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.

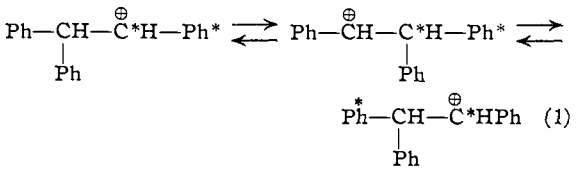
Introduction

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

(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).

hydrolysis, carbinol dehydration and elimination of acetic acid from the acetates. The observed radiochemical results could be explained completely and quantitatively in terms of open carbonium ions which undergo radiochemical isomerization to a varying degree depending on their lifetimes (eq. 1). There was no evidence for the existence of bridged ions[3-6] in any of the reactions studied. In



(1)

certain reactions, *e.g.*, formic acid catalyzed dehydrations of chain- and ring-labeled[2] 1,2,2-triphenylethanols, the intermediates seemed to be sufficiently long-lived to permit statistical redistribution of the radioactive labels prior to irreversible formation of the final olefinic products. In other reactions, for example, hydrolysis or acetolysis of chain- and ring-labeled 1,2,2-triphenylethyl *p*-toluenesulfonates, the shorter-lived intermediates were permitted only a partial equilibration before occurrence of the final irreversible step. In such reactions, the chain-labeled compound proceeded faster toward equilibrium than did the ring-labeled compound and the degree of rearrangement observed during reaction in the chain-labeled system could be calculated with considerable precision, knowing the extent of rearrangement occurring during reaction in the phenyl-labeled system. The calculations were based on a simple kinetic relationship involving equilibrating cationic intermediates.

Acetoxyl group removal from 1,2,2-triphenylethyl acetate appears to be a process in which the equilibration of labeled phenyl groups is complete, during the lifetime of the intermediates.[2] Thus when 1-phenyl-C^{14}-2,2-triphenylethyl acetate (II) is heated with formic acid with or without *p*-toluenesulfonic acid as catalyst, the triphenylethylene obtained is found[2] to have a statistical distribution of the radioactive label

$$\underset{2/3}{\overset{*}{Ph}}_2C{=}CH\overset{*}{Ph}\quad\underset{1/3}{}$$

In addition, both 1,2,2-triphenylethyl-1-C^{14} acetate (I) and 1-phenyl-C^{14}-2,2-triphenylethyl acetate (II), when warmed in acetic acid containing *p*-toluenesulfonic acid, give 1,2,2-triphenylethyl acetate samples having a statistical distribution of radioactivity.[2] The isomerization of this acetate labeled in various positions seemed to offer promise in the study of internal return in the present system for at least one set of conditions. By a comparison of the rates of radioactivity redistribution both of the chain-labeled and of the ring-labeled acetates with the rate of acetoxyl exchange with environment during this reaction, it was hoped that the presence or absence of internal return could be demonstrated, and that, in addition, further information might be obtained regarding the validity of the proposed mechanism.[2] To this end, the triply labeled system of 1,2,2-triphenylethyl acetates, $Ph_2CHC^*H(OAc)Ph$ (I, chain-labeled), $Ph_2CHCH(OAc)Ph^*$ (II, ring-labeled) and $Ph_2CHCH(OCOC^*H_3)Ph$ (III, acetyl-labeled), has been studied kinetically with regard to the comparative rates of label migration and of acetoxyl exchange. Methyl rather than carbonyl labeling in the acetoxyl group of III was selected in order to reduce any possible complications which might arise from an isotope effect during acetoxyl removal.

(3) D. J. Cram, THIS JOURNAL, **71**, 3863 (1949).
(4) J. D. Roberts and C. M. Regan, *ibid.*, **75**, 2069 (1953).
(5) (a) S. Winstein and D. Trifan, *ibid.*, **74**, 1154 (1952); (b) D. J. Cram and F. A. Abd Elhafez, *ibid.*, **75**, 3189 (1953).
(6) F. A. Abd Elhafez and D. J. Cram, *ibid.*, **75**, 339 (1953).

