phenylhydrazone by the addition of 2,4-dinitrophenylhydrazine sulfate solution to ethanolic solutions of the fractions. After chromatography on alumina followed by two crystallizations from ethyl acetate–95% ethanol this was obtained as deep orange needles, m.p. 248.5–249° (dec.),[48] undepressed on admixture with an authentic sample.

(48) C. F. H. Allen, D. M. Young and M. R. Gilbert, J. Org. Chem., **2**, 235 (1937), give m.p. 250° (dec.).

Free Radical Rearrangements in the Decarbonylation of Aldehydes[1a]

BY DAVID Y. CURTIN[1b] AND MARVIN J. HURWITZ

The peroxide-catalyzed free radical decarbonylation of aldehydes has been used to study the 1,2-rearrangements of four free radicals. β,β,β-Triphenylpropionaldehyde when heated with di-t-butyl peroxide has been found to yield only the rearranged hydrocarbon, 1,1,2-triphenylethane. α-Methyl-β,β,β-triphenylpropionaldehyde also gave only rearranged products, 1,1,2-triphenylpropane and 1,1,2-triphenyl-1-propene in approximately equal amounts. β-p-Anisyl-β-phenylpropionaldehyde gave predominately 1-p-anisyl-1-phenylethane with the carbon skeleton unrearranged. β,β-Diphenylbutyraldehyde yielded as the sole product 2,3-dibenzyl-2,3-diphenylbutane, dimer of the rearranged radical. The scope of the synthesis of aldehydes by the reaction of α-chloromercurialdehydes with alkyl chlorides has been extended and stannic chloride has been found to be an effective catalyst in at least one case where the reaction otherwise fails.
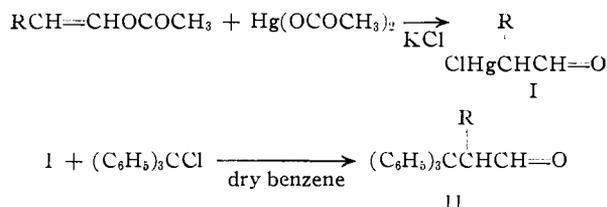
In the course of a general program of study of stereospecific rearrangements it was desirable to examine those involving free radical intermediates. It was first necessary to discover a rearrangement adaptable to this study. A part of this preliminary investigation is described here.

Only a few cases of carbon-to-carbon rearrangements in free radical reactions in solution have been reported thus far. Urry and Kharasch[2] have observed partial migration of the phenyl group of the 2-methyl-2-phenylpropyl (neophyl) radical in the reaction of neophyl chloride with phenylmagnesium bromide in the presence of cobaltous chloride. Of the yield of monomeric hydrocarbons obtained, approximately half was unrearranged (t-butylbenzene) while the other half consisted of saturated and unsaturated products from the rearranged (1-benzyl-1-methylethyl) radical. Similar results with the neophyl radical were obtained by Winstein and Seubold,[3] using a new method for the decarbonylation of aldehydes which had previously been carried out by irradiation.[4] β-Phenylisovaleraldehyde was treated with a peroxide catalyst, resulting in the evolution of carbon monoxide and a 70% yield of a 1:1 mixture of t-butylbenzene (unrearranged) and isobutylbenzene (migration of phenyl). Urry and Nicolaides[5] prepared the p-methylneophyl radical by both of the above methods and obtained rearranged products (again approximately 50% rearrangement). No migration of methyl groups was observed in the cobaltous chloride catalyzed reaction

of 2,2-dimethylbutyl (neohexyl) chloride with ethylmagnesium bromide the only products being neohexane and bineohexane.
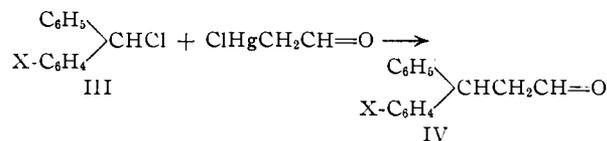
In this study, the peroxide-catalyzed decarbonylation of aldehydes was chosen as the most suitable reaction with which to study the carbon-to-carbon free radical rearrangement.

