additional 2.5 hr. The solvent was removed by distillation at reduced pressure. The residual solid was extracted exhaustively with ethyl ether, and the remaining white solid (0.49 g.) was dried in a vacuum desiccator. The solid was converted by the normal procedures to the N-*p*-tolylsulfonamide derivative, m.p. 53–55°. The infrared absorption and elemental analysis indicated that the compound was 1-propene-1-sulfon-*p*-toluidide (Va).

Anal. Calcd. for $C_{10}H_{13}NO_2S$: C, 56.85; H, 6.20; N, 6.63; S, 15.18. Found: C, 57.13; H, 6.40; N, 6.67; S, 15.06.

B. 1-Propene-1-sulfon-*p*-toluidide (Va).—The diimide reduction of Va was unsuccessful. A solution of Va (0.22 g., 0.0010 mole) and *p*-toluenesulfonyl hydrazine (0.39 g., 0.0021 mole) in 13 ml. of freshly distilled diglyme was refluxed for 1.5 hr. The solvent was removed at reduced pressure, and the residual oil was chromatographed in chloroform on alumina. No material corresponding to IIIa was recovered.

C. 1-Propene-1-sulfon-α-naphthylide (Vb).—The catalytic hydrogenation of Vb was unsuccessful. A solution of Vb in absolute ethanol was shaken with Adams catalyst for 3.5 hr. in a Parr apparatus under 2.5 atm. of hydrogen. Starting material was recovered unchanged.

1-Propyl Methanesulfonate.—The product, b.p. 103° (12 mm.), lit.[29] b.p. 115° (21 mm.), was obtained in 60% yield by the method of Ross and Davis.[29]

Methyl 1-Propanesulfonate.—The product, obtained in 7% yield by the same procedure,[29] was distilled *in vacuo* twice, b.p. 93° (12 mm.), and chromatographed in chloroform on alumina.

Anal. Calcd. for $C_4H_{10}O_3S$: S, 23.20. Found: S, 23.30.

2-Propyl Methanesulfonate.—The product, b.p. 86–88° (12 mm.), $n^{25}D$ 1.4219, was prepared by the same procedure.[29]

N.m.r. Spectra.—Measurements were obtained with a Varian HR-60 instrument at 60 Mc. and 14,100 gauss. Tetramethylsilane was used as internal standard. Spin decoupling experiments were done by a modification of the method of Johnson.[30]

Acknowledgment.—The authors are indebted to Professor C. H. DePuy for assistance with the n.m.r. spectra. We thank Mr. N. E. Fersen, Williams College, for Russian translations.

(29) W. C. J. Ross and W. Davis, *J. Chem. Soc.*, 2420 (1957).

(30) L. F. Johnson, "Proton-proton Spin Decoupling Using the Varian V-3521 Integrator," Varian Associates, Palo Alto, Calif., 1962.

Skeletal Rearrangement Accompanying the Reaction of 2-Phenyl-1-propanol, 1-Phenyl-2-propanol, and 2-Phenyl-ethanol-1-C^{14} with Brominating and Chlorinating Reagents[1]

HERMAN PINES AND FREDERICK SCHAPPELL[2]

Ipatieff High Pressure and Catalytic Laboratory, Department of Chemistry, Northwestern University, Evanston, Illinois

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Under conventional brominating procedures employing phosphorus tribromide or aqueous hydrobromic acid, 2-phenyl-1-propanol is shown to produce up to 85% 1-phenyl-2-bromopropane. Bromination of 1-phenyl-2-propanol yields only small amounts of isomeric bromides. The mechanism of the rearrangement is discussed. The reaction product of 2-phenylethanol-1-C^{14} with the brominating agents consisted of 2-phenyl-1-bromoethane-1-C^{14} containing 0.1 to 6.3% of the rearranged bromide, 2-phenyl-1-bromoethane-2-C^{14}. 2-Phenyl-1-propanol upon treatment with thionyl chloride and pyridine produced 9.3% of the rearranged product, 1-phenyl-2-chloropropane. The same alcohol on reaction with phosphorus trichloride formed the normal and rearranged products in a ratio of 1.3 to 1.

