[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STANFORD UNIVERSITY]

The Dehydroxylation of 1,2,2-Triphenylethanol-1-C^{14} and the Cleavage of 2,3,3-Triphenyl-1-propanol-2-C^{14} with Raney Nickel[1]

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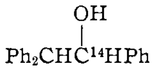
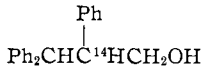
1,2,2-Triphenylethanol-1-C^{14} (I) and 2,3,3-triphenyl-1-propanol-2-C^{14} (II) have each been converted into 1,1,2-triphenylethane-C^{14} by the action of excess Raney nickel in boiling ethanol. The labeled 1,1,2-triphenylethane products have been oxidized to benzoic acid and benzophenone fragments. These in turn have been assayed for radioactivity to determine if and to what extent phenyl redistribution attends such catalytic hydrogenolysis reactions in molecules of these types. In neither the dehydroxylation of I nor in the C1-C2 cleavage of II was any detectable phenyl redistribution noted. Several mechanistic implications of these observations are pointed out.

Recently both Raney nickel-catalyzed dehydroxylation reactions[2-4] and Raney nickel-catalyzed carbon–carbon bond cleavage reactions[5] have been objects of our study, primarily from a stereochemical viewpoint. While we have considered several mechanistic rationalizations of these processes, no experimental criterion has yet appeared compelling an unambiguous choice between them. In the hope of gaining further insight into the mode of Raney nickel action we have now undertaken a study of the effect of Raney nickel in refluxing ethanol on 1,2,2-triphenylethanol-1-C^{14} (I) and 2,3,3-triphenyl-1-propanol-2-C^{14} (II).



$$Ph_2CH\overset{OH}{\overset{|}{C^{14}}}HPh$$

I



$$Ph_2CH\overset{Ph}{\overset{|}{C^{14}}}HCH_2OH$$

II

In accord with the previously observed behavior of benzyl type alcohols[2-4] under these conditions, I has been found smoothly convertible into 1,1,2-triphenylethane by simple dehydroxylation with Raney nickel. Similarly, in keeping with the behavior of 2-aryl primary alcohols, II has been found[5] to undergo C1–C2 bond fission producing 1,1,2-triphenylethane under similar conditions. Our present interest in the dehydroxylation of I and the cleavage of II has been to determine how much, if any, phenyl migration attends such hydrogenolysis processes and if possible to deduce therefrom further mechanistic information.

It has previously been abundantly demonstrated[6] by radiochemical techniques that homogeneous solvolytic reactions in the 1,2,2-triphenylethyl system proceed by way of classical, open 1,2,2-triphenylethyl carbonium ions which tend toward a statistical redistribution of their phenyl nuclei during their transitory lifetimes

$$Ph_2CH\overset{\oplus}{C}{}^{14}HPh \rightleftarrows Ph\overset{\oplus}{C}HC^{14}HPh_2 \qquad (1)$$

It seemed to us of considerable interest to determine if the 1,2,2-triphenylethyl intermediate, whatever its nature, in the heterogeneous catalytic conversion of I and II into 1,1,2-triphenylethane might also be capable of phenyl redistribution during its lifetime on or near the catalyst surface, since the gross structural characteristics, at least, of such an intermediate should permit such nuclear redistribution.

1,2,2-Triphenylethanol-1-C^{14} (I) having a specific radioactivity of 1.984 mc./mole, synthesized by reaction sequences previously described,[6] was converted by the action of Raney nickel in boiling ethanol into a sample of labeled 1,1,2-triphenylethane-C^{14} assaying 1.997 mc./mole. Infrared spectral examination of the crude dehydroxylation product suggested that considerable nuclear reduction had also attended the dehydroxylation process. The purified hydrocarbon product was examined for phenyl redistribution by oxidation into benzoic acid and benzophenone fragments in the manner previously employed.[6] The specific radioactivity of the benzoic acid product (1.930 mc./mole) and of the benzophenone 2,4-dinitrophenylhydrazone product (0.0235 mc./mole) indicated that, at the very most, 1% net phenyl migration accompanied the dehydroxylation of 1,2,2-triphenylethanol under such catalytic conditions.