Synthesis of the Aldehydes Employed.—β,β,β-Triphenylpropionaldehyde (II, R = H) was synthesized by the method of Nesmeyanov, Lutsenko and Tumanova[6] by the treatment of trityl chloride with chloromercuriacetaldehyde (I, R = H) in dry benzene. (I, R = H) was readily prepared by the reaction of vinyl acetate with mercuric acetate and then potassium chloride.

$$RCH{=}CHOCOCH_3 + Hg(OCOCH_3)_2 \xrightarrow[KCl]{} \begin{array}{c} R \\ ClHgCHCH{=}O \\ I \end{array}$$

$$I + (C_6H_5)_3CCl \xrightarrow[\text{dry benzene}]{} \begin{array}{c} R \\ (C_6H_5)_3CCHCH{=}O \\ II \end{array}$$

The method of synthesis was also successful with α-methyl- or ethyl-substituted chloromercurialdehydes to give (II, R = CH₃) or (II, R = C₂H₅).

Benzhydryl chloride (III, X = H) failed to undergo the reaction with (I, R = H) under the above conditions. However, when an equimolar amount of stannic chloride was added to the reaction mixture, reaction proceeded satisfactorily to give a 37% yield of (IV, X = H).

$$\begin{array}{c} C_6H_5 \\ X{\text -}C_6H_4 \end{array}{>}CHCl + ClHgCH_2CH{=}O \longrightarrow \begin{array}{c} C_6H_5 \\ X{\text -}C_6H_4 \end{array}{>}CHCH_2CH{=}O$$

III   IV

(1) (a) Presented in part before the Organic Division of the American Chemical Society in Buffalo in March, 1952. Based on a Dissertation submitted by Marvin J. Hurwitz to Columbia University in partial fulfillment of the requirements for the Ph.D. degree in Chemistry. (b) Department of Chemistry, University of Illinois, Urbana, Illinois.

(2) W. H. Urry and M. S. Kharasch, THIS JOURNAL, **66**, 1438 (1944).

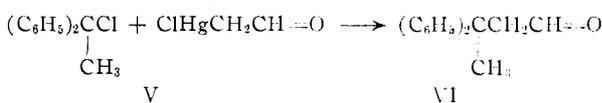(3) S. Winstein and F. H. Seubold, ibid., **69**, 2916 (1947).

(4) E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1946, p. 178 ff.

(5) H. W. Urry and N. Nicolaides, Abstracts of Papers, 118th Meeting, American Chemical Society, 1950, p. 17N.

(6) A. N. Nesmeyanov, I. F. Lutsenko and Z. M. Tumanova, Izvest. Akad. Nauk S.S.R.R. Otdel Khim. Nauk, 601 (1949) [C. A., **44**, 7225c (1950)].

When benzhydryl chloride, *p*-substituted by a single methoxyl group (III, X = CH₃O), was employed, the reaction went smoothly with no added catalyst to give (IV, X = CH₃O) in 70% yield.

The coupling reaction of α,α-diphenylethyl chloride (V) with (I, R = H) gave low yields of (VI), presumably because of the tendency of (V) to undergo dehydrohalogenation. No significant increase in the yield of VI was obtained when

$$(C_6H_5)_2CCl + ClHgCH_2CH=O \longrightarrow (C_6H_5)_2CCH_2CH=O$$
$$\qquad | \qquad\qquad\qquad\qquad\qquad\qquad\qquad |$$
$$\qquad CH_3 \qquad\qquad\qquad\qquad\qquad\qquad CH_3$$
$$\qquad\quad V \qquad\qquad\qquad\qquad\qquad\qquad VI$$

stannic chloride was used in the reaction, the dehydrohalogenation reaction apparently having been catalyzed to approximately the same degree as the coupling.
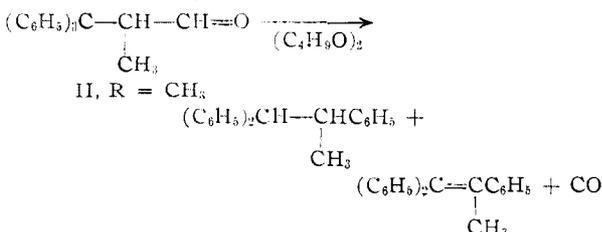
The fact that trityl chloride and *p*-methoxybenzhydryl chloride react with chloromercuriacetaldehyde whereas benzhydryl chloride is stable under the same conditions suggests that the reaction involves a carbonium-type intermediate. The effect of stannic chloride on the reaction of benzhydryl chloride may be to promote the ionization of the chloride or to take part in an exchange reaction with the chloromercurialdehyde leading to an organotin reagent or both. Preliminary attempts to carry out the reaction of *t*-butyl chloride with chloromercuriacetaldehyde in the presence of stannic chloride have been unsuccessful.