In conjunction with the study of some base-catalyzed reactions being carried out in this laboratory it became necessary to synthesize 2-phenyl-1-bromopropane. The usual procedure for converting alcohols to bromides consists of reacting the alcohol with phosphorus tribromide or with concentrated aqueous hydrobromic acid in the presence of sulfuric acid. When applied to secondary alcohols this reaction is accompanied by isomerization. It was found that either 2- or 3-pentanol gives a mixture of 2- and 3-bromopentanes.[3,4]

These procedures were considered to be safe for the synthesis of primary bromides although Whitmore and Rothrock[5] reported that neopentyl alcohol underwent extensive rearrangement to pentyl bromides when treated with hydrobromic acid.

In the present study we found that the primary alcohol, 2-phenyl-1-propanol, undergoes extensive rearrangement upon bromination with either phosphorus tribromide or 48% hydrobromic acid; however, the secondary alcohol, 1-phenyl-2-propanol, rearranges very little upon treatment with either reagent.

In order to determine the effect the methyl group in 2-phenyl-1-propanol may have upon the extent of skeletal isomerism, it was decided to study the reaction of 2-phenylethanol-1-C^{14} with phosphorus tribromide and hydrobromic acid.

Results

I. 2-Phenyl-1-propanol and 1-Phenyl-2-propanol with Phosphorus Tribromide and with Hydrobromic Acid. 1. Reactions with Phosphorus Tribromide.—The bromination of 2-phenyl-1-propanol by conventional procedures[6,7] yields, besides 2-phenyl-1-bromopropane, from 16 to 34% 1-phenyl-2-bromopropane (Table I). The other isomeric bromides, which would be expected to be formed had the rearrangement proceeded by carbonium ion mechanisms 1 and 2, were essentially absent (see p. 1504).

The tertiary bromide, 2-phenyl-2-bromopropane, which would be produced by mechanism 1, was found to be unstable in the presence of water or base, or on

(1) This research was supported in part by the National Science Foundation Grant NSF-G14503.

(2) Monsanto Chemical Co. Predoctoral Fellow, 1962–1963.

(3) H. Pines, A. Rudin, and V. N. Ipatieff, *J. Am. Chem. Soc.*, **74**, 4063 (1952).

(4) J. Cason and J. J. Correia, *J. Org. Chem.*, **26**, 3645 (1961).

(5) F. C. Whitmore and H. S. Rothrock, *J. Am. Chem. Soc.*, **71**, 3431 (1932).

(6) C. R. Noller and R. Dinsmore, "Organic Syntheses," Coll. Vol. II; John Wiley and Sons, Inc., New York, N. Y., 1943, p. 358.

(7) P. A. Levene, R. E. Marker, and A. Rothen, *J. Biol. Chem.*, **100**, 589 (1953).