2,3,3-Triphenyl-1-propanol-2-C^{14} (II) was synthesized starting with *carboxy*-labeled benzoic acid by the sequence of reactions shown in Chart I. The location of the label in II uniquely at C2 is shown by the degradation scheme in Chart I, wherein the methyl 2,3,3-triphenylpropanoate-2-C^{14} precursor of II was, after hydrolysis, oxidized to a benzophenone sample containing only 1% of the base level specific radioactivity. Finally, the data pertaining to the Raney nickel-catalyzed cleavage of II to 1,1,2-triphenylethane-C^{14} are given in Chart I, where it is clearly seen that no detectable phenyl migration accompanies the C1-C2 hydrogenolysis of II with Raney nickel.

The failure to detect a significant phenyl redistribution in the hydrogenolyses of I and II to 1,1,2-triphenylethane-2-C^{14} suggests three alternatives with regard to the mechanism of such heterogeneous catalytic processes: either (1) the mechanism does not involve classical 1,2,2-triphenylethyl carbonium ions of the type known to undergo nuclear redistribution in homogeneous systems, (2) such classical carbonium ions, if involved, are prevented by their adsorption on or proximity to the catalyst surface from exercising the mobility of their phenyl nuclei or (3) such classical ions, if formed, react so rapidly with surface adsorbed hydrogen that phenyl migration

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[1] This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

[2] W. A. Bonner, J. A. Zderic and G. A. Casaletto, THIS JOURNAL, **74**, 5086 (1952).

[3] W. A. Bonner, *ibid.*, **76**, 6350 (1954).

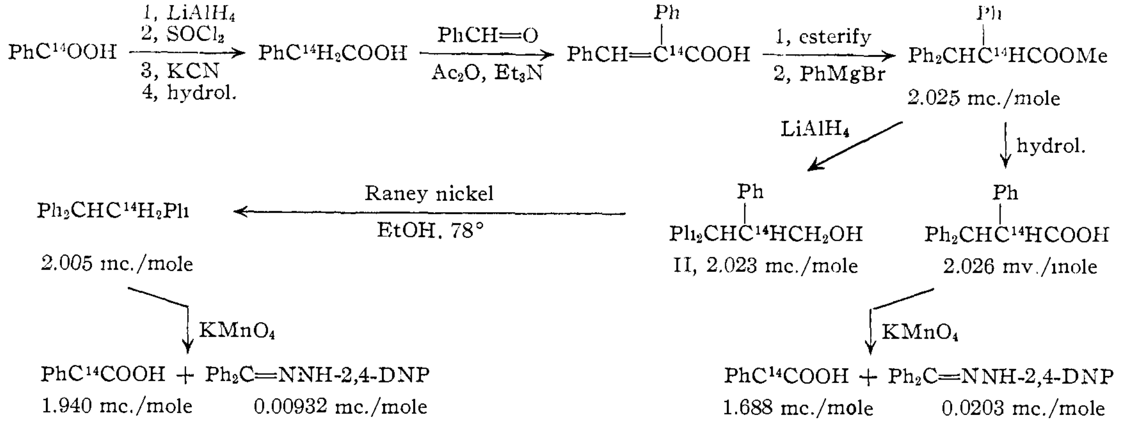
[4] W. A. Bonner and J. A. Zderic, *ibid.*, **78**, 3218 (1956).

[5] J. A. Zderic, W. A. Bonner and T. W. Greenlee, *ibid.*, **79**, 1696 (1957).

[6] W. A. Bonner and C. J. Collins, *ibid.*, **78**, 5587 (1956); **77**, 92, 99 (1955); **75**, 5372, 5379 (1953).

