The Friedel-Crafts Alkylation with 2-Aryl Ethyl-1-C^{14} Chlorides[1]

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The reaction of toluene with 2-phenylethyl-1-C^{14} chloride using aluminum chloride as catalyst gives β-tolylethylbenzene in which 52.0–52.3% of the carbon-14 is contained in the α-position, while 2-phenylethyl chloride recovered from contact with aluminum chloride in toluene had no isotope position rearrangement. The formation of a symmetrical intermediate, whose rate of reaction with toluene is subject to an intramolecular isotope effect, is indicated. The reaction of toluene with 2-(4-nitrophenyl)ethyl-1-C^{14} chloride gives only 8% isotope position rearrangement, while alkylation of naphthalene and of phenol with 2-phenylethyl-1-C^{14} chloride gave 48.7 and 52.7% of the carbon-14 in the α-position.

The Friedel-Crafts alkylation reaction of primary halides continues to present interesting problems. The rearrangements which result in the formation of a large proportion of *sec*-alkyl benzenes were first explained on the basis of a simple carbonium ion mechanism, although some experimental observations could not be interpreted in this way.[2-4] Studies of catalyst complexes and extensive kinetic studies of Friedel-Crafts alkylations led Brown to conclude that alkylations with primary halides proceed by displacement.[5]

The extent of rearrangement which is a significant part of the Friedel-Crafts reaction of most primary halides has been studied by examining the relative amounts of the normal and branched alkylation products. While results described in the older literature often indicate a single product, more refined analytical techniques usually demonstrate the presence of several products, including considerable proportions of those of unrearranged structure.[6,7]

These reactions have also been studied by measuring the extent of carbon-14 isotope position rearrangement. For example, the alkylation of anisole with 2-phenylethyl-1-C^{14} chloride gave a reaction product with nearly equal distribution of carbon-14 in the two alkyl carbons.[8]

In most of these studies, the possibility that halides might rearrange prior to alkylation (a rearrangement which is known to be important in the absence of arenes) has not been excluded.[6,9] The possibility that rearrangement of an alkyl benzene may take place subsequent to reaction has generally been considered slight, since most disproportionations and alkyl group migrations occur with little or no skeletal isomerization.[7,10] Yet, in one instance, partial isotope position rearrangement in an alkyl benzene, without isomerization, was demonstrated to accompany disproportionation.[11a]

There is presently no simple rationalization of many of these observations.[12] The simultaneous operation of S_N1 and S_N2 pathways, rearrangement prior to or subsequent to alkylation or rearrangement within a π-complexed carbonium ion,[13] may be required to explain these results.

Alkylations with 2-phenylethyl halides, which have been little studied, seemed to us to provide opportunity for determining the relative contributions of S_N1 and S_N2 pathways and the extent of phenyl participation to form a symmetrical ion. Studies of reaction kinetics, of isotope position rearrangement, and of the effect of substituents on rates of reaction and rearrangement might all be used to elucidate the mechanism of reaction.

This paper reports studies of isotope position rearrangement in alkylations with 2-phenylethyl-1-C^{14} chloride and 2-(4-nitrophenyl)ethyl-1-C^{14} chloride, using aluminum chloride as a catalyst. The reaction of 2-phenylethyl-1-C^{14} chloride with phenol was first investigated; the high temperatures and long reaction times required led to experiments with alkylation of naphthalene and then of toluene.

Results and Discussion

The reaction of 2-phenylethyl chloride, excess toluene, and aluminum chloride was found to be homogeneous when less than 0.15 mole of aluminum chloride per mole of 2-phenylethyl chloride was used, and to have a rate such that the reaction was more than half complete in 10 min. at 0°.[14] Isotope position rearrangement in this reaction of 2-phenylethyl-1-C^{14} chloride and 2-(4-nitrophenyl)ethyl-1-C^{14} chloride was then studied.

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(1) Abstracted from the Ph.D. thesis of M. A. McMahon, Rensselaer Polytechnic Institute, 1962; Presented at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1962.

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(5) (a) H. C. Brown and M. Grayson, *J. Am. Chem. Soc.*, **75**, 6285 (1953); (b) H. C. Brown and H. Jungk, *ibid.*, **78**, 2182 (1956); (c) H. Jungk, C. R. Smoot, and H. C. Brown, *ibid.*, **78**, 2185 (1956).

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(7) (a) D. V. Nightingale and J. M. Shackelford, *ibid.*, **78**, 1225 (1956); (b) S. H. Sharman, *ibid.*, **84**, 2945 (1962).

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(10) (a) D. A. McCaulay and A. P. Lien, *ibid.*, **75**, 2411 (1953); (b) R. E. Kinney and L. A. Hamilton, *ibid.*, **76**, 786 (1954).

(11) (a) R. M. Roberts and S. G. Brandenberger, *ibid.*, **79**, 5484 (1957); (b) R. M. Roberts, Y. W. Han, C. H. Schmid, and D. A. Davis, *ibid.*, **81**, 640 (1959).

(12) K. L. Marsi and S. H. Willen, *J. Chem. Educ.*, **40**, 214 (1963).

(13) A. Streitwieser, Jr., W. D. Schaeffer, and S. Andreades, *J. Am. Chem. Soc.*, **81**, 1113 (1959).

