titrated with standard sodium hydroxide solution. Plots of the amount of Grignard reagent consumed against time gave straight lines, the slope of which gave the rate.

C^{14}-Labeling Experiments.—1-C^{14}-Isopropyl bromide was prepared by the series of reactions C^{14}H$_3$OH → C^{14}H$_3$I → C^{14}H$_3$MgI → C^{14}H$_3$CHOHCH$_3$ → C^{14}H$_3$CHBrCH$_3$. In each run 4.30 mmoles of Grignard reagent was allowed to react with 4.25 mmoles of halide in the presence of 0.011 mmole of catalyst for copper, 0.033 mmole for cobalt, 0.035 mmole for nickel, and 0.063 mmole for iron. In order to avoid dilution of the products, the gases were collected directly in a 300-ml. reservoir. From the reservoir, 30 ml. of the gas mixture was transferred to the gas chromatograph column. At the instant the propane peak began to appear, the emergent gases were collected in a gas bag, which was left attached to the Aerograph for exactly 5 min. This time was more than sufficient to collect all of the propane. When the propylene appeared on the recorder, a second bag was attached to the Aerograph and the propylene collected for a period of exactly 5 min. The ratio of propane to propylene was determined from the areas under the respective peaks on the chart of the recorder.

The propane fraction was transferred to a reservoir and diluted to a definite volume with nitrogen. The reservoir was connected to an evacuated ionization chamber, and the ionization chamber filled with the gas mixture under atmospheric pressure. The C^{14} assay was made with a Model 31 Cary vibrating-reed electrometer.[9] The activity of the propylene fraction was determined

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

in the same way. The relative activities per mole were calculated from the ratio of the propane to propylene and from the ratio of the activity of propane to the activity of propylene using the equation

$$\text{propane*/propylene*} = \frac{\text{activity of propane}}{\text{activity of propylene}} \times \frac{\text{propylene}}{\text{propane}}$$

Electron Paramagnetic Resonance Spectra.—Ethyl bromide was added to a solution of catalyst in excess ethylmagnesium bromide in the spectrometer sample tube at room temperature. Evolution of gas took place at once and the tube was plunged into liquid nitrogen. The frozen sample was scanned with a Varian Model 4501 e.p.r. spectrometer in the range of 500 gauss on either side of $g = 2$.

A Study of the Decomposition of 3,3,3-Triphenylpropanoyl Peroxide

By Donald B. Denney,[1] Robert L. Ellsworth, and Dorothy Z. Denney

The decomposition of 3,3,3-triphenylpropanoyl peroxide has been studied in the absence of solvent, in carbon tetrachloride, and in a mixture of carbon tetrachloride, iodine, and water. In all cases 3,3,3-triphenylpropanoic acid, 1,1,2-triphenylethylene, 1,1,2-triphenylethane, 1,1,1,4,4,4-hexaphenylbutane, phenyl 3,3-diphenylpropenoate, and carbon dioxide were formed. The relative yields of these substances were considerably affected by the changes in reaction conditions. An oxygen-18 tracer study of the formation of phenyl 3,3-diphenylpropenoate showed that 65% of the original carbonyl label becomes the ether oxygen of the ester. Essentially all of the remaining label was found in the carbonyl group. The formation of 1,1,1,4,4,4-hexaphenylbutane indicates that 2,2,2-triphenylethyl radicals have some stability under the conditions used for their generation. Several novel features of the decomposition are discussed and compared to other diacyl peroxide decompositions.

It seems well recognized that most free radical rearrangements proceed in a stepwise manner which involves generation of the radical followed by rearrangement.[2] This behavior is to be contrasted to many carbonium ion rearrangements in which migration occurs as the electron deficient center is being formed.[3]

Decarbonylation of aldehydes which would have been expected to give the highly substituted radicals (Ia,b)
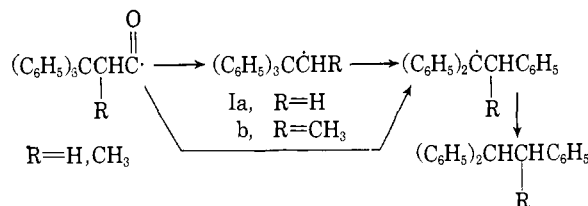
yielded rearranged products exclusively.[4] This could be due to a simultaneous migration of phenyl as carbon monoxide is lost or simply to the fact that the intermediate radicals (Ia,b) rearrange faster than they abstract hydrogen from an aldehydo group of another molecule.

