primary alcohols without isotope-position rearrangement, such intermediates



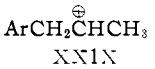
XXVII



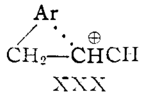
XXVIII

should probably also be involved in SN1 or *Lim.* type[6] solvolysis reactions of 3-aryl-1-propyl derivatives and should be detectable through enhanced solvolysis rates. However, recent kinetic studies by Winstein and co-workers[7] on the solvolysis of 3-aryl-1-propyl derivatives indicate that neighboring group participation does not occur in the rate-determining steps of solvolysis reactions of such systems, and it seems, therefore, that XXVII and/or XXVIII were not important intermediates in the deamination reactions.

If the cation XXIX is an intermediate in our reactions, then XXX is sure to be important also, since Winstein and co-workers have shown that the type of participation indicated by XXX is very significant in solvolysis reactions of the 1-aryl-2-propyl


$ArCH_2\overset{\oplus}{C}HCH_3$

XXIX



XXX

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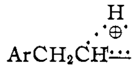
(5) M. S. Kharasch and A. L. Flenner, THIS JOURNAL, **54**, 674 (1932).

(6) S. Winstein, E. Grunwald and H. W. Jones, *ibid.*, **73**, 2700 (1951).

(7) Professor S. Winstein, private communication.

system.[8] However, formation of XXX does not necessarily imply that XXIX was also an intermediate, since XXX could arise directly from XXXI. The present results are compatible with the formation of XXX, but allow no final decision.[9]

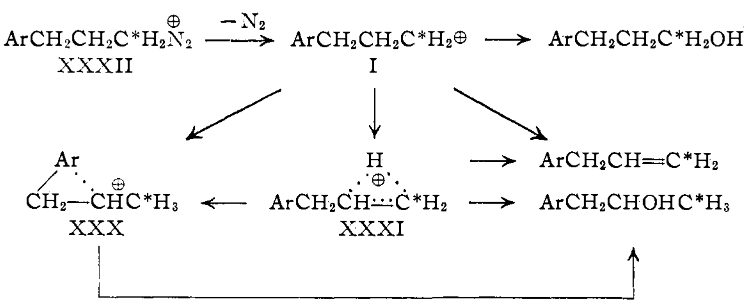


$$ArCH_2\overset{\overset{H}{\cdot\oplus\cdot}}{CH}\text{---}CH_2$$

XXXI

Another possible interpretation of the present results is that the diazonium cation XXXII loses a molecule of nitrogen to form the simple carbonium ion I which may lose a proton to give olefin, react with solvent to give unrearranged product, or go to the "ethyleneprotonium" ion XXXI. Because of its dissymmetry, XXXI would be expected to give only secondary alcohol with water. XXXI could also lose its bridging proton to give olefin, or go to the unsymmetrical phenonium ion XXX. Either the pair of intermediates I and XXXI or the pair I and XXX alone could account for all of the observed products as well as the lack of formation of 1-aryl-1-propanols and 1-arylpropenes.

Part of the primary alcohol product could be formed by reaction of the diazonium cation XXXII with water by the SN2 mechanism, but this seems unlikely in view of the fact that the primary amine–nitrous acid reaction occurs readily with neopentylamine[10] and with bridgehead amines[11] where such a mechanism is not favorable. Furthermore, the extensive rearrangements that occur when *n*-propylamine,[3i,12] *n*-butylamine,[13] 2-phenylethylamine-1-^{14}C[3g] and other primary amines are treated with nitrous acid indicate that direct displacement of nitrogen from the diazonium cation is not usually important.



Ar = C_6H_5– or *p*-$CH_3OC_6H_4$–

Acknowledgment.—We are indebted to Professor S. Winstein of the University of California at Los Angeles for discussions and for information regarding the solvolysis of 3-aryl-1-propyl sulfonates in advance of publication. We are indebted also to Professor George S. Hammond of Iowa State College for pointing out the relationship between some results of the present work and Kharasch's electronegativity series.

Experimental

All melting points reported are corrected.

3-Phenyl-1-propylamine.—Redistilled β-phenylpropionitrile (105 g., 0.80 mole) was reduced with lithium aluminum hydride and the product isolated by the procedure of Amundsen and Nelson.[14] The yield of 3-phenyl-1-propylamine, b.p. 90–91° (8 mm.), was 89 g. (83%).

The ***p*-toluenesulfonamide** was prepared in pyridine solution and recrystallized from methanol, m.p. 64.9–65.3°.

Anal. Calcd. for $C_{16}H_{19}NO_2S$: C, 66.40; H, 6.62; N, 4.84. Found: C, 66.45; H. 6.54; N, 4.85.

