ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY]

On the Distribution of Oxygen-18 in Triphenylmethyl Benzoate from the Reaction of Triphenylmethyl and Benzoyl Peroxide *carbonyl*-^{18}O

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RECEIVED JANUARY 15, 1960

Triphenylmethyl radical reacts with carbonyl-labeled benzoyl peroxide to give triphenylmethyl benzoate in which most of the oxygen-18 remains in the carbonyl group. Accepting the Hammond mechanism for this induced decomposition, one concludes that the initiating attack of triphenylmethyl radical on benzoyl peroxide occurs exclusively at the peroxidic oxygen atom. Predominant attack at the peroxidic oxygen occurs in the formation of α-ethoxyethyl benzoate and cyclohexenyl benzoate in the reactions of benzoyl peroxide with diethyl ether and cyclohexene, respectively. It is significant that this mode of attack involves fewer large changes in bond angles and distances and in π-electronic interactions than the alternate mode of attack at carbonyl oxygen.

In the reaction of triphenylmethyl with benzoyl peroxide in benzene solution,[1,2] the major product is triphenylmethyl benzoate, while the minor products are benzoic acid and tetraphenylmethane, reportedly in equal amount. This paper is concerned with determining which of the two oxygen atoms in benzoyl peroxide is attacked by the triphenylmethyl radical in the formation of trityl benzoate. The question whether the new carbon–oxygen bond in the ester be formed from the *carbonyl*-oxygen or the *ether*-oxygen of the benzoyl peroxide, or both, is relevant to the mechanism of the reaction. With the availability of *carbonyl*-labeled benzoyl peroxide and a method for the analysis of its ^{18}O-content,[3] an answer to this question can be sought.

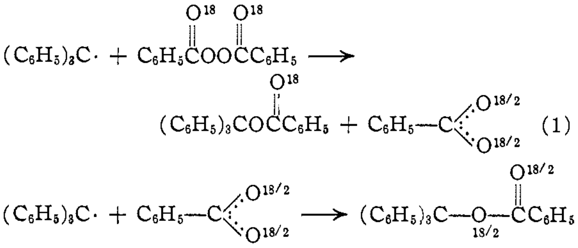
Feasibility of the study depended on the isotopic stability of ^{18}O-labeled triphenylmethyl benzoate, by itself and during analysis. It was anticipated that this solvolytically reactive ester[4] might ionize reversibly so rapidly with loss of isotopic distinction between *carbonyl*-oxygen and *ether*-oxygen that attainment of the goal would be defeated.[5]

Labeled triphenylmethyl benzoate-*carbonyl*-^{18}O was prepared from labeled benzoyl chloride (1.33% ^{18}O)[6] and potassium triphenylmethylate, while triphenylmethyl benzoate-*ether*-^{18}O was obtained from benzoyl chloride and potassium triphenylmethylate-^{18}O (0.85% ^{18}O). Reduction by lithium aluminum hydride in ether at -5 to $-15°$ cleaved the ester to triphenylcarbinol, the ^{18}O-content of which was determined by the method of Doering and Dorfmann.[7]

The *carbonyl*-labeled ester (1.33% ^{18}O) gave triphenylcarbinol, containing 0.03% ^{18}O corresponding to a mixing of 2%. The *ether*-labeled ester (0.85% ^{18}O) gave carbinol of 0.76% ^{18}O corresponding to 11% mixing. Although no effort was made to determine at what point in the transformations mixing had occurred, in a reduction at the boiling point of ether 27% of theoretical mixing resulted. Reasonably, the mixing occurred by reversible ionization in ether solution. In this connection, it is noteworthy that a sample of triphenylmethyl benzoate-*carbonyl*-^{18}O (1.03% ^{18}O) heated (195–210°) above its melting point for two hours had equilibrated completely within the error of analysis.