(14) The kinetics of the reaction in excess toluene were studied by gas chromatographic analysis of the change in concentration of 2-phenylethyl chloride with time. Values for the pseudo-first-order reaction rate constant, calculated by substitution of the peak heights of 2-phenylethyl chloride in the integrated form of the first-order rate expression following,

$$k_1 = \frac{2.303}{t_2 - t_1} \log \frac{C_{t_1}}{C_{t_2}}$$

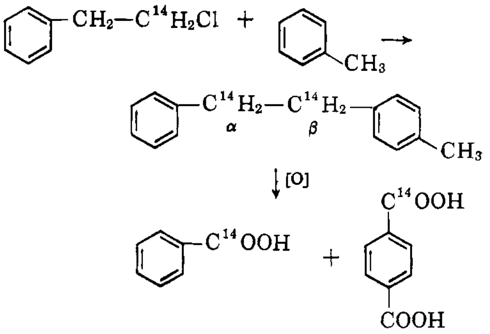
decreased with time. Typical values for the reaction of 2-phenylethyl chloride (1.00 mole/l. of toluene solution) and aluminum chloride (0.014 mole/l. of toluene solution) at −10° were k_1 = 0.0051 sec.$^{-1}$ at 150 sec., 0.0035 sec.$^{-1}$ at 295 sec., 0.0026 sec.$^{-1}$ at 415 sec., and 0.0018 sec.$^{-1}$ at 752 sec. The decrease of k_1 with time may be due to the formation of the loose σ-complex, $C_6H_5CH_3 + HCl + Al_2Cl_6 \rightarrow CH_3C_6H_6^+Al_2Cl_7^-$, which has been observed at −45°.[5a]

TABLE I

REACTION OF TOLUENE WITH 2-ARYL ETHYL-1-C^{14} CHLORIDES. RADIOACTIVITY ANALYSES[a]

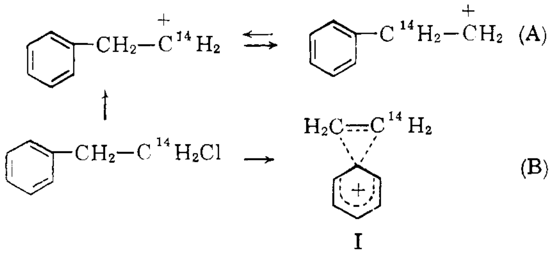
Compound counted	Obsd. c.p.m.	Corrected c.p.m./mmole	Rearrangement, %	$\frac{k^{14}}{k^{12}}$
Reaction 1				
p-$CH_3C_6H_4CH_2CH_2C_6H_5$[b]	1197 ± 11	9.82×10^4		
	576 ± 10	10.09×10^4		
p-$HOOCC_6H_4COOH$	667 ± 7	4.91×10^4		
C_6H_5COOH	683 ± 7	5.30×10^4	52.0	0.92 ± 0.02
Reaction 2				
$C_6H_5CH_2CH_2Cl$[c]	678 ± 6	3.72×10^4		
p-$HOOCC_6H_4COOH$	490 ± 4	1.74×10^4		
	461 ± 4	1.78×10^4		
C_6H_5COOH	568 ± 4	1.96×10^4	52.7	0.90 ± 0.02
Reaction 3				
p-$O_2NC_6H_4CH_2CH_2C_6H_4CH_3$	2117 ± 12	2.014×10^5		
	2478 ± 13	2.003×10^5		
p-$HOOCC_6H_4COOH$	2065 ± 14	1.873×10^5		
	1859 ± 13	1.787×10^5	8.6	

[a] All compounds were counted in the gas phase as carbon dioxide by the general method described by R. C. Anderson, Y. Delabarre, and A. A. Bothner-by, *Anal. Chem.*, **24**, 1298 (1952). [b] Analyses of this compound were poor owing to difficulty in combustion of the liquid. [c] Counted as the urethane derivative of the alcohol from which it was prepared.



The results of radiocarbon assay of the products and their degradation products are given in Table I.

It is evident that a 1,2-phenyl shift has taken place at some stage in the alkylation. 2-Phenylethyl-1-C^{14} chloride which had been in contact with aluminum chloride in toluene was recovered and oxidized; the benzoic acid produced was not radioactive. The formation of a simple carbonium ion (or ion pair) and equilibration of that with one in which a phenyl has shifted (reaction path A) is, therefore, not a possible explanation, unless the reaction of these carbonium ions with toluene is very much faster than their recombination with chloride.



If such were the mechanism of the reaction, one might expect a distribution of activity approaching and perhaps equaling 50% rearrangement. Also, the loss of chloride from 2-phenylethyl-1-C^{14} chloride would presumably be rate-controlling; it would then be subject to an intermolecular isotope effect[15,16] leading, if the reaction were incomplete, to an observation of lowered specific activity of the combined reaction products as compared with starting materials.

In fact in reaction 2, which proceeded to the extent of approximately 60% reaction, no intermolecular isotope effect is observed; instead, an intramolecular isotope is evident in reactions 1 and 2. Thus the distribution of activity is such as to require a different interpretation.

If a symmetrical intermediate (I) is formed, the atomically unsymmetrical ion will produce β-tolylethylbenzene which is carbon-14 rich in the α-position. The magnitude of the observed isotope effect agrees favorably with that expected for an intramolecular isotope effect.

Melander[17] has calculated that an isotope effect should be about half as strong for an SN1 type reaction as for an SN2 type. Although the magnitude of these calculated isotope effects is subject to great uncertainty because of the neglect of solvolytic effects, data on some reactions do show such a difference. The reaction of nucleophiles with methyl-C^{14} iodide showed isotope effects in the range k^{14}/k^{12} = 0.88–0.92,[18] while for the hydrolysis of 2-chloro-2-methylpropane-2-C^{14} in weakly alkaline solution, k^{14}/k^{12} = 0.97.[19]

The observation of an intramolecular isotope effect in the reaction of 2-phenylethyl-1-C^{14} chloride with toluene indicates discrimination in a bond-breaking step in a symmetrical intermediate; the magnitude of this effect, k^{14}/k^{12} = 0.92 (calculable only approximately from these results), indicates that a nucleophilic displacement reaction of this intermediate may be involved.

