fate. Approximately 80% of the solvent was evaporated at reduced pressure, and the residual liquid was then fractionated through the Holzman column to yield 12.4 g. (54%) of ethyl glycidate,[10] b.p. 88–90° (60 mm.).

1,2,5,6-Diepoxyhexane.—To 8.2 g. (0.1 mole) of hexadiene-1,5 in 275 ml. of methylene chloride slurried with 95 g. (0.9 mole) of sodium carbonate was added a solution of peroxytrifluoroacetic acid prepared from 8.2 ml. (0.3 mole) of 90% hydrogen peroxide, 50.8 ml. (0.36 mole) of trifluoroacetic anhydride and 50 ml. of methylene chloride. The addition required 25 minutes and the mixture was then heated under reflux for 30 minutes. The inorganic salts were removed by centrifugation. Most of the solvent was distilled off at atmospheric pressure and the residual liquid was fractionated through the Holzman column to yield 8.0 g. (70%) of 1,2,5,6-diepoxyhexane,[11] b.p. 77–80° (22 mm.).

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[11] S. L. Everett and G. A. R. Kon, *J. Chem. Soc.*, 3131 (1950).

HUNTSVILLE, ALABAMA

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

Molecular Rearrangements. III. The Mechanism of the Wagner–Meerwein Rearrangement in the 1,2,2-Triphenylethyl System[1]

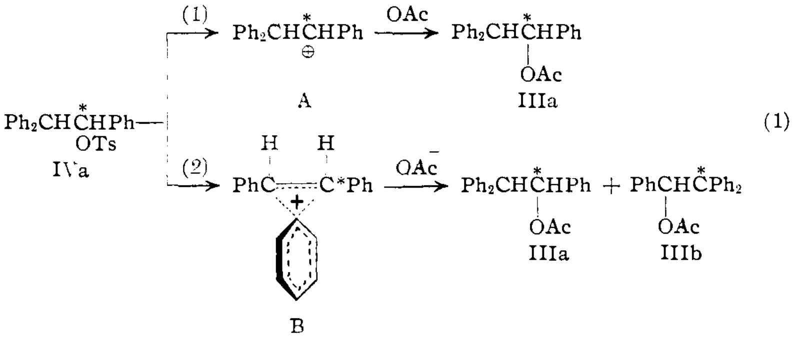
BY CLAIR J. COLLINS AND WILLIAM A. BONNER

RECEIVED APRIL 26, 1954

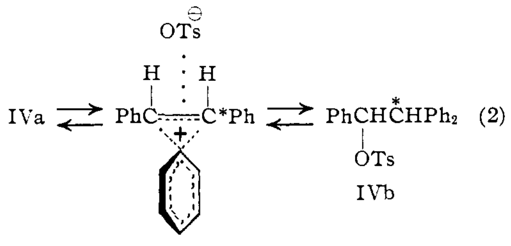
Several reactions of phenyl-labeled 1,2,2-triphenylethanol (IIc), its acetate (IIIc) and its tosylate (IVc) have been carried out under identical reaction conditions used for the chain-labeled analogs, and the radiochemical consequences of these reactions in both systems of labeling have been compared. It has been shown by this novel double-labeling technique that the reactions studied fall into two categories: (1) those in which a statistical redistribution of radioactivity has been achieved and (2) those in which a statistical redistribution has been approached, but not achieved. A simple kinetic relationship has been derived for the latter class of reactions, which allows a calculation of the radiochemical redistributions for various reactions in one series, knowing the results of the other. These calculated values agree with the observed values within experimental error, allowing the data to be rationalized quantitatively in terms of a mechanism involving open carbonium ion intermediates in which the cations undergo partial or complete radiochemical equilibration, depending upon their lifetimes. There is no evidence for bridged ionic intermediates in the reactions studied.

Introduction

The radiochemical results of the solvolytic reactions of 1,2,2-triphenylethyl-1-C^{14} *p*-toluenesulfonate (IVa) in acetone–water, acetic and formic acids have been described previously.[2] The rearrangements attending these solvolyses were tentatively rationalized in terms of two competing processes, one, 1- (step 1), involving an open carbonium ion A, the other, 1- (step 2), involving a symmetrical phenonium ion B, of the type proposed by Cram.[3a] This mechanism seemed likely in view of the results of Cram,[3b,3c] who claims that both open and bridged ions co-exist as intermediates during solvolytic reactions of closely related systems. These processes are illustrated for the acetolysis of tosylate IVa in glacial acetic acid containing sufficient sodium acetate to react with the *p*-toluenesulfonic acid formed

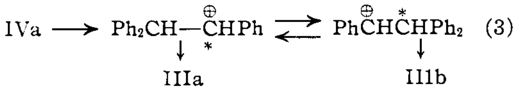


Under these conditions, the acetolysis product was shown[2] by oxidative degradation and subsequent radioactivity assay of the degradation products to consist of approximately 60% of acetate IIIa, and 40% of acetate IIIb. Neither these results, nor the results of the other solvolytic reactions described could be used as supporting evidence for this interpretation, however, since it was not possible



C

by a study of tosylate IVa to distinguish process 1- (step 2) from one involving internal return,[4] in which the ion B and a tosylate anion are thought to exist as an ion pair (C), which may collapse[4b,5] to a mixture of the tosylates IVa and IVb prior to acetolysis (eq. 2). Similarly, neither of the above interpretations could be distinguished from a mechanism (eq. 3) which may be written most simply as an equilibration of two open carbonium ions



$$\text{IVa} \longrightarrow \underset{\text{IIIa}}{\underset{\downarrow}{\text{Ph}_2\text{CH—}\overset{\oplus}{\underset{*}{\text{C}}}\text{HPh}}} \rightleftarrows \underset{\text{IIIb}}{\underset{\downarrow}{\text{Ph}\overset{\oplus}{\text{C}}\text{H}\overset{*}{\text{C}}\text{HPh}_2}} \qquad (3)$$

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

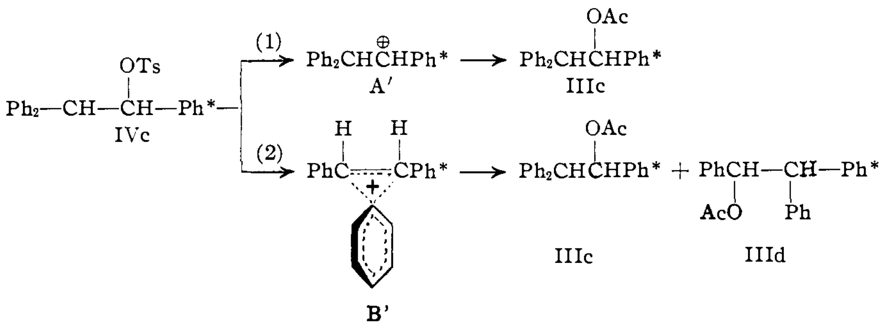
[2] W. A. Bonner and C. J. Collins, THIS JOURNAL, **75**, 5372 (1953).

[3] (a) D. J. Cram, *ibid.*, **71**, 3863, 3875 (1949); (b) F. A. Abd Elhafez and D. J. Cram, *ibid.*, **75**, 339 (1953); (c) D. J. Cram and J. D. Knight, *ibid.*, **74**, 5839 (1952).

[4] (a) S. Winstein and D. Trifan, *ibid.*, **74**, 1154 (1952); (b) S. Winstein and K. C. Schreiber, *ibid.*, **74**, 2165, 2171 (1952); (c) S. Winstein and R. Heck, *ibid.*, **74**, 5584 (1952).