CHART I

SYNTHESIS, RADIOCHEMICAL STRUCTURE PROOF AND RANEY NICKEL-CATALYZED CLEAVAGE OF 2,3,3-TRIPHENYL-1-PROPANOL-2-C^{14} (II)



fails to occur detectibly during the short lifetime of the carbonium intermediate. Unfortunately the data do not permit a distinction between these alternatives, nor do they allow conclusions regarding other possible mechanisms, such as free radical processes.

Experimental

1,2,2,-Triphenylethanol-1-C^{14} (I) was prepared by the lithium aluminum hydride reduction of phenyl benzhydryl ketone-*carbonyl*-C^{14} in the manner previously described.[6,7] The crude product was recrystallized from acetic acid, air-dried and finally dried to constant weight *in vacuo* over phosphoric anhydride. The purified sample had m.p. 83–84° and a radioactivity assay of 1.984 mc./mole.

Action of Raney Nickel on 1,2,2-Triphenylethanol-1-C^{14}.—The above carbinol (6.00 g.) was dissolved in absolute ethanol (200 ml.) and the solution was treated with Raney nickel slurry[8] (*ca.* 140 g.). The mixture was heated under reflux with occasional swirling during 5 hours, whereupon it was filtered (sintered glass funnel) and the catalyst cake was rinsed three times by slurrying with hot ethanol and refiltering. The filtrate and washings were evaporated to dryness yielding 5.40 g. (95.6%) of clear sirup. The infrared spectrum of this sirup in chloroform solution showed no hydroxyl absorption and was identical with that of authentic 1,1,2-triphenylethane, except that the $-CH_2-$ absorption band at 2853 cm.$^{-1}$ for the crude product was much more intense, suggesting that considerable phenyl nucleus reduction had occurred. The product crystallized completely on chilling to 0° for several days. It was recrystallized from ethanol (40 ml.) producing 1.30 g. of solid, m.p. 48–49°. Solvent evaporation from the mother liquors, followed by solution of the residue in 2-propanol (14 ml.), seeding and chilling, yielded a second crop weighing 1.31 g., m.p. 45–57°. The combined crops were recrystallized twice from 2-propanol (10 ml.) to produce 1.38 g. of 1,1,2-triphenylethane-2-C^{14} having m.p. 55–55.5° and a radioactivity assay of 1.997 mc./mole.

Oxidation of 1,2,2-Triphenylethane-2-C^{14} from 1,2,2-Triphenylethanol-1-C^{14}.—The above labeled 1,1,2-triphenylethane (0.34 g.) was dissolved in acetone (13 ml.) and the solution was treated with a mixture of potassium permanganate (0.88 g.) dissolved in water (6 ml.) containing acetic acid (0.03 ml.). After standing at room temperature for 138 hours the oxidation mixture was processed as previously described[6] for its benzoic acid and benzophenone products. The benzoic acid fraction was purified by recrystallization from water and vacuum sublimation prior to radioactivity assay, m.p. 120–121°, 1.930 mc./mole. The crude benzophenone product (0.25 g.) was converted to its 2,4-dinitrophenylhydrazone in the usual manner[6] and the latter was recrystallized twice from dioxane prior to radioactivity assay, m.p. 238° (Fisher block), 0.0235 mc./mole.