The mechanism of the reaction must then be as shown in Scheme I.

The extent of reversibility of the first step is not known. The second step must be irreversible since 2-phenylethyl-1-C^{14} chloride after contact with aluminum chloride in toluene contained no 2-phenylethyl-2-C^{14}

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(15) A. Roe and M. Hellmann, *J. Chem. Phys.*, **19**, 660 (1951).

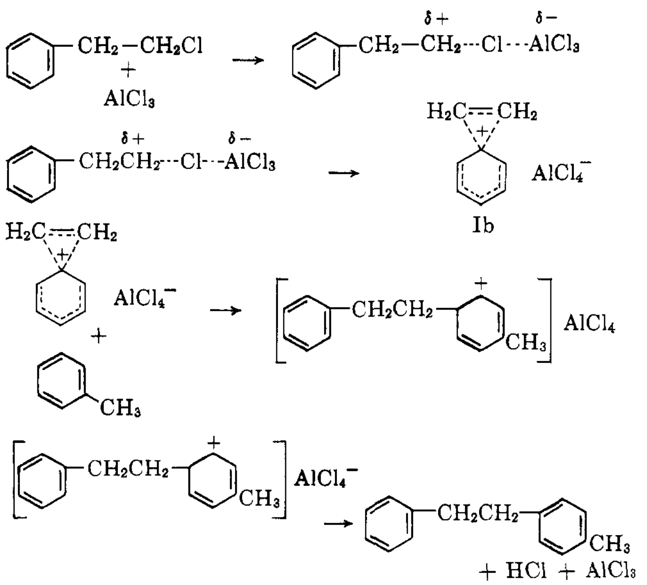
(16) G. A. Ropp and V. F. Raaen, *J. Am. Chem. Soc.*, **74**, 4992 (1952).

(17) L. Melander, "Isotope Effects on Reaction Rates," The Ronald Press Co., New York, N. Y., 1960.

(18) M. L. Bender and D. F. Hoeg, *J. Am. Chem. Soc.*, **79**, 5649 (1957); G. J. Buist and M. L. Bender, *ibid.*, **80**, 4308 (1958).

(19) M. L. Bender and G. J. Buist, *ibid.*, **80**, 4304 (1958).

SCHEME I



chloride. This fact also lends support to a mechanism which involves a stabilized intermediate. If it is assumed that chloride ion becomes a relatively poor nucleophile when involved in the $AlCl_4^-$ complex, this nucleophile will be discriminated against more readily by a stabilized intermediate than by an unstabilized one. Thus the intermediate will react preferentially with toluene, and none of the recovered alkyl halide will be rearranged.

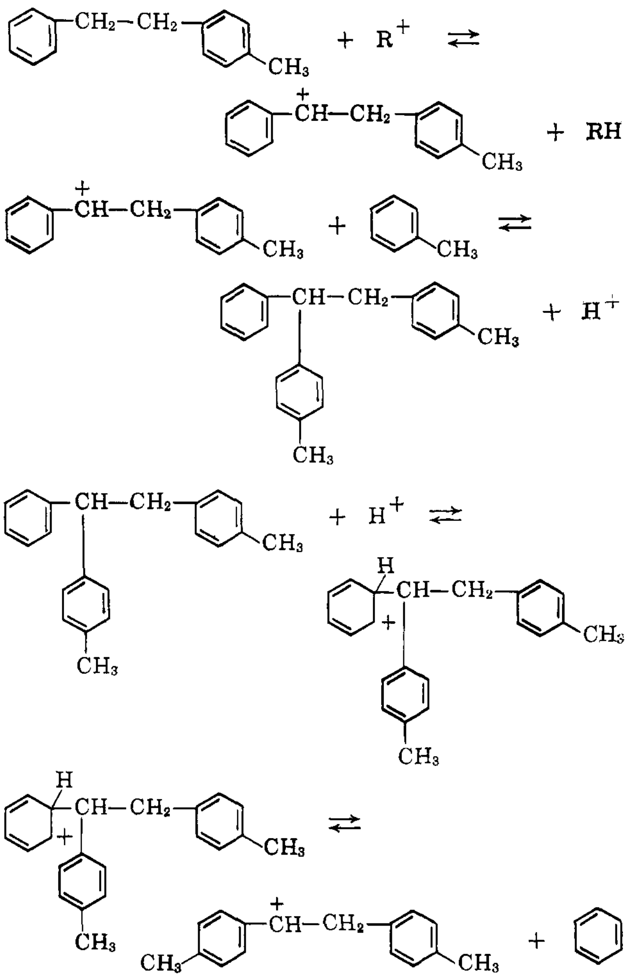
A kinetic study of the aluminum bromide-catalyzed isomerization of 2-phenylethyl-1-C^{14} bromide to 2-phenylethyl-2-C^{14} bromide in carbon disulfide by Adema and Sixma[20] led to the conclusion that the rate-determining step in this fast reaction involved the reaction of a $C_8H_9BrAlBr_3$ particle and an ion formed by ionization of $C_8H_9BrAl_2Br_6$. Their data are not inconsistent with the formulation of $C_8H_9BrAlBr_3$ as a relatively stable ion pair like Ib.

This reaction pathway is unusual in that a first ionization step is not rate determining; because of the slower reaction of the phenonium ion with toluene, the reaction should be first order in 2-phenylethyl chloride and in toluene. Attempts to study the kinetics of this reaction[14] were successful only in part, and gave no certain answer on this point. Other reactions of phenylethyl derivatives may indeed follow different pathways; both displacement[21] and rate-controlling ionization mechanisms (both to bridged[22] or to classical[23] carbonium ions) are known.