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

The present work was undertaken with the hope of resolving these ambiguities, and a study of the previously reported[2] solvolytic reactions using 1-phenyl-C^{14}-2,2-diphenylethyl *p*-toluenesulfonate (IVc) appeared promising for this purpose.



(4)

Thus, if the symmetrical phenonium ion B′ of equation 4- (step 2) were directly formed from IVc as a discrete intermediate[3] which passed directly to product, and if no internal return occurred (see, however, the Discussion for an explanation of the importance of stereospecificity in this relation), the composition of the product should be simply predictable from earlier experiments,[2] that is, the mole fraction of IIIc should equal the mole fraction of IIIa and similarly the fractions of IIId and IIIb should be equal. It was hoped that any deviation from such simple predictability would be a measure of the contribution of equilibration processes such as those shown in equation 3, or possibly of the presence of internal return.

It is our purpose in this paper, and in the paper which follows,[6] to present the experimental results for several reactions of 1,2,2-triphenylethyl derivatives to which the double-labeling technique just outlined has been applied, and to propose a mechanism which explains quantitatively the radiochemical data obtained in all of the reactions to be discussed.

Methods and Results

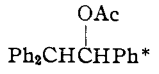
The syntheses of the ring-labeled ketone I, carbinol IIc, acetate IIIc and tosylate IVc were carried out in a manner similar to that employed for the preparation of their chain-labeled analogs[2]

$Ph_2CHCOPh^*$

I

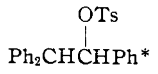
$Ph_2CHCHOHPh^*$

IIc



$Ph_2CH\overset{OAc}{C}HPh^*$

IIIc



$Ph_2CH\overset{OTs}{C}HPh^*$

IVc

with the exception, of course, that non-radioactive diphenylacetyl chloride and carbon-labeled diphenylcadmium were used for the preparation of I. The bromobenzene-C_1^{14} used in the preparation of di-(phenyl-C_1^{14})-cadmium was obtained from benzene-C_1^{14} by a modification of the method of Derbyshire and Waters.[7] The labeled benzene was prepared by a standard method[8] starting with sodium cyanide-C^{14} and pentamethylene dibromide. The radiochemical structures of I, IIc and IIIc were demonstrated by oxidation of these compounds with potassium permanganate, followed by carbon-14 assay of the ensuing benzophenone and benzoic acid fractions.[2,9]

Various reactions were next conducted on the ring-labeled compounds IIc, IIIc and IVc. The products arising from these reactions were analyzed for their distributions of radioactivity by degradation of each product to benzophenone and benzoic acid by procedures previously discussed.[2] Radiochemical assay of the benzophenone fraction from such degradations gave a measure of the rearrangement attending the reaction in question. The results studied were compared with corresponding data from the previous chain-labeled series, and the reactions were found to fall into two categories: (1) those in which a statistical distribution of radioactivity was found in the product, and (2) those in which a statistical distribution was not found. The data pertaining to each category are presented separately in Charts I and II.

The formolysis of tosylate IVa has been shown to proceed with elimination to yield triphenylethylene (Vab) in which a net 50% phenyl migration had taken place, suggesting that the formate of the chain-labeled carbinol IIa is unstable and undergoes elimination to the olefin Vab in formic acid containing *p*-toluenesulfonic acid[2]; confirmation of this is found in Chart I. Thus, when either acetate IIIa (reaction I-1) or acetate IIIc (reaction I-2) was dissolved in warm formic acid, the addition of *p*-toluenesulfonic acid caused the rapid formation of the olefin. Subsequent oxidation and radioactivity assay of the products indicated that in both cases the statistical radioactivity distribution had been obtained. Similarly, when a formic acid solution of the ring-labeled acetate IIIc (reaction I-3) was allowed to stand on a steam-bath, the olefin gradually precipitated during a period of 20 minutes. From the solution the formate VI could be isolated. The statistical radioactivity distribution was again observed in the degradation products thus indicating a complete equilibration at some stage during the formation of V and VI. When the ring-labeled carbinol IIc was heated in formic acid (reaction I-4) statistically equilibrated triphenylethylene again resulted. It was shown independently that the olefin samples in Chart I achieved statistical label redistribution *during* and not subsequent to their formation. Thus, although *p*-toluenesulfonic acid will, in time, effect complete equilibration of discretely labeled triphenylethylene[10] under the conditions of the reactions outlined in Chart I, this isomerization is relatively slow. Formic acid alone also has a negligible isomerizing

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(6) W. A. Bonner and C. J. Collins, THIS JOURNAL, **77**, 99 (1955).

(7) D. H. Derbyshire and W. A. Waters, *J. Chem. Soc.*, 575 (1950).

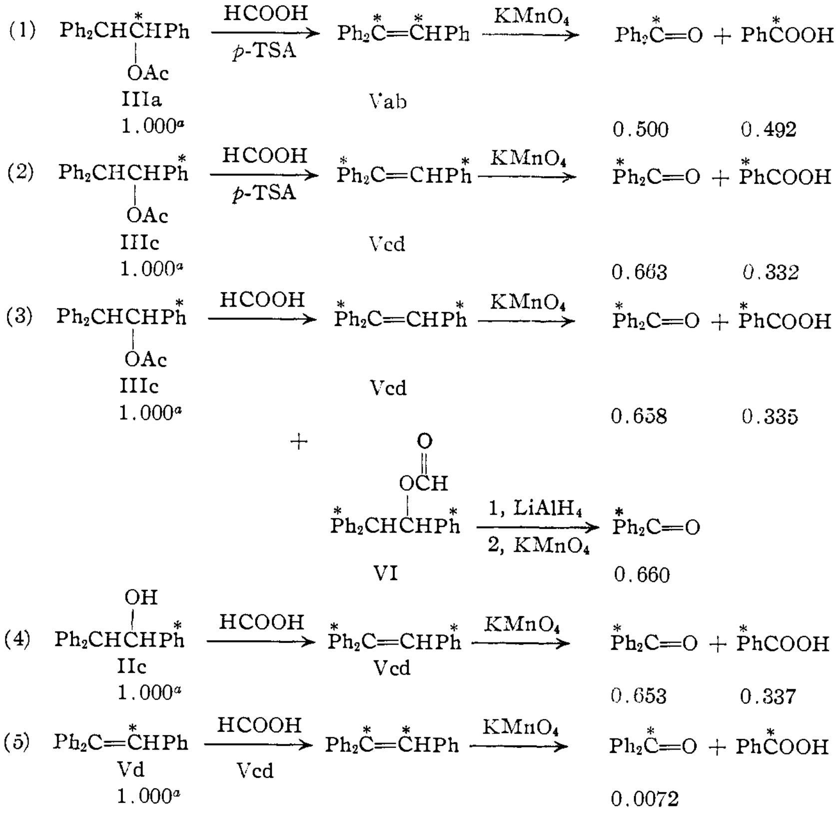
(8) R. J. Speer, N. L. Humphries and A. Roberts, THIS JOURNAL, **74**, 2443 (1952).

(9) C. J. Collins and W. A. Bonner, *ibid.*, **75**, 5379 (1953).

(10) S. F. Clark and C. J. Collins, unpublished work.

