(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]

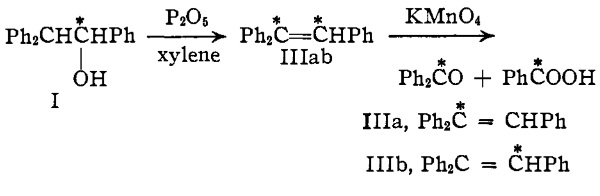
Molecular Rearrangements. II. The 1,1,2-Triphenylethyl System[1]

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



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.

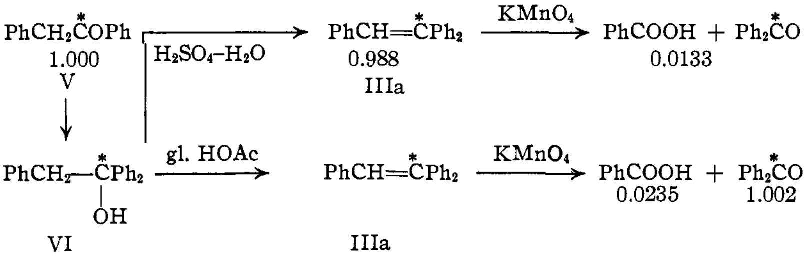


CHART I

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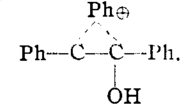
(1) This document is based upon work performed under Contract Number W-7405-eng-26 for the Atomic Energy Commission at the Oak Ridge National Laboratory.

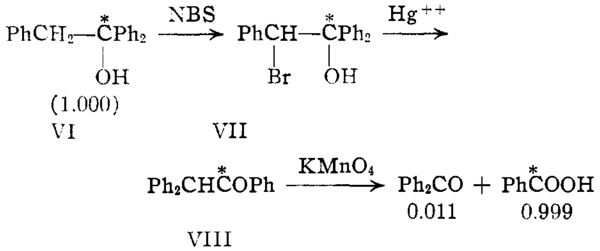
(2) W. A. Bonner and C. J. Collins, THIS JOURNAL, **75**, 5372 (1953).

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

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

As a corollary of the above structure proof, it was convenient to test the prediction of Lane and Walters[5] that the bromohydrin (VII) undergoes semipinacolic dehydrobromination *via* the intermediate 

Thus VII was prepared from VI through the action of N-bromosuccinimide, and converted to phenyl benzhydryl ketone-C^{14} (VIII) by the procedures reported by Lane and Walters[5] (Chart II).



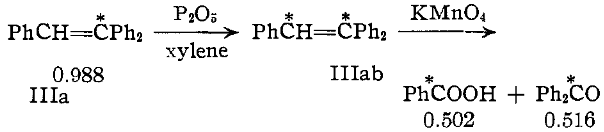
$$\underset{\substack{(1.000)\\ \mathrm{VI}}}{\mathrm{PhCH_2{-}}\underset{\mathrm{OH}}{\overset{*}{\mathrm{C}}}\mathrm{Ph_2}} \xrightarrow{\mathrm{NBS}} \underset{\mathrm{VII}}{\mathrm{Ph}\underset{\mathrm{Br}}{\mathrm{CH}}{-}\underset{\mathrm{OH}}{\overset{*}{\mathrm{C}}}\mathrm{Ph_2}} \xrightarrow{\mathrm{Hg^{++}}}$$

$$\underset{\mathrm{VIII}}{\mathrm{Ph_2CH\overset{*}{C}OPh}} \xrightarrow{\mathrm{KMnO_4}} \underset{0.011}{\mathrm{Ph_2CO}} + \underset{0.999}{\mathrm{Ph\overset{*}{C}OOH}}$$

CHART II

The radiochemical data, given as fractions as in Chart I, completely bear out, within the limits of experimental error, the Lane and Walters prediction that this rearrangement proceeds with exclusive phenyl migration. It was shown independently that only negligible rearrangement occurred during the permanganate oxidation shown in Chart II, by subjecting a sample of phenyl benzhydryl ketone-C^{14} (VIII), prepared as indicated in the previous paper,[2] to the same oxidative conditions.