The Decarbonylation Reaction.—The four aldehydes, (II, R = H), (II, R = CH₃), (IV, X = CH₃O) and (VI) were decarbonylated by the procedure of Winstein and Seubold.[3,7]

Decarbonylation of (II, R = H) gave only the rearranged saturated hydrocarbon, 1,1,2-triphenylethane and recovered aldehyde.
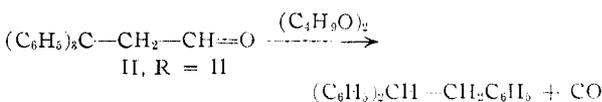
$$(C_6H_5)_3C-CH_2-CH=O \xrightarrow{(C_4H_9O)_2}$$
$$\qquad\qquad II, R = H$$
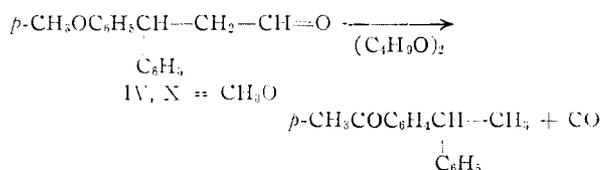$$\qquad\qquad\qquad\qquad (C_6H_5)_2CH-CH_2C_6H_5 + CO$$

From the decarbonylation of (II, R = CH₃), two hydrocarbons, 1,1,2-triphenylpropane and 1,1,-2-triphenylpropene, were obtained in approximately equal amounts. (Both have skeletons formed by rearrangement with migration of phenyl.) The only other material isolated was unreacted aldehyde.
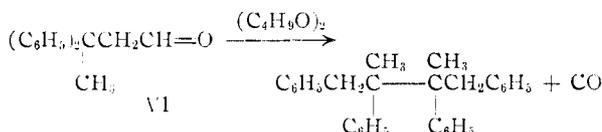
$$(C_6H_5)_3C-CH-CH=O \xrightarrow{(C_4H_9O)_2}$$
$$\qquad\qquad | $$
$$\qquad\quad CH_3$$
$$\qquad II, R = CH_3$$
$$\qquad\qquad (C_6H_5)_2CH-CHC_6H_5 +$$
$$\qquad\qquad\qquad\qquad\qquad | $$
$$\qquad\qquad\qquad\qquad CH_3$$
$$\qquad\qquad\qquad (C_6H_5)_2C=CC_6H_5 + CO$$
$$\qquad\qquad\qquad\qquad\qquad\qquad | $$
$$\qquad\qquad\qquad\qquad\qquad CH_3$$

IV (X = CH₃O), on reaction with di-*t*-butyl peroxide gave an oil which was shown by its infrared spectrum to consist of more than 85%
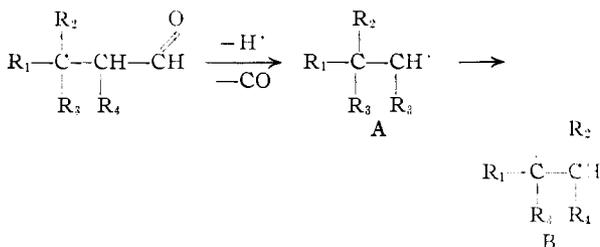
of 1-*p*-anisyl-1-phenylethane (carbon skeleton unrearranged). The reaction may be interpreted as having proceeded largely either without rearrangement or with migration of hydrogen. This point is being further investigated.

$$p\text{-}CH_3OC_6H_4CH-CH_2-CH=O \xrightarrow{(C_4H_9O)_2}$$
$$\qquad\qquad | $$
$$\qquad\quad C_6H_5$$
$$\qquad IV, X = CH_3O$$
$$\qquad\qquad p\text{-}CH_3OC_6H_4CH-CH_3 + CO$$
$$\qquad\qquad\qquad\qquad\qquad | $$
$$\qquad\qquad\qquad\qquad\qquad C_6H_5$$

VI gave, in addition to recovered starting material, only 2,3-dimethyl-1,2,3,4-tetraphenylbutane (presumably formed by dimerization of the radical arising from migration of phenyl).