The reaction of triphenylmethyl radical and benzoyl-^{18}O peroxide (1.30$_5$ atom per cent. excess ^{18}O in each carbonyl group) was carried out following closely the procedure of Hammond, Ravve and Modic.[8] At the prevailing concentrations, the product consisted of 16% of the theoretical amount of benzoic acid and 83% of the theoretical triphenylmethyl benzoate, no attempt having been made to determine the amount of tetraphenylmethane in the product. The triphenylcarbinol obtained by reduction of the ester contained 0.22$_3$% ^{18}O. When corrected for the 3–11% mixing observed in the control experiments, the ^{18}O content in the *ether*-oxygen of the triphenylmethyl benzoate is estimated to be 0.21$_6$–0.19$_8$%, whence, by difference, the *carbonyl*-oxygen contains 1.09–1.11% ^{18}O.

The two steps in Hammond's mechanism by which trityl benzoate is produced are the induced decomposition (1) and the radical combination (2).



$$(C_6H_5)_3C\cdot + C_6H_5\overset{\overset{O^{18}}{\|}}{C}OO\overset{\overset{O^{18}}{\|}}{C}C_6H_5 \longrightarrow (C_6H_5)_3CO\overset{\overset{O^{18}}{\|}}{C}C_6H_5 + C_6H_5{-}C{\overset{\cdot\cdot O^{18/2}}{\underset{\cdot\cdot O^{18/2}}{}}} \tag{1}$$

$$(C_6H_5)_3C\cdot + C_6H_5{-}C{\overset{\cdot\cdot O^{18/2}}{\underset{\cdot\cdot O^{18/2}}{}}} \longrightarrow (C_6H_5)_3C{-}\underset{18/2}{O}{-}\overset{\overset{O^{18/2}}{\|}}{C}C_6H_5 \tag{2}$$

The remaining, more speculative steps are concerned with the formation of benzoic acid and tetraphenylmethane—an interesting problem, but not the concern of the present work.

If reaction 1 is the only path by which benzoyl peroxide is decomposed, 50 parts of the trityl benzoate will be formed by this reaction and 33 parts (the total yield of ester is 83% of theory, the other

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[1] H. Wieland, T. Ploetz and K. Indest, *Ann.*, **532**, 179 (1937).

[2] G. S. Hammond, J. T. Rudesill and F. J. Modic, THIS JOURNAL, **73**, 3929 (1951).

[3] W. von E. Doering and M. Greenbaum, in preparation; *cf.* M. A. Greenbaum, Ph.D. Dissertation, Yale University, 1956, p. 86.

[4] G. S. Hammond and J. T. Rudesill, THIS JOURNAL, **72**, 2769 (1950).

[5] Examination of the possible occurrence of such an ionization in appropriate solvents was stopped on learning of a similar study in progress in the laboratory of Professor C. G. Swain.

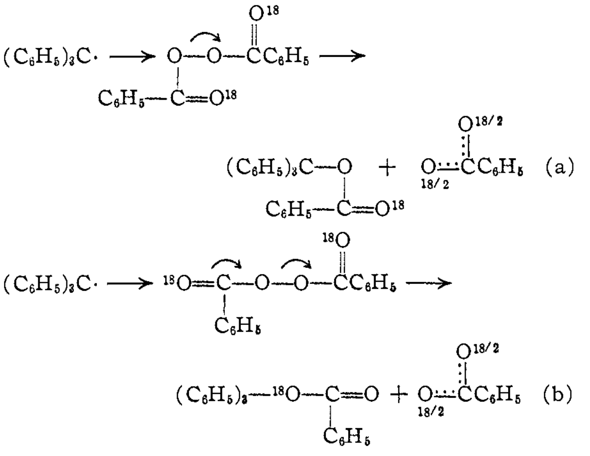
[6] Throughout this paper, the abbreviation "% ^{18}O" signifies "atom per cent. excess ^{18}O over natural abundance."

[7] W. von E. Doering and E. Dorfmann, THIS JOURNAL, **75**, 5595 (1953).