Of the open chain radicals it seems clear that highly arylated systems such as Ia,b will be the most prone

to rearrange. A clear-cut demonstration that such rearrangements are or are not synchronous with generation of the radical seems desirable. In principle there are several ways of attacking such a problem. In the case now being reported, trapping of the radical before rearrangement could occur was selected as the method to be used. The trap was to be another radical generated at the same or essentially the same time and in close proximity to the radical under study. It was believed that decomposition of a diacyl peroxide would provide radicals generated in juxtaposition which could undergo some combination before diffusion.[5] The peroxide chosen was 3,3,3-triphenylpropanoyl peroxide (II) which on decomposition would

$$[(C_6H_5)_3C-CH_2-CO_2]_2 \qquad (C_6H_5)_3C-CH_2-CH_2-C(C_6H_5)_3$$
$$\text{II} \qquad\qquad\qquad\qquad \text{III}$$
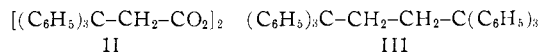
give 1,1,1,4,4,4-hexaphenylbutane (III) if rearrangement of a phenyl group was not synchronous with decomposition and if "cage combination" could occur before diffusion or rearrangement of Ia. It was of interest to study the decomposition of II in its own right and several novel features of this decomposition have been found.

Results

The synthesis of 3,3,3-triphenylpropanoyl peroxide was accomplished from the acid chloride by reaction with sodium peroxide in aqueous acetone[6] or by re-

(1) Rutgers Research Council Faculty Fellow, 1963–1964.

(2) C. Walling, "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 7.

(3) D. J. Cram, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 5.

(4) D. Y. Curtin and M. F. Hurwitz, *J. Am. Chem. Soc.*, **74**, 5381 (1952).

(5) L. Herk, M. Feld, and M. Szwarc, *ibid.*, **83**, 2998 (1961).

(6) S. Gambarajan, *Ber.*, **42**, 4003 (1909).

TABLE I

PRODUCTS OF THE DECOMPOSITION OF II[a]

	Thermal (115–130°)			CCl₄ (77°)[d]			CCl₄ + I₂ (77°)[e]			CCl₄ + I₂ (77°)[f]
3,3,3-Triphenylpropanoic acid[i]	0.72[b]	0.74[c]	0.75[b]	0.21	0.12	..	1.29	1.43	..	1.52
	(.79)	(.77)	(.82)	(.60)	(.59)	..	(1.55)	...	..	(1.60)
1,1,2-Triphenylethane	.014	.013	.016	.006	.006	..	0.002	0.003	..	0.002
1,1,2-Triphenylethylene	.72	.63	.75	.36	.30	..	.10	.14	..	.091
1,1,1,4,4,4-Hexaphenylbutane	.042	.049	.041	.012	.012	..	.012	.015	..	.006
Phenyl 3,3-diphenylpropenoate	.24	.31	.24	.73	.82	..	..	...	0.21[i]	.060
Carbon dioxide	1.20	1.26	1.11	.48	.40	..	0.16	..	..	...
Residue[g]	0.25	0.42	0.23	.46	.57	0.42[h]	0.33	..	0.05[j]	0.10
Total carboxyl groups accounted for, %[i]	108	115	105	71	67	..	83	..	..	80
	(112)	(118)	(109)	(90)	(90)	..	(98)	..	..	(84)
Total triphenylethyl groups accounted for, %[i]	89	90	92	67	63	..	82	..	..	77
	(93)	(93)	(96)	(85)	(86)	..	(95)	..	..	(82)