$$(C_6H_5)_2CCH_2CH=O \xrightarrow{(C_4H_9O)_2}$$
$$\qquad | $$
$$\quad CH_3$$
$$\qquad VI$$
$$\qquad\qquad\qquad CH_3 \quad CH_3$$
$$\qquad\qquad\qquad | \qquad\quad | $$
$$\qquad\qquad C_6H_5CH_2C-CCH_2C_6H_5 + CO$$
$$\qquad\qquad\qquad | \qquad\quad | $$
$$\qquad\qquad\qquad C_6H_5 \quad C_6H_5$$

The probable mechanism of this type of radical rearrangement has been indicated by Winstein and Seubold.[3,8] That part of the mechanism necessary for the present discussion is given below.

$$\begin{matrix} R_2 & O & & R_2 \\ | & \nearrow\!\!/ & -H\cdot & | \\ R_1-C-CH-CH & \xrightarrow{-CO} & R_1-C-CH\cdot & \longrightarrow \\ | \quad | & & | \quad | \\ R_3 \ R_4 & & R_3 \ R_4 \\ & A & & \end{matrix}$$

$$\begin{matrix} & R_2 \\ & | \\ R_1-C-CH \\ & | \quad | \\ & R_3 \ R_4 \\ & B \end{matrix}$$

The factor which determines the fraction of rearranged product is the rate of rearrangement of A to B compared to the rates of competing reactions of A such as chain propagation by reaction with aldehyde, or chain termination by dimerization or disproportionation. It is apparent that the rearrangement can receive additional driving force by any change which stabilizes radical B or destabilizes A with respect to B.

Table I summarizes the work on free radical rearrangements of the type under consideration which have been studied thus far.

It can be seen that the driving force obtained by the transformation of a primary to the more stable tertiary radical is insufficient for the migration of methyl or ethyl (example A) but large enough for partial migration of phenyl (example C). In examples D, E and F the driving force is sufficient for essentially complete rearrangement. Example

(7) In our decarbonylations only 25–40% of the theoretically possible carbon monoxide was evolved, after which reaction virtually stopped. Addition of more di-*t*-butyl peroxide failed to cause further reaction. Dr. W. H. Urry has very kindly pointed out that this effect may be due to a gradual lowering of the reflux temperature by the formation of low-boiling products (acetone and *t*-butanol).

(8) It should be pointed out that the rearrangements of aldehydes (II, R = CH₃) and VI must differ in a significant way from the decarbonylations of (II, R = H) and (IV, R = CH₃O), as well as the reactions studied by Winstein and Urry. The monomeric hydrocarbons formed by disproportionation of the rearranged radical from (II, R = CH₃) and the dimer from VI appear to be products of a chain termination step and the fact that they (rather than the saturated hydrocarbon to be expected from the propagation step) are formed suggests that the termination step almost always competes successfully with propagation. This means that these reactions have degenerated to reactions which, although no longer chain reactions, are very similar in other respects to the chain reactions studied. This does not change the remainder of the discussion in any essential way. We are indebted to Dr. W. H. Urry for valuable discussion of these points.

TABLE I

REARRANGEMENTS IN FREE RADICAL SYSTEMS

	Initial radical	Rearranged radical	Migrating group	Change	Rearrangement, %
A	C_2H_5 ⎮ $(CH_3)_2\overset{.}{C}CH_2\cdot$	$(CH_3)_2\overset{.}{C}CH_2CH_2CH_3$	CH_3CH_2 (or CH_3)	1° → 3° alkyl	0[5]
B	Ph ⎮ $CH_3OC_6H_4\overset{.}{C}HCH_2\cdot$	$CH_3OC_6H_4\overset{.}{C}HCH_2Ph$ or Ph ⎮ $CH_3OC_6H_4\overset{.}{C}—CH_3$	C_6H_5 H	1° → 2° benzyl 1° → 3° benzhydryl	< 15[a] > 85[a]
C	Ph ⎮ $(CH_3)_2C—CH_2\cdot$	$(CH_3)_2\overset{.}{C}—CH_2Ph$	C_6H_5	1° → 3° alkyl	50[2,3,5]
D	$(Ph)_2C—CH_2\cdot$ ⎮ CH_3	$Ph\overset{.}{C}—CH_2Ph$ ⎮ CH_3	C_6H_5	1° → 3° benzyl	100[a]
E	$(Ph)_3C—CH\cdot$ ⎮ CH_3	$(Ph)_2\overset{.}{C}—CHPh$ ⎮ CH_3	C_6H_5	2° → 3° benzhydryl	100[a]
F	$(Ph)_3C—CH_2\cdot$	$(Ph)_2\overset{.}{C}—CH_2Ph$	C_6H_5	1° → 3° benzhydryl	100[a]

[a] Present work.