Phenylacetic-2-C^{14} Acid.—Approximately 0.7 mc. of *carboxy*-labeled benzoic acid in 23.3 g. of benzoic acid was converted to benzyl-α-C^{14} alcohol by reduction in ether solution with lithium aluminum hydride. The crude labeled benzyl alcohol was added dropwise to refluxing thionyl chloride (35 ml.). Refluxing was maintained for an additional hour, whereupon most of the excess thionyl chloride was stripped off *in vacuo* at 100° through a Vigreux column. The dark residue was distilled and the fraction boiling from 120–125° (160 mm.) was collected. The residue was "scavanged" by distilling 11 g. of stock benzyl chloride from it *in vacuo*. The total crude, diluted benzyl-α-C^{14} chloride weighed 25.9 g. (67%) and showed $n^{22}D$ 1.5370. This material was dissolved in ethanol (33 ml.) and the solution was added slowly to a solution of sodium cyanide (13 g.) in hot water (11.7 ml.). The mixture was stirred under reflux for 4 hours, cooled, diluted with water and extracted four times with ether. The ether was evaporated from the extract and the residue was shaken[9] with an equal volume of 50% sulfuric acid at 60° for 5 minutes. The mixture was diluted with water, cooled and extracted four times with ether. The extract was washed with 10% sodium hydroxide solution, dried over anhydrous sodium sulfate, filtered and stripped of solvent. The crude benzyl-α-C^{14} cyanide (24.9 g. (104%)) was distilled and the fraction boiling at 124–128° (30 mm.) was collected. The residue was "scavanged" by distilling 5.1 g. of non-radioactive benzyl cyanide from it. The total distillate weighed 25.5 g. (85%). This was treated with 20% potassium hydroxide solution (150 ml.) and the mixture was stirred magnetically under reflux for 4 hours, after which it had become homogeneous and the liberation of ammonia was no longer evident. The alkaline solution was cooled and extracted twice with ether. Evaporation of the ether extract led to 2.9 g. of benzyl alcohol. The alkaline layer was made strongly acidic with sulfuric acid, cooled and extracted three times with ether. The extract was washed with water, dried over anhydrous sodium sulfate, filtered and stripped of solvent, last traces *in vacuo*. The crude phenylacetic-2-C^{14} acid product weighed 25.4 g. (99%), had m.p. 70–71° and gave a radioactivity assay of 2.99 mc./mole. It was used in the condensation below without further purification.

α-Phenylcinnamic-α-C^{14} Acid.—The above phenylacetic-2-C^{14} acid (24.1 g.) was diluted with unlabeled phenylacetic acid (12.9 g.). The acids were treated with alkali-washed benzaldehyde (27.5 ml.), anhydrous triethylamine (27 ml.) and acetic anhydride (54 ml.). The mixture was heated under reflux for 5.5 hours, then processed for product according to the procedure of Buckles and Bremer.[10] The crude acid product weighed 42.5 g. (70%), had m.p. 161–162° and was esterified below without further purification.

Methyl α-Phenylcinnamate-α-C^{14}.—The above crude acid (42.5 g.) was dissolved in methanol (250 ml.) containing sulfuric acid (20 ml.). The mixture was refluxed for a 2-hour period, then cooled and poured into water (800 ml.) with

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(7) We are indebted to Dr. Clair J. Collins of Oak Ridge National Laboratory for furnishing us with a sample of this ketone.

(8) R. Mozingo, *Org. Syntheses*, **21**, 15 (1941).

(9) R. Adams and A. F. Thal, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., p. 107.

(10) R. E. Buckles and K. Bremer, *Org. Syntheses*, **33**, 70 (1953).

stirring. The slurry was neutralized by the addition of sufficient concentrated sodium hydroxide solution, then chilled overnight. The crude solid was filtered, air-dried and recrystallized from a mixture of ethanol (175 ml.) and water (25 ml.). There resulted 33.3 g. (74%) of methyl α-phenylcinnamate-α-C^{14} having m.p. 75–76°. The m.p. reported for this product[11] is 77–78°.