It was considered that the observed rearrangement might be attributed to an alternate mechanism involving reversible hydride transfers and alkylations. Reactions of the types involved in this reaction sequence (Scheme II) are known to take place, although they may require higher temperatures, catalyst concentrations, and reaction times.[24]

It is evident that biphenyl could be produced by a similar path. These transformations would lead to oxidation products with specific activities indicating 1,2-phenyl shifts.

SCHEME II



The product of the reaction of 2-phenylethyl-1-C^{14} chloride with toluene was isolated by distillation; although it was free of chloride, it could not readily be crystallized and it was assayed without further purification. Examination of infrared spectra of the reaction product, of bibenzyl, of pure 4-methylbibenzyl, and of 4,4'-dimethylbibenzyl as solutions in carbon disulfide showed that there was no important amount of 4,4'-dimethylbibenzyl present in the reaction product, whose spectrum differed from that of 4-methylbibenzyl only by weak absorptions at 11.1, 12.8, and 13.9 μ which are attributable to small amounts of the *ortho* and *meta* isomers.[25]

Gas chromatography gave confirmation that no significant amounts of bibenzyl or 4,4'-dimethylbibenzyl were present in the reaction product. In a mixture of bibenzyl, 4-methylbibenzyl, and 4,4'-dimethylbibenzyl, all three components gave well-separated peaks (retention volumes 368, 572, and 810 cc., respectively) at 208° using an Apiezon M liquid phase (10% on Chromosorb P); the reaction product gave a single peak corresponding to 4-methylbibenzyl. It

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[20] E. H. Adema and F. L. Sixma, *Rec. trav. chim.*, **81**, 323, 336 (1962).

[21] (a) H. Hart and H. S. Eleuterio, *J. Am. Chem. Soc.*, **76**, 516 (1954); (b) H. Hart, W. L. Spliethoff, and H. S. Eleuterio, *ibid.*, **76**, 4547 (1954).

[22] (a) D. J. Cram, *ibid.*, **74**, 2159 (1952), and earlier papers; (b) S. Winstein and K. C. Schreiber, *ibid.*, **74**, 2165 (1952), and earlier papers.

[23] C. J. Collins, W. A. Bonner, and C. T. Lester, *ibid.*, **81**, 466 (1959).

[24] (a) H. Pines and J. T. Arrigo, *ibid.*, **80**, 4369 (1958); (b) L. Schmerling, J. P. Luvisi, and R. W. Welch, *ibid.*, **81**, 2718 (1959); (c) A. Streitwieser, Jr., and L. Reif, *ibid.*, **82**, 5003 (1960); (d) A. Streitwieser, Jr., and W. J. Downs, *J. Org. Chem.*, **27**, 625 (1962); (e) E. Unseren and P. Wolf, *ibid.*, **27**, 1509 (1962).

[25] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958.

was estimated that 1.0% of bibenzyl or 4,4′-dimethylbibenzyl would have been detected.

It is not likely that randomization of carbon-14 in 4-methylbibenzyl could occur by processes involving reversible alkylations and be followed by the exclusive formation of 4-methylbibenzyl at equilibrium.

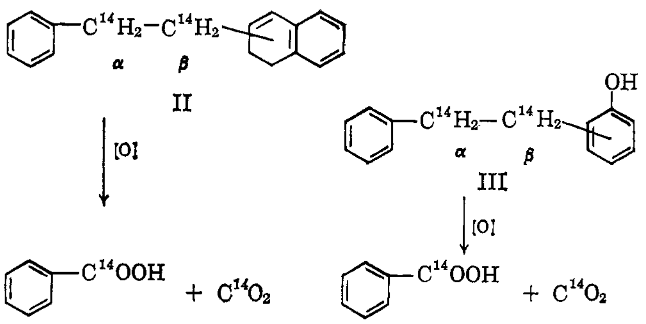
A second way in which apparent scrambling of carbon-14 between α- and β-positions might occur is represented by an intramolecular migration of both phenyl and *p*-tolyl in protonated 4-methylbibenzyl. A reaction of this type was postulated[11] to explain a partial rearrangement of *n*-propylbenzene-β-C^{14} to *n*-propylbenzene-α-C^{14}, and the interconversion of *sec*-butylbenzene and isobutylbenzene. This reaction was found to be significant, in the case of *n*-propylbenzene, only with large amounts of aluminum chloride at reflux for several hours, and it was accompanied by the formation of a relatively large amount of di-*n*-propylbenzene. At room temperature where isotopic position rearrangement of *n*-propylbenzene-β-C^{14} was slight after 6.5 hr., disproportionation was still extensive. The absence of biphenyl and bi-*p*-tolyl and the fact that the reaction products included less than 11% of higher boiling material makes it unlikely that a reaction of this type could explain the distribution of carbon-14 activity in the 4-methylbibenzyl.

The results of the alkylation of toluene with 2-(4-nitrophenyl)ethyl-1-C^{14} chloride indicate a considerably smaller contribution from a symmetrical ion, whose stability would be decreased by the electron withdrawing group. In this case, a displacement reaction or a reaction of a nonrearranging open carbonium ion (evidence from kinetic studies[26] indicates the former) competes importantly with the formation of the symmetrical intermediate.

Experiments with aluminum chloride-catalyzed alkylations of naphthalene and of phenol,[27] which preceded the study of the alkylation of toluene, indicate (although not unequivocally) that a similar mechanism obtains in these cases also.

