sublimations only 0.10 g. remained, m.p. 86–92° (reported 86°).[4]

Acknowledgment.—The authors wish to express their appreciation to Professor W. C. Vosburgh for his advice and encouragement and to the Duke University Research Council for a grant to one of them (A.W.) during the course of this investigation. The authors also wish to thank the referee for his valuable comment.

Durham, N. C.

[Contribution from the Chemistry Division, Oak Ridge National Laboratory]

Molecular Rearrangements. I. The 1,2,2-Triphenylethyl System[1]

By William A. Bonner and Clair J. Collins

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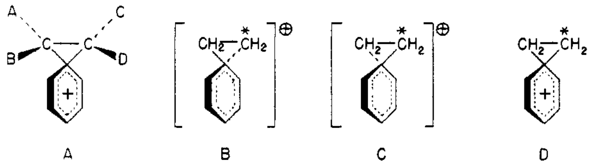
1,2,2-Triphenylethanol-1-C^{14} (I) has been acetylated and the acetate (II) deacetylated with no radiochemical rearrangement. When the carbinol (I) was dehydrated with phosphoric anydride in xylene, the resulting 1,1,2-triphenylethylene-1,2-C_1^{14} (III) had an equal distribution of radioactivity in the ethylenic carbons. Similarly, when one mole of the acetate (II) was warmed in glacial acetic acid containing a mole of *p*-toluenesulfonic acid, the reisolated acetate contained an equal amount of carbon-14 in each ethylenic position. This rearrangement of acetate II was not observed when sodium acetate was present in the reaction mixture. Formolysis of the tosylate (IV) of carbinol I proceeded with elimination, yielding olefin III in which a net 50% phenyl migration had taken place. Acetolysis of tosylate IV proceeded with 39% phenyl migration, whereas hydrolysis of IV in aqueous acetone proceeded with 22% phenyl migration. The lithium aluminum hydride reduction of IV was attended by 9% phenyl migration. These results are discussed in terms of the presumed symmetrical phenonium ion intermediates.

Introduction

Amplifying the concept of a bridged cationic intermediate originally suggested[2] by Lane and Wallis to account for the stereochemical consequences of certain intramolecular rearrangements, Cram in 1949 introduced[3,4] the concept of the symmetrical phenonium ion (A) as a discrete reaction intermediate of geometrical stability to explain the clear-cut stereochemical results he observed on acetolyzing the *p*-toluenesulfonate esters of the diastereomeric 3-phenyl-2-butanols. This simple interpretation was later expanded[5] to the view that bridged cations such as A existed in solution with tosylate anions as ion pairs. Later the stereochemical consequences of the solvolyses of various 4-phenyl-3-hexanol derivatives[6] and the radiochemical consequences of the nitrous acid deamination of 2-phenylethylamine-1-C^{14} were studied,[7] and the results of neither investigation could be explained in terms of a symmetrical phenonium ion alone. Roberts, in fact, proposed[7] structures similar to B and C as symbolic of the cationic intermediate formed during nitrous acid conversion of 2-phenylethylamine-1-C^{14} to 2-phenylethanol-1,2-C_1^{14}, and suggested that cation B underwent reaction with hydroxyl ion more rapidly than it equilibrated with C. This hypothesis rationalized Roberts' observation that neither phenyl nor substituted phenyl migration ever approached 50% as should be the case if the symmetrical phenonium ion D were in fact the sole intermediate.



In a series of investigations[8] originated with the intention of providing facile synthetic routes to carbon-14 labeled polynuclear aromatic hydrocarbons we became interested in the comparative migration ratios of phenyl and substituted phenyl groups, as well as in the nature of the intermediate formed during dehydration–rearrangement of carbon-14 labeled 2,2-diarylethanols. Following an unsuccessful attempt[9,10] to obtain mechanistic information on such reactions in the acenaphthene series, we report in the present paper, and the one following, our results on rearrangement studies in the triphenylethanol series. These observations, we believe, have a direct bearing on the present concept of the symmetrical phenonium ion.

Methods and Results

In order to have an "open chain" analog of the 2-phenyl-1-acenaphthenol-1-C^{14} previously studied,[10] the synthesis of 1,2,2-triphenylethanol-1-C^{14} (I) was undertaken. It was anticipated that the 1,2,2-triphenylethyl system would offer nearly optimum chemical reactivity for phenyl group participation during the solvolyses and elimination reactions, particularly since either one of two neighboring phenyl groups might participate in the rate-determining steps. If the formation of a symmetrical phenonium ion[3] were not a general phenomenon, then there was considerable promise that more than 50% phenyl migration might occur during one of the reactions studied. Such an observation, of course, would prove the nongenerality of the symmetrical phenonium ion concept. As indicated in Chart I, carbinol I was readily prepared from benzhydryl chloride, the

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[1] This document is based upon work performed under Contract Number W-7405-eng-26 for the Atomic Energy Commission at the Oak Ridge National Laboratory. Reprint requests should be addressed to C. J. C.

[2] J. F. Lane and E. S. Wallis, This Journal, **63**, 1674 (1941).

[3] D. J. Cram, *ibid.*, **71**, 3863, 3875 (1949).

[4] D. J. Cram and R. Davis, *ibid.*, **71**, 3871 (1949).

[5] D. J. Cram, *ibid.*, **74**, 2129, 2137, 2195 (1952).

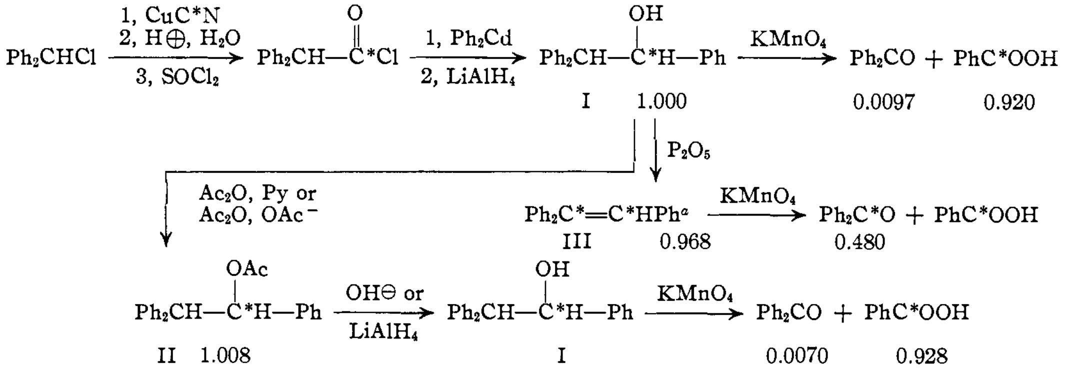
[6] D. J. Cram and F. A. Abd Elhafez, *ibid.*, **75**, 3189 (1953).

[7] J. D. Roberts and Clare M. Regan, *ibid.*, **75**, 2069 (1953).

[8] Paper VI, C. J. Collins and B. M. Benjamin, *ibid.*, **75**, 1644 (1953).

[9] W. A. Bonner and C. J. Collins, *ibid.*, **75**, 2308 (1953).