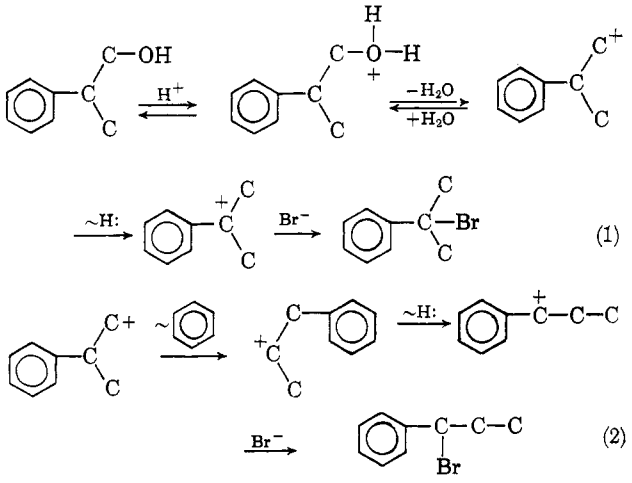
TABLE I

BROMINATION OF PHENYLPROPANOL

	Experiment[a]									
	1[c]	2	3a[d]	3b[e]	3c[f]	4	5[m]	6[n]	7	8
Alcohol used; kind[b]	2-Ph-1-P	2-Ph-1-P		2-Ph-1-P		1-Ph-2-P	2-Ph-1-P	2-Ph-1-P	2-Ph-1-P	1-Ph-2-P
Alcohol used; g. (mole)	10 (0.07)	8.3 (0.06)		10 (0.07)		20 (0.15)	9.5 (0.07)	9.5 (0.07)	9.5 (0.07)	13.6 (0.1)
PBr_3 used; g. (mole)	15 (0.05)	5.8 (0.02)		7.3 (0.07)		14.6 (0.05)				
Aqueous HBr, 48%, g.							38	38	38	43
	Product Formed, Mole%[h]									
Ph—C—C—C	1.1[i]	(3.0)		0.8	2.7			2.0[j]	7.6[k] (1.5)	6.1[e] (2.8)
Ph—C(C)—C		2.5					0.9			(1.3)
Ph—C(C)—C—Br	64.7 (63.8)	79.3 (73.6)	84.4	71.4	70.2	(1.7)	13.6	16.2 (12.9)	17.7 (13.3)	3.0 (4.0)
Ph—C—CBr—C	34.2 (34.1)	19.8 (20.4)	15.6	27.8	27.3	100 (93.5)	85.5	81.8 (83.2)	74.7 (75.7)	90.2 (83.4)
Ph—CBr—C—C	(2.1)	(0.5)				(4.8)		(3.9)	(9.5)	(9.5)

[a] Unless indicated the procedures used are those described in the Experimental part. [b] 2-Ph-1-P corresponds to 2-phenyl-1-propanol; 1-Ph-2-P corresponds to 1-phenyl-2-propanol. [c] The reagents were mixed at 0° and the mixture was allowed to stand overnight and then heated to 100° and maintained at this temperature for 1 hr. This procedure was analogous to that of Levene, *et. al.*[7] [d] This sample was analyzed immediately after the PBr_3 addition was complete. The unchanged materials found were alcohol, 45.5%; phosphites, 29.5%. [e] The product was analyzed after the reaction mixture was allowed to stand for 20 hr. at room temperature. Unchanged material in the form of organophosphites composed 11.8% of the reaction product. [f] After distillation. [g] Sulfuric acid, 96%, was used in amounts equivalent to the moles of alcohol used. [h] The data given in the parentheses are based on n.m.r. analysis; those without parentheses were obtained from gas chromatography. [i] Composed of allylbenzene, 0.2%; *trans*-β-methylstyrene, 0.9%. [j] Composed of *cis*-β-methylstyrene, 1.4%; *trans*-β-methylstyrene, 0.6%. [k] Composed of *cis*-β-methylstyrene, 2.0%; *trans*-β-methylstyrene, 5.6%. [l] Composed of allylbenzene, 0.2%; *trans*-β-methylstyrene, 5.9%. [m] The bromide was washed with sulfuric acid during work-up. [n] When this reaction was carried out without sulfuric acid an 80% rearrangement was observed. The product distribution was 1-phenyl-2-bromopropane, 60%; allylbenzene, 1%; β-methylstyrene, 19%.

gas chromatographic analysis. Hence, its presence could be detected only as a stable decomposition product, namely as α-methylstyrene; this compound was generally absent from all reactions.



The isomeric bromide which could arise from mechanism 2 was found to occur to the extent of 2.1% at a maximum; its formation could also be ascribed, however, to a noncarbonium ion mechanism, as described below.

All the reactions with phosphorus tribromide gave high yields of brominated products. Using the usual brominating procedure and an internal standard, it was found by gas chromatography that 93% of the 2-phenyl-1-propanol reacted with an 83% conversion to the bromides, and only 6.1% of the starting alcohol could not be accounted for.

The effect of the ratio of phosphorus tribromide to 2-phenyl-1-propanol used was investigated. It was found that the ratio 2-phenyl-1-bromopropane to the rearranged bromide, 1-phenyl-2-bromopropane, decreases with the amount of phosphorus tribromide used (Table II). Upon standing, after the addition of a stoichiometric amount of phosphorus tribromide, this ratio decreases (Table I, expt. 3). However, neither of these effects can be explained on the basis of isomerization of the bromides since under identical brominating conditions preformed 2-phenyl-1-bromopropane did not rearrange.

TABLE II

RATIOS OF 2-PHENYL-1-BROMOPROPANE FORMED AS A FUNCTION OF PHOSPHORUS TRIBROMIDE TO 2-PHENYLPROPANOL USED

Theoretical amount of PBr_3 used[a]	1/3	2/3	1
2-Phenylpropanol reacted, mole %	17	53	93
Ratio of $\frac{\text{2-Phenyl-1-bromopropane}}{\text{1-Phenyl-2-bromopropane}}$ formed	8.1	4.3	3

[a] For experimental conditions see Experimental.