[a] Entries are moles of product per mole of peroxide. [b] Peroxide decomposed, 5.000 g., 0.0083 mole. [c] Peroxide decomposed, 10.000 g., 0.0166 mole. [d] Peroxide decomposed, 2.000 g., 0.0033 mole. [e] Peroxide decomposed, 2.000 g., 0.0033 mole; 10 ml. of water; 2.0 g (0.008 mole) of iodine. [f] Peroxide decomposed, 2.000 g., 0.0033 mole; 10 ml. of water; 16.5 g. (0.066 mole) of iodine. [g] Reported in grams. [h] For analytical purposes, only the residue was isolated. [i] Peroxide decomposition products extracted with five portions of 10% aqueous sodium hydroxide. No attempt was made to isolate the other products from the subsequent chromatography. [j] Numbers within parentheses represent recalculated values based on the residue containing 81% acid or potential acid.

action with hydrogen peroxide in the presence of pyridine.[7] The later technique seemed to give more reproducible results. The decomposition of II was effected by heating the solid to 115° at which temperature a vigorous evolution of carbon dioxide occurred. Decomposition in carbon tetrachloride was effected by refluxing for 5 hr. The results of these experiments are compiled in Table I as are the results of decompositions conducted in the presence of iodine and water.
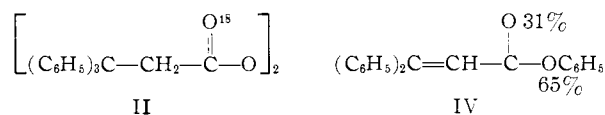
The structural assignment for 1,1,1,4,4,4-hexaphenylbutane is based on the elemental analysis, the infrared spectrum, the n.m.r. spectrum, and the concordance of physical properties with a sample prepared by the reaction of 3,3,3-triphenylpropyl iodide with triphenylmethyl bromide in the presence of magnesium.[8]

The formation of phenyl 3,3-diphenylpropenoate (IV) was not completely unexpected.[9] In order to investigate its mode of formation a sample of II labeled with oxygen-18 in the carbonyl groups was prepared and decomposed. The ester IV was hydrogenated and the crude saturated ester was converted to 3,3-diphenylpropanoic acid hydrazide and phenol by reaction with anhydrous hydrazine. The oxygen-18 analytical data are collected in Table II. The ana-

$$\left[(C_6H_5)_3C{-}CH_2{-}\overset{\overset{O^{18}}{\|}}{C}{-}O\right]_2 \qquad (C_6H_5)_2C{=}CH{-}\overset{\overset{O\ 31\%}{\|}}{C}{-}\underset{65\%}{O}C_6H_5$$

$$\text{II} \qquad\qquad\qquad \text{IV}$$

of II becomes bonded to the rearranged phenyl ring and essentially all of the remainder is found in the carbonyl group of IV.

The other products obtained from the decomposition are those to be expected. During the course of isolating them it became apparent that considerable difficulty was being encountered in recovering the acid from the reaction mixtures.[10] This was due in part to the insolubility of the sodium salt in water. Repeated extractions with base ultimately gave little residue and led to increased yields of acid. It should be noted that this could be due to hydrolysis of a material which gives acid, for example the anhydride.

Discussion

The formation of 1,1,1,4,4,4-hexaphenylbutane (III) clearly indicates that 2,2,2-triphenylethyl radicals were present and underwent geminate combination.[11] The yields of III are considerably less than those usually found for similar products derived from diacyl peroxides. For example, bis-δ-valeryl peroxide[12] yields 20% of dimeric hydrocarbon when it is decomposed in boiling carbon tetrachloride and 31% in boiling benzene. Acetyl peroxide yields 6% of ethane by geminate combination when decomposed in isooctane at 65°[5] and propionyl peroxide yields 30–40% of "cage" products from the ethyl radicals.[13] The explanation advanced to explain these differences in yields postulates that in the main they are due to the different rates of diffusion of the radicals involved; i.e., the larger radicals diffuse more slowly.[5] The very low yield of III compared to the other peroxides is probably due in part to rearrangement of the 2,2,2-triphenylethyl radicals which competes with geminate combination. Internal trapping of the 3,3,3-triphenylpropanoyloxy radicals which lowers the rate of decarboxylation is undoubtedly another major factor which contributes to the low yields of III. It is interesting to note that the highest yields of III were obtained in the melt at higher temperatures than were used in the solution decom-