Methods and Results

The kinetic studies were conducted at 54.6 ± 0.4°, using the appropriate 1,2,2-triphenylethyl acetate, in acetic acid solution containing one equivalent of *p*-toluenesulfonic acid. Aliquots of the reaction mixture were then quenched in aqueous sodium chloride solutions after various time intervals. The acetate from each aliquot was recovered and, for those runs in which it was necessary to determine carbon-14 at this point, crystallized one or two times. The crude acetate obtained quantitatively on quenching the aliquots was quite pure; recrystallization prior to radioactivity assay was carried out chiefly to remove *p*-toluenesulfonic acid and sodium chloride which might possibly have been occluded during the quenching procedure. The extent of carbon-14 equilibration in the chain- and ring-labeled acetates was ascertained by deacetylating the recovered acetate, oxidizing the resulting carbinol and assaying the benzophenone oxidation product for radioactivity. The extent of acetoxyl exchange of the acetyl-labeled acetate with its non-radioactive environment was ascertained by assaying for total radioactivity the acetate recovered from each aliquot. Both isomerization reactions, as well as the acetoxyl exchange reaction, were found to obey first-order kinetic expressions with respect to acetates I, II or III under the reaction conditions employed. First-order rate constants at the time of each aliquot removal were calculated as described in the Experimental section. The results of these kinetic experiments are presented in Tables I–III.

Examination of Tables I–III indicates that the first-order rates of equilibration of the chain-labeled acetate and the ring-labeled acetate are equal within experimental error and each is essentially the same as the first-order rate of acetoxyl exchange for the acetyl-labeled acetate, although the data for acetoxyl exchange seem to be subject to a larger external error than do the data of Tables I or II. These results demonstrate that during the *p*-toluenesulfonic acid catalyzed isomerization of labeled 1,2,2-triphenylethyl acetates, *statistical equilibration of each label occurs each time an acetoxyl group is removed from the discretely labeled starting material.*

Although the possibility was considered extremely unlikely, there was a chance that a consistent external error was operative during the gathering of the data of Tables I and II which would make it seem that the rates of equilibration of the ring-labeled and chain-labeled acetates

TABLE I

FIRST-ORDER RATE CONSTANTS FOR THE EQUILIBRATION OF 1,2,2-TRIPHENYLETHYL-1-C^{14} ACETATE

	$k_I \times 10^2$, hours^{-1}
Run 1	2.22 ± 0.02
Run 2	2.22 ± .06
Average	2.22 ± .05

TABLE II

FIRST-ORDER RATE CONSTANTS FOR THE EQUILIBRATION OF 1-PHENYL-C^{14}-2,2-DIPHENYLETHYL ACETATE

	$k_{II} \times 10^2$, hours^{-1}
Run 1	2.22 ± 0.09
Run 2	2.08 ± .07
Average	2.15 ± .08

TABLE III

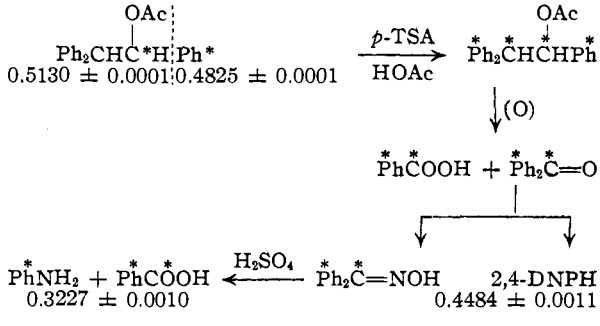
FIRST-ORDER RATE CONSTANTS FOR ACETOXYL EXCHANGE OF 1,2,2-TRIPHENYLETHYL ACETATE-2-C^{14}

	$k_{III} \times 10^2$, hours^{-1}
Run 1	1.97 ± 0.06
Run 2[a]	2.56 ± .03
Run 3[b]	2.39 ± .07
Average	2.31 ± .05

[a] Value obtained running the ring-labeled and acetyl-labeled 1,2,2-triphenylethyl acetates in the same reaction vessel. [b] One-half of the value obtained using two equivalents of *p*-toluenesulfonic acid.