Chart I

Irreversible Reactions Proceeding with Statistical Redistribution of Radioactivity



$$\text{(1)}\quad \mathrm{Ph_2CH\underset{\underset{OAc}{|}}{\overset{*}{C}}HPh} \xrightarrow[p\text{-TSA}]{\text{HCOOH}} \mathrm{Ph_2\overset{*}{C}{=}\overset{*}{C}HPh} \xrightarrow{\text{KMnO}_4} \mathrm{Ph_2\overset{*}{C}{=}O + Ph\overset{*}{C}OOH}$$

IIIa, 1.000[a]; Vab; 0.500, 0.492

$$\text{(2)}\quad \mathrm{Ph_2CH\underset{\underset{OAc}{|}}{C}H\overset{*}{Ph}} \xrightarrow[p\text{-TSA}]{\text{HCOOH}} \mathrm{\overset{*}{Ph_2}C{=}CH\overset{*}{Ph}} \xrightarrow{\text{KMnO}_4} \mathrm{\overset{*}{Ph_2}C{=}O + \overset{*}{Ph}COOH}$$

IIIc, 1.000[a]; Vcd; 0.663, 0.332

$$\text{(3)}\quad \mathrm{Ph_2CH\underset{\underset{OAc}{|}}{C}H\overset{*}{Ph}} \xrightarrow{\text{HCOOH}} \mathrm{\overset{*}{Ph_2}C{=}CH\overset{*}{Ph}} \xrightarrow{\text{KMnO}_4} \mathrm{\overset{*}{Ph_2}C{=}O + \overset{*}{Ph}COOH}$$

IIIc, 1.000[a]; Vcd; 0.658, 0.335

$$+\ \mathrm{\overset{*}{Ph_2}CH\overset{\overset{\overset{O}{\|}}{OCH}}{\overset{|}{C}}H\overset{*}{Ph}} \xrightarrow[2,\ \text{KMnO}_4]{1,\ \text{LiAlH}_4} \mathrm{\overset{*}{Ph_2}C{=}O}$$

VI; 0.660

$$\text{(4)}\quad \mathrm{Ph_2CH\overset{\overset{OH}{|}}{C}H\overset{*}{Ph}} \xrightarrow{\text{HCOOH}} \mathrm{\overset{*}{Ph_2}C{=}CH\overset{*}{Ph}} \xrightarrow{\text{KMnO}_4} \mathrm{\overset{*}{Ph_2}C{=}O + \overset{*}{Ph}COOH}$$

IIc, 1.000[a]; Vcd; 0.653, 0.337

$$\text{(5)}\quad \mathrm{Ph_2C{=}\overset{*}{C}HPh} \xrightarrow{\text{HCOOH}} \mathrm{Ph_2\overset{*}{C}{=}\overset{*}{C}HPh} \xrightarrow{\text{KMnO}_4} \mathrm{Ph_2\overset{*}{C}{=}O + Ph\overset{*}{C}OOH}$$

Vd, 1.000[a]; Vcd; 0.0072

[a] Radioactivity assay of reactant expressed as unity, and degradation product assays reported as fractions thereof.

Chart II

Irreversible Reactions Proceeding without a Statistical Distribution of Radioactivity

$$\text{(1)}\quad \mathrm{Ph_2CHC^*H(OTs)Ph} \xrightarrow[\text{NaOAc}]{\text{HOAc}} \mathrm{Ph_2C^*HC^*H(OAc)Ph} \longrightarrow \mathrm{Ph_2C^*O + PhC^*OOH}$$

IVa, 1.000[a]; IIIab; 0.395[b] (0.593)[c]

$$\text{(2)}\quad \mathrm{Ph_2CHCH(OTs)Ph^*} \xrightarrow[\text{NaOAc}]{\text{HOAc}} \mathrm{Ph_2{}^*CHCH(OAc)Ph^*} \longrightarrow \mathrm{Ph_2{}^*CO + Ph^*COOH}$$

IVc, 1.000; IVcd; 0.471 (0.517)[c]

$$\text{(3)}\quad \mathrm{Ph_2CHC^*H(OTs)Ph} \xrightarrow[\text{Me}_2\text{CO}]{\text{H}_2\text{O}} \mathrm{Ph_2C^*HC^*H(OH)Ph} \longrightarrow \mathrm{Ph_2C^*O + PhC^*OOH}$$

IVa, 1.000; IIab; 0.222[d] (0.744)[c]

$$\text{(4)}\quad \mathrm{Ph_2CHCH(OTs)Ph^*} \xrightarrow[\text{Me}_2\text{CO}]{\text{H}_2\text{O}} \mathrm{Ph_2{}^*CHCH(OH)Ph^*} \longrightarrow \mathrm{Ph_2{}^*CO + Ph^*COOH}$$

IVc, 1.000; IIIcd; 0.236 (0.738)[c]

$$\text{(5)}\quad \mathrm{Ph_2CHC^*H(OH)Ph} \xrightarrow[\text{Xylene}]{p\text{-TSA}} \mathrm{Ph_2C^* = C^*HPh} \longrightarrow \mathrm{Ph_2C^*O + PhC^*OOH}$$

IIa, 1.000; 1 hour; Vab; 0.479 (0.524)[a]

$$\text{(6)}\quad \mathrm{Ph_2CHCH(OH)Ph^*} \xrightarrow[\text{Xylene}]{p\text{-TSA}} \mathrm{Ph_2{}^*C{=}CHPh^*} \longrightarrow \mathrm{Ph_2{}^*CO + Ph^*COOH}$$

IIc, 1.000; 1 hour; Vcd; 0.602 ...

[a] Radioactivity assay of reactant expressed as unity, and degradation product assays reported as fractions thereof. [b] Value obtained by careful reassay of derivative of previous paper (ref. 2), using the high precision technique reported in the Experimental section. [c] As previously reported (ref. 2) the benzoic acid assays are less reliable criteria of extent of migration than the benzophenone assays. Benzoic acid assays were performed as a rough check and are included parenthetically. [d] Value obtained in previous paper (ref. 2).

effect on the olefin, as indicated by reaction I-5 in which the olefin, warmed for 15 minutes in formic acid, was found to be rearranged to the extent of only 0.72%.

Irreversible reactions not proceeding with statistical redistribution of radioactivity are given in Chart II for both the chain-labeled and ring-labeled triphenylethyl systems. It has already been shown[2] that 1,2,2-triphenylethyl-1-C^{14} acetate is not rearranged under the acetolyzing conditions of reactions II-1 and II-2, so long as at least one molar equivalent of sodium acetate is present. 1,2,2-Triphenylethanol-1-C^{14} is likewise not rearranged after treatment with acetone–water and *p*-toluenesulfonic acid under the hydrolysis conditions of reactions II-3 and II-4. It was further found[10] that statistical radiochemical equilibration of 1,1,2-triphenylethylene-1-C^{14} with *p*-toluenesulfonic acid in xylene requires several days time[10] under experimental conditions similar to reactions II-5 and II-6. Thus the distributions of radioactivity found in the products of reactions 1–6 of Chart II are uncomplicated by subsequent equilibration of the products, once these products have been formed.