[10] W. A. Bonner and C. J. Collins, *ibid.*, **75**, 3831 (1953).



[a] As in accord with previous practice,[8] double asterisks here and in Chart II indicate a mixture of the two singly labeled radiochemical isomers $Ph_2C^*{=}CHPh$ (IIIa) and $Ph_2C{=}C^*HPh$ (IIIb) and *not* a doubly labeled structure.

CHART I

carbon-14 being introduced on conversion of the chloride to diphenyl-(acetonitrile-1-C^{14}) using cuprous cyanide-C^{14}. The radiochemical structure of carbinol I was confirmed by its oxidation to benzophenone and benzoic acid. As seen in Chart I, where the relative radioactivity assays of the pertinent products are indicated as fractions of the base radioactivity of carbinol I, only 0.97% of the radioactivity was found in the supposedly non-radioactive benzophenone fraction. This small amount is in all probability the consequence of slight phenyl migration during the oxidative degradation of carbinol I. The benzoic acid fraction in this oxidation shows a radioactivity assay, however, only 92% that of the base level. The low assay here and also in the benzoic acid fraction in the bottom line of Chart I was found by the application of carrier technique to be the consequence of partial oxidation of the benzophenone fraction under the oxidative conditions employed. Thus when benzophenone-α-C^{14} was subjected to our oxidizing conditions and the unprocessed oxidation mixture was treated with non-radioactive benzoic acid, the benzoic acid reisolated was found radioactive to an extent permitting calculation that 8% of the benzophenone-α-C^{14} had been oxidized. In view of this result we place greater reliability on the radioactivity assay of the benzophenone fractions from such oxidations as an indication of the extent of phenyl migration during the reactions discussed below.

The carbinol I was found capable of acetylation to form 2-acetoxy-1,1,2-triphenylethane-1-C^{14} (II). The acetate II could be deacetylated with lithium aluminum hydride or with dilute alcoholic alkali to regenerate the carbinol I. Similar oxidative degradation of regenerated I showed that no phenyl migration occurred during the acylation or deacylation reactions. While these results would be anticipated, the facile migration of the phenyl group observed in other reactions described later necessitated unambiguous experimental confirmation that phenyl migration was indeed absent in the present case, since deacylation, at least, is an important tool in the experiments described below.

On dehydration of carbinol I with phosphoric anhydride in boiling xylene 1,1,2-triphenylethylene-1,2-C$_1^{14}$ (III) resulted in good yield. Permanganate oxidation of the olefin III gave ketone and acid fractions of essentially equal radioactivity assay, thus indicating clearly that phenyl migration occurred during or after the dehydration of carbinol I to the extent of 50%.

Tosylation of carbinol I was accomplished by its conversion in liquid ammonia solution to the sodium salt, followed by reaction of the latter with *p*-toluenesulfonyl chloride. The resulting 1,2,2-triphenylethyl-1-C^{14} *p*-toluenesulfonate (IV) was subjected to the reactions indicated in Chart II. The molar radioactivities relative to original carbinol I given under the pertinent products in Chart II permit calculation of the percentage of phenyl migration occurring during each of the reactions studied. These percentages are summarized in the right hand column of Chart II. In the acetolysis experiments with tosylate IV it is seen that the extent of phenyl migration depends on the reaction environment, reaching a maximum of approximately 50% when pure acetic acid is the solvolyzing medium. The result in glacial acetic acid was shown to be due to the catalytic effect of the *p*-toluenesulfonic acid formed during the solvolysis of the acetate, since when the discretely labeled acetate (II) was heated in glacial acetic acid containing an equivalent quantity of *p*-toluenesulfonic acid, the reisolated acetate again showed a 50-50 distribution of carbon-14 between the ethylenic carbons. The acetate (II) exhibited no tendency for phenyl migration, however, under solvolytic conditions in which one or more moles of sodium acetate were present for each mole of II. In this instance the acetate reisolated had the starting radiochemical structure. While rate studies have not been made, the acetolysis reaction is apparently quite rapid, since in one instance we have observed conversion of tosylate IV to acetate II on mere quick recrystallization from acetic acid.

In order for our migration figures during tosylate acetolysis to have full validity it was desirable to establish unambiguously the radiochemical structure of tosylate IV. While its method of preparation argues for the indicated radiochemical structure, the possibility of partial migration of a phenyl group during the preparation of IV made our migration figures open to some question and hence we have attempted to establish the radiochemical structure of IV by other reactions. Hydrolysis of tosylate IV in aqueous acetone solution produced

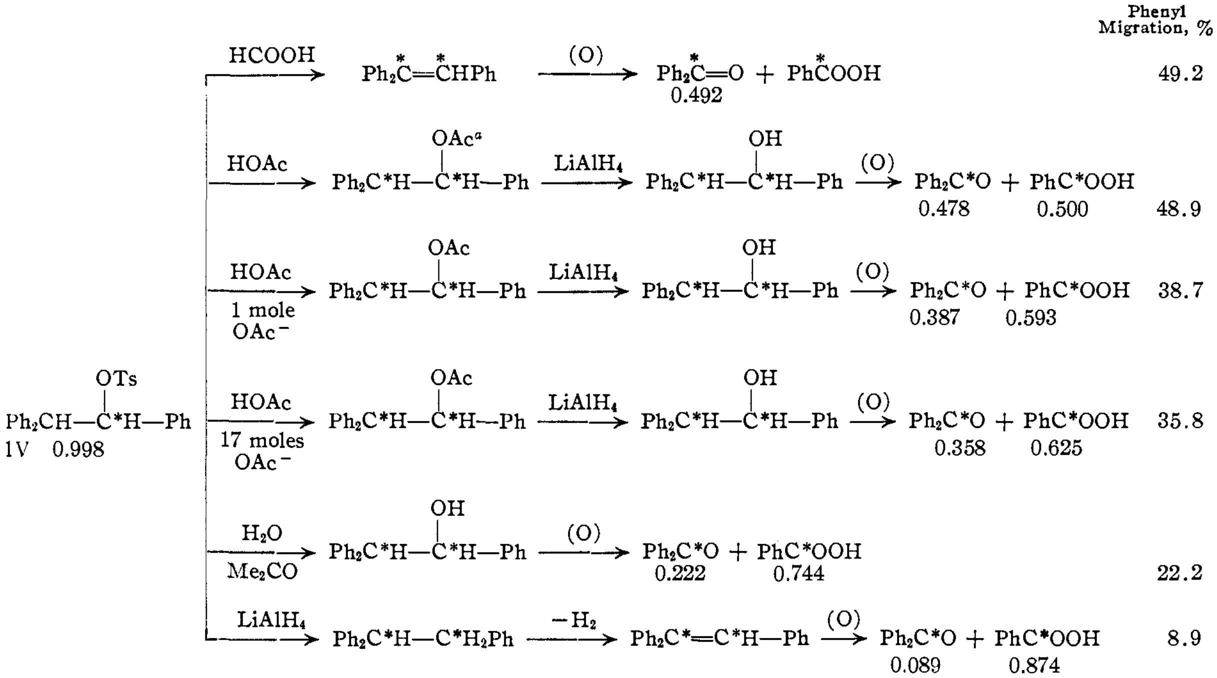


CHART II

[a] See footnote, Chart I.

carbinol I whose degradation indicated, assuming the proposed structure for IV, phenyl migration to the extent of 22%. Lithium aluminum hydride action on tosylate IV led to radioactive 1,1,2-triphenylethane in good yield. Dehydrogenation of the latter with chloranil in refluxing xylene, followed by oxidation of the resulting olefin produced acid and ketone fractions whose radioactivity assays, assuming structure IV, indicated phenyl migration during hydride reduction to the extent of about 9%. Since Cram has found[11] that phenyl migration may accompany tosylate reduction to the hydrocarbon stage using lithium aluminum hydride, it is logical to conclude that the 9% figure we indicate for this reaction in Chart II is due to partial migration during reduction and that the radiochemical structure of tosylate IV is indeed as indicated. In the unlikely event that our reduction proceeded *without* such rearrangement, we are in a position to say that at least 91% of our tosylate has the radiochemical structure indicated in Chart II.