3-Phenyl-1-propyl *p*-Nitrobenzoate.—A commercial sample of hydrocinnamyl alcohol was distilled through a 54 × 0.7-cm. column provided with a tantalum spiral, and a fraction, b.p. 129° (19.3 mm.) (lit.,[15] b.p. 132° (21 mm.)), was taken for physical properties and infrared spectrum, $n^{25.9}D$ 1.5237 (lit.,[15] $n^{20}D$ 1.5278). The ***p*-nitrobenzoate** was prepared in pyridine solution and recrystallized from methanol, m.p. 46–47°.

Anal. Calcd. for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30; N, 4.91. Found: C, 67.28; H, 5.33; N, 5.06.

Benzylmethylcarbinol and Derivatives.—Benzyl methyl ketone[16] was reduced with excess lithium aluminum hydride. Distillation gave 13 g. (65%) of benzylmethylcarbinol, b.p. 100–101° (14.5 mm.), $n^{24.5}D$ 1.5198. Another sample of benzyl methyl ketone was reduced by the Meerwein-Ponndorf-Verley method.[17] The yield of benzylmethylcarbinol, b.p. 97–104.5° (15 mm.), was 83%. Redistillation through a 54 × 0.7-cm. column packed with a tantalum spiral gave material of b.p. 101–102° (13 mm.), $n^{25}D$ 1.5188 (lit.,[8] b.p. 97° (10.5 mm.), $n^{25}D$ 1.5181–1.5182). The *p*-toluenesulfonate had m.p. 90.9–91.4° after recrystallization from petroleum ether (lit.,[8] m.p. 93.7–94°).

The *p*-nitrobenzoate was prepared in pyridine solution and recrystallized from methanol, m.p. 60.8–61.4°.

Anal. Calcd. for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30; N, 4.91. Found: C, 67.28; H, 5.32; N, 4.99.

Allylbenzene.—Hydrocinnamyl acetate, b.p. 133° (18 mm.) (61 g., 0.34 mole) was passed over glass wool heated at 460–485°. The pyrolysis product was washed with aqueous sodium carbonate solution, dried and distilled at atmospheric pressure. The yield of allylbenzene, b.p. 150–160°, was 31 g. (76%). On redistillation through a 36 × 1-cm. spinning-band column, most of the olefin was collected at 59–59.5° (23.5 mm.), $n^{25}D$ 1.5097, Siwoloboff b.p. 159.0° (759 mm.) (lit.[18] b.p. 158.6° (760 mm.), $n^{20}D$ 1.5110).

The Reaction of 3-Phenyl-1-propylamine with Nitrous Acid.—A stirred solution of 33.8 g. (0.25 mole) of 3-phenyl-1-propylamine and 24.3 g. (0.35 mole) of sodium nitrite in 250 ml. of 1.0 *M* perchloric acid and 50 ml. of water was heated to 80–90° for one hour. The reaction mixture was allowed to cool somewhat and 63 ml. of 1.0 *M* perchloric acid was added to the reaction flask. The mixture was again heated to 80–90° for a short time, then cooled and extracted with ether. The combined ether extracts were washed with dilute sulfuric acid, then with dilute sodium carbonate solution, finally with water, and dried. The residue from evaporation of ether was boiled under reflux with methanol to convert organic nitrites into the corresponding carbinols. Methanol was removed by distillation and the residue was distilled under reduced pressure to give 1.65 g. (5.6%) of allylbenzene, b.p. 55–56° (20 mm.), $n^{25.5}D$ 1.5087; 20.7 g. (61%) of a carbinol mixture, b.p.

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(8) S. Winstein, M. Brown, K. C. Schreiber and A. H. Schlesinger, THIS JOURNAL, **74**, 1140 (1952).

(9) XXX would lead to secondary alcohol without isotope-position rearrangement.[8] The corresponding intermediate from 3-aryl-1-butylamine-1-^{14}C, if formed, would probably be symmetrical and lead to secondary alcohol showing isotope-position rearrangement.

(10) (a) M. Freund and F. Lenze, *Ber.*, **23**, 2865 (1890); **24**, 2150 (1891); (b) L. Tissier, *Ann. chim. phys.*, [6] **29**, 335 (1893).

(11) D. E. Applequist and J. D. Roberts, *Chem. Revs.*, **54**, 1065 (1954).

(12) F. C. Whitmore and R. S. Thorpe, THIS JOURNAL, **63**, 1118 (1941).

(13) F. C. Whitmore and D. P. Langlois, *ibid.*, **54**, 3441 (1932).

(14) L. H. Amundsen and L. S. Nelson, *ibid.*, **73**, 242 (1951).

(15) F. A. Hochstein and W. G. Brown, *ibid.*, **70**, 3484 (1948).

(16) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 391.

(17) A. L. Wilds in Adams, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 178.

(18) M. G. Voronkov, A. S. Broun and G. B. Karpenko, *J. Gen. Chem.* (*U.S.S.R.*), **19**, 1927 (1949); *C. A.*, **44**, 1956 (1950).