were equal when in reality they should bear the 0.75 ratio which might be predicted on the basis of the previously derived kinetic reaction.[2] This possibility has now been definitely and completely excluded by the results of an experiment in which the two differently labeled acetate samples, I and II, were mixed homogeneously in solution and then subjected to the conditions of the acid-catalyzed isomerization in the same reaction vessel. The degradative procedure and the radiochemical results of this experiment are outlined in Chart I. Radioactivity data are shown for each molecule or for each portion thereof as millicuries per mole. The reaction conditions were identical to those employed in gathering the data of Tables I and II except that only one aliquot was removed—after 72 hours. From these data k_I is calculated to be 0.0203 ± 0.0012 hour^{-1}, while k_{II} is calculated as 0.0211 ± 0.008 hour^{-1}. The errors in the values of the two constants are calculated from the average errors of the radioactivity determinations shown in Chart I. Allowing for these average errors, the ratio k_{II}/k_I = 1.04 lies between the extreme limits 0.945 and 1.14, excluding the ratio 0.75 as a possibility.

CHART I

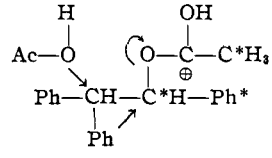


Discussion

The kinetic data of the preceding section allow the following conclusions to be drawn concerning the nature of the intermediates in the isomerization of the several labeled species of 1,2,2-triphenylethyl acetate: (1) Internal return[5] does not occur during the isomerization, since the rate of acetoxyl loss is the same as the rate of equilibration of the acetates I and II. If internal return should take place during these reactions, then the rate of acetoxyl loss, k_{III}, would be expected to be considerably slower than the two equilibration rates k_I and k_{II}. This conclusion might have been anticipated, since the leaving group is undoubtedly an acetic acid molecule. Thus an ion pair is not formed on ionization and ion-pair collapse is, of course, impossible. These same considerations do not apply to the solvolyses reported in the preceding paper,[2] during which it is possible that internal return does occur.

(2) Symmetrical[3] or unsymmetrical[4,5] bridged ions can be ruled out as the sole cationic intermediates since, in the absence of internal return, and whether or not they demonstrate stereospecificity,[7] their postulation would demand that k_I should be *greater than* k_{II}.[8] In the event that the *trans*-phenonium ion were formed to the complete exclusion[2] of the *cis*-phenonium ion, then the ring-labeled acetate II could never exhibit more than 50% rearrangement of the radioactive label.

(3) A completely concerted process in which one phenyl group migrates totally as it assists in the removal of an acetoxyl group



is excluded as an explanation for the present data since it would require that the rate of *isomerization* of both the ring-labeled and chain-labeled acetates be equal to the rate of acetoxyl exchange (k_{III}). Such a mechanism would then require that the rate of *equilibration* (k_I) of the chain-labeled acetate be twice the rate of acetoxyl exchange, and the rate of *equilibrium* (k_{II}) for the ring-labeled acetate be 3/2 the rate of acetoxyl exchange, again contrary to observation.

(4) The general mechanism proposed in the previous paper[2] in which the classical carbonium ion intermediates undergo more or less equilibration, depending upon their lifetimes, receives support. During the isomerizations of acetates I and II, it is obvious from the present kinetic data, that the ionic intermediates are sufficiently long-lived in

(7) 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); D. J. Cram and F. A. Abd Elhafez, *ibid.*, **76**, 30 (1954). See also discussion of stereospecificity in ref. 2.

(8) A symmetrical phenonium-ion mechanism in which a complete lack of stereospecificity is postulated would require that the rate of equilibration for the chain-labeled acetate be given by the relation $k_I = 2k = (1/t) \ln (x_e/x_e - x)$, and that for the ring-labeled acetate by the relation of $k_{II} = 3k/2 = (1/t) \ln y_e/(y_e - y)$ where k, x_e, x, y_e and y have the same significance as in the identical relations derived in the preceding (ref. 2) paper. Thus, $k_I : k_{II}$ should be in the ratio 4:3.

acetic acid solution, in the absence of acetate ion, to permit statistical redistribution of both the chain and ring labels before reaction of these intermediates with non-radioactive acetic acid. Thus, each mole of acetate product is fully equilibrated radiochemically for each mole of radioactive acetoxyl lost.