Naphthalene reacted with 2-phenylethyl chloride sufficiently rapidly that catalysis by aluminum chloride in benzene solution at 0–5° for 30 min. gave 19% of a solid mixture of 2-phenylethylnaphthalenes, after removal of reactants and other products by reduced pressure distillation. The competing alkylation of benzene gave a large amount of bibenzyl in this case.

Chromic acid oxidation of the product (II) formed from 2-phenylethyl-1-C^{14} chloride and naphthalene converted it to benzoic acid and carbon dioxide, which was swept by a stream of nitrogen into a trap cooled by liquid nitrogen. Benzoic acid, obtained from the oxidation mixture by dilution and purified by vacuum sublimation, was found to have 48.7% of the radioactivity; the carbon dioxide, 51.3%.



The reaction of 2-phenylethyl chloride with excess phenol in the presence of catalytic amounts of aluminum chloride was accomplished only by long heating at 180–190°. After distillation of phenol from the reaction mixture, the residue was dissolved in base and precipitated by addition of acid. In a typical experiment the yield of mixed 2-phenylethylphenols (III) was 66%.

Degradation of the product of the reaction of phenol with 2-phenylethyl-1-C^{14} chloride was also accomplished by chromic acid oxidation. The purified benzoic acid contained 49.6% of the activity of the reaction product and the carbon dioxide contained 44.8%. These results are comparable with the nearly symmetrical distribution of carbon-14 in the ethane carbons found in the product of the alkylation of anisole with 2-phenylethyl-1-C^{14} chloride at intermediate temperatures,[8] which was reported after our study with phenol was initiated.

These results are those of single experiments with the labeled materials and are not precise, but they show approximately the distribution of activity which is expected if a symmetrical bridged ion is an intermediate.

It should be pointed out that in neither of these cases was it found possible to isolate unchanged 2-phenylethyl-1-C^{14} chloride under the reaction conditions, and it is therefore possible that a prior rearrangement of 2-phenylethyl-1-C^{14} chloride may have given a symmetrical distribution of activity in the ethane carbon atoms of the products.

Experimental[28]

Phenylacetic Acid-1-C^{14}.—The reaction of carbon dioxide generated from 23 mg. of $BaC^{14}O_3$ with 56 mmoles of benzylmagnesium chloride, followed by addition of inactive solid carbon dioxide gave a 78% yield (25% radiochemical yield) of phenylacetic acid-1-C^{14}.[29]

2-Phenylethanol-1-C^{14}.—Lithium aluminum hydride (10.5 g., 0.29 mole) was added to 150 ml. of ether in a 2-l. flask fitted with a stirrer, condenser, and addition funnel. A solution of 33 g. (0.244 mole) of phenylacetic acid-1-C^{14} in 350 ml. of ether was added to the slurry during 2 hr. The reaction mixture was stirred for an additional 4 hr., and the excess lithium aluminum hydride was decomposed by the dropwise addition of water, followed by 15% sulfuric acid. The clear layers were separated, and the aqueous layer was extracted with two 250-ml. quantities of ether. The ether solutions were combined and washed with saturated

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(26) A kinetic study of the reaction of 2-(4-nitrophenyl)ethyl bromide with toluene in 1,2,4-trichlorobenzene catalyzed by aluminum bromide will be separately reported. The reaction exhibits marked retardation after 25–35% reaction, attributed in this case to removal of toluene by separation of the insoluble σ-complex, $CH_3C_6H_6{}^+Al_2Br_7{}^-\cdot 6C_6H_5CH_3$.[9] In the early stages of the reaction the rate was shown to be proportional to the concentrations of both 2-(4-nitrophenyl)ethyl bromide and toluene. This result, together with the relatively small amount of isotope position rearrangement found in alkylation of toluene with 2-(4-nitrophenyl)ethyl chloride, suggests that the reactions of the 4-nitrophenylethyl halides follow a displacement mechanism for the greater part.

(27) This part of the work is a portion of the B.S. theses of E. Umgelter (1957) and R. Lorenz (1958) at Rensselaer Polytechnic Institute.

(28) All reactions with carbon-14 compounds were conducted first with inactive compounds. Elemental analyses for carbon were routinely performed on all samples combusted for radioassay; results agreed within 0.5% with the calculated value. Boiling points are uncorrected; melting points are corrected [S. C. Bunce, *Anal. Chem.*, **25**, 825 (1953)]. For gas chromatography, a Perkin-Elmer 154C vapor fractometer was used.

(29) W. G. Dauben, *J. Org. Chem.*, **13**, 313 (1948).

sodium chloride solution and 8% sodium bicarbonate solution. After drying over sodium sulfate, the ether was distilled, and the residual liquid was distilled at reduced pressure through a 10-in. Vigreux column. 2-Phenylethanol, 26.5 g. (85%), was collected at 110° (17 mm)., lit.[30a] b.p. 104° (14 mm.).

2-Phenylethanol-1-C^{14} (0.5 g.) was converted[31] to the phenylurethane for isotopic assay. The crude derivative was dissolved in petroleum ether (b.p. 70–90°), treated with Norit A, and filtered. After three recrystallizations, the material melted at 78.0–79.5°, lit.[30a] m.p. 79°.

2-Phenylethyl-1-C^{14} Chloride.[32]—A solution of 25 g. (0.2 mole) of 2-phenylethanol in 100 ml. of pyridine was placed in a 300-ml. flask fitted with a thermometer, addition funnel, and mechanical stirrer. The contents of the flask were cooled to 0° while 50 ml. (0.7 mole) of purified thionyl chloride was added slowly. The solution was then heated on a steam bath for 5 min., cooled to room temperature, and allowed to stand for 30 min. The reaction was quenched by the slow addition of ice–water, while the solution was cooled in an ice bath. The aqueous solution was extracted with two 300-ml. portions of ether and the ether solutions were combined and washed successively with water, dilute hydrochloric acid, saturated sodium chloride, 6% sodium bicarbonate, and water. After drying over sodium sulfate, the ether was distilled, and the residual liquid was distilled at reduced pressure through a 15-in. Vigreux column. The product, 24.5 g. (83.5%), was collected at 88° (18 mm.), $n^{21}\mathrm{D}$ 1.5284; lit.[30b] b.p. 91° (20 mm.), $n^{20}\mathrm{D}$ 1.5294.