B which involves the change from primary to secondary benzyl should be intermediate between A and C. In this case rearrangement with migration of phenyl may have occurred to a slight extent (< 15%). However, the principal reaction involved either migration of hydrogen (with a change from a primary to a tertiary benzhydryl radical) or no rearrangement of any kind. This point is being investigated further.

It is not yet clear to what extent the driving forces for rearrangements C, D, E and F come from relief of steric strain present in the initial radicals rather than more favorable distribution of the odd electron in the product radicals. It may be noted that rearrangement might occur simultaneously with loss of carbon monoxide. However, even if this should be the case the arguments used in the discussion of Table I still apply in a modified form.

Experimental[9]

Preparation of Enol Acetates.—The procedure followed was in general that employed by Bedoukian[10] for the preparation of isobutenyl acetate. Two moles of the aldehyde which had been dried over sodium sulfate and distilled, 306 g. (3.0 moles) of acetic anhydride, and 24 g. (0.25 mole) of freshly fused potassium acetate were refluxed vigorously for eight hours, cooled, washed with 5% sodium carbonate solution and with water. The resultant oil was dried over magnesium sulfate and distilled through a packed column of approximately five theoretical plates.

(a) **1-Propenyl Acetate.**—Propionaldehyde, b.p. 49–50°, was used in the above procedure modified as follows. After refluxing, the solution was distilled slowly through a packed column. After the unreacted propionaldehyde had been distilled, the fraction boiling between 80 and 118° was collected, and that fraction was washed, dried and distilled as described above. The yield of the fraction boiling at 104–106° was 24 g. (12%), $n^{25.8}D$ 1.4090, $n^{19}D$ 1.4118.

Anal. Calcd. for $C_5H_8O_2$: C, 60.0; H, 8.0. Found: C, 59.7; H, 8.2.

(b) **1-Butenyl Acetate.**—The yield of the fraction boiling at 122–125°, based on 144 g. (2.0 moles) of starting n-butyraldehyde, b.p. 75–76°, was 73 g. (32%), $n^{20}D$ 1.4170.

(9) All melting points are corrected. Microanalyses were carried out by the Clark Microanalytical Laboratories, the Schwarzkopf Microanalytical Laboratories and Mrs. K. Pih and Mrs. E. Fett of the University of Illinois Microanalytical Laboratory.

(10) P. Z. Bedoukian, THIS JOURNAL, 66, 1325 (1944).

Anal. Calcd. for $C_6H_{10}O_2$: C, 63.2; H, 8.8. Found: C, 63.2; H, 8.9.

Preparation of Chloromercurialdehydes.—The procedure followed was an adaptation of that employed by Nesmeyanov[6] in making chloromercuriacetaldehyde. To 450 ml. of water was added 96 g. (0.3 mole) of mercuric acetate and the mixture was shaken to effect as complete solution as possible. To this mixture was added 0.3 mole of the enol acetate. To the solution 22.8 g. (0.3 mole) of potassium chloride was added and the flask shaken vigorously. The copious white precipitate of chloromercurialdehyde was washed with water and dried for several hours in an oven.

(a) **Chloromercuriacetaldehyde** (I, R = H).—This compound was dried at 80° for four hours. The yield of (I, R = H), m.p. 129–130° (dec.), based on 25.8 g. (0.3 mole) of vinyl acetate, was 73 g. (87%).

(b) **α-Chloromercuripropionaldehyde** (I, R = CH_3).—Since this substance tended to come out of solution as an oil, a modified procedure was used in its isolation. To the chilled solution of acetoxymercuriacetaldehyde in 250 ml. of water was added slowly the potassium chloride in 200 ml. of cold water until a trace of oil appeared. This was removed and triturated until crystalline after which it was used to seed the remainder of the solution. The product was dried under vacuum at room temperature for several days. The yield of (I, R = CH_3), m.p. 60–70° (dec.), from 30.0 g. (0.3 mole) of 1-propenyl acetate was 63 g. (71%).

Anal. Calcd. for C_3H_5OClHg: C, 12.3; H, 1.7; Cl, 12.1. Found: C, 12.2; H, 1.6; Cl, 11.8.