[8] G. S. Hammond, A. Ravve and J. F. Modic, *Anal. Chem.*, **24**, 1373 (1952).

16% being benzoic acid) by reaction 2. With most of the ^{18}O initially located in the *carbonyl* group of the benzoyl group in fact appearing in the *carbonyl* group of the trityl benzoate, it may be assumed that reaction 1 proceeds exclusively by attack on ether-oxygen. On the further assumption that all trityl benzoate formed by step 2 will have ^{18}O equally distributed between the two oxygen atoms, a simple calculation shows that 1.05% ^{18}O should have appeared in the *carbonyl*-oxygen. The discrepancy between 1.05 and 1.09–1.11% ^{18}O is probably within experimental error, but, if not, lies in the direction requiring more retention of oxygen-18 in the carbonyl group, rather than less. It is concluded that the attack of trityl radical on benzoyl peroxide in step 1 occurs entirely at the *peroxide*-oxygen atom.

Such a reaction is best described as a concerted radical displacement in which attack at the peroxidic oxygen atom is accompanied by release of the benzoyloxy radical (path a). An alternate mechanism involves attack at a carbonyl group producing, either as a transition state or as an intermediate, a structure of the benzyl radical type (path b). Although it does not appear possible to make a logically valid comparison of the relative activation energies of paths a and b, the significant feature of this calibrating experiment may well lie in the fact that reaction has proceeded more rapidly by that path (a) involving the smaller interference in bond distances and electronic interactions. In reaction by path b, bond distance and electronic interaction in a carbonyl group are disturbed to a far greater extent than they are in path a. Stated most simply, one more arrow is required to represent reaction path b than is required by path a.



Attention should be directed to the related work of Drew and Martin[9] on the induced decomposition of benzoyl peroxide in ether. In a decomposition carried out for 90 hours at the boiling point of ether, 1-ethoxyethyl radicals react with benzoyl peroxide at the peroxidic oxygen atom at least to the extent of 71%. In a similar experiment carried out for 168 hours, we have observed a minimum of 60% attack on the peroxidic oxygen. The difference is to be ascribed to scrambling of benzoate oxygen atom in the α-ethoxyethyl benzoate catalyzed by free benzoic acid. Although we had been unaware of this phenomenon until it was pointed out by Drew and Martin, it can now be used in a crude, simply extrapolative way to set 83% as a figure close to the minimum measure of the extent of peroxidic attack. The obvious crudities in this extrapolation deserving no further comment it need only be said that Drew and Martin promise the quantitative solution to the problem.

Our study of the decomposition of benzoyl peroxide *carbonyl*-^{18}O in cyclohexene also deserves mention here. Carried out at reflux in cyclohexene, according to the procedure of Hermans and van Eyk,[10] the decomposition led to a mixture (54% of theoretical benzoyloxy groups) of cyclohexenyl benzoate (1 part) and cyclohexyl benzoate (14 parts) which was analyzed by reduction with lithium aluminum hydride. The ^{18}O content of benzyl alcohol from the mixture of esters and of cyclohexenol and cyclohexanol (separated on a g.l.p.c. column specially packed to avoid the otherwise quite general dehydration of the cyclohexenol) was determined. In two runs, each involving duplicate analyses, benzoyl peroxide *carbonyl*-^{18}O with 1.37_5 and 1.35_5% ^{18}O (in each carbonyl group) led to benzyl alcohol with 0.73_0 and 0.65_5% ^{18}O, cyclohexanol with 0.62_5 and 0.63_5% ^{18}O, and cyclohexenol with 0.41_0 and 0.39_5% ^{18}O. Correcting the benzyl alcohol values for the presence of cyclohexenyl benzoate, the ^{18}O content of benzyl alcohol from cyclohexyl benzoate and, consequently, the ^{18}O content of the carbonyl group in the ester becomes 0.71 and 0.63, respectively. These values of the ^{18}O content of the carbonyl group in the cyclohexyl benzoate are nearly equal to those of the ether oxygen. This result is consistent with a mechanism in which benzoyloxy radical with equivalently distributed ^{18}O adds to the double bond of cyclohexene to give a 2-benzoyloxycyclohexyl radical which proceeds to the ester by removing an allylic hydrogen from cyclohexene.