Discussion

It is obvious that, in the absence of internal return,[4] symmetrical phenonium ions[3] cannot be the sole cationic intermediates that intervene in reactions 1–4 of Chart I. Such a mechanism would require an equal distribution of radioactivity between the two phenyl-labeled products in each case, rather than the observed $^2/_3$–$^1/_3$ statistical distribution. These reactions could occur through bridged ions as the sole cationic intermediates, provided only that internal return[4] *via* ion-pair collapse[4b,5] proceeds at a rate much greater than that at which the bridged cations react irreversibly to produce their ultimate products. By inference then, it would be expected that the open or "classical" carbonium ion intermediates must be present in these reactions. The clearest evidence which demands the presence of these intermediates in reactions of the 1,1,2-triphenylethyl system may be developed through a study of the reactions of Chart II. Let us consider the implications of the possibility that the reactions of Chart II proceed through the classical open ions indicated in equations 5 and 6 and again use as examples the acetolyses of IVa and IVc. The values x and y are the concentrations of the rearranged cations of equations 5 and 6, respectively, a being the original concentration of IVa which, under the conditions employed, is identical with the original concentration of IVc. We make the additional assumption that the ratio of rearranged to unrearranged product is the same as the ratio of rearranged to unrearranged cationic intermediate. Since all other concentration functions cancel under the identical reaction conditions employed, we obtain as rate expressions for the appearance of the rearranged cations in the two cases

$$dx/dt = k(a - x) - kx, \text{ and} \tag{7}$$

$$dy/dt = k(a - y) - (k/2)y \tag{8}$$

where k is the specific rate constant as defined in equations 5 and 6. Integrating equations 7 and 8 and substituting equilibrium values of x and y into the integrated expressions[11] we find

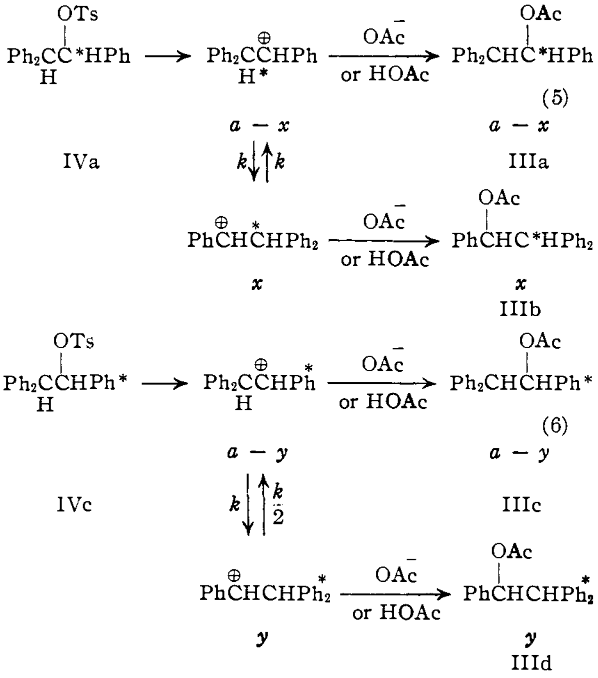
$$k = \frac{1}{2t} \ln \frac{x_e}{x_e - x} \text{ and} \tag{9}$$

$$k = \frac{2}{3t} \ln \frac{y_e}{y_e - y} \tag{10}$$

where x and y are the amounts of the isotopically rearranged cations (products) at time t, and x_e and y_e have the equilibrium values $0.500a$ and $0.667a$, respectively. Since under identical reaction conditions the time interval t must be the same for reactions of the chain- and ring-labeled analogs, we may equate relations 9 and 10. Converting concentration values to mole fractions (*i.e.*, $a = 1$), we may write

$$\frac{1}{2} \log \frac{0.500}{0.500 - x} = \frac{2}{3} \log \frac{0.667}{0.667 - y} \tag{11}$$

From equation 11 we see that if the preceding treatment is correct and generally applicable to all of the reactions of Chart II, then it should be possible knowing y, the amount of carbon-14 migration attending reaction in the ring-labeled series, to predict x, the carbon-14 migration attending the same reaction in the chain-labeled series. Such predictions are made in Table I, where the calculated carbon-14 migration values for the chain-labeled series are compared with the values actually observed.



NOTE ADDED IN PROOF.—Since the submission of this paper, 1,2,2-triphenylethanol-2-C^{14} has been prepared, and the isotope effect during its oxidation to benzophenone with permanganate has been determined. Although a small isotope effect was shown to exist, the yields obtained during the degradative reactions of chart II were sufficiently high that the errors owing to this effect are smaller than the experimental error inherent in the method of radioactivity assay.

TABLE I

COMPARISON OF OBSERVED DISTRIBUTION OF RADIOACTIVITY IN PRODUCTS FROM REACTIONS IN THE CHAIN-LABELED TRIPHENYLETHYL SYSTEM WITH DISTRIBUTION CALCULATED FROM DATA OBTAINED IN THE RING-LABELED TRIPHENYLETHYL SYSTEM

	Mole fraction of isomerized structure in reaction, product		
		Chain-labeled, x^a	
Reaction	Ring-labeled, y^a	Calcd. from eq.[11b]	Found
Tosylate hydrol. II-4	0.236 ± 0.0005	....	....
Tosylate hydrol. II-3	....	0.222 ± 0.001	0.222 ± 0.002
Tosylate acetol. II-2	.471 ± .003	....	....
Tosylate acetol. II-1	....	.403 ± .006	.395 ± .002
Carbinol dehydr. II-6	.602 ± .0005	....	....
Carbinol dehydr. II-5	....	.477 ± .001	.479 ± .002

[a] Taken as the radioactivity assay of the 2,4-dinitrophenylhydrazone of the benzophenone fraction obtained on oxidative degradation of the reaction product, divided by the molar radioactivity of starting material. [b] It is more accurate to predict chain-label reaction results from ring-label reaction observations than to do the reverse, since the value $(0.667 - y)$ is always larger than $(0.500 - x)$, and errors involving the benzophenone fraction assay are not magnified as greatly in the larger difference. The errors shown after each value represent average deviations from the mean value of two or more radioactivity assays. The experimental error is estimated to be ±0.5–0.8%.

The extremely close agreement between the calculated and observed values of x shown in Table I allows the following conclusions to be made concerning the nature of the intermediates in these reactions: (1) The intermediates cannot be *solely* bridged cations of either the symmetrical[3] or of the unsymmetrical[12] variety, nor can such bridged

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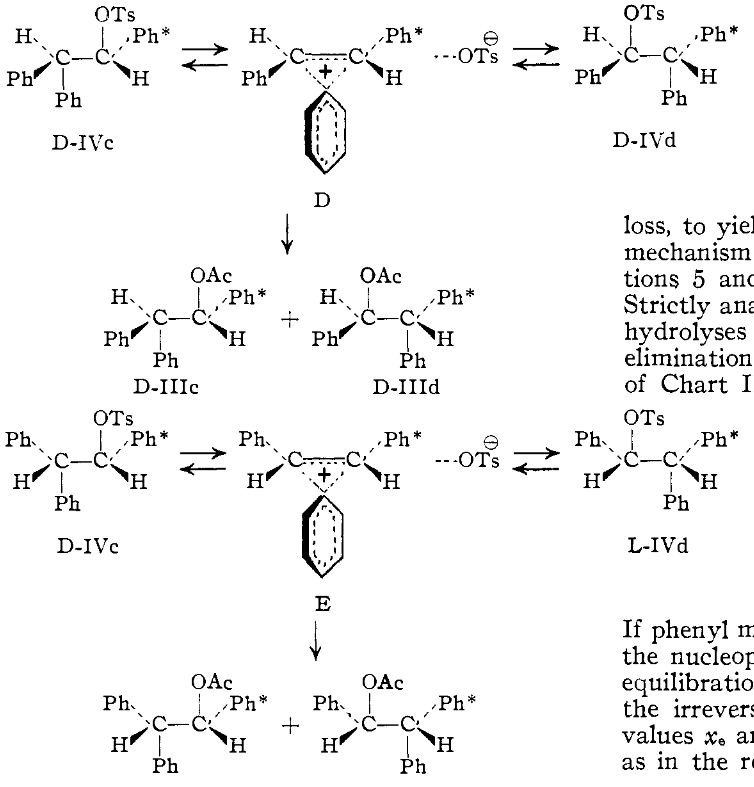
(11) K. J. Laidler, "Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 20.