The bromination of 1-phenyl-2-propanol (expt. 4) went essentially to completion. The reaction product consisted mainly of 1-phenyl-2-bromopropane. In this reaction 4.8% of the bromides was composed of 1-phenyl-1-bromopropane, a product resulting probably from a carbonium ion mechanism, and only 1.7% of the skeletally rearranged 2-phenyl-1-bromopropane was produced.

2. Reactions with Hydrobromic Acid–Sulfuric Acid.—When 2-phenyl-1-propanol was refluxed with 48% hydrobromic acid and sulfuric acid, according to conventional procedures,[8a,b] a rearrangement to 1-phenyl-2-bromopropane was found to occur to the extent of about 76% and to 1-phenyl-1-bromopropane to the extent of 9.5% (expt. 7).

(8) (a) O. Kamm and C. S. Marvel, "Organic Synthesis," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 30; (b) B. Elpern, L. N. Gardner, and L. Grumbach, *J. Am. Chem. Soc.*, **79**, 1951 (1957).

In order to ascertain whether the 1-phenyl-2-bromopropane was a primary reaction product or whether it arose from the isomerization of 2-phenyl-1-bromopropane, a series of experiments was carried out in which the reaction time was varied from 1 min. to 2 hr. It was found that 1-phenyl-2-bromopropane formed immediately in the reaction in large excess over the expected product. At 2-hr. reaction time, the reaction had gone 99% to completion, material balance had been maintained, and the ratio of the normal and rearranged products was essentially that found in the longer reactions (Fig. 1).

When preformed 2-phenyl-1-bromopropane was refluxed with a threefold excess of 48% hydrobromic acid, it was found that some loss of product occurred after 70-min. reaction time. However, at this point only 13.8% of the 2-phenyl-1-bromopropane had isomerized. This rate of isomerization is far too slow to account for the rapid buildup of 1-phenyl-2-bromopropane early in the reaction.

The absence of a carbonium ion character in the brominations employing 48% hydrobromic acid–sulfuric acid was strikingly illustrated by reaction of 1-phenyl-2-propanol (expt. 8, Table I). This alcohol reacted to form only 9.5% carbonium ion products in the form of 1-phenyl-1-bromopropane. The product of a phenyl migration, 2-phenyl-1-bromopropane, was found to the extent of 4.0%, while bromination went to completion.

Discussion

From the data presented in Table I it is obvious that the bromination of phenylpropanol, unlike that of 2- and 3-pentanol,[3] does not proceed *via* a classical carbonium ion mechanism. The bromination reaction of 2-phenyl-1-propanol resembles very much the solvolysis and rearrangement of 2-phenyl-1-propyl-*p*-benzenesulfonate described by Winstein and Schreiber,[9] and could probably be explained by an SN1 process, *via* a phenonium intermediate, or by a competition of SN1 and SN2 processes.

The observation that in the bromination reaction the ratio of 2-phenyl-1-bromopropane to the rearranged bromide isomer decreases as a function of phosphorus tribromide to 2-phenylpropanol used can be explained by a consideration of the reactive species present at various times in the reaction and/or the change in the dielectric constant of the medium. The effect of variation in medium upon the rate of participation was found to influence the rate of solvolytic reactions.[10]

The rearrangement occurring during the bromination of 2-phenyl-1-propanol with hydrobromic acid–sulfuric acid can also be explained by the mechanism described above. The bromides once formed undergo little rearrangement; this is indicated by Fig. 1.

The very small participation of the classical carbonium ion mechanism in the bromination of phenylpropanols was not predictable in view of the early work on the bromination of 2- and 3-pentanols by means of either phosphorus tribromide or hydrobromic acid.[3,4,11] In each case a mixture of 2- and 3-bromopentane was obtained. On the other hand the bromination of 2-butanol formed the unrearranged *sec*-butyl bromide, as determined by the use of carbon-14.[12,13] These incongruous results were rationalized by a steric argument, bromination of *sec*-butyl alcohol being less sterically hindered to the transition state of an SN2 reaction.[4] However, neopentyl alcohol was converted to neopentyl bromide in the presence of an excess of quinoline.[14] When a base was not present extensive rearrangement was found to occur. Similarly, the bromination of neopentyl alcohol with hydrobromic acid leads to isomeric pentyl bromides.[5]