It next became necessary to determine whether the 50:50 skeletal isomerization noticed[2] on dehydration of 1,2,2-triphenylethanol-1-C^{14} (I) could have occurred *after* the dehydration step. It has now been demonstrated that such isotope position isomerization can, in fact, occur. Thus 1,1,2-triphenylethylene-1-C^{14} (IIIa), was heated under reflux in dry xylene for 30 minutes with an approximately equal weight of phosphorus pentoxide. The regenerated triphenylethylene (IIIab) was oxidized with permanganate (Chart III) to yield benzophenone and benzoic acid of essentially equal molar radioactivities. Therefore, even though boiling aqueous sulfuric or glacial acetic acids fail to bring about this isomerization, phosphoric anhydride in boiling xylene causes complete interconversion. Thus, in the presence of the latter reagents, *all of the olefin, 1,1,2-triphenylethylene-1-*C^{14} *(IIIa) must have passed through a state of symmetry during its conversion to 1,1,2-triphenylethylene-1,2-*C_1^{14} *(IIIab).*



$$\underset{\substack{0.988\\ \mathrm{IIIa}}}{\mathrm{PhCH{=}\overset{*}{C}Ph_2}} \xrightarrow[\text{xylene}]{\mathrm{P_2O_5}} \underset{\mathrm{IIIab}}{\mathrm{Ph\overset{*}{C}H{=}\overset{*}{C}Ph_2}} \xrightarrow{\mathrm{KMnO_4}} \underset{0.502}{\mathrm{Ph\overset{*}{C}OOH}} + \underset{0.516}{\mathrm{Ph_2\overset{*}{C}O}}$$

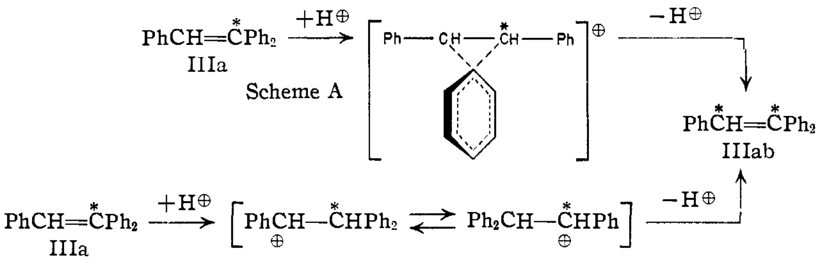
CHART III

While the radiochemical consequences of the solvolytic reactions reported in the previous paper[2] are probable best interpreted in terms of bridged cationic intermediates, at least two possibilities exist (Schemes A and B) for explaining the isomerization of olefin IIIa (Scheme B.)

It might be argued that the various cations indicated in Scheme B almost surely pass through a transition state represented by the single bridged cation of Scheme A, and that therefore there is no essential difference between these two mechanisms. The dissimilarity, of course, is to be found in the fact that the symmetrical phenonium ion of Scheme A is not considered[3] to represent a transition state, but rather a single, discrete intermediate.

It is not possible, on the basis of present tracer data, to distinguish between these two alternate possibilities. Experiments are now in progress, however, which should assist in gathering more information concerning the mechanism of this olefinic isomerization.

An additional observation is worthy of note. When the olefin IIIa was heated under reflux for 30 minutes in xylene containing much less than an equal weight of phosphoric anhydride, only 27% of IIIa was converted to IIIb. Since the phosphoric anhydride dehydration is a heterogeneous reaction and since in addition it is difficult to store, weigh, and transfer phosphoric anhydride under strictly anhydrous conditions, it has not been possible to gather quantitative data concerning this transformation. The isomerization of olefin IIIa with other dehydrating agents, however, is now being studied with the view of obtaining such quantitative data.