TABLE II

Compound	Atom % excess oxygen-18
3,3,3-Triphenylpropanoic acid	0.63, 0.64
3,3,3-Triphenylpropanoyl peroxide	.57, .57, 0.60, 0.53
Phenyl 3,3-diphenylpropenoate	.63, .64
3,3-Diphenylpropanoic acid hydrazide	.20, .21
Phenyl phenylurethan	.41, .42

lytical data for the peroxide are low and somewhat erratic. Because of the good agreement between the values obtained from the other compounds the percentage scrambling has been calculated using these data. The results show that during the rearrangement ca. 65% of the excess oxygen-18 in the carbonyl group

(7) L. S. Silbert and D. Swern, J. Am. Chem. Soc., 81, 2364 (1959).

(8) A material which was claimed to be III was synthesized by H. Wieland, Ann., 514, 145 (1934). The reported properties do not agree with those found in this study. Wieland's compound was isolated from a reaction mixture of 1,1,1-triphenyl-2,2,2-trichloroethane with zinc. It seems likely that rearrangement occurred in this reaction and thus it is not difficult to believe that III was not obtained.

(9) (a) H. Breederveld and E. C. Kooyman, Rec. trav. chim., 76, 297 (1957); (b) E. C. Kooyman, Record Chem. Progr., 24, 98 (1963); (c) J. W. Wilt and D. D. Oathoudt, J. Org. Chem., 23, 218 (1958); (d) J. W. Wilt and J. L. Finnerty, ibid., 26, 2173 (1961).

(10) Full details can be found in the Experimental; see also footnote j, Table I.

(11) This conclusion is valid irrespective of whether II decomposes by one-, two-, or three-bond cleavage or some combination of these modes of decomposition.

(12) D. F. DeTar and C. Weis, J. Am. Chem. Soc., 78, 4296 (1956).

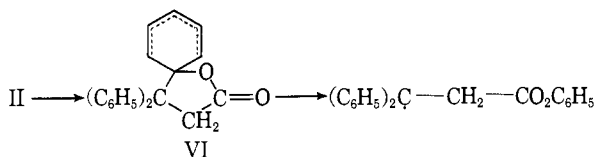(13) J. Smid and M. Szwarc, ibid., 78, 3322 (1956).

positions. This might be due to a greater rate of decarboxylation at the higher temperatures and a lower rate of diffusion of the 2,2,2-triphenylethyl radicals in this more viscous medium.

It seems reasonable to conclude that decomposition of II yielded 2,2,2-triphenylethyl radicals and that there was no anchimeric assistance by a migrating phenyl group.

Another point of interest which has emerged from this study is the apparent lack of formation of 2,2,2-triphenylethyl 3,3,3-triphenylpropanoate (V) which is the ester expected if geminate combination of 2,2,2-triphenylethyl radicals and 3,3,3-triphenylpropanoyloxy radicals occurred. Acetyl peroxide gives *ca.* 20% methyl acetate[5] by geminate combination and bis-δ-phenylvaleryl peroxide yields 15–20% of δ-phenylbutyl δ-phenylvalerate.[12] Although a small amount of V might have escaped isolation, quantities of the magnitude found in other peroxide decompositions should have been detected. It does not seem likely that the esters would have decomposed under the conditions used for isolation.[14] Again, rearrangement of the 2,2,2-triphenylethyl radicals may contribute to the apparent lack of formation of V. Intramolecular stabilization of the 3,3,3-triphenylpropanoyloxy radicals might also make them less susceptible to geminate combination.