In the hope of finding a reaction which might proceed with more than 50% phenyl migration, we have attempted to study the formolysis of tosylate IV. When IV was heated in 99% formic acid an insoluble oil was rapidly produced. This could not be crystallized and so was treated with ethereal lithium aluminum hydride. The resulting product was not carbinol I in that it failed to crystallize and was identified as the olefin III, which was quite rapidly oxidizable to benzophenone and benzoic acid. Radioactivity assay of the former oxidation fragment again indicated phenyl migration to the extent of 50% during the reaction of formic acid with tosylate IV.

One point pertaining to carbinol I is noteworthy. The literature records[12] the m.p. of 1,2,2-triphenylethanol as 87.5–88.5°. Our samples of carbinol I have been recrystallized from acetic acid and have shown m.p. values in accord with this figure. On standing, however, the m.p. of carbinol I thus purified has been observed to drop and broaden, and the sample to lose weight corresponding to one molar equivalent of acetic acid. Freshly recrystallized samples of radioactive carbinol I also showed a molar radioactivity corresponding to carbinol solvation by one molecule of acetic acid, and approached base level radioactivity only after desiccation. When non-desiccated samples of freshly recrystallized carbinol were allowed to react with *p*-toluenesulfonyl chloride in pyridine, or with phosphoric anhydride in hot xylene, only the acetate of I was isolated, indicating that under dehydrating conditions non-desiccated carbinol I undergoes acetylation with its own solvent of crystallization.

Discussion

While the phosphoric anhydride dehydration of carbinol I led to essentially 50% phenyl migration, we have found also, as indicated in the following paper, that the olefinic product III is itself capable of radiochemical isomerization under our dehydrating conditions. Thus we cannot say from our present data whether the 50:50 distribution of carbon-14 in the olefin III is due to phenyl migration during dehydration or to isomerization following dehydration. This problem is under further investigation.

The data summarized in Chart II may be rationalized in terms of two competing processes, (a) one involving the symmetrical phenonium ion E, and (b) one involving the classical carbonium

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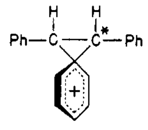
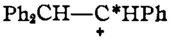
[11] D. J. Cram, THIS JOURNAL, **74**, 2149, 2152 (1952).

[12] J. S. Boyle, A. McKenzie and W. Mitchell, *Ber.*, **70B**, 2153 (1937).

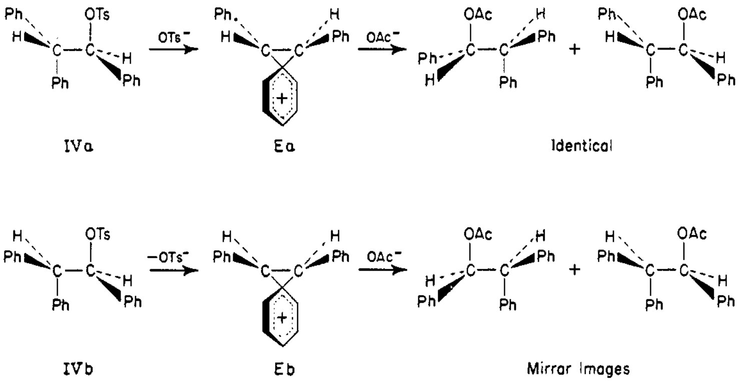
ion F. Although the stereochemical studies of Cram[3-5] have precluded the contribution of ions like F in similar solvolyses, the radiochemical data of Chart II indicate that during acetolysis of tosylate IV, the ion F must be involved to the extent of approximately 22%. That this approximately 22% acetolysis which proceeds without phenyl migration does not occur through a second-order displacement of tosylate by acetate ion is suggested by the fact that increasing the acetate ion concentration several-fold does not appreciably diminish the extent of phenyl migration.


E


$Ph_2CH—\overset{+}{C^*}HPh$

F

The formolysis of tosylate IV resulted in the formation of the olefin III. Since the olefin obtained was found to have a 50–50 distribution of carbon-14 over its ethylenic skeleton and since Winstein has shown[13] that the degree of phenyl participation is greater in formic than in acetic acid, it is reasonable to suppose that the contribution of the bridged ion E is important and that of the classical ion F negligible during the present reaction. The fact that the formolysis of tosylate IV appears to proceed exclusively with elimination, however, has thus far precluded a study of the tendency of the formate of carbinol I to exhibit an equilibration similar to that of acetate II in the presence of p-toluenesulfonic acid. It is thus not possible at present to state decisively that the net 50% phenyl migration during formolysis of tosylate IV was not a consequence of equilibration of the formate of I brought about by p-toluenesulfonic acid prior to elimination forming olefin III. That under the conditions of our formolysis experiment the olefin might rearrange further once formed is rendered unlikely, however, by the observation, to be published subsequently, that in a variety of solvents the olefin III is radiochemically isomerized only very slowly by action of p-toluenesulfonic acid.



The nature of the intermediate in the solvolysis of IV, together with such questions as internal return[14] are presently being studied with (a) phenyl-labeled derivatives of carbinol II and (b) stereochemical techniques.

On the basis of his observation that the diastereomeric 3-phenyl-2-butyl p-toluenesulfonates gave rise to the same (+)-2-phenylbutane when treated with lithium aluminum hydride, Cram has concluded[11] that the predominant mechanism of this reduction is a simple nucleophilic displacement of the tosylate group by the aluminum hydride ion. The high survival of optical activity suggested that the phenonium ion path made only a limited contribution during such reductions. Our finding that only 9% phenyl migration attends the lithium aluminum hydride reduction of our tosylate IV is thus in excellent agreement with Cram's findings and conclusions. We also, however, are unable to decide whether the small degree of phenyl migration accompanying tosylate reduction is due to a competing mechanism proceeding *via* the symmetrical phenonium ion, or to internal return[14] arising by regenerative collapse of the phenonium ion–tosylate ion pairs.