Scheme A

Scheme B

Experimental

1,1,2-Triphenylethanol-1-C^{14} (VI).—This carbinol was prepared by the method of Klages and Heilmann[6] by the addition of an ether solution of 7.00 g. of phenyl-(aceto-1-C^{14})-phenone[3] (2.398 mc. per mole) to the Grignard reagent prepared from 8 g. of bromobenzene and 2 g. of magnesium. On crystallization from ether–hexane, 6.40 g. (65%) of VI was obtained. After one recrystallization from hexane the m.p. was 88–89° (lit.[6] 88°). On desiccation over phosphorus pentoxide for several days, VI undergoes partial dehydration to the olefin (IIIa) with an attendant lowering in melting point. This fact was unknown at the time of preparation, so carbinol VI was not assayed for carbon-14.

1,1,2-Triphenylethylene-1-C^{14} (IIIa). 1. By the Method of Adkins and Zartman.[7]—The carbinol VI (758 mg.) was heated under reflux with 8 cc. of water and 2 cc. of sulfuric acid for 8 hours. It was found that by extending the reflux period from the 2 hours recommended by Adkins and Zartman, the vacuum distillation operation could be dispensed

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(5) J. F. Lane and D. R. Walters, THIS JOURNAL, **73**, 4234 (1951).

(6) A. Klages and S. Heilmann, *Ber.*, **37**, 1455 (1904).

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

with, and an olefin of higher purity could be obtained, since on concentration the product in the ethereal extract spontaneously crystallized; yield 594 mg. (84%). One crystallization from ethanol gave 504 mg. of VI whose m.p. was 67–69° (lit.[7] 68–89°), assay, 2.370 mc. carbon-14 per mole.

2. **By the Method of Lane and Walters.**[5]—The carbinol (VI) could also be dehydrated by simple crystallization from glacial acetic acid.[5] One sample prepared in this way melted at 71–72°.

Rearrangement of 2-Bromo-1,1,2-triphenylethanol-1-C^{14} (VII).—The bromohydrin (VII), prepared from VI by the method of Lane and Walters, was converted to phenyl benzhydryl ketone-C^{14} (VIII) as reported by these same authors, by allowing 714 mg. of VII and 326 mg. of mercuric nitrate in 85 cc. of 70% aqueous dioxane to stand at room temperature for six days. The yield of once-crystallized ketone was 273 mg.; m.p. 136–137.5° (lit.[5] 137–139°).

Isomerization of IIIa with Phosphorus Pentoxide. Experiment No. 1.—The olefin (IIIa, 500 mg.) was allowed to react with approximately 0.5 g. of phosphorus pentoxide in boiling xylene for 30 minutes. The mixture was cooled and 100 cc. of water was added, followed by 100 cc. of hexane. The layers were separated, and the hexane layer was washed with water until the washings were neutral to litmus paper. The concentrated, dried olefin (IIIab) was not further purified, but was immediately subjected to a permanganate oxidation as indicated in Table I. **Experiment No. 2.**—The olefin (IIIa, 743 mg.) was heated under reflux for 30 minutes with 0.3–0.4 g. of phosphorus pentoxide in 17 cc. of xylene. The mixture was cooled, and treated as in experiment No. 1 above. From the concentrated hexane mixture there was isolated 362 mg. of IIIab; m.p. 67–69°. This was subjected to permanganate oxidation as indicated in Table I.

Permanganate Oxidations of Various 1,1,2-Triphenylethyl Derivatives.—In a typical oxidation experiment, 500 mg. of olefin (III) and 800 mg. of potassium permanganate were allowed to react at room temperature in 25 cc. of acetone and 10 cc. of water containing 1 cc. of glacial acetic acid. The reaction was complete within an hour. The excess of permanganate was decomposed with bisulfite, and the mixture was filtered. The concentrated filtrate was made alkaline and continuously extracted with ether. The concentrated ether extract was dissolved in 5 cc. of alcohol and to it was added a solution of 400 mg. of 2,4-dinitrophenylhydrazine in 2 cc. of H_2SO_4 and 1 cc. of water. The solution was warmed on the steam-bath. The 2,4-dinitrophenylhydrazone (217 mg., 31%) crystallized almost immediately. After one crystallization from dioxane it melted at 238–239°. The aqueous layer from the ether extraction was acidified and re-extracted with ether, yielding 108 mg. (45%) of benzoic acid. After one crystallization from water the benzoic acid had a m.p. of 121–122°.