It should be noted that the yields of both III and V could be low if the major path for decomposition of II involves induced decomposition. Although induced decomposition cannot be entirely eliminated with the data presently available, two factors argue against it. Addition of iodine should inhibit induced decomposition and might therefore lead to increased yields of these products.[15] Furthermore, the decompositions in carbon tetrachloride were conducted at concentrations which have been reported to overcome this difficulty to a large degree.[12]

The oxygen-18 tracer experiment shows that no more than 60–65% of the rearranged ester IV can be derived from free 3,3,3-triphenylpropanoyloxy radicals. The rest must be formed by some process which allows the carbonyl oxygen to preserve its integrity in its path to becoming the phenol oxygen of the ester. Several explanations can be offered to account for these results. It seems clear that some sort of specific interaction between a phenyl group and a carbonyl oxygen is required at least part of the time. A σ-complex (VI) is undoubtedly involved in the rearrangement.[9] Whether

$$\text{II} \longrightarrow (C_6H_5)_2C \overset{O}{\underset{CH_2}{\diagdown}} C=O \longrightarrow (C_6H_5)_2C-CH_2-CO_2C_6H_5$$

VI

or not it is in equilibrium with the 3,3,3-triphenylpropanoyloxy radical, a π-complex or even a charge-transfer complex cannot be answered as yet.[16]

The effect of iodine–water on the yield of 3,3,3-triphenylpropanoic acid is quite striking. It is quite

clear that iodine is very efficient in capturing and converting the 3,3,3-triphenylpropanoyloxy radicals or related radicals into acid. In general, iodine is not able to trap acyloxy radicals from diacyl peroxide decompositions with anything near the efficiency found here.[17] The behavior found with II can be taken as support for the contention that there is slower decarboxylation than with most other acyloxy radicals.[18]

Experimental[19]

3,3,3-Triphenylpropanoic Acid.—The procedure of Hellerman[20] gave an average yield of 45% of the acid, m.p. 165–179° (lit.[20] 180°).

The following procedure gave the best results. A mixture of triphenylcarbinol (200.0 g., 0.77 mole), 130.0 g. (0.80 mole) of malonic acid, and 75 ml. (0.80 mole) of acetic anhydride was heated at 150–160° for 3 hr. The acetic acid and acetic anhydride were distilled and the residue was heated for 3 hr. at 150–160°. The residue was taken up in 2 l. of a warm 2.5% solution of sodium hydroxide. The solution was filtered to recover unreacted triphenylcarbinol. The filtrate was acidified with 10% sulfuric acid to give crude acid. The acid was crystallized from ethanol to give 204.0 g. (88%) of product, m.p. 182–183°.

3,3,3-Triphenylpropanoyl Chloride.—A mixture of 3,3,3-triphenylpropanoic acid (115.0 g., 0.38 mole) and 145 ml. (2.0 moles) of thionyl chloride was heated under reflux for 3 hr. The solution was allowed to cool slowly, and the resulting acid chloride was removed by filtration through a sintered glass funnel. Evaporation of the filtrate afforded a second batch of acid chloride. Occasionally, 25 ml. of dry benzene was added in order to remove the last traces of thionyl chloride. Recrystallization of the combined fractions from dry hexane–benzene gave 82.0 g. (67%) of acid chloride, m.p. 133–135° (lit.[20] 132°).

3,3,3-Triphenylpropanoyl Peroxide (II).—To a stirred ice-cold solution of 1.9 g. (0.024 mole) of sodium peroxide in 100 ml. of water was added over a period of 30 min. a solution of 14.6 g. (0.048 mole) of 3,3,3-triphenylpropanoyl chloride in 100 ml. of acetone. The mixture was stirred for an additional 1.5 hr. at 0 to −5°. The white solid which separated was removed by filtration and washed with two 50-ml. portions of cold acetone. The crude peroxide, m.p. 128–131°, was dissolved in chloroform at room temperature and extracted with three 100-ml. portions of 5% sodium hydroxide solution. Acidification of the aqueous extract with dilute sulfuric acid gave a white solid, m.p. 175–179°. The melting point was raised to 181° after one recrystallization from ethanol. No depression of the melting point was observed when mixed with an authentic sample of 3,3,3-triphenylpropanoic acid. The chloroform solution was evaporated to dryness at room temperature. The residue was crystallized by dissolving it in excess acetone at room temperature and the resulting solution was concentrated in a stream of nitrogen. The peroxide, 8.7 g. (62%), was crystallized as fine needles, m.p. 133.5 dec. The infrared spectrum had carbonyl bands at 1815 and 1790 cm.⁻¹.