Our interest in 1,2,2-triphenylethanol-1-C^{14} rearrangements has been augmented by an interesting and noteworthy stereochemical aspect of this system. Depending on the constellation, IVa or IVb, of one of the enantiomorphic forms of tosylate IV prior to symmetrical ion formation, one might expect diastereomeric structures Ea and Eb of the phenonium intermediate to result. Ea represents an optically active intermediate, while Eb is a *meso* form, optically inactive by virtue of its plane of symmetry. Random attack of acetate ion or acetic acid on the equivalent carbon atoms of the ethane skeleton in Ea or Eb would lead to different stereochemical consequences, Ea producing an optically active acetate and Eb a racemic product. An investigation of the extent of racemization of optically active tosylate IV on solvolysis under conditions where the extent of phenyl migration can be radiochemically established might permit evaluation of the relative importance of the bridged intermediates Ea and Eb.

Acknowledgment.—We take pleasure in acknowledging the helpful suggestions made during the course of this work by Prof. John D. Roberts.

Experimental

Radioactivity Determinations.—Carbon-14 determinations were performed in the usual[8-10] manner. It will be noted however that the assays given for the related compounds reported in this paper do not agree with one another with the precision attainable[15] using the vibrating-reed method. This lower degree of precision is the consequence of three factors: (a) the occurrence of isotope effects during the permanganate oxidations,[9] (b) secondary oxidation of the benzophenone fractions (see Discussion) to benzoic acid under the oxidative conditions employed, and (c) an increased weighing error. Since our preliminary results indicated the importance of factors (a) and (b) above, an ordi-

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[13] S. Winstein, M. Brown, K. C. Schreiber and A. H. Schlesinger, THIS JOURNAL, **74**, 1140 (1952), have shown that phenyl migration increases as a function of solvolytic medium in the order $H_2O < HOAc < HCOOH$.

[14] S. Winstein and K. C. Schreiber, *ibid.*, **74**, 2165 (1952); S. Winstein and R. Heck, *ibid.*, **74**, 5584 (1952).

[15] V. F. Raaen and G. A. Ropp, *Anal. Chem.*, **25**, 174 (1953).

nary analytical balance was subsequently used in preference to a microanalytical balance for weighing the samples for combustion. The use of such a balance with somewhat larger samples greatly increases the speed and ease of performance of the radioactivity assays.

Diphenylacetyl-*carbonyl*-C^{14} Chloride.—Freshly distilled benzhydryl chloride (54 g., 0.266 mole) (prepared by action of thionyl chloride on benzhydrol in benzene solution) was treated with cuprous cyanide-C^{14} (20.6 g., 0.239 mole; approximate radioactivity assay, 13 mc./mole) (prepared by adaptation of the procedure of Barber[16]) and the mixture was immersed in an oil-bath preheated to 200–210°. Heating was continued with occasional swirling during a two-hour period. The mixture was diluted with acetone, filtered and the residual cake rinsed thoroughly with acetone. The filtrate and washings were distilled until free of solvent and the residue was treated with 50% (by volume) sulfuric acid (250 ml.). The mixture was stirred vigorously under reflux for 3.5 hours, cooled and continuously extracted ether. Ether was distilled from the extract and the residue was stirred vigorously with warm, saturated sodium bicarbonate solution. After the bicarbonate mixture had stood for several days the undissolved material was filtered and rinsed with water. The filtrate was acidified and the precipitated material was collected, washed with water and dried. The crude diphenylacetic-*carboxy*-C^{14} acid thus obtained weighed 25.2 g. (50%), had m.p. 145–146.5°, and showed a radioactivity assay of 9.56 mc./mole. This material was diluted to our tracer level (*ca.* 2.7 mc./mole) with non-radioactive diphenylacetic acid prior to conversion to the acid chloride.

The above tracer level diphenylacetic-*carboxy*-C^{14} acid (50 g.) was dissolved in boiling, dry, thiophene-free benzene (150 ml.), and the solution was treated gradually with thionyl chloride (80 ml.). The mixture was refluxed for 7 hours, after which the residual thionyl chloride was removed by evacuation at 100°, last traces by vacuum codistillation with benzene (125 ml.). The residue was dissolved in hot hexane (150 ml.), and the solution was clarified with Norit and allowed to crystallize at 0° after seeding. The first crop material weighed 42.1 g. (78%) and had m.p. 56–56.6°, in agreement with the recorded value.[17]

Phenyl Benzhydryl Ketone-C^{14}.—The conditions for this reaction, as well as those for all reactions discussed later in this paper, were previously worked out with non-radioactive analogs. In general, only the results of the experiments with the radioactive species are herein reported. Phenylmagnesium bromide (0.402 mole, 10% excess) was prepared from magnesium (9.80 g.) and bromobenzene (42.5 ml.) in dry ether (300 ml.). After reaction was complete the Grignard solution was cooled in ice and treated slowly with anhydrous cadmium chloride (36.9 g., 0.201 mole), then with glass beads. The mixture was stirred for 10 minutes (Hershberg stirrer) at 0°, then for 15 minutes at room temperature, after which the ether was distilled while stirring until the residue was nearly solvent-free. Dry, thiophene-free benzene (275 ml.) was added, and distillation was continued with stirring until the vapor temperature had risen to 68°, whereupon an additional 50 ml. of benzene was added. The mixture was then cooled in ice and stirred vigorously during gradual addition (10 minutes) of a solution of the above diphenylacetyl-*carbonyl*-C^{14} chloride (42.1 g.) in benzene (90 ml.). The mixture was stirred for one hour at room temperature, then for 30 minutes under gentle reflux, after which it was cooled in ice. Excess water was added dropwise with stirring, followed by hydrochloric acid in quantity sufficient to dissolve the magnesium salts. The benzene layer was washed with water, 5% sodium hydroxide solution, then again water, after which it was dried (sodium sulfate) and decolorized (Norit). The solvent was flash distilled, leaving 57.6 g. of amber solid. This was dissolved in hot benzene (58 ml.) and the solution was poured into hot ethanol (370 ml.). Cooling for 2 days at 0° produced 39.9 g. (79%) of the desired ketonic product, m.p. 136–136.5°, unchanged by further recrystallization, in agreement with the literature.[18] The product gave a radioactivity assay of 2.688 mc./mole. The above procedure is adapted from that of Cason.[19]

1,2,2-Triphenylethanol-1-C^{14} (I).—Lithium aluminum hydride (7 g.) was placed in a 2-l. 3-necked flask equipped with Hershberg stirrer, glass beads, reflux condenser ($CaCl_2$), and dropping funnel, and was covered with dry ether (235 ml.). The above phenyl benzhydryl ketone-C^{14} (35 g.) was dissolved in warm benzene (235 ml.) and the warm solution was added dropwise with stirring to the lithium aluminum hydride slurry over a period of 20 minutes. Stirring was continued for 45 minutes, when the excess hydride was decomposed by the cautious addition of ethyl acetate, followed by water, then hydrochloric acid. After washing, drying and decolorizing, the solvents were evaporated from the organic layer, leaving 36.4 g. (103%) of clear oil. Crystallization was accomplished from acetic acid (155 ml.), resulting in a first crop, 35.1 g., m.p. 79–84°, and, after slight dilution, a second crop, 3.8 g., m.p. indistinct above 80°. Recrystallization from acetic acid (150 ml.) gave pure carbinol I, m.p. 87.5–88.5° in agreement with the literature.[12] The combined second crops from the above crystallizations (10.5 g.) were treated with ethanol (18 ml.), and 1.0 g. of insoluble material removed by filtration, m.p. 80–205°. The filtrate was freed of solvent and the residue was crystallized from acetic acid (35 ml.), yielding an additional 7.7 g. of carbinol I, m.p. 87.5–88.5°.