120–140° (31 mm.); and 6.4 g. of a high-boiling residue. Fractionation of the carbinol mixture in a 36 × 1-cm. spinning-band column under reduced pressure gave a 25% over-all yield of hydrocinnamyl alcohol and a 15% over-all yield of benzylmethylcarbinol, both identified by the melting points of their *p*-nitrobenzoates. The hydrocinnamyl alcohol was treated with aqueous alkali to remove a small amount of a nitro-compound contaminant and redistilled through a semi-micro column,[19] b.p. 129–130° (20.7 mm.), $n^{25}\text{D}$ 1.5242–1.5245. The infrared spectrum was essentially identical with that of a sample of authentic hydrocinnamyl alcohol except for a weak band at 6.45 μ. The crude benzylmethylcarbinol product was shaken with ammoniacal silver oxide solution to oxidize an aldehyde impurity. Distillation through a semi-micro column[19] gave material of b.p. 107° (17.5 mm.) and $n^{25}\text{D}$ 1.5185 which had an infrared spectrum like that of authentic benzylmethylcarbinol except for a weak band at 10.25 μ.

Preparation and Diazotization of 3-Phenylpropylamine-1-^{14}C.—β-Phenylpropionitrile-1-^{14}C was prepared from 2-phenylethyl bromide (2.5 g., 13.5 mmoles) and sodium cyanide-^{14}C (0.5 mmole containing 5×10^2 μcuries of ^{14}C-activity) in 80% ethanol. The reaction mixture was boiled under reflux for 20 hours and the radioactive nitrile was recovered with the aid of 32.4 g. of inactive β-phenylpropionitrile as carrier after dilution of the reaction mixture with half-saturated calcium chloride solution and extraction with chloroform. β-Phenylpropionitrile-1-^{14}C was purified by distillation at reduced pressure, b.p. 129–130.5° (16.5 mm.).

Reduction of β-phenylpropionitrile-1-^{14}C was carried out as with the inactive nitrile. The yield of 3-phenyl-1-propylamine-1-^{14}C, b.p. 100.5–101.5° (13.5 mm.), was 91%.

Sodium nitrite (19.4 g., 0.28 mole) in 100 ml. of water was added over a period of 1.5 hours to a stirred solution of 26.5 g. (0.196 mole) of 3-phenyl-1-propylamine-1-^{14}C in 250 ml. of 1.0 *M* perchloric acid at 50–55°. The reaction mixture was stirred at 50–55° for an additional two hours, cooled, acidified and extracted with ether. The crude products were treated with aqueous sodium hydroxide to remove alkyl nitro compounds, then boiled under reflux with dry methanol to convert organic nitrites into the corresponding carbinols. Inactive hydrocinnamyl alcohol (2.3 g.), benzylmethylcarbinol (1.4 g.) and allylbenzene (1.3 g.) were added to the product mixture to act as carriers; the mixture was treated with silver nitrate and sodium hydroxide in aqueous alcohol to oxidize any aldehydes present and then fractionated in a 36 × 1-cm. spinning-band column under reduced pressure. The yields of the several products were calculated from the amount of isotope dilution.

Degradation of Hydrocinnamyl-*x*-^{14}C Alcohol.—Hydrocinnamyl-*x*-^{14}C alcohol (6.5 g., 48 mmoles) was oxidized with chromium trioxide in 95% acetic acid.[20] The yield of hydrocinnamic-*x*-^{14}C acid, m.p. 47–48.5°, was 2.2 g. (31%). Hydrocinnamic-*x*-^{14}C acid (0.1 g.) was oxidized with alkaline permanganate to benzoic acid which had m.p. 121.5–122.5° after two recrystallizations from water.

The degradation of hydrocinnamic-*x*-^{14}C acid is outlined in Fig. 1a. The methyl ester was prepared by treating 1.5 g. (10 mmoles) of hydrocinnamic-*x*-^{14}C acid with a slight excess of a dry ether solution of diazomethane. The oily crude product from the reaction of methyl hydrocinnamate-*x*-^{14}C with excess phenylmagnesium bromide was dissolved in petroleum ether. When cooled, the petroleum ether solution deposited 1.43 g. (5.0 mmoles) of 1,1,3-triphenylpropane-1-ol-*x*-^{14}C. This carbinol (0.88 g., 2.9 mmoles) was dehydrated at the steam-bath temperature with 20% sulfuric acid. Inactive 1,1,3-triphenylpropene (0.35 g., 1.2 mmoles), b.p. 178–181° (1.1 mm.), was added to the active olefin to act as carrier. Hydroxylation of the active olefin with 1.0 ml. of 30% hydrogen peroxide in 15 ml. of 98–100% formic acid gave, after saponification, 0.65 g. (2.1 mmoles) of **1,1,3-triphenylpropane-1,2-diol-*x*-^{14}C**, m. p. 143–148°. A sample of the active diol (100 mg.) was recrystallized from benzene–petroleum ether for activity measurements, m.p. 150.4–150.8°.