Experimental

1,2,2-Triphenylethyl-1-C^{14} Acetate.—A synthesis for this acetate was employed which differs slightly from that previously reported.[9] 1,2,2-Triphenylethanol-1-C^{14} (4.5 g.) was dissolved in pyridine (20 ml.) and the solution was treated with acetic anhydride (15 ml.). The mixture was allowed to stand for 24 hours, then diluted with water and the product was filtered, rinsed and dried. The crude product was dissolved in excess hot acetone, then the solution was concentrated and treated with an equal volume of hot ethanol. The pure acetate (5.14 g., 99%, m.p. 155–156°) crystallized as splendid needles. In other experiments giving comparable results, the original reaction mixture was allowed to stand for one hour, then heated on the steam-bath for one hour prior to dilution. Such procedures were employed in the synthesis of all three alternatively labeled acetates studies except, of course, that radioactive acetic anhydride was employed in the preparation of the acetyl-labeled acetate. The radiochemical structure of one of the acetates prepared by this method was confirmed by deacetylation and oxidative degradation of the resulting carbinol. Isolation and assay of the benzophenone fraction from the oxidation by the usual procedures indicated that only 0.66% of the total radioactivity was found in the supposedly non-radioactive fraction, a result in accord with our previous observations.

RADIOACTIVITY ASSAYS OF THE THREE ALTERNATIVELY LABELED ACETATE SPECIES

	Assay, mc./mole
1,2,2-Triphenylethyl-1-C^{14} acetate	2.161 ± 0.006
1-Phenyl-C^{14}-2,2-diphenylethyl acetate	0.991 ± .004
1,2,2-Triphenylethyl acetate-2-C^{14}	0.549 ± .003

Kinetic Investigations.—The kinetic experiments leading to the rate data in Table I–III were conducted as follows. The 1,2,2-triphenylethyl acetate under study (3.000 g.) was dissolved in hot glacial acetic acid (70.00 ml.) and the solution was allowed to reach the thermostat temperature of 54.6 ± 0.4°. At this point 6.00 ml. of catalyst solution was added, and the time was recorded. The catalyst solution consisted of 9.89 g. of desiccated *p*-toluenesulfonic acid dissolved in 32.4 ml. of glacial acetic acid containing 4.00 ml. of acetic anhydride. The reaction mixture was thus 0.1260 *M* in *p*-toluenesulfonic acid and 0.1250 *M* in starting acetate. At various time intervals 15.0-ml. aliquots were pipetted from the thermostated reaction mixture and drained into water. In those runs in which the recovered acetate was assayed for carbon-14, the precipitate was filtered and crystallized from an acetone–alcohol mixture. For acetoxyl-exchange data the acetate was assayed at this point, or after a second recrystallization. For phenyl equilibration data the acetate (including that recovered from the recrystallization mother liquors) was deacetylated with ethereal lithium aluminum hydride, and the crude carbinol obtained was oxidized in the usual fashion[2] with an acetone–water solution of potassium permanganate. The benzophenone oxidation fraction was isolated as usual and converted to its 2,4-dinitrophenylhydrazone, which was recrystallized once or twice from dioxane prior to radioactivity assay.

In one acetoxyl exchange run the volume of catalyst solution employed was doubled and the volume of acetic acid decreased accordingly, giving a solution 0.2714 *M* in *p*-toluenesulfonic acid and 0.1250 *M* in starting acetate. In several of the experiments the size of the run was scaled to exactly $^2/_3$ that indicated above.

Kinetic Calculations.—The rates of equilibration for the chain-labeled acetate were calculated by means of the integrated first-order expression

$$k_I = \frac{2.303}{t} \log \frac{x_e}{x_e - x}$$

where k_I is the specific rate for the conversion of 1,2,2-triphenyl-1-C^{14} acetate I into an equilibrium mixture of 1,2,2-triphenylethyl-1,2-C$_1^{14}$ acetate, x is the radioactivity assay of the benzophenone fraction isolated at time t, and x_e is the radioactivity assay of the benzophenone fraction at complete equilibrium (0.500 times the assay of the starting acetate).