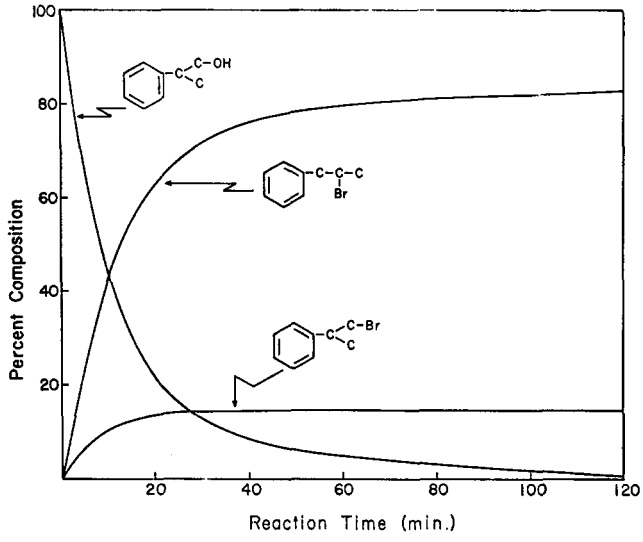


Fig. 1.—Composition of product from 2-phenyl-1-propanol with hydrobromic acid–sulfuric acid at 123°.

II. 2-Phenylethanol-1-C^{14}.—The reactions of the title compound with hydrobromic acid, hydrobromic acid–sulfuric acid, and with phosphorus tribromide were made under experimental conditions described above. In each case over 95% of the alcohol was converted to 2-phenyl-1-bromoethane; the only impurity detected was styrene, which ranged from 0.2 to 1.1%. The isomeric bromide 1-phenyl-1-bromoethane was not detected among the products of the reaction.

The reaction product consisted of 2-phenyl-1-bromoethane-1-C^{14} containing smaller amounts of the rearranged product 2-phenyl-1-bromoethane-2-C^{14}. The extent of isomerization (Table III) was determined by oxidizing the phenylethyl bromide to benzoic acid by means of alkaline potassium permanganate solution. The activity of the benzoic acid, as compared with the parent bromide, gave the measure of the degree of rearrangement. Before counting, the bromide was purified from small amounts of the unreacted phenylethanol by passing it over a column of alumina powder; the alcohol was retained by the alumina.

A comparison of the present results with those obtained from the reaction of 2-phenyl-1-propanol (Table III) demonstrates the effect of the methyl group upon the extent of isomerization. These observations are in agreement with the relative stabilities

(9) S. Winstein and K. C. Schreiber, *J. Am. Chem. Soc.*, **74**, 217 (1952).
(10) S. Winstein and H. Marshall, *ibid.*, **74**, 1120 (1952).
(11) J. Cason and R. H. Mills, *J. Am. Chem. Soc.*, **73**, 1354 (1951).
(12) A. T. Shulgin, *ibid.*, **77**, 2338 (1955).
(13) P. S. Skell, R. G. Allen, and G. L. Helmkamp, *ibid.*, **82**, 410 (1960).
(14) L. H. Sommer, H. D. Blankman, and P. C. Miller, *ibid.*, **76**, 803 (1954).

TABLE III

THE REARRANGEMENT OF 2-PHENYLETHANOL-1-C^{14} UPON REACTION WITH BROMINATING REAGENTS[a]

	Reagent		
	48% HBr	48% HBr-H_2SO_4	PBr_3
Activity [b]of 2-phenylethyl bromide $\times 10^{-3}$ μc./mmole	2107	2146	2000
Activity of benzoic acid, $\times 10^{-3}$ μc./mmole	102	136	2.8
Per cent rearrangement	4.7	6.3	0.14
Per cent rearrangement of 2-phenyl-1-propanol to 1-phenyl-2-bromopropane	60	76	20

[a] The activity of the 2-phenylethanol-1-C^{14} used as a starting material for all experiments was 2129 $\times 10^{-3}$ μc./mmole. [b] All activities are corrected for a background radiation of 1.11 $\times 10^{-15}$ amp.

of the nonsymmetrical phenonium ions mentioned previously and by other investigators.[15]

The phenyl migration accompanying the reaction of 2-phenylethanol-1-C^{14} was in accord with the observations made by Lee and Spinks,[16] who observed 5.3–7.0% isomerization on treatment of the cited alcohol with hydrobromic acid, and about 50% with thionyl chloride.