Anal. Calcd. for $C_{42}H_{34}O_4$: C, 83.69; H, 5.69. Found: C, 83.60; H, 5.70.

Oxygen-18 Labeled 3,3,3-Triphenylpropanoic Acid.—To a solution of 92 g. (0.288 mole) of crude acid chloride in 200 ml. of dry pyridine was added 18 g. of water containing 1.6 atom % oxygen-18. After stirring under reflux for 12 hr., the mixture was poured onto 1000 g. of ice and 260 ml. of concentrated hydrochloric acid. The solid was dried to give 75 g. of crude 3,3,3-triphenylpropanoic acid, m.p. 135–168°. Recrystallization from benzene–pentane of this material and 15 g. of crude labeled acid from another run gave material, m.p. 180–181°.

Oxygen-18 Labeled II.—The acid chloride was prepared from the above acid and converted to the peroxide by Silbert and Swern's method[7] in 69% yield, m.p. 129–130° dec. The analytical sample had m.p. 133–135°.

Decomposition of II in the Absence of Solvent.—A 250-ml. flask, equipped with a condenser and gas inlet tube, containing 5.000 g. (0.0083 mole) of II, was immersed in an oil bath. The temperature of the bath was slowly raised to 115°, at which temperature a vigorous evolution of carbon dioxide occurred. The

(14) S. Winstein, B. Morse, E. Grunwald, K. Schreiber, and J. Corse, *J. Am. Chem. Soc.*, **74**, 1113 (1952), report that 2,2,2-triphenylethyl *p*-toluenesulfonate is readily prepared and easily handled.

(15) It is recognized that iodine is not necessarily a completely efficient trap: see P. D. Bartlett and C. Rüchardt, *ibid.*, **82**, 1756 (1960); however, since the yield of IV was markedly diminished by added iodine it is quite clear that it is having some effect.

(16) It is interesting to note that no rearranged ester similar to IV can be isolated from the reaction mixture from the decomposition of 3,3-diphenyl-propanoyl peroxide (unpublished experiments of J. Giacin). An inspection of models shows that in II there is no conformation in which a phenyl group is not brought into close proximity to a carbonyl oxygen. This is not true of the disubstituted peroxide.

(17) D. F. DeTar and R. C. Lamb, *J. Am. Chem. Soc.*, **81**, 122 (1959), and references cited therein.

(18) In the case of trapping acetyloxy radicals from acetyl peroxide with iodine–water, misleading results were obtained because of hydrolysis of the acetyl peroxide: H. Shine, J. A. Waters, and D. M. Hoffman, Abstracts of Papers, 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1961, p. 72Q. It is not likely that this is a factor here because of the extreme insolubility of II in water.

(19) Melting points are uncorrected. Analyses by G. Robertson, Florham Park, N. J.

(20) L. Hellerman, *J. Am. Chem. Soc.*, **49**, 1738 (1927).

evolved carbon dioxide was swept out of the reaction flask by nitrogen and precipitated as barium carbonate by passing the gases into a saturated solution of barium hydroxide. In some cases the gases were bubbled through a solution of carbonate-free sodium hydroxide to which there was later added barium chloride solution. After the evolution of carbon dioxide had subsided, the temperature of the bath was raised to 135° and maintained at that temperature for 3 hr.

The residue from the decomposition was dissolved in 100 ml. of ether and was extracted with three 100-ml. portions of 5% sodium hydroxide solution. Acidification of the alkaline fraction with dilute sulfuric acid gave a white solid, m.p. 165–175°, which was crystallized from ethanol to give material, m.p. 179–181°, which showed no depression of melting point with an authentic sample of 3,3,3-triphenylpropanoic acid.