The high-melting insoluble material above was recrystallized by dissolving in boiling acetone, concentrating the solution and diluting with hot ethanol. Two such recrystallizations gave pure 1,1,2,2-tetraphenylethanol, m.p. 235.5° in agreement with the recorded value.[20] The occurrence of this by-product is explainable if one assumes that the conversion of phenylmagnesium bromide to phenylcadmium was not quite complete in the ketone synthesis above, since the action of phenylmagnesium bromide on diphenylacetyl chloride is known[20] to produce 1,1,2,2-tetraphenylethanol.

Anal. Calcd. for $C_{26}H_{22}O$: C, 89.12; H, 6.30; mol. wt., 350.5. Found: C, 89.11, 89.06; H, 6.38, 6.34; mol. wt., 357.

When our freshly recrystallized 1,2,2-triphenylethanol-1-C^{14}, m.p. 87.5–88.5° (0.1159 g.) was dried to constant weight *in vacuo* over sulfuric acid, weight loss (0.0186 g.) corresponded approximately to one molar equivalent of acetic acid; calcd. weight loss, 17.96%; found, 16.05%. The desiccated sample of carbinol I showed m.p. 82.5–83.5° and a radioactivity assay, 2.682, 2.686, average, 2.684 mc./mole, in agreement with that of its parent ketone. When this material was recrystallized from acetic acid the m.p. again rose to 87.5–88.5° and the radioactivity assay of the freshly recrystallized sample was 2.630 mc./mole, calculated on the basis of one molecule of acetic acid of solvation. In view of these results the bulk sample of carbinol I above was dried *in vacuo* over sulfuric acid until the acetic acid odor was no longer noticeable, prior to its employment in further reactions.

1-Acetoxy-1,2,2-triphenylethane-1-C^{14} (II).—The above carbinol I (1.54 g.) was dissolved in pyridine (7 ml.). Acetic anhydride (4 ml.) was added, and the solution was allowed to stand for 2 days. Water was slowly added, after which the precipitated solid was filtered and dried, 1.70 g. (96%), m.p. 150–153°. Two recrystallizations from ethanol (16 ml.) gave the pure acetate, m.p. 156.5–157°.

Anal. Calcd. for $C_{22}H_{20}O_2$: C, 83.52; H, 6.38; radioactivity assay, 2.684 mc./mole. Found: C, 83.24, 83.39; H, 6.29, 6.32; radioactivity assay, 2.708 mc./mole.

In another experiment carbinol I (1.00 g.) was dissolved in hot acetic acid (10 ml.), and the solution was treated with anhydrous sodium acetate (0.2 g.) and acetic anhydride (5 ml.). The mixture was heated on the steam-bath for 16 hours, then diluted slightly with water and allowed to crystallize. There resulted 1.13 g. (99%) of pure acetate, white needles, m.p. 156.5–157°. Deacetylation of the present acetate sample, followed by oxidative degradation of the resulting carbinol, gave results, as indicated below, which proved that the conditions of acetylation and deacetylation, which we have employed exert no isomerizing effect on the molecular skeleton involved.

1,2,2-Triphenylethyl-1-C^{14} *p*-Toluenesulfonate (IV).—Liquid ammonia (*ca.* 85 ml.) was added to a precooled (Dry Ice-methanol) three-necked flask containing glass beads

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(16) H. J. Barber, *J. Chem. Soc.*, 79 (1943).

(17) H. Staudinger, *Ber.*, **38**, 1737 (1905).

(18) H. Biltz, *ibid.*, **26**, 1957 (1893).

(19) J. Cason, THIS JOURNAL, **68**, 2080 (1946); *Chem. Revs.*, **40**, 15 (1947).

(20) A. Orekhoff, *Bull. soc. chim.*, [4] **25**, 188 (1919).

(*ca.* 25 g.) and equipped with Hershberg stirrer, reflux condenser ($CaCl_2$) and dropping funnel. A small quantity (*ca.* 0.1 g.) of sodium shot was added, while stirring vigorously under cooling. When the sodium had dissolved a portion of a solution of the above desiccated carbinol I (5.00 g.) in anhydrous ether (100 ml.) was added dropwise to the liquid ammonia mixture. Addition was continued until the blue color of the sodium had been discharged, whereupon an additional small quantity of sodium shot was added and the carbinol solution addition was continued. This process was repeated until all of the carbinol solution had been added, when any remaining sodium color was discharged by the addition of a small quantity of solid carbinol. An additional quautity of dry ether (50 ml.) was added. The cooling bath was then removed and the flask was warmed gently allowing the liquid ammonia to evaporate slowly through the condenser, after which the remaining ether suspension was stirred under reflux, finally for a brief period in the presence of an air stream, to remove residual ammonia. To the stirred suspension was next added dropwise a solution of distilled *p*-toluenesulfonyl chloride (4.00 g.) in dry ether (35 ml.). Stirring under reflux was continued for 30 minutes, when the slurry was filtered (Celite) and the cake was rinsed three times by resuspension in boiling ether and refiltration. The filtrate was evaporated to *ca.* 50 ml. and allowed to crystallize, producing 2.57 g. of the desired tosylate IV, m.p. 74–75°. A second crop, 0.20 g., m.p. 70–71°, was obtained on concentrating the mother liquors to 10 ml. and diluting with 30 ml. of ligroin. The combined crops were recrystallized by dissolving in acetone (8 ml.) and diluting with ligroin (30 ml.), yielding 2.45 g. of product having m.p. 78–79°. In similar preparations the highest m.p. noted for tosylate IV was 82.5–83°. The freshly prepared material seemed to deteriorate on standing, in that the m.p. dropped to lower and broader values. Consequently analysis, radiochemical assay, and all subsequent chemical reactions were conducted on freshly prepared samples of tosylate IV which had stood, at most, for an hour or so before use.

Anal. Calcd. for $C_{27}H_{24}O_3S$: C, 75.70; H, 5.65; S, 7.48; radioactivity assay, 2.684 mc./mole. Found: C, 75.60, 75.45; H, 5.80, 5.84; S, 7.48, 7.62; radioactivity assay, 2.680 mc./mole.

Succinoylation of 1,2,2-Triphenylethanol.—Non-radioactive, desiccated 1,2,2-triphenylethanol (5.00 g.) was dissolved in pyridine (25 ml.) and the solution was treated with succinic anhydride (7.5 g.). The solution was heated on the steam-bath for 24 hours, then poured slowly with stirring into water (200 ml.) containing a little sodium chloride. After stirring for 80 minutes the solid was filtered, rinsed and dried, 7.2 g. (105%), m.p. 176–177°. The material was recrystallized from a mixture of acetic acid (70 ml.) and water (20 ml.), filtering before the dilution. There resulted 6.70 g. of needles, m.p. 177.5–178°.