Anal. Calcd. for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62. Found: C, 82.81; H, 6.65.

1,1,3-Triphenylpropane-1,2-diol-*x*-^{14}C was stirred with the calculated amount of lead tetraacetate and excess anhydrous potassium carbonate in dry benzene. Phenylacetaldehyde was obtained as the dimethone derivative by the general procedure of Horning and Horning,[21] m.p. 168–169.3° (lit. m.p. 164–165°,[22] m.p. 164–166°[23]) after two recrystallizations from methanol. The mother liquors from the preparation of the dimethone derivative of phenylacetaldehyde were diluted with aqueous calcium chloride and extracted with ether. The ether was evaporated and the residue dissolved in acetone and allowed to stand for two days with potassium permanganate. Benzophenone-*x*-^{14}C was recovered from the acetone solution and converted into the 2,4-dinitrophenylhydrazone, m.p. 240.3–241.5° (lit.[24] m.p. 239.5–240°) after recrystallization from dioxane containing a little ethanol.

Excess sodium azide was added in small portions to a mechanically stirred mixture of 0.49 g. (3.3 mmoles) of hydrocinnamic-*x*-^{14}C acid, 25 ml. of chloroform and 5 ml. of concentrated sulfuric acid. The mixture was stirred at room temperature for one hour, then at 40–45° for one hour. A low yield of 2-phenylethylamine was obtained from the reaction mixture as the benzoyl derivative, m.p. 113–115°.

Preparation and Degradation of Hydrocinnamyl-1-^{14}C Alcohol.—Hydrocinnamic-1-^{14}C acid, m.p. 47.5–48.5°, was obtained by the alkaline hydrolysis of β-phenylpropionitrile-1-^{14}C. Hydrocinnamyl-1-^{14}C alcohol was obtained by reduction of the active acid with lithium aluminum hydride. Oxidation[20] of hydrocinnamyl-1-^{14}C alcohol with chromium trioxide in acetic acid gave hydrocinnamic-1-^{14}C acid which was degraded by means of the Schmidt reaction as described in the previous section.

Degradation of Benzylmethylcarbinol-*x*-^{14}C.—Benzylmethylcarbinol-*x*-^{14}C (5.5 g., 0.041 mole) was stirred overnight at room temperature with 2.8 g. (0.028 mole) of chromium trioxide in 20 ml. of 80% acetic acid. Fractionation[19] of the crude mixture of products under reduced pressure gave 0.3 g. of benzaldehyde (octahydroxanthene derivative, m.p. 205.5–206°), 2.0 g. of benzyl methyl ketone, and 1.2 g. of a mixture of benzylmethylcarbinol (*p*-toluenesulfonate, m.p. 90.8–91°) and benzyl methyl ketone (2,4-dinitrophenylhydrazone, m.p. 152–153°).

The benzyl methyl ketone fraction was diluted with 2.0 g. of inactive benzyl methyl ketone and heated to 230° for 2.5 hours with an equivalent amount (3.1 g.) of *o*-phenylenediamine.[25] The highly colored reaction mixture yielded a small amount of 2-methylbenzimidazole-*x*-^{14}C, m.p. 175–175.7° after sublimation and recrystallization from water, as the only pure product. 2-Methylbenzimidazole-*x*-^{14}C was diluted with inactive 2-methylbenzimidazole and degraded by the procedure of Roseman[26] to benzimidazole, m.p. 171.8–172.2° (lit.[27] m.p. 170°). The picrate was recrystallized from ethanol, m.p. 229–230° (lit.[28] m.p. 225–226°).

Degradation of Allylbenzene-*x*-^{14}C.—Allylbenzene-*x*-^{14}C (0.30 g., 2.5 mmoles) was stirred with 5 ml. of 98–100% formic acid and 0.9 ml. of 30% hydrogen peroxide. The reaction became homogeneous in about 15 minutes and was then allowed to stand at room temperature for several hours. The formic acid was removed under reduced pressure and the residue boiled under reflux with 20% aqueous sodium hydroxide containing a little ethanol. The saponification reaction mixture was diluted with water and the 3-phenylpropane-1,2-diol-*x*-^{14}C removed by continuous ether extraction. The ether was removed from a portion of the active diol solution and the residue stirred at room temperature with lead tetraacetate and anhydrous potassium carbonate in 5 ml. of benzene. The resulting formaldehyde was extracted from the reaction mixture with water and converted into the dimethone derivative, m.p. 191–191.6° after recrystallization from methanol. The benzene layer from the

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[19] C. W. Gould, Jr., G. Holzman and C. Niemann, *Anal. Chem.*, **20**, 361 (1948).