Oxidation of 2-Phenylethyl-1-C^{14} Chloride.—2-Phenylethyl chloride (2.0 g., 0.014 moles) was added to 250 ml. of 3% potassium permanganate containing 0.5 g. of potassium hydroxide. The reaction mixture was stirred at reflux for 4 hr. The solution was cooled to room temperature, filtered, and acidified with 20 ml. of 20% sulfuric acid. The benzoic acid, 0.51 g. (29.2%), was filtered and washed with ice–water. After drying and vacuum sublimation, it melted at 121.1–122.1°. It was found to be inactive, a 2-mg. sample having 100 ± 4 c.p.m. while background was 101 ± 4 c.p.m.

Alkylation of Toluene with 2-Phenylethyl-1-C^{14} Chloride.—A solution of 6 g. (42 mmoles) of 2-phenylethyl-1-C^{14} chloride in 50 ml. of reagent grade toluene was cooled to 0° in a three-necked flask equipped for mechanical stirring and protected by drying tubes. To this solution was added 0.802 g. (5.9 mmoles) of sublimed aluminum chloride. The solution became yellow and then orange. After allowing the reaction to stir for 20 min., it was quenched by the addition of 100 ml. of ice–water. The layers were separated, and the organic layer was washed with saturated salt solution and 8% sodium bicarbonate until neutral. After drying, the toluene was distilled. The residual liquid was then distilled through a 12-in. Vigreux column. Two fractions were collected: less than 155° (13 mm.), 3.3 g.; 155–156°, 4 g., $n^{20}\mathrm{D}$ 1.5628.

A second run was performed in a similar manner. Two fractions were collected: less than 148° (12 mm.), 1 g.; 148–151° (12 mm.), 5 g. The highest boiling fraction was redistilled, and three fractions were collected: 137–147° (11 mm.), 2 g.; 147° (11 mm.), 2 g., $n^{20}\mathrm{D}$ 1.5629; 147° (11 mm.), 2 g., $n^{20}\mathrm{D}$ 1.5629. Pure 4-methylbibenzyl had $n^{20}\mathrm{D}$ 1.5635.

Alkylation of Toluene with 2-Phenylethyl-1-C^{14} Chloride and Isolation of Unchanged 2-Phenylethyl Chloride.—In a three-necked flask equipped with a mechanical stirrer and drying tubes at all openings, were placed 80 g. of toluene and 13.6 g. (96 mmoles) of 2-phenylethyl-1-C^{14} chloride. This solution was cooled to −6°. While the stirrer was in motion, 0.31 g. (2.3 mmoles) of sublimed aluminum chloride was added. The solution became a deep orange, the temperature rose to −4° and was maintained at −5° for the remainder of the reaction. After 10 min., the reaction was quenched by the addition of ice–water. The organic phase which was separated remained yellow. It was washed with two 75-ml. portions of 8% sodium bicarbonate and with water, and dried. The toluene was distilled through a 15-in. Vigreux column. Three higher boiling fractions were then collected: 105° (50 mm.), 6.5 g.; 105–130° (50 mm.), 4.3 g., $n^{21.5}\mathrm{D}$ 1.5251; 130–135° (50 mm.), 2.2 g. $n^{21.5}\mathrm{D}$ 1.5267. These were distilled again through the same column and three fractions were collected: 87° (14 mm.); 88–91° (14 mm.), $n^{22.4}\mathrm{D}$ 1.5287; 100–105° (14 mm.). The reported[30b] physical constants of 2-phenylethyl chloride are b.p. 89° (10 mm.), $n^{20}\mathrm{D}$ 1.5294. When the sample, b.p. 88–91° (14 mm.), was oxidized to benzoic acid, the acid was found to be inactive (3-mg. sample, 94 ± 4 c.p.m.; background, 93 ± 4 c.pm.). The specific activity of the 2-phenylethyl chloride-1-C^{14} which was oxidized was 10.50 × 10^4 c.m.p./mmole.

4-Methylbibenzyl.—Benzyl *p*-tolyl ketone, m.p. 108.6–109.6° (lit.[30c] m.p. 110°), was prepared[33] in 51% yield by the reaction of benzylmagnesium chloride and *p*-tolunitrile.

A mixture of 2.1 g. (10 mmoles) of the ketone, 2.1 g. (30 mmoles of hydrazine hydrate, and 2.2 g. (30 mmoles) of potassium hydroxide in 30 ml. of diethylene glycol was slowly heated from 121 to 225° while a small amount of volatile material distilled. After 3 hr., the clear solution was cooled, diluted with water, and extracted three times with ether. The combined ether solutions were washed with dilute hydrochloric acid, dried, and distilled. The residue, 1.7 g. (87%) of crude 4-methylbibenzyl, crystallized at low temperature. Recrystallization from ethanol at 0° gave 0.7 g., m.p. 33.5–34.5°, lit.[34] m.p. 27°.

4,4′-Dimethylbibenzyl.—The oxidation of 24 g. (0.25 mole) of *p*-xylene with 33 g. (0.12 mole) of potassium persulfate[35] gave 14 g. (50%) of 4,4′-dimethylbibenzyl, m.p. 78–79° after recrystallization from ethanol, lit.[35] m.p. 80–81°.