Anal. Calcd. for $C_{24}H_{22}O_4$: C, 77.00; H, 5.93. Found: C, 76.79, 76.84; H, 5.93, 6.01.

This half ester was further characterized by conversion to its phenylethylammonium salt. The half succinate (0.50 g.) and DL-1-phenethylamine (0.162 g., one mole) were dissolved in ethanol (3 ml.) and the solution was allowed to crystallize slowly, resulting in 0.41 g. (62%) of product, m.p. 145.5–146.5°, unraised by further crystallization.

Anal. Calcd. for $C_{32}H_{33}O_4N$: C, 77.58; H, 6.71. Found: C, 77.55, 77.65; H, 6.76, 6.72.

Dehydration of 1,2,2-Triphenylethanol-1-C^{14}.—Desiccated carbinol I (1.25 g.) was dissolved in dry, refluxing xylene (15 ml.). Phosphoric anhydride (*ca.* 0.5 g.) was added, and the mixture allowed to reflux for 30 minutes, after which it was cooled. The decanted xylene layer was washed with water, dried (sodium sulfate), and passed through a 1 × 20 cm. column of alumina, rinsing with benzene (50 ml.). Solvent was evaporated from the effluent, leaving 1.20 g. of clear oil which was crystallized from acetic acid (6 ml.) after seeding with 1,1,2-triphenylethylene. There resulted 0.83 g. of product having m.p. 63–66°. Recrystallization from acetic acid (4 ml.) produced 0.41 g. of pure 1,1,2-triphenylethylene-1,2-C_1^{14} (III) having m.p. 66.5–67.5° in agreement with the literature.[21] Radioactivity assay, calcd. 2.684 mc./mole, found 2.598 mc./mole. On standing the mother liquors produced a small quantity (*ca.* 0.02 g.) of material, m.p. 82–84°, apparently unremoved carbinol I. The above olefin III was oxidized in the manner described below, with the radiochemical consequences summarized in Table II.

Deacetylation of 1-Acetoxy-1,2,2-triphenylethane-1-C^{14}.—The acetate II (1.00 g.) was dissolved in hot ethanol (20 ml.) and the solution was treated with 20% sodium hydroxide solution (10 ml.). After refluxing for an hour the mixture was cooled, diluted with water and extracted with ether. Solvent evaporation from the washed extract gave 0.88 g. (101%) of sirup which, on crystallization from acetic acid (6 ml.), produced 0.81 g. of carbinol I, m.p. 88–88.5°. The oxidation of this material is described below, and the radiochemical data are given in Table II.

In another experiment the acetate II (1.13 g.) obtained by the previous Ac_2O-NaOAc acetylation was added in small portions to a stirred slurry of excess lithium aluminum hydride in ether, stirring for 5 minutes on completion of the addition. The excess hydride was decomposed by cautious addition of acetone, followed by water and hydrochloric acid. Evaporation of the washed ether layer gave 0.98 g. (100%) of clear sirup which gave pure carbinol I, m.p. 88–89°, on recrystallization from acetic acid. The oxidation of this product is described below, with radiochemical data in Table II.

Acetolyses of 1,2,2-Triphenylethyl-1-C^{14} *p*-Toluenesulfonate.—In general the freshly prepared tosylate IV was dissolved in the acetolyzing mixture indicated in Table I, and the resulting solution was heated on the steam-bath for the indicated period of time. Water was then added to the mixture until slightly turbid, whereupon the rearranged acetate II was permitted to crystallize. Investigation of the acetate mother liquors from an acetolysis similar to run 2 in Table I, conducted on a non-radioactive sample of tosylate IV, failed to indicate the presence of any by-product 1,1,2-triphenylethylene formed during the acetolysis reaction. The acetates from such acetolyses were subjected to deacetylation with lithium aluminum hydride in the manner described above, and the resulting samples of 1,2,2-triphenylethanol-1,2-C_1^{14} were purified by recrystallization from acetic acid prior to the oxidative degradations described below. The results of the acetolysis experiments are summarized in Table I. The radiochemical consequences on oxidation of the carbinol products in Table I are given in Table II below.

Hydrolysis of 1,2,2-Triphenylethyl-1-C^{14} *p*-Toluenesulfonate.—Tosylate IV (1.00 g.) was dissolved in acetone (30 ml.). Water (10 ml.) was added, and the solution was heated under reflux for 4 hours, then diluted with water and heated in an air stream to remove the acetone. The aqueous residue was extracted with ether. Solvent removal from the extract left 0.66 g. (103%) of sirup which gave 0.56 g. of 1,2,2-triphenylethanol-1,2-C_1^{14}, m.p. 84–86° on crystallization from acetic acid. The radiochemical data pertaining to the oxidation products from this carbinol sample are given in Table II below.

Formolysis of 1,2,2-Triphenylethyl-1-C^{14} *p*-Toluenesulfonate.—Tosylate IV (0.90 g.) was treated with E.K.Co. 98–100% formic acid (8 ml.), heating the mixture on the steam-bath. Homogeneous solution was rapid, but after several minutes the mixture turned milky and in a short time an oil separated and the mixture darkened. Heating was continued for an hour when the mixture was cooled, diluted with water and extracted with ether. The extract was washed with water and sodium bicarbonate solution. Solvent removal left 0.55 g. of amber oil which could not be crystallized. This was accordingly dissolved in ether, and the solution was added with stirring to an ether slurry of lithium aluminum hydride. Decomposition of the excess hydride, followed by product isolation as described above led to 0.49 g. of oil which failed to crystallize. This was dissolved in benzene (10 ml.) and the solution was passed through a 1 × 25 cm. column of alumina, rinsing with 40 ml. of benzene. Solvent evaporation from the effluent led to a quantitative recovery of oil which again failed to crystallize. The material at this point was subjected to permanganate oxidation in the manner described below. The radiochemical consequences of the experiment are summarized in Table II. The material appeared to be a radiochemically isomerized sample of olefin III, in that underwent oxidation with permanganate much more rapidly than samples of 1,2,2-triphenylethanol.

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[21] H. Adkins and W. Zartman, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 606.

TABLE I

ACETOLYSES OF TOSYLATE IV UNDER VARYING CONDITIONS

No.	Tosylate, G.	Tosylate, Mmoles	Sodium acetate, G.	Sodium acetate, Mmoles	Sodium acetate / tosylate	Acetic acid,[a] ml.	Time, min.	Acetate G.	Acetate %	Acetate M.p., °C.	Carbinol G.	Carbinol %	Carbinol M.p., °C.
1	0.90	2.10	0.00	0.00	0.00	8	60	0.43	59	142–145[b]	0.34	100	.....[c]
2	1.10	2.58	0.20	2.44	0.95	10	45	.64	79	154–155	.53[d]	95[d]	86–87
3	1.24	2.90	4.00	48.8	16.9	20	60	.83	91	154–155	.66[d]	93[d]	87–88.5

[a] Containing 0.1 ml. of acetic anhydride. [b] Recryst. from dil. acetic acid to give 0.39 g., m.p. 154–155°. [c] Oxidized without recrystallization. [d] Refers to purified, crystalline product.