Methyl 2,3,3-Triphenylpropanoate-2-C^{14}.—Phenylmagnesium bromide (20% excess) was prepared in anhydrous ether (150 ml.) from bromobenzene (17.6 ml.) and magnesium (4.08 g.). The above methyl α-phenylcinnamate-α-C^{14} (33.2 g.) was dissolved in anhydrous ether (200 ml.), and the resulting solution was added with stirring to the Grignard reagent over a period of 15 minutes. The mixture was stirred under reflux for 30 minutes, then treated gradually with sufficient water to destroy the Grignard adduct, then slowly with sufficient 50% hydrochloric acid to dissolve the precipitated magnesium salts. The crude product, a gray solid, had precipitated at this point. It was filtered and rinsed with ether, 35.6 g., m.p. 163–164°. The ether filtrate was washed with water, dried over anhydrous sodium sulfate and concentrated to a volume of 50 ml., whereupon an additional 1.0 g. of product, m.p. 159–160°, crystallized. The total yield was 36.6 g. (83%). The crude product was dissolved in boiling acetone (300 ml.) and the solution was filtered (Celite) from residual magnesium salts. On cooling the filtrate deposited 6.7 g. of pure methyl 2,3,3-triphenylpropanoate-2-C^{14}, m.p. 163.5–164°. The filtrate was boiled down to a volume of *ca.* 120 ml., when crystallization started. Water (10 ml.) was added and the mixture was chilled, producing a main crop of product weighing 19.0 g., m.p. 163–164°. The initial 6.7-g. crop was recrystallized from acetone (30 ml.), giving 5.8 g. of product having m.p. 163.5–164° and a radioactivity assay of 2.025 mc./mole. Kohler and Heritage[12] give m.p. 159° for methyl 2,3,3-triphenylpropanoate, prepared in the same manner.

In earlier pilot experiments a 100% excess of phenylmagnesium bromide was employed. In these experiments the crude ester product was contaminated with considerable quantities of phenyl 1,2,2-triphenylethyl ketone. This neutral product could be readily isolated by alkaline hydrolysis of either the crude ester or the residues left after its recrystallization. The crude ketone so obtained had m.p. 178–179°. Recrystallization from acetone led to pure phenyl 1,2,2-triphenylethyl ketone having m.p. 180.5–181°.

Anal. Calcd. for $C_{27}H_{22}O$: C, 89.12; H, 6.29. Found: C, 89.14, 89.22; H, 6.23, 6.28.

Not previously observed[12] by action of phenylmagnesium bromide on methyl α-phenylcinnamate, this ketone, m.p. 182°, has been reported[13] to result by action by phenylmagnesium bromide on phenyl α-phenylcinnamate.

2,3,3-Triphenylpropanoic-2-C^{14} Acid.—The above methyl ester (3.00 g.) was treated with ethanol (50 ml.) and a solution of potassium hydroxide (15 g.) in water (35 ml.). After stirring under reflux for 2 hours the ethanol was stripped off *in vacuo*, 100 ml. of 5% aqueous potassium hydroxide was added, and stirring under reflux was continued for 5 hours. The hot solution was poured into excess dilute sulfuric acid, chilled and filtered. The crude acid weighed 2.85 g. (99%) and had m.p. 205–210°. This was recrystallized from benzene (75 ml.) to produce 2.61 g. of product having m.p. 216.5–217°. A second recrystallization from benzene gave pure 2,3,3-triphenylpropanoic-2-C^{14} acid having m.p. 220.5° (Fisher block) and showing a radioactivity assay of 2.022, 2.030 mc./mole. Kohler and Heritage[12] report m.p. 211° for this acid.

2,3,3-Triphenyl-1-propanol-2-C^{14} (II).—The above methyl 2,3,3-triphenylpropanoate-2-C^{14} (6.00 g.) was dissolved in warm benzene (50 ml.) and the resulting solution was added slowly with stirring to a suspension of excess lithium aluminum hydride in anhydrous ether (150 ml.). After an additional 45 minutes of stirring water was cautiously added and the product was isolated as usual, 5.67 g. (103%) of white solid. This was recrystallized from a mixture of ethanol (30 ml.) and water (10 ml.), producing 5.50 g. of white needles. A second recrystallization yielded pure 2,3,3-triphenyl-1-propanol-2-C^{14} having m.p. 108–108.5° and radioactivity assays of 2.010, 2.036 mc./mole.

Anal. Calcd. for $C_{21}H_{20}O$: C, 87.46; H, 6.99. Found: C, 87.10, 87.05; H, 7.33, 7.42.