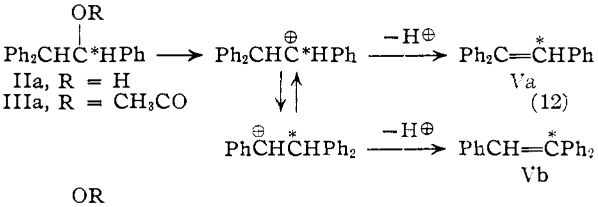
(12) (a) J. D. Roberts and C. M. Regan, THIS JOURNAL, **75**, 2069 (1953); (b) D. J. Cram and F. A. Abd Elhafez, *ibid.*, **75**, 3189 (1953).

cations be formed competitively with the open carbonium ions and then be disposed of directly by going to product as postulated previously,[2] since such bridged intermediates, whether or not they undergo internal return,[4] would lead to less than the observed amount of carbon-14 rearrangement in the phenyl-labeled series. This follows of necessity from a consideration of the stereospecific requirements of such cations in the 1,2,2-triphenylethyl system. Thus, the ring-labeled tosylate D-IVc, on acetolysis would be expected to go preferentially through the *trans*-phenonium ion D, rather than through the *cis*-phenonium ion E. The tosylate D-IVd formed through internal return would, therefore, solvolyze through the same *trans*-phenonium ion D if the solvolysis were completely stereospecific. Curtin[13] has demonstrated such stereospecificity in pinacol-type rearrangements, and Cram[14] has demonstrated stereospecificity to a high degree in the Wagner–Meerwein rearrangement of D-(+)-1,1-diphenyl-2-propanol. It can be seen that if ion D is formed to the exclusion of its *cis*-isomer E, then the labeled phenyl group can never migrate during acetolysis of IVc nor, for that matter, during any of the reactions shown in Chart II. The amount of radiochemically rearranged products in the phenyl-labeled series should, under these conditions, exactly equal the amount of rearranged product in the chain-labeled series. The same conclusions would be drawn in the hypothetical yet improbable event that the entire reaction proceeded *via* the *cis*-phenonium ion E.[15] The only conditions, therefore, under which equation 11 and, therefore, the experimental results of Table I, would be compatible with the existence of phenonium-ions as the sole intermediates, or as competitive intermediates which pass directly to product, are those in which (a) the *cis*- and *trans*-phenonium ions were always formed with equal frequency (that is, under conditions completely lacking in stereospecificity) and in which (b) the rate of internal return was very much greater than the rate of product formation. This is true because the rate of carbon-14 redistribution during solvolytic reactions of chain-labeled tosylate IVa should be unaffected by the presence or absence of stereospecificity.

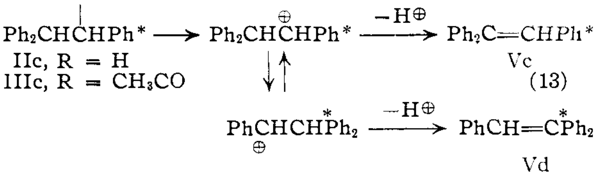
CHART III



(2) The simplest mechanism which fits quantitatively the data of Charts I and II and Table I appears to be one in which the open carbonium ion intermediates undergo radiochemical isomerization and then ultimately suffer either (a) nucleophilic attack by a foreign molecule or ion or (b) proton loss, to yield irreversibly the final product. This mechanism already has been symbolized in equations 5 and 6 for the acetolyses of IVa and IVc. Strictly analogous equations may be written for the hydrolyses of these same two tosylates. For the elimination reactions 1–4 of Chart I and 5 and 6 of Chart II, we may write equations 12 and 13. The extent of redistribution of the radioactive label during each reaction depends, in such schemes, upon the ratio of the rate of phenyl migration in the cationic intermediates to the rate of nucleophilic attack by the solvent (or in the elimination reactions, the rate of proton loss by the cation). If phenyl migration is sufficiently fast compared to the nucleophilic attack (or proton loss), then the equilibration of the cations will be complete before the irreversible step occurs, and the equilibrium values x_e and y_e (of equation 11) will be achieved as in the reactions of Chart I. If the attack by



$$\begin{array}{lll} \mathrm{Ph_2CH\overset{OR}{\overset{|}{C}}{}^*HPh} \longrightarrow & \mathrm{Ph_2CH\overset{\oplus}{C}{}^*HPh} & \xrightarrow{-\mathrm{H}^{\oplus}} \mathrm{Ph_2C{=}\overset{*}{C}HPh} \\ \text{IIa, R = H} & \quad\big\downarrow\!\uparrow & \qquad\qquad \text{Va} \\ \text{IIIa, R = CH}_3\text{CO} & & \qquad\qquad\qquad (12) \\ & \mathrm{Ph\overset{\oplus}{C}H\overset{*}{C}HPh_2} & \xrightarrow{-\mathrm{H}^{\oplus}} \mathrm{PhCH{=}\overset{*}{C}Ph_2} \\ & & \qquad\qquad \text{Vb} \end{array}$$



$$\begin{array}{lll} \mathrm{Ph_2CH\overset{OR}{\overset{|}{C}}HPh^*} \longrightarrow & \mathrm{Ph_2CH\overset{\oplus}{C}HPh^*} & \xrightarrow{-\mathrm{H}^{\oplus}} \mathrm{Ph_2C{=}CHPh^*} \\ \text{IIc, R = H} & \quad\big\downarrow\!\uparrow & \qquad\qquad \text{Vc} \\ \text{IIIc, R = CH}_3\text{CO} & & \qquad\qquad\qquad (13) \\ & \mathrm{Ph\overset{*}{C}H\underset{\oplus}{C}HPh_2} & \xrightarrow{-\mathrm{H}^{\oplus}} \mathrm{PhCH{=}\overset{*}{C}Ph_2} \\ & & \qquad\qquad \text{Vd} \end{array}$$

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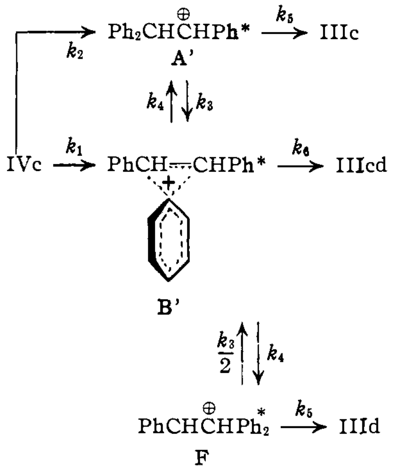
[13] P. I. Pollak and D. Y. Curtin, THIS JOURNAL, **72**, 961 (1950); D. Y. Curtin and P. I. Pollak, *ibid.*, **73**, 992 (1951); D. Y. Curtin, E. E. Harris and P. I. Pollak, *ibid.*, **73**, 3453 (1951); D. Y. Curtin and E. K. Meislich, *ibid.*, **74**, 5905 (1952); D. Y. Curtin and D. B. Kellom, *ibid.*, **75**, 6011 (1953).

[14] D. J. Cram and F. A. Abd Elhafez, *ibid.*, **76**, 30 (1954).

[15] Although the enantiomorphic structure D-IVc has been used to illustrate these facts, the conclusions apply equally as well to the solvolysis of racemic IVc.

solvent (or proton loss) is fast compared to phenyl migration, however, then the final products will contain less than the equilibrium concentrations x_e and y_e of rearranged structures, as in the reactions of Chart II.