[20] L. Rugheimer, *Ann.*, **172**, 122 (1874).

[21] E. C. Horning and M. G. Horning, *J. Org. Chem.*, **11**, 95 (1946).

[22] K. H. Lin and R. Robinson, *J. Chem. Soc.*, 2005 (1938).

[23] E. B. Hershberg, *Helv. Chim. Acta*, **17**, 351 (1934).

[24] W. A. Bonner and C. J. Collins, THIS JOURNAL, **75**, 5372 (1953).

[25] This reaction was patterned after that of R. C. Elderfield and F. J. Kreysa, THIS JOURNAL, **70**, 44 (1948). The use of a full equivalent of *o*-phenylenediamine is probably the cause of the difficulty in purification of the product.

[26] S. Roseman, *ibid.*, **75**, 3854 (1953).

[27] A. Bistrzycki and G. Przeworski, *Ber.*, **45**, 3483 (1912).

[28] S. Skraup, *Ann.*, **419**, 70 (1919).

lead tetraacetate cleavage was filtered and benzene removed by evaporation. The residual phenylacetaldehyde was converted into the dimethone derivative, m.p. 168.5–169.8° after recrystallization from methanol.

The ether was removed from the remaining 3-phenylpropane-1,2-diol-*x*-^{14}C solution (about two-fifths of the original amount) and the residue dried by azeotropic distillation of the water with benzene. The dried diol was warmed with 0.5 g. (2 mmoles) of *p*-phenylazobenzoyl chloride in 8 ml. of dry pyridine. The reaction mixture was allowed to stand overnight at room temperature and the crude **bis-*p*-phenylazobenzoyl derivative** recrystallized first from cyclohexane then from ethanol–ethyl acetate, m.p. 155–156°.

Anal. Calcd. for $C_{35}H_{28}N_4O_4$: C, 73.93; H, 4.96. Found: C, 73.95; H, 5.00.

***p*-Methoxyhydrocinnamyl Alcohol.**—Lithium aluminum hydride (10.4 g., 0.27 mole) and 600 ml. of dry ether were placed in a flask equipped with a mechanical stirrer and a bulb surmounted by a reflux condenser. An extraction thimble containing 26.7 g. (0.15 mole) of *p*-methoxycinnamic acid was placed in the bulb, the mixture stirred and heated under reflux until all of the organic acid was extracted. Distillation of the product gave a small fraction (1.7 g.), b.p. 128–131° (2.8 mm.), and a main fraction (16.7 g., 69%) of *p*-methoxyhydrocinnamyl alcohol, b.p. 138° (3.5 mm.), n^{25}D 1.5309. The main fraction was redistilled in a 36 × 1 cm. spinning-band column. After a small forerun, there was obtained 15.0 g. of the carbinol, b.p. 134.5–135.5° (4.3 mm.) (lit.[29] b.p. 162° (15 mm.)), n^{25}D 1.5305. The N-phenylcarbamate of *p*-methoxyhydrocinnamyl alcohol melted at 66–66.2° (lit.[29] m.p. 67°).

***p*-Methoxybenzylmethylcarbinol.**—Anisylacetone[8] was reduced with a slurry of lithium aluminum hydride in ether. Distillation of the crude product under reduced pressure gave an 87% yield of *p*-methoxybenzylmethylcarbinol, b.p. 140–141° (13 mm.), $n^{22.5}$D 1.5258 (lit.[8] b.p. 119° (4 mm.), n^{25}D 1.5261).

p-Methoxybenzylmethylcarbinyl *p*-toluenesulfonate was prepared in pyridine solution and recrystallized twice from petroleum ether, m.p. 80.0–80.8° (lit.[8] m.p. 80.0°).

The N-phenylcarbamate of *p*-methoxybenzylmethylcarbinol melted at 74.5–75° after four recrystallizations from petroleum ether.

Anal. Calcd. for $C_{17}H_{19}NO_3$: C, 71.56; H, 6.71. Found: C, 71.68; H, 6.76.

***p*-Methoxyallylbenzene.**—*p*-Methoxyhydrocinnamyl alcohol (8.31 g., 0.05 mole) was boiled under reflux for 2.5 hours with 10 g. of acetic anhydride and 1.0 ml. of pyridine. The resulting *p*-methoxyhydrocinnamyl acetate was freed of acetic acid and passed over glass wool heated to 400°. The crude pyrolysis product was washed with base and distilled through a semi-micro column[19] to give 2.4 g. (32% over-all) of *p*-methoxyallylbenzene, b.p. 100–102° (16 mm.), n^{25}D 1.5239 (lit.[30] b.p. 98–100° (14 mm.), n^{17}D 1.5190).