2-(4-Nitrophenyl)ethyl-1-C^{14} Chloride.—Into a 500-ml. flask equipped with a thermometer, addition funnel, and a mechanical stirrer was placed 200 ml. of concentrated nitric acid (Sp. Gr. 1.42). This was stirred at 85–90° while 21 g. (0.15 mole) of 2-phenylethyl-1-C^{14} chloride was added over a period of 1 hr. After allowing the reaction to continue for an additional 15 min., it was poured into 600 ml. of ice–water. Water was extracted with two 250-ml. quantities of ether. The ether was washed with 8% sodium bicarbonate and saturated salt solution. After drying over sodium sulfate, the ether was evaporated; the residual orange oil was dissolved in ethanol. The oily crystals which formed on cooling were recrystallized four times from ethanol. The yield was 8.4 g. (31%), m.p. 47.0–47.3°, lit.[36] m.p. 48°.

Alkylation of Toluene with 2-(4-Nitrophenyl)ethyl-1-C^{14} Chloride.—A solution of 7.2 g. (39 mmoles) of 2-(4-nitrophenyl)ethyl-1-C^{14} chloride in 100 ml. of dry toluene was added over a 10-min. period to a slurry of 11 g. (83 mmoles) of aluminum chloride in 150 ml. of toluene. The temperature rose 1°, but remained constant thereafter. The reaction was stirred at room temperature for 2.5 hr., then quenched by the addition of ice–water. The layers were separated, the aqueous layer was extracted with 250 ml. of ether, and the combined organic layers were washed with saturated salt solution and 8% sodium bicarbonate solution. After drying over sodium sulfate, the toluene and ether were distilled and the residual liquid was distilled at reduced pressure. Three fractions were collected: 120–170° (3 mm.), 3 g.; 170–192° (3 mm.), 1. g.; 192–203° (3 mm.), 3.5 g. The highest boiling fraction was an oil at room temperature. It was crystallized in ethanol, and recrystallized eight times yielding 150 mg. of 4-nitro-4′-methylbibenzyl, m.p. 68.0–68.5°.[37]

Anal.[38] Calcd. for $\mathrm{C_{15}H_{15}NO_2}$: C, 74.66; H, 6.27. Found: C, 74.93; H, 6.03.

Oxidation of 4-Methylbibenzyl.—4-Methylbibenzyl-C^{14} (2.0 g., 0.01 mole) was added to 500 ml. of 3% potassium permanganate containing 4 g. of potassium hydroxide. This mixture was stirred at reflux for 120 hr. After cooling to room temperature, the manganese dioxide was filtered from the solution. The filtrate was acidified with 20% sulfuric acid, cooled, and filtered. The resulting crystals were washed with ice–water and air dried. The white powder was extracted with two 100-ml. quantities of carbon tetrachloride. The carbon tetrachloride was decanted and evaporated to dryness. The residue (5.3 mg.) melted at 110–117°. The original acidic aqueous solution was extracted

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(30) (a) I. Heilbron and H. Bunbary, "Dictionary of Organic Compounds," Vol. IV, Oxford University Press, New York, N. Y., 1953, p. 125; (b) Vol. I, p. 500; (c) Vol. III, p. 363.

(31) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 227.

(32) C. C. Lee, M. C. Hamblin, and N. James, *Can. J. Chem.*, **36**, 1597 (1958).

(33) E. E. Turner, *J. Chem. Soc.*, **107**, 1459 (1915). We are indebted to R. Brown for this preparation.

(34) W. Mann, *Ber.*, **14**, 1645 (1881).

(35) C. Moritz and R. Wolffenstein, *ibid.*, **32**, 2531 (1899). We are indebted to S. D. Clemans for this preparation.

(36) H. Sobotka, *ibid.*, **62B**, 2191 (1929).

(37) Preparation of the nonradioactive compound, on which the analysis is reported, gave 4%, m.p. 68.5–69.0° after six recrystallizations.

(38) Analysis by Dr. G. Weiler and Dr. F. B. Strauss, Analytical Laboratory, 164 Banbury Road, Oxford, England.

with three 150-ml. quantities of carbon tetrachloride. The carbon tetrachloride was evaporated and the residue was extracted with 75 ml. of hot water. After decanting and cooling, white crystals resulted. Upon filtering and drying, 60 mg. of material melting at 110–117° was isolated. The total crude benzoic acid isolated corresponded to a 5% yield. Vacuum sublimation gave material with m.p. 119.5–121.0°.

The solid material which was insoluble in carbon tetrachloride was heated and stirred for 2 hr. in ethanol. After filtering and cooling, 0.2 g. of white crystals was isolated. An additional 0.11 g. was obtained as second and third crops. This crude yield (19%) of terephthalic acid was further purified by vacuum sublimation.

Oxidation of 4-Nitro-4′-methylbibenzyl.—To a solution of 75 ml. of saturated potassium permanganate containing 0.5 g. of potassium hydroxide was added 140 mg. (0.58 mmole) of 4-nitro-4′-methylbibenzyl-C^{14}. This mixture was stirred at reflux for 120 hr. The basic solution was acidified with 20% hydrochloric acid, filtered, and the manganese dioxide was extracted with two 50-ml. quantities of 10% sodium hydroxide. Acidification of the solution gave 15 mg. of white powder. The acidified filtrates were combined and extracted with two 200-ml. quantities of ether. The ether was evaporated to 50 ml. and extracted with 50 ml. of 10% sodium hydroxide. This yielded 30 mg. of solid material upon acidification and filtration. All of the solid material was combined and extracted with three 50-ml. portions of ether. When the ether was evaporated to dryness, approximately 2–3 mg. of oily material remained. The solid which remained after ether extraction was extracted with two 30-ml. quantities of hot ethanol. Evaporation of the ethanol extracts and cooling resulted in a first crop of white crystals (approximately 10 mg.); further concentration gave 4 mg., and evaporation to dryness yielded an additional 3 mg. of material. The first crop of crystals would not sublime, but the second two crops yielded 4 mg. of terephthalic acid after sublimation. *p*-Nitrobenzoic acid was not isolated.