Assuming that the cyclohexenyl benzoate is the product of reaction of cyclohexenyl radical with benzoyl peroxide (and not the result of the combination of cyclohexenyl radical and benzoyloxy radical), the distribution of ^{18}O indicates that at least 70 ± 1% of the attack had occurred at the peroxidic oxygen. Since no correction was made for allylic rearrangement in the already formed cyclohexenyl benzoate, for exchange with free benzoic acid or for formation of ester in part by the combination of radicals, this value is again a minimum one. Conservatively, one concludes that the cyclohexenyl radical and the α-ethoxyethyl radical react *predominantly* with the peroxidic oxygen of benzoyl peroxide. One cannot say whether, on close inspection of the necessary corrections, it will appear that these radicals, like triphenylmethyl, react *exclusively* at the peroxidic oxygen.

We wish to thank the National Science Foundation for its generous support of this work.

Experimental[6,11]

Benzoyl chloride-*carbonyl*-^{18}O was prepared most conveniently by adapting an old procedure.[12] To a well-stirred

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[9] E. H. Drew and J. C. Martin, *Chemistry & Industry*, 925 (1959); see also D. B. Denney and G. Feig, This Journal, **81**, 5322 (1959).

[10] P. K. Hermans and J. van Eyk, *J. Polymer Sci.*, **1**, 407 (1946).

[11] Microanalyses by Schwarzkopf Microanalytical Laboratory,

mixture of 100 g. of benzotrichloride and 0.2 g. of ferric chloride hexahydrate heated on the steam-bath and protected by a reflux condenser, 10 cc. of water containing somewhat more than 1.4% ^{18}O was added, dropwise, over a period of 1 hour. Hydrogen chloride evolution ceased after another hour of heating and stirring. Two distillations *in vacuo* of the product gave 27.5 g. of labeled benzoyl chloride (1.33% ^{18}O).

Triphenylmethyl Benzoate-*carbonyl*-^{18}O.—A solution of potassium triphenylmethoxide was prepared in a three-necked flask with stirrer, reflux condenser with drying tube and dropping funnel by refluxing a mixture of 1.95 g. of potassium with 14.6 g. of triphenylcarbinol in 250 cc. of dried xylene under a nitrogen atmosphere for 48 hours. Benzoyl chloride-*carbonyl*-^{18}O (7.0 g.) then was added dropwise at −10 to −5° over a period of 40 min. After filtration and evaporation of the solvent, crystalline triphenylmethyl benzoate precipitated (14.6 g., m.p. 167–172°). A second crop of 2.8 g. brought the yield to 96% based on benzoyl chloride.

A solution of 2.8 g. of this material in 300 cc. of anhydrous ether was added slowly at −15 to −5° to a solution of 8.5 g. of lithium aluminum hydride in 600 cc. of anhydrous ether. After standing overnight at 20°, the mixture was decomposed at −10 to −5° with 20 cc. of water. The filtered, ethereal solution was concentrated to give 2.3 g. of crystalline triphenylcarbinol which was recrystallized from benzene: 1.0 g., m.p. 160–162°, mixed m.p. with authentic material 160–162°, 0.030% ^{18}O.

Anal. Calcd. for $C_{19}H_{16}O$: C, 87.7; H, 6.2. Found: C, 87.8; H, 6.3.

Triphenylmethyl Benzoate-*ether*-^{18}O.—Labelled triphenylcarbinol was prepared by refluxing triphenylmethyl chloride at 100° in dried dioxane containing labeled water: m.p. 161–162°, 0.836 and 0.856% ^{18}O in duplicate assays. By a procedure identical with that above, triphenylmethyl benzoate *ether*-^{18}O was prepared and reduced with lithium aluminum hydride to triphenylcarbinol, m.p. 162–163°, 0.742 and 0.768% ^{18}O in duplicate analyses; C, 87.5; H, 6.3.