(3) These data require the postulation of open, or "classical" carbonium ions as intermediates in the reactions studied. These data also rule out as intermediates bridged ions which are formed directly from reactant and then pass directly to product without entering into ionic equilibrium with the open cations.[2] The question still remains however, whether, during the reactions of Chart II, the data of Table I will permit the conclusion that bridged ions, if they are present in these reactions, could be formed directly from reactant in competition with the open ions, and then enter into equilibrium with open ions. This formulation is shown in equation 14 for the acetolysis of IVc.



(14)

It is clear from a study of equation 14 that the *direct* formation of the ion B′ from reactant even though this bridged ion B′ subsequently enters into an equilibrium with the open ions A′ and F, is manifestly incompatible with the data of Table I. The direct formation of B′ from reactant followed by its conversion to A′ and F implies that there exists an alternate path for the formation of F other than from A′, and that the ratio of F to A′ so formed is unity. Such an alternate path would destroy the relationship between x and y expressed in equation 11 and experimentally verified by the data of Table I.

(4) There is no evidence, from the present experiments, for the existence of bridged ions during any of the reactions studied, despite a mechanism involving such ions which the authors proposed tentatively in an earlier paper.[2] Even so, one might be tempted to explain the somewhat surprising ease of interconversion of the cations A′ and F by assuming the intervention of the bridged ion B′ between these two classical ions. Such a rationalization is clearly unnecessary if it is assumed that a high energy barrier does not exist between A′ and F. In the absence of any knowledge concerning the relative magnitude of such an energy barrier, it would be misleading to suggest the existence of bridged ionic intermediates in the reactions of 1,2,2-triphenylethanol and its derivatives.[16]

Acknowledgment.—The authors wish to acknowledge the assistance of Dr. J. D. Roberts through several stimulating discussions of the data of the present paper, as well as through his criticism of many of the authors' interpretations of that data. One of us (C. J. C.) acknowledges helpful discussions with Dr. J. F. Eastham.

Experimental

Radioactivity Determinations.—Although no particular effort was exerted to obtain highly precise data for Chart I, it was of major importance that the net phenyl migrations reported in Chart II be of the utmost accuracy, and that the radioactivity data suporting these migration values be obtained under conditions permitting highest precision. To this end, only the molar radioactivities of the 2,4-dinitrophenylhydrazone derivatives (of benzophenone fractions obtained on permanganate oxidation of the reaction products) were used for these calculations, since it had been shown previously that the benzoic acid fractions were diluted with benzoic acid arising as a result of secondary oxidation.[2] The weighing error for these 2,4-DNPH derivatives was made negligible by combusting samples as large as 50 mg., which had been carefully weighed on a microanalytical balance. The level of radioactivity for each sample combusted was carefully chosen in order that the ion-current produced would fall within the range in which the vibrating-reed electrometer gives highest accuracy. Whenever possible, radioactivity determinations were performed only on those days during which the vibrating-reed electrometer was most stable, as indicated by frequent reference to a standard ion-chamber, after the general procedure employed in this Laboratory, and previously described by Raaen and Ropp.[17]

Bromobenzene-C_1^{14}.—Benzene-C_1^{14} prepared by the method of Speer, *et al.*,[8] was converted to labeled bromobenzene by a modification of the procedure of Derbyshire and Waters.[7] Since in our preparation it was undesirable to have benzene-C^{14} present in a one-mole excess, several model runs were made in order to determine the optimum conditions for this bromination on an equimolar basis. The following procedure was found to give uniformly reproducible results: Distilled water (200 ml.), 65 ml. of concd. nitric acid and 22 ml. (0.222 mole) of benzene-C_1^{14} were placed in a one-liter 3-neck flask equipped with a reflux condenser, stirring motor and dropping funnel. The flask was surrounded with an ice-bath and after allowing sufficient time for cooling, 13 ml. (0.253 mole) of bromine was introduced into the flask. The apparatus was protected from light, and over a period of 5 hours a solution of 44 g. of silver nitrate in 200 ml. of distilled water was added dropwise while the mixture was vigorously stirred. An excess (130 g.) of solid Na_2SO_3 was then added and the contents of the flask were stirred an additional half-hour. The heterogeneous mixture was subjected to a continuous ether extraction for 16 hours while vigorous stirring was maintained. The ether layer was concentrated and steam distilled until crystals of dibromobenzene began to appear in the condenser. The yield of bromobenzene-C_1^{14} was 34 g. The combined steam distillates from three identical runs were dried over magnesium sulfate and distilled under vacuum yielding 84.3 g. of pure bromobenzene-C_1^{14} (63% yield of purified product). A portion of this (7.48 g.) was converted to 1,1,2-triphenylethylene-1-phenyl-C_1^{14} (Vd) as previously described.[9] Permanganate oxidation of this olefin[9] to benzophenone was followed by conversion of the benzophenone to the 2,4-dinitrophenylhydrazone.

Radioactivity assay: 1.264, 1.252 mc. of carbon-14 per mole. The bromobenzene was diluted with non-radioactive bromobenzene to a molar radioactivity of 0.9907 mc./mole prior to use in the reaction described below.

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[16] It has been pointed out quite properly by H. C. Brown and R. B. Kornblum, THIS JOURNAL, **76**, 4514 (1954), that the concept of non-classical or bridged ions should be used with caution, lacking definite experimental evidence that these ions actually exist in the particular system under study.

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

Phenyl-C^{14} Benzhydryl Ketone (I).—This ketone was prepared in the synthetic fashion previously described,[2] converting the above bromobenzene-C^{14} to diphenylcadmium and allowing the latter to react with diphenylacetyl chloride in dry benzene. From 39.2 g. (0.25 mole) of bromobenzene-C^{14} and 22.4 g. (0.097 mole) of diphenylacetyl chloride there resulted 21.3 g. (80%) of once recrystallized phenyl-C^{14} benzhydryl ketone, m.p. 136–137°.[18] The phenyl-C^{14} benzhydryl ketone had a radioactivity assay of 0.991 mc. per mole.[19] When an attempt was made to carry out the reaction under conditions in which the diphenylcadmium and diphenylacetyl chloride were in a mole ratio of 0.5 to 1.0 instead of *ca.* 1.3 to 1.0 (with the aim toward conserving radioactive bromobenzene) unsatisfactory results were obtained.

1-Phenyl-C^{14}-2,2-diphenylethanol (IIc).—The ring-labeled carbinol (radioactivity assay: 0.991 mc. per mole)[18] was prepared as before by reduction of the above ketone with ethereal lithium aluminum hydride. Yields, after recrystallization of the crude product from dilute acetic acid, averaged about 90% for this reaction.

The radiochemical structure of the carbinol IIc was confirmed at this point by oxidative degradation. One gram of the above carbinol was dissolved in acetone (40 ml.) and treated with potassium permanganate (2.30 g.) in water (20 ml.) containing acetic acid (0.1 ml.). The solution was permitted to stand at room temperature for four days, then processed as previously described[2] for the oxidation fragments, benzophenone and benzoic-phenyl-C^{14} acid.[20] The purified acid fragment had a radioactivity assay of 0.979 mc. per mole, while the benzophenone 2,4-dinitrophenylhydrazone gave an assay of 0.0206 mc. per mole. As pointed out previously,[2] the benzoic-phenyl-C^{14} acid assay is slightly low due to contamination with non-radioactive benzoic acid produced by concomitant benzophenone oxidation. The benzophenone shows a slight radioactivity due probably to occlusion of radioactive benzoic acid by the 2,4-dinitrophenylhydrazone.

1-Phenyl-C^{14}-2,2-diphenylethyl Acetate (IIIc).—The acetylation of the above carbinol was conducted readily using acetic anhydride and sodium acetate in the manner previously recorded.[2] Lithium aluminum hydride deacetylation followed by oxidation of the regenerated carbinol was used to show[2] that such acetylation is not attended by isomerization.