The ether solution was dried over anhydrous magnesium sulfate and evaporated to dryness. Separation of the mixture was achieved by chromatography on silica gel (mesh 60–200). Elution of the crude residue with 350 ml. of benzene–hexane (1:9) gave a clear oil which solidified upon standing. The material was crystallized from ethanol to give a white solid, m.p. 64–66°. The reported melting points for the possible products are: 1,1,2-triphenylethane,[21] 54.5°; 1,1,2-triphenylethylene,[21] 72–73°; 1,1,1-triphenylethane,[22] 93.8–95°. Further recrystallization of the solid material did not alter the melting point. This material quickly decolorized potassium permanganate solution (0.5%) and reacted with bromine in carbon tetrachloride. Its ultraviolet spectrum possessed $\lambda_{max}^{CHCl_3}$ 300 mμ ($\lambda_{max}^{CHCl_3}$ 300 mμ for 1,1,2-triphenylethylene).[23] The material was reduced with hydrogen at atmospheric pressure using ethanol as a solvent and palladium–charcoal as catalyst. The catalyst was removed by filtration and the solution was concentrated to give a white solid, m.p. 54.5°. From the above information it was concluded that the original material was a mixture of 1,1,2-triphenylethylene and 1,1,2-triphenylethane. The percentage of each was calculated from the volume of hydrogen absorbed during the reduction. The results (98% 1,1,2-triphenylethylene and 2% 1,1,2-triphenylethane) checked closely with that calculated from the ultraviolet absorbance of the mixture and the known extinction coefficient of the olefin.

Further elution of the column with 350 ml. of benzene–hexane (1:3) gave a white crystalline solid which was recrystallized from benzene to give a material, m.p. 287°. The infrared spectrum of this material showed only C–H and phenyl absorption.

Anal. Calcd. for $C_{40}H_{34}$: C, 93.34; H, 6.66. Found: C, 93.20; H, 6.70.

A mixture melting point with 1,1,1,4,4,4-hexaphenylbutane synthesized as described below showed no depression. The infrared spectra of these two compounds were identical. The n.m.r. spectrum in a very dilute solution in trifluoroacetic acid had phenyl absorption at τ 3.1 and a distinguishable peak at τ 7.77.[24]

Further elution with 500 ml. of benzene gave a colorless oil which solidified upon standing. The melting point after one recrystallization from benzene–petroleum ether (30–60°) was 123–124°; reported[25] for phenyl 3,3-diphenylpropenoate, 123.5°. The infrared spectrum had peaks at 1736, 1618, 1594, and 1579 cm.$^{-1}$. Wilt and Oathoudt[9c] report the same maxima for phenyl 3,3-diphenylpropenoate. The compound quickly decolorized potassium permanganate solution (0.5%) and gave a positive hydroxamic acid test.[26]

Anal. Calcd. for $C_{21}H_{16}O_2$: C, 83.98; H, 5.37. Found: C, 84.48; H, 5.27.

Saponification of the ester with 20% alcoholic potassium hydroxide solution gave an acid which after two recrystallizations from ethanol melted at 160–162°; reported[27] for 3,3-diphenylpropenoic acid, 161°. The infrared spectrum was consistent with the assigned structure. Reduction of the acid by hydrogen at atmospheric pressure using ethanol as a solvent and palladium on barium sulfate as catalyst, gave a white crystalline material, m.p. 153°; reported[28] for 3,3-diphenylpropanoic acid, 155°. The infrared spectrum was consistent with the assigned structure.

Elution of the column with 500 ml. of acetone gave a brown oil which appeared to be mainly 3,3,3-triphenylpropanoic acid (see experiment below).

Decomposition of II in Carbon Tetrachloride in the Presence of Iodine and Water.—A solution of 2.0 g. (0.008 mole) of iodine,

2.000 g. (0.0033 mole) of II, 10 ml. of water, and 300 ml. of carbon tetrachloride was refluxed for 5 hr. Carbon dioxide was determined as before. The carbon tetrachloride solution was cooled to room temperature and decolorized with aqueous sodium thiosulfate. The carbon tetrachloride solution was concentrated to 50 ml. and extracted with three 100-ml. portions of 5% sodium hydroxide solution. The analysis of the products from the residue was the same as above with the exception that sulfur was obtained upon elution of the column with hexane.