β-(*p*-Methoxyphenyl)-propionamide was prepared by the general procedure of Boissonnas.[31] Ethyl chloroformate (44 g., 0.405 mole) was added to a stirred solution of 73 g. (0.405 mole) of *p*-methoxyhydrocinnamic acid (m.p. 103–104°) and 37 g. (0.405 mole) of triethylamine in one liter of chloroform at 0°. The solution was stirred for 15 minutes, then a stream of ammonia was passed slowly into the reaction mixture for 10 minutes. The ice-bath was removed and agitation continued for one hour. The reaction mixture was filtered and the chloroform evaporated. The residue was recrystallized from water to give 52.5 g. (65%) of β-(*p*-methoxyphenyl)-propionamide, m.p. 121–123° (lit.[32] m.p. 123–125°).

3-(*p*-Methoxyphenyl)-1-propylamine.—β-(*p*-Methoxyphenyl)-propionamide was reduced with excess lithium aluminum hydride in 750 ml. of ether by the extraction procedure used for *p*-methoxyhydrocinnamyl alcohol. Distillation under reduced pressure gave 18 g. (55%) of 3-(*p*-methoxyphenyl)-1-propylamine, b.p. 124.5° (5.5 mm.)–128° (6.5 mm.).

The *p*-toluenesulfonamide was prepared in pyridine solution and recrystallized from aqueous methanol and benzene–cyclohexane, m.p. 65.7–66.5°.

Anal. Calcd. for $C_{17}H_{21}NSO_3$: C, 63.93; H, 6.63. Found: C, 64.20; H, 6.75.

β-(*p*-Methoxyphenyl)-propionitrile was prepared by the general procedure of English and co-workers.[33] A solution of 10 g. (0.056 mole) of β-(*p*-methoxyphenyl)-propionamide and 27 g. (0.18 mole) of phosphorus oxychloride in 160 ml. of ethylene chloride was boiled under reflux for one hour. The hot reaction mixture was poured onto ice and the layers were separated. The organic layer was washed with potassium carbonate solution then with water and dried. Ethylene chloride was removed by evaporation and the high-boiling residue was distilled under reduced pressure to give 8.0 g. (89%) of β-(*p*-methoxyphenyl)-propionitrile, b.p. 135° (3.1–3.2 mm.).

3-(*p*-Methoxyphenyl)-1-propylamine-1-^{14}C.—*p*-Methoxyphenylacetonitrile (17.6 g., 0.12 mole) was hydrolyzed by the procedure of Wenner.[34] The yield of crude *p*-methoxyphenylacetic acid was 17.9 g. (90%). One recrystallization from benzene–ligroin gave a product melting at 84–85.4°.

p-Methoxyphenylacetic acid was reduced with a slurry of lithium aluminum hydride in ether. The reaction of *p*-toluenesulfonyl chloride with the resulting crude 2-(*p*-methoxyphenyl)-ethanol in pyridine solution at 0° gave a 70% over-all yield of crude 2-(*p*-methoxyphenyl)-ethyl *p*-toluene sulfonate. After one recrystallization from benzene-petroleum ether, this material melted at 57–58° (lit.[35] m.p. 57–58°).

Sodium cyanide-^{14}C (0.5 mmole containing 5 × 10^2 μcuries of ^{14}C) was diluted with 0.27 g. (5.5 mmoles) of inactive sodium cyanide and boiled under reflux overnight with 2.8 g. (9 mmoles) of 2-(*p*-methoxyphenyl)-ethyl *p*-toluenesulfonate in 80% ethanol. Inactive β-(*p*-methoxyphenyl)-propionitrile (8.0 g., 0.05 mole) was added to the reaction mixture to act as carrier and the mixture was poured into chloroform. The chloroform solution was extracted with half-saturated calcium chloride solution, dried, and the solvent removed by evaporation. Distillation under reduced pressure gave 8.5 g. (0.051 mole) of β-(*p*-methoxyphenyl)-propionitrile-1-^{14}C, b.p. 129–133° (2.8 mm.).

β-(*p*-Methoxyphenyl)-propionitrile-1-^{14}C (6.76 g., 0.042 mole) was reduced with lithium aluminum hydride in the usual manner. Inactive 3-(*p*-methoxyphenyl)-1-propylamine (10.3 g.) was added to the reaction mixture to act as carrier. Distillation under reduced pressure gave 13.4 g. of 3-(*p*-methoxyphenyl)-1-propylamine-1-^{14}C, b.p. 110–111° (2.5 mm.).

3-(*p*-Methoxyphenyl)-1-propylamine-1-^{14}C with Nitrous Acid.—The products of the reaction of 3-(*p*-methoxyphenyl)-1-propylamine with excess nitrous acid at 55 ± 2° were *p*-methoxyallylbenzene, *p*-methoxybenzylmethylcarbinol and *p*-methoxyhydrocinnamyl alcohol. These products were isolated and identified as described in the reaction of 3-phenyl-1-propylamine with nitrous acid.