The rates of equilibration for the ring-labeled acetate were calculated by means of the equation

$$k_{II} = \frac{2.303}{t} \log \frac{y_e}{y_e - y}$$

where k_{II} is the specific rate constant for the conversion of acetate II to its equilibrium mixture, y is the radioactivity assay of the benzophenone fraction at time t, and y_e is the assay of the benzophenone fraction at complete equilibrium (0.667 times the assay of the starting acetate).

The rates of acetoxyl exchange for the acetyl-labeled acetate were calculated by the first-order expression

$$k_{III} = \frac{2.303}{t} \log \frac{a}{a - x}$$

where a is the original radioactivity assay of the starting acetyl-labeled acetate, and x is the quantity of radioactive acetoxyl lost at time t. The radioactivity assay of the acetate recovered at time t thus defines the value of $a - x$.

Kinetic Data.—In Tables IV–VI are given the equilibration or exchange rates calculated for each time t from the corresponding radioactivity assays of the products isolated at each time t. The averages of these values appear in Tables I–III.

TABLE IV

EQUILIBRATION CONSTANTS FOR 1,2,2-TRIPHENYLETHYL-1-C^{14} ACETATE

Run	Assay of starting acetate, mc./mole	Time, hours	Ph_2C^*O assay (x), mc./mole	$k_I \times 10^2$, hours^{-1}
1	2.161	6	0.172	(2.900)
	(x_e 1.081)	22	.419	2.229
		30	.529	2.243
		46	.689	2.207
		70	.848	2.192
				2.218 ± 0.018
2	1.000	9	0.0996	(2.460)
	(x_e 0.500)	21	.191	2.296
		44	.314	2.250
		48	.317	2.130
		52	.347	2.280
		57.5	.365	2.272
		70	.398	2.268
		76	.402	2.130
		95	.435	2.164
				2.224 ± 0.062

Isomerization of $Ph_2CHC^*HPH^*$.—The doubly labeled acetate (2.4459 g. containing 0.5130 ± 0.001 mc./mole carbon-14 in the C-1 ethyl carbon and 0.4825 ± 0.0001 mc./mole in the C-1 phenyl group) was dissolved in 57 ml. of glacial acetic acid in a 200-ml. flask and, after having been placed in a thermostat at 54.6 ± 0.4° for one hour, 4.9 ml. of the catalyst solution (described previously in this section) was added, and the mixture was well shaken to ensure homogeneity. After 72 hours, a 32-ml. aliquot was removed, and poured into excess water containing sodium chloride to congeal the precipitate. The acetate was filtered, dried and added to an ethereal solution of lithium aluminum hydride, from which the carbinol was recovered. The crude carbinol was dissolved in 60 ml. of acetone, and to it was added 3.8 g. of $KMnO_4$ in 32 ml. of water containing 0.2 ml. of acetic acid. After four days, the oxidation mixture was worked up in the usual fashion. The benzo-

(9) W. A. Bonner and C. J. Collins, THIS JOURNAL, **75**, 5376 (1953).

TABLE V

EQUILIBRATION CONSTANTS FOR 1-PHENYL-C^{14}-2,2-DIPHENYLETHYL ACETATE

Run	Assay of starting acetate, mc./mole	Time, hours	1.009 × Ph_2*CO assay (y), mc./mole	$k_{II} \times 10^2$, hours^{-1}
1	0.991	6	0.107	(2.950)
	(y_0 0.661)	22	.270	2.385
		30	.318	2.190
		46	.419	2.186
		71.5	.510	2.100
				2.215 ± 0.092
2	0.991	9	0.119	2.208
	(y_0 0.661)	21	.241	2.162
		44	.399	2.102
		48	.414	2.120
		52	.435	2.062
		57.5	.457	2.045
		70	.501	2.028
		76	.518	2.018
		95	.560	1.978
				2.080 ± 0.070