As was already discussed above, a symmetrical phenonium ion cannot explain the results of the reaction; however, a competition between an SN2 process and a symmetrical phenonium ion could explain the results of the bromination of phenylethanol. Similarly, Roberts and Regan[15] were able to explain the deamination of 2-phenylethyl-1-C^{14} amine in terms of a mechanism in which the symmetrical phenonium ion was a transition state rather than an intermediate.

However, the small amount of hydride migration products found in this work, in the reactions of phenylpropanols described above, and in the work of Roberts and Regan[15] is somewhat puzzling if one assumes an ionization step prior to the formation of the phenonium ion. Hence, it seems that either the unsymmetrical phenonium ion forms directly without any hydride migration or perhaps a concerted mechanism is involved in the competition with the SN2 process.

It was reported that the reaction of 2-phenylethanol-1-C^{14} [16] and 2-*p*-anisylethanol-1-C^{14} [17] with thionyl chloride is accompanied by 46–50% of skeletal isomerization involving phenyl migration. When the reaction was carried out in the presence of pyridine as a solvent less than 0.5% rearrangement occurred.

III. 2-Phenyl-1-propanol with Thionyl Chloride.—As would be expected in the light of the existing data, 2-phenyl-1-propanol, upon treatment with thionyl hcloride and pyridine according to the procedure of Whitmore and Karnatz,[18] produced 9.3% of the rearranged product 1-phenyl-2-chloropropane (Table IV). This experiment confirms the observation that a methyl group attached to the β carbon atom in phenylethanol exerts an effect upon phenyl migration.

It is interesting to note that phosphorus trichloride treatment of 2-phenyl-1-propanol produced a reaction

(15) J. D. Roberts and C. M. Regan, *J. Am. Chem Soc.*, **75**, 2069 (1953).
(16) C. C. Lee and J. W. T. Spinks, *Can. J. Chem.*, **32**, 1005 (1954).
(17) C. C. Lee, D. Newman, and D. P. Thornhill, *ibid.*, **41**, 620 (1963).
(18) F. C. Whitmore and F. A. Karnatz, *J. Am. Chem. Soc.*, **60**, 2536 (1938).

TABLE IV

COMPOSITION OF PRODUCTS FROM THE REACTIONS OF 2-PHENYL-1-PROPANOL WITH THIONYL CHLORIDE AND PHOSPHORUS TRICHLORIDE

	Reagent		
Products	$SOCl_2$-pyridine	$SOCl_2$-$CHCl_3$	PCl_3
2-Phenyl-1-chloropropane	90.7	5.3	33.7
1-Phenyl-2-chloropropane	9.3	32.6	26.6
Olefins		10.1	12.7
2-Phenyl-1-propanol		32.2	27.0
High boiling compounds		19.8	

mixture containing a normal to rearranged chloride ratio of 1.27. The reaction of this alcohol with thionyl chloride in chloroform solution in the absence of pyridine showed a normal to rearranged chloride ratio of only 0.163 (Table IV).

Analytical Procedure. A.—Gas chromatography was carried out on an F and M Model 300 gas chromatograph (F and M Scientific Corporation, Avondale, Pennsylvania). When the analyses were performed using the standard siliceous solid supports, the bromides underwent extensive dehydrobromination to form aryl olefins. In order to minimize this reaction pretreated Tide (commercial detergent) was used as a solid support.[19]

The experimental conditions of analysis and relative retention times are given in Table V.

TABLE V

RELATIVE RETENTION TIMES OF PHENYLBROMOPROPANES[a]

Compound	Relative retention times
n-Hexylbenzene	1.00
1-Phenyl-1-bromopropane	2.59
1-Phenyl-2-bromopropane	2.60
2-Phenyl-1-bromopropane	3.06
3-Phenyl-1-bromopropane	4.18
2-Phenyl-2-bromopropane	decomposes

[a] Column, 6 mm. × 4 m. filled with 10% Carbowax 20M on 40–60-mesh pretreated Tide; temp. 100°; carrier gas, helium with a flow rate of 156 ml./min.