3-(*p*-Methoxyphenyl)-1-propylamine-1-^{14}C (13.2 g., 0.080 mole) was treated with excess aqueous nitrous acid at 60 ± 2°. To the slightly acidic reaction mixture was added 1.38 g. of *p*-methoxyallylbenzene, 6.8 g. of *p*-methoxybenzylmethylcarbinol and 6.6 g. of *p*-methoxyhydrocinnamyl alcohol to act as carriers. The products were isolated as described for those of the 3-phenyl-1-propylamine-1-^{14}C–nitrous acid reaction. Fractionation through a 36 × 1-cm. spinning-band column gave 1.8 g. of *p*-methoxyallylbenzene-*x*-^{14}C, b.p. 101–102° (18.5 mm.); 2.7 g. of an intermediate fraction, boiling from 90 to 139° (10.1 mm.); 7.7 g. of *p*-methoxybenzylmethylcarbinol-*x*-^{14}C, boiling from 133° (7.5 mm.) to 138° (8.2 mm.) (N-phenylcarbamate, m.p. 74.5–77°); 1.8 g. of an intermediate fraction boiling from 141 to 150° (9.6 mm.); and 6.9 g of *p*-methoxyhydrocinnamyl-*x*-^{14}C alcohol, b.p. 133.5–136.5° (4.3 mm.) (N-phenylcarbamate, m.p. 65.7–66°). Refractionation of the column holdup and intermediate fractions in a semi-micro column[19] gave *p*-methoxyallylbenzene-*x*-^{14}C (0.4[illegible] g.), *p*-methoxybenzylmethylcarbinol-*x*-^{14}C (2.5 g.) and *p*-methoxyhydrocinnamyl-*x*-^{14}C alcohol (0.8 g.). The yields (Table I) were calculated from the extent of isotope dilution. The starting material not accounted for (34%) was presumed

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(32) J. Lee, A. Ziering, L. Berger and S. D. Heineman, *Jubilee Vol., Emil Barell*, 264 (1946); *C. A.*, **41**, 6253 (1947).

(33) J. P. English, J. H. Clark, R. G. Shepherd, H. W. Marson, J. Krapcho and R. O. Roblin, Jr., THIS JOURNAL, **68**, 1039 (1946).

(34) W. Wenner, *J. Org. Chem.*, **15**, 548 (1950).

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to be converted into organic nitro compounds, aldehyde and/or nitroso secondary amine.

Degradation of *p*-Methoxyhydrocinnamyl-x-^{14}C Alcohol.—The acetylation and pyrolysis of *p*-methoxyhydrocinnamyl-x-^{14}C alcohol was carried out as described in the preparation of inactive *p*-methoxyallylbenzene. From 6.4 g. (0.038 mole) of the active carbinol, there was obtained 2.0 g. (35%) of *p*-methoxyallylbenzene-x-^{14}C.

To a stirred solution of 1.5 g. (10 mmoles) of *p*-methoxyallylbenzene-x-^{14}C in 20 ml. of 98–100% formic acid was added 0.9 ml. of 30% hydrogen peroxide solution. The mixture was stirred for 10 minutes, an additional 0.9 ml. of 30% hydrogen peroxide solution was added and the reaction allowed to continue at room temperature for 40 minutes. The solvent was removed under reduced pressure, the residue was boiled under reflux for 30 minutes with aqueous methanolic sodium hydroxide and the product was recovered by continuous ether extraction. The crude 3-(*p*-methoxyphenyl)-propane-1,2-diol-x-^{14}C was stirred for 2 hours at room temperatures with 1.5 g. of anhydrous potassium carbonate and 4.4 g. (10 mmoles) of lead tetraacetate in about 10 ml. of benzene. Formaldehyde-^{14}C was recovered from the reaction mixture by extraction with water and converted[21] into its dimethone derivative, m.p. 191.2–191.7° after recrystallization from methanol. The benzene was evaporated from the filtered solution of *p*-methoxyphenylacetaldehyde and the residue taken up in 80% ethanol, filtered and treated with excess methone.[21] **The dimethone derivative of *p*-methoxyphenylacetaldehyde** was recrystallized from aqueous methanol, cyclohexane and finally from methanol, m.p. 152.5–154.5°.

Anal. Calcd. for $C_{25}H_{32}O_5$: C, 72.79; H, 7.82. Found: C, 73.00; H, 7.91.

A sample of *p*-methoxyhydrocinnamyl-x-^{14}C alcohol was oxidized with alkaline permanganate to anisic acid, m.p. 183.8–184.2° after recrystallization from benzene.