Action of *p*-Toluenesulfonic Acid on 1-Phenyl-C^{14}-2,2-diphenylethyl Acetate in Acetic Acid.—The acetate IIIc (0.991 mc./mole) (1.46 g., 4.62 mmoles) was dissolved in warm acetic acid (17 ml.) and the solution was treated with *p*-toluenesulfonic acid hydrate (0.88 g., 5.0 mmoles) and acetic anhydride (0.5 ml., 4.9 mmoles). The mixture was heated on the steam-bath for 1.25 hours, diluted slightly with water, and allowed to crystallize. The crude acetate (1.13 g., 78%) was recrystallized to give 0.94 g. of pure product, m.p. 153–154°. The latter was deacetylated as usual with ethereal lithium aluminum hydride, giving 0.88 g. of crude 1,2,2-triphenyl-C_1^{14}-ethanol. This was oxidized in the manner described above, and both oxidation fragments were assayed. The benzoic-*phenyl*-C^{14} acid had a radioactivity assay of 0.363 mc. per mole, while the benzophenone-*phenyl*-C_1^{14} 2,4-dinitrophenylhydrazone showed 0.631 mc. per mole, corresponding to 36.3 and 63.7%, respectively, of the total radioactivity. Here, as in the previously reported[2] isomerization of 1,2,2-triphenylethyl-1-C^{14} acetate, reaction proceeded essentially to a statistical distribution of the radioactivity.

Action of *p*-Toluenesulfonic Acid on Labeled Triphenylethylacetate (IIIa) and (IIIc) in Formic Acid.—Acetate IIIc (600 mg.) was dissolved in warm formic acid (10 ml.) and to the solution was added 400 mg. of *p*-toluenesulfonic acid monohydrate. Within three seconds, droplets of the olefin Vcd appeared. The mixture was warmed on a steam-bath for 7 minutes and then poured into water. The resulting mixture was extracted with hexane, and the dried hexane was passed through a column of alumina. The eluate was concentrated to dryness, yielding 381 mg. of an oil which on crystallization from 1.7 ml. of ethanol gave 218 mg. of olefin Vcd, m.p. 69–72°; no m.p. depression when mixed with authentic olefin V. The 218 mg. of Vcd was oxidized with $KMnO_4$ as previously described,[2] to yield benzophenone and benzoic acid fractions. The benzophenone 2,4-dinitrophenylhydrazone was assayed for carbon-14: 0.655 mc. per mole; assay of benzoic acid fraction: 0.3275 mc. per mole. These values correspond to 66.1% of the radioactivity in the benzophenone fraction and 33.1% in the benzoic acid fraction.

A similar experiment on 600 mg. of the chain-labeled acetate IIIa (2.703 mc. per mole) produced benzophenone 2,4-dinitrophenylhydrazone (1.350 mc. per mole) and benzoic acid (1.326 mc. per mole) corresponding to 50.0 and 49.2%, respectively, of the original molar radioactivity of acetate IIIa.

Action of Formic Acid on 1-Phenyl-C^{14}-2,2-Diphenylethyl Acetate.—The acetate IIIc (1.00 g.) was dissolved in hot 99.5% formic acid (10 ml.) and the solution was placed on the steam-bath. Within six minutes an oil appeared. After 30 minutes the mixture was cooled, poured into water, and the oil was extracted into ether. The extract was washed well with water, and sodium bicarbonate solution, then dried. Distillation of the solvent left 0.90 g. of sirup. This was crystallized from ligroin to produce 0.14 g. of 1,2,2-triphenyl-C_1^{14}-ethyl formate (VI), m.p. 110–114°. Recrystallization from an ethanol–ligroin mixture gave 0.10 g. of formate of m.p. 118–119°. The ligroin mother liquor was passed through an alumina column, rinsing with ligroin (75 ml.). Solvent evaporation produced 0.42 g. of oil. The latter was crystallized readily from ethanol (3 ml.) to produce 0.28 g. of 1,1,2-triphenyl-C_1^{14}-ethylene, m.p. 69.5–70°, mixed m.p. with an authentic sample 69–70°. Further elution of the alumina column with acetone resulted in 0.23 g. of oil which failed to crystallize when seeded with either the above formate or olefin.

The olefin was oxidized as usual, resulting in benzoic-phenyl-C^{14} acid showing a radioactivity assay of 0.332 mc. per mole and benzophenone-phenyl-C_1^{14} assaying 0.650 mc. per mole. These values correspond to 33.5 and 65.8% of the radioactivity, respectively, of the olefinic product.

The formate VI (0.10 g.) was deformylated, using lithium aluminum hydride in ether, producing 0.09 g. of crude 1,2,2 triphenyl-C_1^{14} -ethanol. The latter was oxidized to produce benzophenone-*phenyl*-C_1^{14} having a radioactivity assay of 0.654 mc. per mole, corresponding to 34.0 and 66.0%, respectively, of the radioactivity. The original acetate thus underwent reaction to yield olefin and ester products both of which contained a statistical distribution of radioactivity.

In a parallel reaction employing non-radioactive 1,2,2-triphenylethyl acetate as starting material, the 1,2,2-triphenylethyl formate showed a constant m.p. of 119.5–120° after three recrystallizations from ethanol.

Anal. Calcd. for $C_{21}H_{18}O_2$: C, 83.41; H, 6.01. Found: C, 83.46, 83.57; H, 5.99, 6.00.

Action of Formic Acid Alone on Ring-labeled 1,2,2-Triphenylethanol (IIc).—To 10 ml. of formic acid was added 600 mg. of the carbinol IIc. The solution was warmed on the steam-bath for one hour, then poured into water. The aqueous mixture was treated exactly as in the preceding section, yielding 217 mg. of recrystallized olefin Vcd, m.p. 70–72.5°, not depressed by authentic sample. The 2,4-dinitrophenylhydrazone of the benzophenone fraction obtained on oxidation of the 217 mg. of olefin Vcd contained 0.644 mc. per mole of carbon-14, while the benzoic acid fraction contained 0.333 mc. per mole. These values correspond to 65.0 and 33.6%, respectively, of the original radioactivity of IIc. Careful examination of the residues—including chromatography with alumina—failed to reveal the presence of any of the formate VI.

Action of Formic Acid on Chain-labeled Triphenylethylene (Va).—In order to see how much olefin equilibration takes place under the conditions of reaction I-3 and I-4, 500 mg. of 1,1,2-triphenylethylene-2-C^{14} (Va, 0.257 mc. per mole)[21] was suspended in 10 ml. of 99% formic acid, and the flask containing this mixture was put on a steam-bath for 15 minutes. The mixture was then poured into water. The aqueous suspension was extracted with ether, and the ether layer was washed with aqueous bicarbonate solution, then water. The olefin obtained on concentrating the ether

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[18] All melting points reported are uncorrected.

[19] The radioactivity assay reported for this compound and others in the ring-labeled series is taken as the over-all average of all of the assays of all of the products prepared in this series.

[20] All subsequent oxidations described below for compounds I, II and III have employed approximately the same ratios of reactants and were conducted similarly.