Heating Triphenylmethyl Benzoate-*carbonyl*-^{18}O.—A 2.5-g. sample of ester containing 1.03% ^{18}O in the carbonyl group was heated at 195–210° for 2 hours in a stream of dry nitrogen. The residue was extracted with ether and reduced with lithium aluminum hydride to triphenylcarbinol: 0.49% ^{18}O. Within experimental error, mixing was essentially complete.

Benzoyl peroxide *carbonyl*-^{18}O was prepared and analyzed according to a previously unpublished procedure of Doering and Greenbaum.[3] To a vigorously stirred mixture of 200 g. of cracked ice, 200 g. of water and 52 g. of sodium peroxide in a 1-l. three-necked flask equipped with thermometer, dropping funnel and stirrer, 62.0 g. of benzoyl chloride *carbonyl*-^{18}O (1.33% ^{18}O) in 60 cc. of benzene was added. After 30 minutes, during which the temperature rose to 30°, crystals of benzoyl peroxide were filtered and combined with an additional crop obtained after partial evaporation of the benzene solvent (50 g., 94% of theor.). This material was recrystallized from a mixture of 200 cc. of chloroform and 200 cc. of methanol.

The benzoyl peroxide was converted to methyl benzoate,[13] the O^{18} content of which then was determined (1.30 and 1.31% ^{18}O per carbonyl group).

Reaction of Triphenylmethyl Radical and Benzoyl Peroxide-*carbonyl*-^{18}O.—Triphenylmethyl radical was prepared according to Hammond, Ravve and Modic[8] by stirring a mixture of 6.5 g. of trityl chloride (m.p. 105–108°), 11.0 g. of mercury and 50 cc. of dried benzene in a 125-cc. erlenmeyer flask under a nitrogen atmosphere for 20 hr. The mixture was filtered through glass wool under nitrogen and treated with a solution of 2.50 g. of benzoyl peroxide-*carbonyl*-^{18}O in 50 cc. of benzene. The concentration of trityl radical was determined by weighing the trityl peroxide remaining after evaporation of a 1-cc. aliquot of the radical solution. About 2.11 equivalents of trityl radical was used for each molar equivalent of benzoyl peroxide. After 1 hour at room temperature, the pale yellow reaction mixture was washed with two 50-ml. portions of 4% aqueous sodium bicarbonate and with two 50-ml. portions of saturated aqueous sodium chloride until the washings became neutral to litmus. The benzene solution was dried with magnesium sulfate and evaporated under reduced pressure to give a yellow, viscous mass (7.7 g., 94%) which became solid. On being dissolved in 30 ml. of acetone, this solid deposited 750 mg. of insoluble crystals (m.p. > 190°) which were separated. Concentration of the mother liquors gave 5.3 g. of oil which was reduced with lithium aluminum hydride (see below) without further purification.

After acidification of the sodium bicarbonate extracts with 10% sulfuric acid, 400 mg. (16% of theoretical benzoate groups) of benzoic acid (m.p. 121–122°) was obtained. Titration of the filtrate with 0.10 *N* silver nitrate showed that only 0.47% of the starting trityl chloride had remained unreacted in the benzene solution of trityl radical.

Before being dissolved in acetone, a part of the reaction product (273.5 mg. from 7.7 g.) was hydrolyzed with 1 ml. of 0.226 *N* hydrochloric acid in 5.0 ml. of dioxane at 70–80° for one hour. The liberated acid was titrated with 5.51 ml. of 0.110 *N* aqueous sodium hydroxide. From these results, trityl benzoate was calculated to account for 83% of the starting benzoate groups.