Lithium Aluminum Hydride Reduction of **1,2,2-Triphenylethyl-1-C^{14} *p*-Toluenesulfonate.**—Tosylate IV (1.15 g.) was added in small portions to a stirred slurry of lithium aluminum hydride in ether, stirring for an additional 10 minutes following completion of the addition. The excess hydride was decomposed with acetone, and the product, 0.68 g., isolated in the usual way. The sirupy material was dissolved in ligroin and its solution was passed through a 1 × 20 cm. column of alumina, rinsing with ligroin. Solvent evaporation from the effluent led to 0.48 g. of white oil. Further elution of the column with methanol produced an additional small quantity of oil which could not be crystallized readily from acetic acid and hence did not appear to be 1,2,2-triphenylethanol. The 0.48 g. of oil above was crystallized from *ca.* 3 ml. of ethanol, producing a first crop weighing 0.11 g., m.p. 51–52°, mixed m.p. with authentic 1,1,2-triphenylethane (m.p. 54–55°, prepared by catalytic reduction of 1,1,2-triphenylethylene), 53.5–55°. A second crop of less pure material, 0.18 g., m.p. 48–49°, was obtained by placing the mother liquors at 0°. The combined crops (0.28 g.) were dissolved in xylene (3 ml.) and treated with chloranil (0.28 g.). The mixture was refluxed gently for three days, when it was diluted with ether and passed through an alumina column. Solvent removal left 0.27 g. of thin oil. This was subjected to oxidation with potassium permanganate in the general fashion described below, resulting in the isolation of 0.08 g. of benzoic acid and 0.317 g. of benzophenone 2,4-dinitrophenylhydrazone, both of correct m.p. The radiochemical assays of these products are shown in Table II.

Oxidative Degradations of 1,2,2-Triphenylethanol-C^{14} and 1,1,2-Triphenylethylene-C^{14} Samples.—The radiochemical structure of our originally synthesized sample of carbinol I was established by the following oxidation. Carbinol I (1.00 g.) was dissolved in C.P. acetone (40 ml.) and the solution was treated with a solution of potassium permanganate (2.30 g., 100% excess) in water (20 ml.). Acetic acid (0.1 ml.) was added, and the mixture was allowed to stand at room temperature. After 4 days the remaining permanganate was destroyed by addition of sufficient concentrated sodium bisulfite solution, after which the manganese dioxide was filtered and rinsed with acetone and hot water. The filtrate and washings were heated on the steam-bath in an air stream to remove the majority of the acetone. The aqueous residue was extracted by stirring well with ether. The ether extract was stirred thoroughly with saturated sodium bicarbonate solution to remove the acidic component, and the ether layer was evaporated to dryness, leaving 0.69 g. (103%) of benzophenone. The bicarbonate solution was acidified with hydrochloric acid and extracted several times by thorough stirring with ether. Evaporation of the ether solution left 0.44 g. (99%) of crude benzoic acid. The latter was recrystallized twice from water to give a pure sample, m.p. 122–122.5°; radioactivity assay, 2.437, 2.497; average, 2.467 mc./mole. The benzophenone fraction was converted to its 2,4-dinitrophenylhydrazone in the usual fashion yielding 0.86 g. (63%), m.p. 235–237°. Recrystallization from dioxane gave the pure sample, m.p. 239.5–240°; radioactivity assay, 0.0261 mc./mole.

Oxidations of our other samples of 1,2,2-triphenylethanol-C^{14} whose radiochemical structures concerned us were in general conducted in the fashion outlined above, with variations only in the quantities of materials depending on the size of the sample being oxidized. The results, with minor variations in yields, were essentially as indicated for the oxidation above. The radiochemical data pertaining to these experiments are summarized in Table II.

Oxidations of the various samples of 1,1,2-triphenylethylene-1,2-C^{14} obtained from several of the experiments previously discussed were conducted in an identical fashion, using approximately twice the calculated quantity of potassium permanganate in dilute acetone solution. These olefinic oxidations proceeded rather more rapidly than the above carbinol oxidations and it generally sufficed to permit the oxidation mixture to stand only 24 hours in order to isolate acceptable yields of benzoic acid and benzophenone oxidation products. The radiochemical data applying to the oxidation products from olefin oxidations are summarized in the lower half of Table II.

All of our oxidations gave products in sufficiently high yields such that the possibility of isotopic fractionation during oxidation[9] could not be considered a serious source of error in our results.

TABLE II

RADIOCHEMICAL DATA FOR OXIDATION PRODUCTS FROM VARIOUS 1,2,2-TRIPHENYLETHANOL-C^{14} AND 1,1,2-TRIPHENYLETHYLENE-C^{14} SAMPLES

	Radioactivity assay,[a] mc./mole	
Carbinol from	Benzoic acid	Benzophenone 2,4-DNPH
NaOH hydrolysis of acetate II	2.499 ± 0.020	0.0190
LiAlH$_4$ deacetylation of acetate II	2.482	0.0184
Tosylate acetolysis, run No. 1	1.281 ± 0.004	1.341
Tosylate acetolysis, run No. 2	1.591 ± 0.009	1.038 ± 0.002
Tosylate acetolysis, run No. 3	1.675	0.964
Tosylate hydrolysis	1.995	0.595 ± 0.004
Olefin from		
Dehydration of carbinol I	...	1.287 ± 0.001
Tosylate formolysis	...	1.342
Tosylate reduction with LiAlH$_4$ then dehydrogenation	2.343	0.240 ± 0.002

[a] All radioactivity assays reported in this paper were conducted on a vibrating reed electrometer after the usual wet combustion procedure (O. K. Neville, THIS JOURNAL, **70**, 3501 (1948), modified to handle compounds of high nitrogen content (W. A. Bonner and C. J. Collins, *ibid.*, **75**, 3693 (1953).

Action of *p*-Toluenesulfonic Acid on 1-Acetoxy-1,2,2-triphenylethane-1-C^{14}.—The radioactive acetate II described above (0.73 g.) was diluted with non-radioactive acetate II (0.73 g.) and the mixture (4.62 mmoles) was dissolved in warm glacial acetic acid (17 ml.). Acetic anhydride (0.5 ml.) was added, then *p*-toluenesulfonic acid hydrate (0.88 g., 4.65 mmoles). The solution was heated for one hour on the steam bath, a little water was added, and crystallization was allowed to proceed. The recovered acetate weighed 1.36 g. (93%). The entire sample of acetate was deacetylated using lithium aluminum hydride as described above. The crude carbinol product was recrystallized from dilute acetic acid to give 0.88 g. of pure product, m.p. 87.5–88 5°. An additional 0.17 g. of carbinol, m.p. 87–88°, was obtained from the mother liquors. The first crop of carbinol (0.88 g.) was oxidized using potassium permanganate (2.30 g.) in a 1:1 acetone–water mixture containing 0.1 ml. of acetic acid, in the fashion previously described. The benzoic acid fraction (0.20 g., 51%) had m.p. 121–122° after recrystallization from water, and showed a radioactivity assay of 0.694 mc./mole. The benzophenone fraction (0.50 g., 85%) was converted to its 2,4-dinitrophenylhydrazone. The crude derivative was recrystallized twice from dioxane to give a pure sample having m.p. 239.5–240° and a radioactive assay of 0.674 mc./mole. Thus 49.3% of the total carbon-14 was observed in the benzoic acid fraction and 50.7% in the benzophenone fraction.