Alkylation of Naphthalene.—A solution of 12.8 g. (0.1 mole) of naphthalene in 150 ml. of benzene was stirred at 0° while 13.2 g. (0.1 mole) of aluminum chloride and 14.0 g. (0.1 mole) of 2-phenylethyl-1-C^{14} chloride in 15 ml. of benzene were added. The addition required 6 min. and the mixture was stirred for a total time of 30 min. at 0–5°, then poured onto ice. The benzene layer was washed thoroughly, dried with calcium chloride, and distilled. After removal of benzene and naphthalene at reduced pressure, 1.5 g. (19%) of the product, b.p. 140–144° (2.5 mm.), was obtained. Recrystallization from alcohol and from petroleum ether to constant specific activity gave material of 132×10^3 c.p.m./mmole.

Chromic Acid Oxidation.—To a mixture of 10 ml. of water, 5.5 ml. of concentrated sulfuric acid, and 4.5 g. (15 mmoles) of potassium dichromate there was added 0.16 g. (0.7 mmole) of reaction product. Nitrogen was used to flush the lines which led to a Dry Ice-cooled water trap and a liquid nitrogen trap; after addition the mixture was heated to reflux for 3 hr. The carbon dioxide in the nitrogen trap was purified by transfers on a vacuum line then counted by proportional counting in the gas phase.[39] The activity was 61.3×10^2 c.p.m./mmole, compared with an activity of $132 \times 10^3 \div 11$, or 120×10^2 c.p.m./mmole, to be expected if all of the carbon-14 were in the β-position. After dilution, the oxidation mixture was extracted with ether and the ether solution was extracted with 10% sodium hydroxide. The benzoic acid obtained by acidification was in turn extracted with ether; after drying and removal of the solvent, two vacuum sublimations gave material of 64.2×10^3 c.p.m./mmole, compared with 132×10^3 c.p.m./mmole to be expected if all of the carbon-14 were in the α-position.

Alkylation of Phenol.—In preliminary investigations of the reaction of 2-phenylethyl chloride (0.1 mole) with phenol (0.12 mole) and aluminum chloride (0.24 mole), no reaction was noted at 25° in nitroethane, nitrobenzene, or *n*-heptane solution. Slow evolution of hydrogen chloride was noted at 180° when excess phenol was used as the solvent. A mixture of 56.5 g. (0.6 mole) of phenol, 18 g. (0.127 mole) of 2-phenylethyl-1-C^{14} chloride (282×10^3 c.p.m./mmole), and 0.3 g. of aluminum chloride was heated at 180–190° for 78 hr. After cooling, the mixture was dissolved in ether and washed with dilute hydrochloric acid. After distillation of the ether, phenol was separated by distillation from a Claisen flask (b.p. 95° at 35 mm.). The cooled solid residue was dissolved in dilute sodium hydroxide solution, washed with ether, treated with decolorizing carbon, and filtered. Addition of hydrochloric acid at 0° gave 16.8 g. (66%), m.p. 70–75°, 240×10^3 c.p.m./mmole. Both the melting point and infrared spectra indicated that this product was a mixture, including *ortho*, *para*, and probably some *meta* isomers. Oxidation with chromic acid gave carbon dioxide with activity 15.4×10^3 c.p.m./mmole, compared with an activity of $240 \times 10^3 \div 7$ or 34.3×10^3 c.p.m./mmole to be expected if all the carbon-14 were in the β-position. The acid fraction, obtained as previously described, except that sodium bicarbonate rather than sodium hydroxide was used, gave benzoic acid which, after sublimation, had m.p. 120° and an activity of 118×10^3 c.p.m./mmole.

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[39] See footnote *a* in Table I.

Anchimerically Accelerated Bond Homolysis. IV.[1] Participation of a Neighboring Olefinic Double Bond in the Decomposition of a *t*-Butyl Perester

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First-order rate constants for the decompositions of a series of *o*-vinyl-substituted benzoyl peroxides and *t*-butyl perbenzoates have been determined. All compounds studied decompose faster than unsubstituted benzoyl peroxide or, in the case of the peresters, *t*-butyl perbenzoate. The accelerations are ascribed to neighboring group participation by the olefinic groups in the homolytic cleavage of the O–O bond. Solvent and substituent effects support the postulated charge separation in the transition state. Products isolated from one of the peresters and one of the peroxides are compatible with the proposed bonding interaction in the transition state leading to free-radical fragments.

Previous studies[3,4] have shown that the first-order rate constants observed in the thermal decomposition of *o*-methylthio-, *o*-iodo-, and *o*-phenylthio-substituted *t*-butyl perbenzoates are unusually large. This acceleration has been attributed to a stabilization of the transition state leading to radical intermediates by means of a bonding interaction between the perester group and the neighboring group. The postulation of charge separation in the transition state for the decomposition of the *o*-phenylthio perester has been well supported by studies of the variation in the first-order

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(1) For paper III, see D. L. Tuleen, W. G. Bentrude, and J. C. Martin, *J. Am. Chem. Soc.*, **85**, 1938 (1963).

(2) National Science Foundation Cooperative Fellowship, 1962–1963.

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