phenone fraction was dissolved in 8 ml. of ethanol, treated with Norit and filtered through Celite, then 1.5 ml. of this solution was converted to the 2,4-dinitrophenylhydrazone (189 mg.) which was twice crystallized from dioxane and dried in an Abderhalden. The radioactivity assay was: 0.4495; 0.4473 average 0.4484 ± 0.0011 mc./mole. The remaining 6.5 ml. of ethanolic benzophenone was heated under reflux for 24 hours with 1 ml. of pyridine and 0.5 g. of hydroxylamine hydrochloride. The mixture was then poured into water and filtered, yielding 647 mg. of crude benzophenone oxime. This was not purified, since several model experiments had demonstrated that the crude oxime gave satisfactory yields in the Beckmann rearrangement. The oxime was dissolved in 12 ml. of concd. sulfuric acid and the solution was warmed on a steam-bath for one hour, after which time the cooled solution was poured over crushed ice. The resulting mixture was extracted three times with ether, the ether was clarified and concentrated, yielding 232 mg. of pure benzoic acid. This was twice crystallized from water, and identified by melting point and mixed melting point. The radioactivity assay was: 0.3238; 0.3217, average 0.3227 ± 0.0010 mc./mole of carbon-14. From these data it was calculated that $k_I = 2.03 \pm 0.12 \times 10^{-2}$ hours^{-1}, and $k_{II} = 2.11 \pm 0.08 \times 10^{-2}$ hours^{-1}, and that $k_{II}/k_I = 1.04 \pm 0.095$.

TABLE VI

ACETOXYL EXCHANGE CONSTANTS FOR 1,2,2-TRIPHENYLETHYL ACETATE-2-C^{14}

Run	Assay of starting acetate, mc./mole	Time, hours	Assay of recovered acetate ($a - x$) mc./mole	$k_{III} \times 10^2$, hours^{-1}
1	0.549	6.5	0.483	1.982
		23	.344	2.035
		30.75	.293	2.042
		47	.224	1.905
		54	.198	1.890
				1.971 ± 0.059
2	0.495	6	0.382	(4.318)
		22	.278	2.621
		30	.230	2.560
		46	.153	2.553
		71.5	.083	2.500
				2.558 ± 0.032
3	0.549	4.5	0.438	5.00
	(p-toluenesulfonic acid	23	.178	4.90
	concn. doubled)	27	.151	4.77
		30	.137	4.51
				4.79 ± 0.15
		(Divided by 2)		2.39 ± 0.07

Radioactivity Determinations.—These were carried out in the normal fashion as described in the previous paper.[2] For the determination of the isomerization of doubly labeled acetate (I and II) described in the preceding section, the highest precision was necessary. This was obtained by weighing large samples (20–50 mg.) of analytical material on a micro-balance, and using the technique described for previous double-labeling experiments.[2]

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The Reaction of 1-Alkynes with Organometallic Compounds. I. 1-Hexyne with Some Alkyl and Alkenylmagnesium Halides

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In the reactions of some Grignard reagents with 1-alkynes the rate of the evolution of gas was measured. The following relative rates were found: MeMgI, 6; MeMgBr, 6; MeMgCl, 16; n-PrMgBr, 59; EtMgI, 71; EtMgBr, 100; EtMgCl, 155; i-PrMgBr, 210; AllylMgBr, 435. A possible explanation of these relative rates is proposed.

In our laboratory we had many times the opportunity to prepare 1-hexynylmagnesium bromide in five mole quantities. The preparation consists of treating 1-hexyne (I) with a Grignard reagent such as methyl (II) or ethylmagnesium bromide (III) in boiling ether. The completeness of reaction was noted by the termination of evolved gas (methane or ethane). We have observed that the reaction with ethylmagnesium bromide was finished shortly after the completion of addition whereas with methylmagnesium bromide we needed more than 24 hours before we considered the reaction to be finished. It was the purpose of this investigation to establish the rate of reaction of some Grignard reagents with 1-alkynes.

$$C_4H_9C{\equiv}C{-}H + R{-}MgX \longrightarrow C_4H_9C{\equiv}C{-}MgX + R{-}H(gas)$$

R = CH_3 (II), C_2H_5 (III)

The literature contains two studies of the relative reactivities of Grignard reagents with compounds containing an "active" (acidic) hydrogen. Thus, the reactions with chloromagnesium phenyl-

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