The oxidations of the ketone (VIII) were parallel to the above described experiment with the exception that (a) appropriately more permanganate was employed and (b) the oxidations required four days for completion. The data for all of these oxidative degradations are summarized in Table I.[8]

TABLE I[8]

SUMMARY OF DATA FOR PERMANGANATE OXIDATIONS OF IIIa, IIIab AND VIII

Compound oxidized	Radioactivity assay of fraction isolated, mc. per mole	
	Benzophenone 2,4-DNPH	Benzoic acid
IIIa[a]	. . .	0.0322
IIIa[b]	2.432	0.0564
IIIab[c]	1.238, 1.238	1.203
IIIab[d]	. . .	0.645, 0.628
VIII[e]	0.026	2.392
VIII[f]	0.022	2.485[g]

[a] Prepared by the method of Adkins and Zartman (ref. 7). [b] Prepared by the method of Lane and Walters (ref. 5). [c] From the phosphorus pentoxide isomerization of IIIa, experiment No. 1. [d] From the phosphorus pentoxide isomerization of IIIa, experiment No. 2. [e] From rearrangement of the bromohydrin VII. [f] From direct synthesis (ref. 2). [g] This molar radioactivity is not consistent with the molar radioactivities of the other compounds described in this paper because of the different origin (ref. 2) of the sample of VIII oxidized.

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(8) It is apparent from Table I that the benzoic acid fractions isolated upon permanganate oxidation of the olefin IIIa contain approximately 1–2% of the total molar radioactivity of the original olefin. Since this same order of radioactivity is also present in the benzophenone fractions obtained upon permanganate oxidation of compound VIII and its derivatives, we have concluded that an approximate 1% phenyl migration must occur during the oxidation reaction. The benzoic acid fraction isolated upon permanganate oxidation of phenyl benzhydryl ketone-C^{14} (VIII, last reaction in Table I) has a molar radioactivity lower by several per cent. than the base level of radioactivity (2.688 mc. per mole; see ref. 2). This has been shown (ref. 2) to be in all probability the consequence of dilution with non-radioactive benzoic acid arising by slight oxidation of the non-radioactive benzophenone fraction. This explanation seems inapplicable, however, to the low level of radioactivity found in the benzoic acid fraction arising on oxidation of IIIa, since these olefin oxidations appear essentially complete within less than an hour, hardly enough time (ref. 2) to allow appreciable oxidation of benzophenone to benzoic acid.

OAK RIDGE, TENN.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF G. D. SEARLE AND COMPANY]

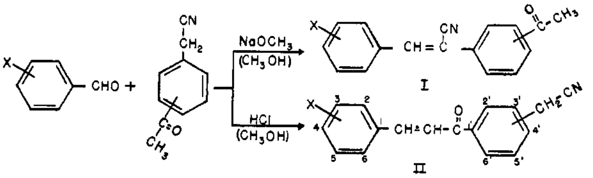
Condensations of Substituted Benzaldehydes with *m*- or *p*-Acetylphenylacetonitrile[1]

BY KURT RORIG

RECEIVED JUNE 5, 1953

Sodium methoxide in methanol catalyzes the reaction of various benzaldehydes with *m*- or *p*-acetylphenylacetonitrile to give substituted α-acetylphenylcinnamonitriles (I). Methanolic hydrogen chloride, however, catalyzes the formation of substituted 4′-cyanomethylchalcones (II) from *p*-acetylphenylacetonitrile and substituted benzaldehydes.

In the presence of alkaline catalysts aromatic aldehydes react with phenylacetonitrile to give α-phenylcinnamonitriles, whereas they react with acetophenone to give chalcones. Thus it was of interest to determine which of these two types of compound, I or II (or both), would be formed from substituted benzaldehydes and *m*- or *p*-acetylphenylacetonitrile in alkaline media.



The use of sodium methoxide catalyst in methanol yielded as the principal products the substituted α-acetylphenylcinnamonitriles (I). The

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(1) Presented before the Division of Organic Chemistry at the 123rd Meeting of the American Chemical Society, Los Angeles, California, March, 1953.