Degradation of *p*-Methoxyallylbenzene-x-^{14}C.—*p*-Methoxyallylbenzene-x-^{14}C (1.7 g., 11 mmoles) was hydroxylated and cleaved as described in the degradation of *p*-methoxyhydrocinnamyl-x-^{14}C alcohol. The yield of the dimethone derivative of formaldehyde-^{14}C, m.p. 191.3–191.7°, was 1.6 g. (50% over-all). The yield of the dimethone derivative of *p*-methoxyphenylacetaldehyde-^{14}C, m.p. 153.5–155.5°, was 1.3 g. (28% over-all).

Degradation of *p*-Methoxybenzylmethylcarbinol-x-^{14}C.—*p*-Methoxybenzylmethylcarbinol-x-^{14}C (6.3 g., 0.038 mole) was oxidized with 3.9 g. (0.039 mole) of chromium trioxide in aqueous acetic acid at room temperature. The crude product of the oxidation was diluted with inactive anisylacetone (6.3 g.). Distillation under reduced pressure gave a forerun (1.2 g.) which was discarded and 7.1 g. of anisylacetone-x-^{14}C, b.p. 114–117° (4.3 mm.). The 2,4-dinitrophenylhydrazone was prepared for ^{14}C-activity measurements and had m.p. 107.7–108.1° after several recrystallizations from ethanol.

Anal. Calcd. for $C_{16}H_{16}N_4O_5$: C, 55.81; H, 4.68; N, 16.27. Found: C, 55.69; H, 4.74; N, 16.20.

Anisylacetone-x-^{14}C (6.8 g., 0.039 mole) was heated with 2.2 g. (0.020 mole) of *o*-phenylenediamine under an atmosphere of nitrogen for several hours at 250°. Several recrystallizations of the crude product from aqueous methanol followed by two sublimations gave about 0.5 g. of **2-(*p*-methoxybenzyl)-benzimidazole**, m.p. 165.5–166°.

Anal. Calcd. for $C_{15}H_{14}N_2O$: C, 75.60; H, 5.92; N, 11.66. Found: C, 75.62; H, 5.94; N, 11.76.

The picrate of 2-(*p*-methoxybenzyl)-benzimidazole was prepared in ethanol solution and recrystallized from ethanol, m.p. 188–189°.

Anal. Calcd. for $C_{21}H_{17}N_5O_8$: N, 15.52. Found: N, 15.52.

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[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

An Oxygen-18 Tracer Study of the Rearrangement of *p*-Methoxy-*p*′-nitrobenzoyl Peroxide

BY DONALD B. DENNEY[1]

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p-Methoxy-*p*′-nitrobenzoyl peroxide (III) labeled with oxygen-18 in the anisoyl carbonyl has been rearranged to *p*-methoxyphenyl-*p*-nitrobenzoyl carbonate (IV). Upon hydrolysis IV afforded *p*-methoxyphenol containing no excess oxygen-18. These results exclude the formation of a positive anisate fragment VI as an intermediate in the rearrangement, but are in agreement with a mechanism which involves a concerted shift of *p*-methoxyphenyl to oxygen as the O–O bond undergoes heterolysis.

Within the last few years, it has been shown by many workers that certain compounds containing the peroxidic linkage can decompose or rearrange by heterolysis as well as homolysis of the O–O bond.[2]

Considerable interest has been expressed concerning the nature of the oxygen cation which could be an intermediate in these reactions. It has been recognized[2a] that if the oxygen cation does exist, it is probably a very short lived entity. Recent work from this and other laboratories[3–5] has shown that the rearrangement of 9-decalyl perbenzoate proceeds in such a manner that the formation of a free oxygen cation as an intermediate is very unlikely; the reaction is however definitely ionic in character. Bassey[6] and co-workers have studied the acid-catalyzed decomposition of 1-phenylethyl hydroperoxide in H_2O^{18}. They found that recovered hydroperoxide did not contain excess oxygen-18. They conclude that the reaction probably does not involve the formation of the oxygen cation as an intermediate, as it would presumably react with water to reform hydroperoxide which in their experiment should contain excess oxygen-18.

Leffler[7] has shown that *p*-methoxy-*p*′-nitrobenzoyl peroxide (III) can decompose in a homolytic or heterolytic manner, the mode of decomposition being governed to a large degree by the polarity of the solvent. When thionyl chloride is used as the solvent, the main product of the reaction is the mixed carbonate IV. It has been postulated that this reaction proceeds by heterolysis of the O–O bond to give the cation VI and *p*-nitrobenzoate ion.

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(1) School of Chemistry, Rutgers University, New Brunswick, N. J.

(2) For several examples of these reactions and pertinent discussions see (a) P. D. Bartlett, *Rec. Chem. Progr.*, **11**, 47 (1950); (b) J. E. Leffler, *Chem. Revs.*, **45**, 385 (1949); (c) A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954, pp. 107–122.

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