[21] The details of the preparation of olefin V labeled in the 2-position will be published in a forthcoming paper.

solution was dried under vacuum, and then oxidized in 35 ml. of acetone, 10 ml. of water and 0.1 ml. of acetic acid with 750 mg. of $KMnO_4$. After four days the mixture was worked up in the standard fashion. The benzophenone obtained was converted to its 2,4-DNPH (484 mg.) which was once crystallized from dioxane. The m.p. of the derivative was 237–238°. Radioactivity assay showed the 2,4-DNPH to contain 0.0104 mc. per mole of carbon-14. Since the olefin Va, before treatment with formic acid yielded, after oxidation and derivative preparation, a 2,4-DNPH of activity 0.00854 mc. per mole, it can be calculated that the olefin, on the above treatment, underwent only 0.72% isomerization.

1-Phenyl-C^{14}-2,2-diphenylethyl *p*-Toluenesulfonate (IVc).—Thoroughly desiccated 1-phenyl-1-C^{14}-2,2-diphenylethanol (5.00 g.) was converted to its tosylate as previously described,[2] by allowing the sodium salt of the alcohol to react with *p*-toluenesulfonyl chloride in anhydrous ether. The crude product weighed 1.93 g., had m.p. 79–80°, and was used without further purification. It has been shown previously[2] that no isomerization attends the tosylation reaction so conducted.

Acetolysis of 1-Phenyl-C^{14}-2,2-diphenylethyl *p*-Toluenesulfonate (IVc).—The tosylate IVc (1.00 g., 2.33 mmoles) was added to a hot mixture of acetic acid (10 ml.), acetic anhydride (0.1 ml.) and anhydrous sodium acetate (0.57 g., 6.98 mmoles, threefold excess). The mixture was heated for 45 minutes on a steam-bath, then diluted slightly with water and allowed to crystallize. The resulting 1,2,2-triphenyl-C$_1^{14}$-ethyl acetate (0.61 g., 82%, m.p. 155–156°) was deacetylated as before with lithium aluminum hydride producing 1,2,2-triphenyl-C$_1^{14}$-ethanol which, after recrystallization from dilute acetic acid, weighed 0.46 g. (87%) and had m.p. 87–88°. The latter was oxidatively degraded in the usual manner to produce benzoic-phenyl-C^{14} acid showing a m.p. of 122–123° and a radioactivity assay of 0.510 mc./mole after one recrystallization from water, and benzophenone - phenyl - C$_1^{14}$ 2,4 - dinitrophenylhydrazone showing m.p. 240.5–241.5° and an assay of 0.4665 ± 0.003 mc per mole after two recrystallizations from dioxane. These values correspond to a 47.1 and 52.9% distribution of radioactivity, respectively. It has been established previously[2] that no further rearrangement of the acetate product occurs when sodium acetate is present in the reaction mixture to buffer the *p*-toluenesulfonic acid produced during acetolysis.

Hydrolysis of 1-Phenyl-C^{14}-2,2-diphenylethyl *p*-Toluenesulfonate.—The ring-labeled tosylate IVc (0.93 g.) was dissolved in an acetone (25 ml.)-water (8 ml.) mixture, which was then refluxed for 2.5 hours. After allowing the mixture to stand overnight the acetone was evaporated in an air-steam, water was added and the product was extracted into ether. The ethereal solution was washed with water, dried and the solvent evaporated, yielding 0.60 g. (100%) of crude 1,2,2-triphenyl-C$_1^{14}$-ethanol. This was recrystallized from dilute acetic acid to give 0.58 g., m.p. 87–88°. The purified carbinol was oxidized with permanganate to give benzoic-*phenyl*-C^{14} acid, m.p. 121–122°, assay 0.728 mc. per mole after one recrystallization, and benzophenone-*phenyl*-C$_1^{14}$ 2,4-dinitrophenylhydrazone, m.p. 240.5–241.5°, assay 0.2330 and 0.2340 (average 0.2335 ± 0.0005) after two recrystallizations. These values correspond to a radioactivity distribution of 76.5 and 23.6%, respectively.

Action of *p*-Toluenesulfonic Acid on 1,2,2-Triphenylethanol-1-C^{14} (IIc) in Acetone–Water.—To see if the *p*-toluenesulfonic acid produced during hydrolysis of tosylate IVc might have any further isomerizing action on the carbinol formed, 1,2,2-triphenylethanol-1-C^{14} (0.60 g., radioactivity assay 1.000 mc. per mole) was dissolved for 2.5 hours in a refluxing mixture of acetone (25 ml.), water (8 ml.) and *p*-toluenesulfonic acid hydrate (0.42 g., 1 molar equivalent). The carbinol was re-isolated and its oxidation was conducted as described above. The benzophenone derivative from the oxidation showed a radioactivity assay of 0.0119 mc. per mole. Thus the isomerized carbinol produced on tosylate hydrolysis undergoes no further isomerization under the reaction conditions.

Dehydration of 1,2,2-Triphenylethanol (IIa) and (IIc) in Xylene with *p*-Toluenesulfonic Acid.—Ring-labeled 1,2,2-triphenylethanol (IIc) (700 mg.) was dissolved in 27 ml. of dry xylene containing 550 mg. of anhydrous *p*-toluenesulfonic acid. This mixture was boiled one hour, at which time excess water was added to the flask, and the separated xylene layer was diluted with ether, washed with bicarbonate solution and concentrated. Hexane was added to the concentrate, and the solution was passed through a column of alumina, and the eluate was evaporated yielding 312 mg. of olefin Vcd, m.p. 68–70°. No depression with authentic sample. The benzophenone 2,4-dinitrophenylhydrazone obtained upon oxidation of the 312 mg. of olefin Vcd, followed by preparation of the derivative was assayed for carbon-14 with the following results: 0.5975, 0.5965 mc. per mole, average 0.5970 ± 0.0005 mc. per mole, corresponding to 60.2% of the original radioactivity of IIc. The benzoic acid fraction was discarded.

A reaction similar in every respect was carried out on the chain-labeled 1,2,2-triphenylethanol-1-C^{14} (IIa). The benzophenone 2,4-dinitrophenylhydrazone resulting was assayed for carbon-14 with the following results: 0.4772, 0.4778, 0.4815, average 0.4788 ± 0.0017 mc. per mole, corresponding to 47.88% of the original radioactivity. The benzoic acid fraction, assayed as a rough check on the total radioactivity, contained 0.5370 mc. per mole (single determination).

OAK RIDGE, TENNESSEE

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

Molecular Rearrangements. IV. Triple-labeling Experiments on the Isotope Position Isomerization of 1,2,2-Triphenylethyl Acetate[1]

BY WILLIAM A. BONNER AND CLAIR J. COLLINS

RECEIVED APRIL 26, 1954

1,2,2-Triphenylethyl acetate, separately labeled in the chain, phenyl and acetate portions of the molecule, has been studied kinetically with respect to the rates of radiochemical isomerization and of acetoxyl exchange under the influence of an acid catalyst. Confirmatory experiments, using combinations of these three differently labeled species, have also been carried out. It is found that the rates of radiochemical equilibration of the ring-labeled and chain-labeled acetates are equal, and each is identical to the rate of loss of the labeled acetoxyl group. The data are explainable in terms of open carbonium ion intermediates in which the cation undergoes radiochemical isomerization prior to product formation. It is shown that, as expected, no internal return accompanies the isomerization.

Introduction

In the previous paper[2] a study was reported of a number of irreversible carbonium ion-type processes with doubly labeled 1,2,2-triphenylethyl derivatives. That is, a comparison was made of the distributions of the radioactive labels when derivatives of 1,2,2-triphenylethanol-1-C^{14} and of 1-phenyl-C^{14}-2,2-diphenylethanol undergo certain irreversible carbonium ion-type reactions. These reactions have included tosylate acetolysis, tosylate

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

[2] C. J. Collins and W. A. Bonner, THIS JOURNAL, **77**, 92 (1955).