B. Nuclear Magnetic Resonance.—This technique allowed the quantitative determination of 1-phenyl-1-bromopropane in the presence of 1-phenyl-2-bromopropane since these isomers were inseparable by gas chromatography. It also served as a check on the amount of decomposition which took place upon gas chromatographic analysis. Quantitative measurements were accomplished by cutting and weighing of the peaks.

τ-Values[20] of the phenylbromopropanes and of methylstyrenes are listed in Table VI.

C. Infrared Analysis.—Since uncomplicated analytical bands did not occur for the bromides involved in this research, infrared analysis served only to determine the presence of olefins or unchanged alcohols and phosphite esters in the reaction mixture.

D. Radioactivity Assay.—Both the phenylethyl bromide and the benzoic acid resulting from the alkaline potassium permanganate oxidation of this compound were converted to gaseous carbon dioxide by

(19) A. W. Decora and G. U. Denneen, U. S. Department of Interior, Bureau of Mines, Report of Investigations 5768.
(20) G. V. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

TABLE VI

N.M.R. ANALYSIS. τ-VALUES OF PURE BROMIDES AND OLEFINS

Compound	Peak assignment	τ-value
2-Phenyl-1-bromopropane	$-CH_3$	8.61[a]
1-Phenyl-2-bromopropane	$-CH_3$	8.38[a]
	—CHBr—	5.85[a]
1-Phenyl-1-bromopropane	$-CH_3$	8.87[b]
		9.02[c]
	—CHBr—	4.77[c]
3-Phenyl-1-bromopropane	$-CH_2Br$	6.68[c]
α-Methylstyrene	$-CH_3$	7.92
β-Methylstyrene	$-CH_3$	8.22[d]

[a] Calculated from the midpoint of the adsorbance. [b] Calculated from the lowest peak of the absorbance. [c] Calculated from the central peak of the absorbance. [d] Calculated from the upper peak of the absorbance.

wet combustion according to the procedure of Van Slyke.[21,22]

The apparatus and techniques employed for measuring the radioactivity of carbon dioxide have been described previously.[23]

Experimental

1. **Preparation of Alcohols. A.—2-Phenyl-1-propanol** was prepared by hydrogenation of hydrotropaldehyde with an equal volume of ethanol as solvent with 10% by weight copper chromite as catalyst. The reaction was carried out in a 1350-ml. rocking autoclave at 170° and an initial hydrogen pressure of 100 atm. The alcohol distilled at 92–93° (4 mm.), $n^{25}D$ 1.5245.

B.—1-Phenyl-2-propanol was obtained by hydrogenation of phenylacetone at 118° according to the procedure described above; b.p. 82° (9 mm.), $n^{25}D$ 1.5194.

C.—1-Phenyl-1-propanol was prepared from propiophenone by hydrogenation, according to the above described procedure. The alcohol distilled at 90–91° (6 mm.), $n^{25}D$ 1.5212.

D.—2-Phenyl-2-propanol was synthesized by a Grignard reaction from 47.4 g. (0.3 mole) of bromobenzene, 6.9 g. (0.3 g.-atom) of magnesium, and 16.5 g. (0.28 mole) of acetone; the complex was decomposed with an ammonium chloride solution. The alcohol, 52% yield, distilled at 71° (7 mm.), $n^{25}D$ 1.5206.

E.—2-Phenylethanol-1-C^{14} [24].—Phenylacetic acid-1-C^{14} was prepared by the reaction of benzylmagnesium chloride and carbon dioxide C^{14} obtained from barium carbonate C^{14}. **2-Phenylethanol-1-C^{14}** was prepared from the phenylacetic acid obtained above by reduction with lithium aluminum hydride. A 60% yield of this alcohol was received based on the amount of barium carbonate used.

2. **Preparation of Bromides. A.—2-Phenyl-1-bromopropane** was prepared by treating 184 g. (2.4 moles) of benzene with 88 g. (1.36 moles) of allyl bromide in the presence of 41 ml. of 96% sulfuric acid, according to the procedure of Adams and Garber.[25] The bromide was over 95% pure according to gas chromatography; b.p. 99.5° (11 mm.), $n^{25}D$ 1.5470.