The crude reaction product (5.2 g.) was dissolved in 150 ml. of anhydrous ether and added to a solution of 4.0 g. of lithium aluminum hydride in 400 cc. of anhydrous ether at −5 to −10°. The mixture was allowed to stand at −5 to −10° for 30 min. and at 25° for 20 hr., and then was hydrolyzed with 5.0 ml. of water at −30°. After the filtration of inorganic salts, the ether was distilled, leaving 4.4 g. of solid material. After several recrystallizations from carbon tetrachloride, 120 mg. of a first crop, m.p. 160–161°, and 100 mg. of a second crop, m.p. 160.5–161.5°, both showing no depression of m.p. on admixture with authentic triphenylcarbinol, were obtained. The ^{18}O content of the first crop was 0.231 and 0.215 atom % excess in duplicate assays.

Anal. Calcd. for $C_{19}H_{16}O$: C, 87.7; H, 6.2. Found: C, 87.5; H, 6.2.

Decomposition of Benzoyl Peroxide-*carbonyl*-^{18}O in Ethyl Ether.—Following the method described by Cass,[14] a mixture of 22.0 g. of benzoyl peroxide-*carbonyl*-^{18}O containing 1.37% ^{18}O and 453 g. of anhydrous ether was refluxed for one week in a 1-l. round-bottomed flask equipped with a reflux condenser and a drying tube. After 400 ml. of ether had been distilled from the reaction mixture, the residue was washed with 100 ml. of a 10% aqueous sodium bicarbonate solution. Acidification of the water layer gave 7.9 g. of benzoic acid. Concentration of the ether solution gave an oil, distillation of which afforded crude α-ethoxyethyl benzoate: 14.95 g., 42.2% of benzoyloxy radicals, b.p. 69–79° at 0.6 mm. Two further distillations gave 13.45 g. of ester, b.p. 68–72° at 0.4 mm., n^{25}D 1.4870.

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.0; H, 7.3. Found: C, 68.1; H, 7.2.

Duplicate analyses of the α-ethoxyethyl benzoate showed 1.34 and 1.34% ^{18}O calculated for one oxygen atom.

Reduction of α-Ethoxyethyl Benzoate-^{18}O with Lithium Aluminum Hydride.—To 10.4 g. of lithium aluminum hydride under a nitrogen atmosphere in a 2-l. three-necked flask equipped with a reflux condenser, a drying tube, a dropping funnel and a magnetic stirrer, 640 ml. of anhydrous ether was added. After 3 hr. of stirring, 9.5 g. of α-ethoxyethyl benzoate-^{18}O in 100 ml. of dry ether was added to the mixture over a period of 20 min. After being stirred for 5 hr. and standing overnight, the reaction mixture was diluted with 12 ml. of water to give a precipitate which was filtered and washed with ether. Concentration of the combined ether solutions afforded an oily material which was distilled *in vacuo* to give 3.7 g. of benzyl alcohol, b.p. 109–110° at 28 mm., n^{25}D 1.5370. Duplicate samples of benzyl alcohol contained 0.796 and 0.796% ^{18}O.

Anal. Calcd. for C_7H_8O: C, 77.8; H, 7.5. Found: C, 77.6; H, 7.5.

Decomposition of Benzoyl Peroxide-*carbonyl*-^{18}O in Cyclohexene.—By the method described by Hermans and van Eyk,[10] 20 g. of benzoyl peroxide-*carbonyl*-^{18}O containing 1.37% ^{18}O was dissolved in 80.0 g. of distilled cyclohexene in a 250-ml., round-bottomed flask equipped with a reflux con-

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Woodside 77, N. Y. Oxygen-18 analyses according to W. von E. Doering and E. Dorfmann.[7]

[12] Badische Anilin- und Soda-Fabrik, German Patent, 331,696 (*Chem. Zentr.*, **98**, II, 558 (1921)).

[13] H. Gilman in "Organic Syntheses," Coll. Vol. I, John Wiley and Sons. Inc., New York. N. Y., 1941, p. 431.