In a second experiment *p*-toluenesulfonic acid hydrate

(0.88 g., 4.65 mmoles), sodium acetate (3.8 g., 46.2 mmoles), and acetic anhydride (0.5 ml.) were dissolved in warm acetic acid (21 ml.). 1-Acetoxy-1,2,2-triphenylethane-1-C^{14} (1.46 g., 4.62 mmoles; radioactivity assay, 2.708 mc./mole) was added, and the solution was heated on the steam-bath for one hour. The acetate was re-isolated and deacetylated and the carbinol, 1.34 g., m.p. 87–87.5°, was obtained as in the paragraph above. A 0.90 g. portion of this was oxidized, producing 0.53 g. of benzoic-*carboxy*-C^{14} acid which after recrystallization had m.p. 120–120.5° and radioactivity assay, 2.580 mc./mole. The benzophenone from the oxidation showed a radioactivity assay of 0.0312 mc./mole after conversion to its 2,4-dinitrophenylhydrazone. These data correspond very closely to those obtained on oxidative degradation of the pure carbinol I, indicating that excess sodium acetate completely hinders the isomerizing action of *p*-toluenesulfonic acid on the acetate II.

Test Oxidation of Benzophenone-α-C^{14}.—To determine if the low radiochemical assays obtained for the benzoic acid fraction resulting on oxidation of unrearranged samples of 1,2,2-triphenylethanol-1-C^{14} might be due to partial oxidation of the concomitantly produced non-radioactive benzophenone under the conditions of the oxidations, the following carrier experiment was conducted. Benzophenone-α-C^{14} (0.50 g., radioactivity assay, 1.570 mc./mole) was dissolved in acetone (30 ml.) and the solution was treated with a solution of potassium permanganate (1.80 g.) in water (15 ml.) containing acetic acid (0.1 ml.). The mixture was allowed to stand for 3 days, after which non-radioactive benzoic acid (0.50 g.) was added. The oxidation mixture was then processed in the usual manner, and the ketonic and acidic fractions were separated as described above. The benzoic acid fraction weighed 0.44 g., and was recrystallized from water (Norit clarification) to yield 0.16 g. of purified product, m.p. 122–122.5°; radioactivity assay, 0.0851 mc./mole. This uptake of radioactivity by the carrier benzoic acid permits calculation that 8.1% of the original benzophenone-α-C^{14} had undergone oxidation to benzoic acid under the conditions employed.

OAK RIDGE, TENN.

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

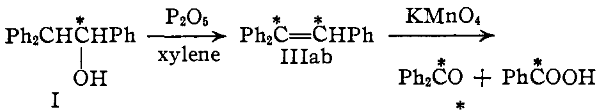
Molecular Rearrangements. II. The 1,1,2-Triphenylethyl System[1]

BY CLAIR J. COLLINS AND WILLIAM A. BONNER

RECEIVED MAY 1, 1953

1,1,2-Triphenylethanol-1-C^{14} (VI) has been dehydrated by means of aqueous sulfuric or glacial acetic acids to yield the unrearranged olefin, 1,1,2-triphenylethylene-1-C^{14} (IIIa). When this olefin was heated under reflux with dry xylene containing an equal weight of phosphoric anhydride, a complete isotopic position isomerization occurred, yielding a 50:50 mixture of IIIa and 1,1,2-triphenylethylene-2-C^{14} (IIIb). This observation can probably best be rationalized in terms of Cram's symmetrical phenonium ion. The semipinacolic dehydrobromination of 2-bromo-1,1,2-triphenylethanol-1-C^{14} (VII) to phenyl benzhydryl ketone-C^{14} (VIII) has been shown to take place with exclusive phenyl migration.

The radiochemical consequences of the solvolysis of the *p*-toluenesulfonate of 1,2,2-triphenylethanol-1-C^{14} (I) under various reaction conditions have been discussed in the previous paper.[2] It was also reported that when I was dehydrated with phosphoric anhydride in boiling xylene, 1,1,2-triphenylethylene-1,2-C_1^{14} (IIIab in which IIIa and IIIb were present in equal amounts) was obtained. This was demonstrated by permanganate oxidation of the olefin, and subsequent radioactivity assay of the oxidation fragments



$$\text{IIIa, } Ph_2\overset{*}{C} = CHPh$$

$$\text{IIIb, } Ph_2C = \overset{*}{C}HPh$$

All of the observations recorded could be rationalized in terms of a symmetrical phenonium ion of the type first proposed by Cram[3] to explain his stereochemical results during Wagner–Meerwein rearrangements in the 3-phenyl-2-butanol system. Owing to the ease with which this symmetrical intermediate, whatever its nature, is apparently formed, it became necessary to test the degradative method used[2] on 1,2,2-triphenylethylene-1,2-C_1^{14} (IIIab), in order to demonstrate conclusively and unambiguously that the phenyl migration, leading to a 50:50 distribution of carbon-14 in the ethylenic carbons, had occurred *prior to* and not *during* the degradative reaction. Accordingly, carbonyl labeled desoxybenzoin (V) was prepared[4] and then converted by means of the Grignard reaction to 1,1,2-triphenylethanol-1-C^{14} (VI), which could be dehydrated to the olefin (IIIa) by means of aqueous sulfuric or glacial acetic acids. These reactions, as well as the radiochemical data for the oxidative degradation of IIIa are summarized in Chart I. Radioactivity data are shown under each structure as fractions of the molar radioactivity of compound V. The radiochemical data indicate the correctness of assignment of the labeled positions in the compounds of Chart I, and confirm that no serious skeletal rearrangement took place during the permanganate oxidation of the olefin IIIa.

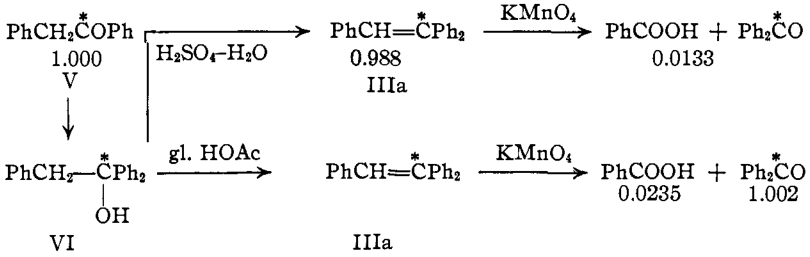


CHART I

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[1] This document is based upon work performed under Contract Number W-7405-eng-26 for the Atomic Energy Commission at the Oak Ridge National Laboratory.

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

[3] D. J. Cram, *ibid.*, 71, 3863 (1949).

[4] C. J. Collins and O. K. Neville, *ibid.*, 73, 2471 (1951).