B.—1-Phenyl-2-bromopropane was synthesized by treating the tosyl ester of 1-phenyl-2-propanol with calcium bromide. The tosylate was prepared from 7.3 g. of the alcohol with 22.8 g. of *p*-toluenesulfonyl chloride in pyridine solvent, according to the procedure of Streitwieser, *et al.*[26] The crude ester, 88% yield, was then treated with calcium bromide using dimethylformamide as a solvent.[27] A 33% yield of pure 1-phenyl-2-bromopropane was obtained, $n^{25}D$ 1.5418.

C.—1-Phenyl-1-bromopropane was prepared from 8.3 g. (0.06 mole) of 1-phenyl-1-propanol with 5.8 g. (0.02 mole) of phosphorus tribromide, according to Noller and Dinsmore.[6] The bromide, 85% yield, distilled at 89.5° (6 mm.), $n^{25}D$ 1.5494.

D. 2-Phenyl-2-bromopropane.—Several attempts were made to prepare the bromide from 2-phenyl-2-propanol with either phosphorus tribromide, 48% hydrobromic acid, or hydrogen bromide. In the latter case the water liberated from the reaction was already sufficient to cause the decomposition of the bromide to α-methylstyrene and to the starting alcohol.

Similarly, the reaction of hydrogen bromide with α-methylstyrene in the presence and absence of acetic acid failed to form pure 2-phenyl-2-bromopropane.

Bromination Procedure. A. Phosphorus Tribromide.—The bromination reactions, unless otherwise indicated in Table I, were carried out in a 100-ml., three-necked, round-bottom flask following the procedure of Noller and Dinsmore.[6] The phosphorus tribromide was added dropwise to the alcohol which was cooled to −5°. The rate of addition was controlled for the temperature of the reaction not to exceed 0°. Stirring was maintained throughout the reaction and for 30 min. after the addition of the phosphorus tribromide was completed.

The reaction mixture, which was allowed to warm to room temperature and to stand overnight, was decomposed by pouring it over ice. The organic phase was diluted with benzene, separated, neutralized with 10% aqueous sodium bicarbonate, and dried over potassium carbonate; the benzene was stripped under reduced pressure in the presence of anhydrous potassium carbonate.

B. Hydrobromic Acid (48%)–Sulfuric Acid (96%).—Brominations with the title reagent were carried out according to the procedure of Kamm and Marvel.[8]

The alcohol to be brominated was refluxed with a solution containing a threefold excess of hydrobromic acid and an amount of sulfuric acid equivalent to the moles of alcohol used. After 4-hr. refluxing at 123° the aqueous phase was diluted with water and the organic phase was diluted with benzene, separated, washed with a 10% aqueous sodium bicarbonate until neutral, and dried over potassium carbonate. The benzene was then removed under reduced pressure in the presence of anhydrous potassium carbonate.

C. Miscellaneous Reactions. 3-Phenyl-1-propanol, 2-Phenyl-1-bromopropane, and Phosphorus Tribromide.—Following the general procedure, 8.3 g. (0.06 mole) of the alcohol and 5.8 g. (0.02 mole) of phosphorus tribromide were treated in the presence of 3.8 g. of preformed 2-phenyl-1-bromopropane. The final reaction product showed a 90% yield of 3-phenyl-1-bromopropane and none of the 2-phenyl-1-bromopropane initially present in the reaction had isomerized.

Use of Variable Amounts of PBr_3 on Bromination of 2-Phenyl-1-propanol.—Following the general procedure, 20 g. (0.15 mole) of 2-phenyl-1-propanol was treated with 14.6 g. (0.054 mole) of phosphorus tribromide in the presence of an internal standard (1,2,3,4-tetrahydronaphthalene, 6.7 g.). Samples were taken from the reaction mixture for analysis when the addition of PBr_3 was one-third complete, two-thirds complete, and complete. These samples were allowed to stand at room temperature for 20 hr. After this time, all the samples were decomposed and analyzed. Analysis of the third sample showed the yield of bromides to be 83.1%. Only 6.1% of the material could not be accounted for. Analytical results are summarized in Table II.

2-Phenyl-1-bromopropane and HBr–H_2SO_4.—A solution of preformed 2-phenyl-1-bromopropane containing 8% 1-phenyl-2-bromopropane was refluxed with a threefold excess of 48% hydrobromic acid and sulfuric acid for periods of time ranging from 30 min. to 5 hr. After 70 min., substantial material was lost through charring. However, in this period of time only 13.8% of the preformed 2-phenyl-1-bromopropane had undergone isomerization.

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