Decomposition of II in Carbon Tetrachloride.—The decomposition and product analysis were the same as above. The brown oil obtained by elution with acetone, 0.42 g., was partially identified as a mixture containing 81% of acid or material which gave acid easily. Identification was achieved by sublimation which yielded a material whose infrared spectrum was identical with that of acid and which showed no depression of melting point when mixed with pure 3,3,3-triphenylpropanoic acid. The residue was then dissolved in 50 ml. of ether and was extracted with three 50-ml. portions of 10% sodium hydroxide. Acidification of the alkaline layer with 10% sulfuric acid gave, when combined with the sublimed material, a total of 0.34 g. The ether layer was washed with 50 ml. of water, dried over anhydrous magnesium sulfate, and evaporated to yield 0.08 g. of a carbonyl-containing material. The infrared spectrum of the mixture was identical with those obtained from other experiments. Therefore, in order to calculate the total carboxyl groups and $(C_6H_5)_3C-CH_2-$ groups accounted for, it was assumed in all cases that the brown oil contained 81% of acid or acid-forming materials.

Isolation of Oxygen-18 Labeled IV.—Two 10-g. portions of labeled peroxide were decomposed and a total of 1.6 g. of labeled IV was isolated, m.p. 122–123°; 1 g. of less pure material was obtained. Hydrogenation of 2.5 g. was carried out in 100 ml. of anhydrous ethanol with platinum catalyst. After removal of the catalyst, excess anhydrous hydrazine was added and the mixture was heated under reflux for 16 hr. The solvent was removed *in vacuo* and the resulting semisolid was triturated with ether. Two recrystallizations from benzene gave 3,3-diphenylpropanoic acid hydrazide, m.p. 123–124° (lit.[29] 127–128°). The infrared spectrum of this material was entirely consistent with the assigned structure.

The ether solution was concentrated to dryness. Sublimation of a portion of the residue gave 0.25 g. of phenol which was heated with 0.30 g. of phenyl isocyanate and 1 drop of pyridine for 30 min. Recrystallization from benzene–pentane gave phenyl phenylurethan, m.p. 124–125° (lit.[30] 126°). The infrared spectrum was identical with that of a known sample of phenyl phenylurethan.

3,3,3-Triphenylpropanol.—A solution of 20.0 g. (0.07 mole) of 3,3,3-triphenylpropanoic acid in 500 ml. of dry ether was slowly added to a stirred slurry of 2.8 g. (0.08 mole) of lithium aluminum hydride in 250 ml. of anhydrous ether. The solution was refluxed for 3 hr. with stirring after completion of the addition. The flask was then cooled in an ice bath, and 50 ml. of water was added, the first few milliliters with extreme caution. A sulfuric acid–ice mixture was then added slowly. The ethereal layer was separated, washed with dilute sulfuric acid, aqueous sodium bicarbonate and water, and was then dried over anhydrous magnesium sulfate. Evaporation of the solvent gave 9.8 g. (52%) of alcohol, m.p. 107–108° (lit.[31] 107–108°) after three recrystallizations from petroleum ether (30–60°).

3,3,3-Triphenylpropyl Iodide.—The procedure of McPhee and Lindstrom[31] yielded 81% of the iodide, m.p. 173–175° (lit.[25] 173.5–174.5°).

1,1,1,4,4,4-Hexaphenylbutane.—Into a 250-ml., three-necked flask equipped with reflux condenser, mechanical stirrer, addition funnel, and gas inlet tube was placed a solution of 1.65 g. (0.004 mole) of 3,3,3-triphenylpropyl iodide in 50 ml. of anhydrous benzene–dibutyl ether (1:1), and 0.24 g. (0.01 mole) of magnesium. The mixture was stirred rapidly for 2 hr. under an atmosphere of nitrogen. A solution of 1.30 g. (0.004 mole) of triphenylmethyl bromide in 50 ml. of anhydrous benzene was added and stirring was continued for an additional 24 hr. at room temperature. The flask was placed in an ice bath and the mixture was acidified with dilute sulfuric acid. The benzene–dibutyl ether layer was separated, washed with dilute aqueous sodium hydroxide and water, and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave 0.85 g. (43%) of product, m.p. 287° after two recrystallizations from benzene.

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