Oxidation of 2,3,3-Triphenylpropanoic-2-C^{14} Acid.—In order to provide a radiochemical structure proof demonstrating the location of the label at C2 in the series under study, and to show that no significant rearrangement attended any of the syntheses involved, the permanganate oxidation of the above 2,3,3-triphenylpropanoic-2-C^{14} acid to benzophenone and benzoic acid was undertaken.

The above acid (1.00 g.) was dissolved in warm 5% potassium hydroxide solution (50 ml.) and the mixture was treated with a solution of potassium permanganate (2.8 g.) in water (25 ml.), then heated on the steam-bath for a period of 5 days. Customary processing of the reaction mixture led to 0.30 g. of benzophenone and 0.52 g. of a crude acid fraction.

The benzophenone was converted in the usual fashion to its 2,4-dinitrophenylhydrazone which, purified by two recrystallizations from dioxane, had m.p. 237.5–238° (Fisher block). Its radioactivity assay, 0.0203 mc./mole, was about 1% of the base level for the series of compounds in question, indicating no significant quantity of label at the C3 position.

On recrystallization from water (10 ml.) the acid oxidation product was found to contain considerable unreacted starting acid, which was filtered from the hot solution, 0.10 g., m.p. 195–200°. The chilled filtrate afforded 0.10 g. of benzoic acid, m.p. 122°, which was further purified by vacuum sublimation. Its low radioactivity assay, 1.688 mc./mole, was presumably, due to its dilution with non-radioactive benzoic acid formed by concomitant oxidation of the benzophenone product, a feature of such oxidations which has been previously studied and discussed.[6]

Action of Raney Nickel on 2,3,3-Triphenyl-1-propanol-2-C^{14}.—Four grams of the above 2,3,3-triphenyl-1-propanol-2-C^{14} was treated with Raney nickel slurry (*ca.* 100 g.) in absolute ethanol (150 ml.). The mixture was heated under reflux for 8.5 hours, then processed for product as described in the Raney nickel reaction above. The crude product was 3.53 g. (97.5% calculated as 1,1,2-triphenylethane) of clear sirup whose infrared spectrum in chloroform showed no hydroxyl band and appeared essentially identical with the spectrum of the crude product obtained in the Raney nickel dehydroxylation above. The sample was dissolved in 2-propanol, seeded and chilled, affording 0.40 g. of solid m.p. 50–51°. This was recrystallized from 2-propanol (2 ml.) yielding 0.28 g. of pure 1,1,2-triphenylethane, m.p. 55°. Its radioactivity assay, 2.005 mc./mole, agreed within 1% with the base level assay of this series of compounds, indicating that no label was born at the hydroxymethylene carbon (Cl) which was cleaved off during the reaction. From the mother liquors of the above recrystallizations an additional 0.31 g. of product was obtained.

Oxidation of 1,1,2-Triphenylethane-2-C^{14} from 2,3,3-Triphenyl-1-propanol-2-C^{14}.—The product from the above Raney nickel reaction was oxidized to benzophenone and benzoic acid in a manner identical to that described in the third Experimental paragraph above. The recrystallized and sublimed benzoic acid product, m.p. 121.5°, had a radioactivity assay of 1.940 mc./mole. The twice recrystallized benzophenone 2,4-dinitrophenylhydrazone, m.p. 235°, had an assay of 0.00932 mc./mole, indicating that no phenyl rearrangement had attended the above cleavage of 2,3,3-triphenyl-1-propanol-2-C^{14} to 1,1,2-triphenylethane-2-C^{14}.

Radioactivity assays were accomplished by wet combustion of the above labeled samples to carbon dioxide,[14] followed by counting[15] the latter in an ionization chamber with the aid of a Cary model 31 vibrating reed electrometer.

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(11) A. G. Cabella, *Gazz. chim. ital.*, **14**, 114 (1884).

(12) E. P. Kohler and Gertrude Heritage, *Am. Chem. J.*, **33**, 156 (1905).

(13) E. P. Kohler and Gertrude Heritage, *ibid.*, **34**, 571 (1906).

(14) O. K. Neville, THIS JOURNAL, **70**, 3501 (1948).

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