[14] W. E. Cass, THIS JOURNAL, **69**, 500 (1947).

denser fitted with a calcium chloride tube. The cyclohexene previously had been refluxed over potassium and distilled through a 30-cm. Vigreux column; b.p. 82.1°, $n^{25}D$ 1.4440. After 24 hr. under reflux in a nitrogen atmosphere, the solution was concentrated by distillation at 60 mm. The residue was dissolved in ether, extracted with four 25-ml. portions of 5% aqueous sodium hydroxide, washed with three 25-ml. portions of water, dried, and concentrated. The residue (34.5 g.) was fractionally distilled *in vacuo*, giving 17.75 g. of a fraction, b.p. 92–110° at 0.6 mm., which was redistilled to give 16.45 g. of the mixture of cyclohexyl and cyclohexenyl benzoate, b.p. 108.5–114.3° at 0.8 mm. Duplicate analyses of this sample indicated 1.36 and 1.35% ^{18}O calculated for one oxygen atom.

The second run carried out under the same conditions with 20.0 g. of labeled peroxide and 64.9 g. of cyclohexene afforded 12.72 g. of a mixture of cyclohexyl and cyclohexenyl benzoate, b.p. 114.0–119.0° at 1.0 mm. containing 1.39 and 1.36% ^{18}O in duplicate analyses.

Reduction of the Mixture of Cyclohexyl and Cyclohexenyl Benzoate-^{18}O with Lithium Aluminum Hydride.—A mixture of 9.5 g. of lithium aluminum hydride in a 2-l., three-necked flask equipped with a reflux condenser, a drying tube, a dropping funnel and a magnetic stirrer and 640 ml. of anhydrous ether was stirred for 2 hr. under a nitrogen atmosphere and treated with 14.5 g. of the mixture of cyclohexyl and cyclohexenyl benzoate-^{18}O in 200 ml. of dry ether over a period of 10 min. After stirring for 5 hours and allowing to stand overnight, the mixture was treated with 20 ml. of water, added over a period of 1 hour. The precipitated material was filtered and washed with 300 ml. of ether, and the combined ether solution was concentrated. The residue (17.0 g.) was distilled under reduced pressure to give 5.15 g. of a mixture of cyclohexanol and cyclohexenol, b.p. 75–90° at 25 mm., and 6.05 g. of a fraction, b.p. 90–106° at 25 mm., consisting mainly of benzyl alcohol. Redistillation of this fraction gave 4.30 g. of benzyl alcohol, b.p. 105.0–106.5° at 25 mm., $n^{25}D$ 1.5378, containing 0.724 and 0.734% ^{18}O in duplicate analyses.

Anal. Calcd. for C_7H_8O: C, 77.8; H, 7.5. Found: C, 77.9; H, 7.4.

A fraction of b.p. 75–79° at 27.0 mm. obtained by redistillation of the mixture of cyclohexanol and cyclohexenol was separated by gas–liquid partition chromatography on a 2.5-m. column (6 mm. i.d.) packed with 40–60 mesh firebrick supporting one-quarter its weight of monohydroxyethyltrihydroxypropylethylenediamine (Visco Products, Inc., Houston, Tex.). Samples of 0.13–0.15 ml. were diluted with one-half their volume of *n*-pentane and separated in the column at 110° and 20 p.s.i. Thirty-six runs (4.1 g. of the mixture) gave 295 mg. of material with retention times of 80–84 min. (mainly cyclohexenol) and 3.80 g. of cyclohexanol with retention times of 60–70 min. The cyclohexenol fractions were refractionated twice under the same conditions to give 77 mg. of pure cyclohexanol, $n^{25}D$ 1.4832, 0.420 and 0.405% ^{18}O.

Anal. Calcd. for $C_6H_{10}O$: C, 73.4; H, 10.3. Found: C, 73.3; H, 10.3.

A portion of the combined cyclohexanol fractions was refractionated under the same conditions to give pure cyclohexanol, $n^{25}D$ 1.4632, 0.615 and 0.635% ^{18}O.

Anal. Calcd. for $C_6H_{12}O$: C, 71.9; H, 12.2. Found: C, 72.2; H, 12.2.

The mixture of cyclohexyl and cyclohexenyl benzoate-^{18}O (12.0 g.) obtained in the second experiment gave benzyl alcohol containing 0.658 and 0.654% ^{18}O, cyclohexenol, 0.392 and 0.400% ^{18}O and cyclohexanol, 0.647 and 0.622% ^{18}O.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

"1,3-Shifts" in Rearrangements of 3,4,4-Trimethyl-2-pentyl Derivatives[1]

BY WILLIAM H. SAUNDERS, JR., AND GERARD L. CARGES

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The dehydration of 3,4,4-trimethyl-2-pentanol (I) has been studied under a variety of conditions. Product identification was accomplished by gas chromatography and infrared spectra, using independently-prepared olefins as reference samples. Under conditions where the dehydration of I is irreversible, nearly all of the product has the same carbon skeleton as I. Significant amounts of product having the 2,3,4-trimethylpentane skeleton result only under conditions strenuous enough to cause isomerization of the first-formed products. Thus the apparent "1,3-shift" is most probably a succession of 1,2-shifts rather than a direct process.

All but a handful of the many examples of carbonium-ion rearrangements are simple 1,2-shifts or combinations of 1,2-shifts. Among the few apparent exceptions to this rule have been the 1,3-shifts of methyl groups reported in certain highly-branched systems.[2,3,4] Schneider and Kennedy[5] have argued that most of these examples can be explained as successive 1,2-shifts. Mosher and Cox,[6] however, examined a system in which the distinction could be made and reported results consistent only with a direct 1,3-shift.

Our aim in the present work was to define more clearly the conditions for 1,3-shifts. In addition, more positive separation and identification of products is possible through the use of gas chromatography. We could thus eliminate the possibility that observed rearrangements might be artifacts of the degradative procedures used by earlier workers.

The simplest system which gives apparent 1,3-shift is 3,4,4-trimethyl-2-pentyl.[7] The corresponding alcohol, 3,4,4-trimethyl-2-pentanol (I) was therefore chosen for our work so as to minimize the task of separating and identifying the products. This substance resulted from the lithium aluminum hydride reduction of 3,4,4-trimethyl-2-pentanone, which in turn was obtained by the action of dimethylcadmium on the acid chloride of the known[8] methyl-*t*-butylacetic acid. Further details of the synthesis of I will be found under Experimental.

Since I has two asymmetric carbons (C_2 and C_3) it should be capable of existing in two diastereomeric

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[1] This work was supported in part by the Office of Ordnance Research, U. S. Army. G. L. C. received a stipend from the has. Pfizer and Co. grant during part of the period of this work.

[2] F. C. Whitmore, K. C. Laughlin, J. F. Matuszeski and J. D. Surmatis, THIS JOURNAL, **63**, 756 (1941).

[3] F. C. Whitmore and W. A. Mosher, *ibid.*, **68**, 281 (1946).

[4] N. L. Drake, G. M. Kline and W. G. Rose, *ibid.*, **56**, 2076 (1934).

[5] A. Schneider and R. M. Kennedy, *ibid.*, **73**, 5017, 5024 (1951).

[6] W. A. Mosher and J. C. Cox, Jr., *ibid.*, **72**, 3701 (1950).

[7] The 3,4,4-trimethyl-2-pentyl carbonium ion was undoubtedly an intermediate in the acid-catalyzed copolymerization of *sec*-butyl and *t*-butyl alcohols,[2] in which 2,3,4-trimethyl-2-pentene, the result of a 1,3-shift, was a major product.

[8] C. G. Overberger and M. B. Berenbaum, THIS JOURNAL, **74**, 3293 (1952).