(c) **α-Chloromercuributyraldehyde** (I, R = C_2H_5).—Since this compound separated as an oil initially, the precipitation procedure above was used. The yield of (I, R = C_2H_5), m.p. 93–96° (dec.), from 34.2 g. (0.3 mole) of 1-butenyl acetate, was 85 g. (92%).

Anal. Calcd. for C_4H_7OClHg: C, 15.6; H, 2.3; Cl, 11.5. Found: C, 15.5; H, 2.4; Cl, 11.4.

Preparation of Aldehydes.—The coupling procedure used was a modification of that employed by Nesmeyanov[6] in making β,β,β-triphenylpropionaldehyde. Under strictly anhydrous conditions, 0.3 mole of the substituted chloride was dissolved in 600 ml. of dry benzene. To this solution was added with stirring 0.3 mole of the chloromercurialdehyde. The mixture was stirred at room temperature overnight and then refluxed for 2 hours and cooled. The benzene solution was filtered to remove the insoluble mercuric salts, then washed repeatedly with 10% sodium carbonate until all the mercuric salts, which had been precipitated by the washing, were removed. The solution was then washed with water and filtered to remove any suspended particles. The benzene was distilled, leaving an anhydrous residue.

(a) **β,β,β-Triphenylpropionaldehyde** (II, R = H).—The triphenylmethyl chloride used in this synthesis had been freshly prepared from triphenylcarbinol and acetyl chlo-

ride,[11] and melted at 111-112°. Upon the addition of (I, R = H) (84 g., 0.30 mole) to the benzene solution of trityl chloride (84 g., 0.30 mole), there was produced an immediate bright yellow color which persisted throughout the reaction. The product was recrystallized from hexane and then from methanol. The yield of (II, R = H), m.p. 99.5-102°, was 60 g. (65%). The oxime was prepared and its m.p. of 187-191° agreed with that previously reported.[12]

(b) β-p-Anisyl-β-phenylpropionaldehyde (IV, X = CH₃-O).—p-Methoxybenzhydryl chloride, m.p. 62-63°, was prepared from p-methoxybenzhydrol[13] with hydrogen chloride gas.[14] In the reaction with choromercuriacetaldehyde the solution immediately became bright orange, then bright yellow and finally faded after a few hours. The residue after removal of the benzene was a yellow oil which was twice distilled under vacuum. The yield of colorless liquid, b.p. 206-209° (13 mm.), $n^{25.5}D$ 1.5786, $n^{23.6}D$ 1.5773 from 70 g. (0.3 mole) of p-methoxybenzhydryl chloride and 84 g. (0.3 mole) of (I, R = H) was 50 g. (70%). The aldehyde solidified in the refrigerator but remelted when brought to room temperature.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 80.0; H, 6.7. Found: C, 80.1; H, 6.7.

The 2,4-dinitrophenylhydrazone[15] was bright yellow and melted at 153.5-155°.

Anal. Calcd. for $C_{22}H_{20}O_5N_4$: C, 62.9; H, 4.8; N, 13.3. Found: C, 63.2; H, 4.6; N, 12.7.

(c) β,β-Diphenylpropionaldehyde (IV, X = H). (1) Attempted Preparation by Above Procedure.—The benzhydryl chloride, b.p. 160-161° (14 mm.), $n^{23}D$ 1.5944, used in this synthesis had been freshly prepared from benzhydrol by treatment with hydrogen chloride gas.[12] No color was produced upon the addition of (I, R = H) to the benzene solution. The residue from the reaction was taken up in petroleum ether, from which a solid crystallized melting at 108-109°. Infrared analysis of this solid gave absorption peaks at 6.22, 6.68 and 9.27 μ (S), showing the presence of phenyl groups and a possible ether linkage only. This and the analysis indicated the compound to be dibenzhydryl ether.

Anal. Calcd. for $C_{26}H_{22}O$: C, 89.2; H, 6.3. Found: C, 89.1; H, 6.4.

Mixed melting points with dibenzhydryl ether, m.p. 108-109°, made by treating benzhydrol with phosphoric acid,[16] showed no depression. The yield of the ether was 50 g. (95%). The reaction was repeated, this time refluxing overnight, and the ether was again the only product obtained; no coupling had taken place.

(2) Preparation Using Stannic Chloride.—The above general procedure was modified as follows: After the addition of all the reactants to the flask, 27.7 ml. (0.33 mole) of anhydrous stannic chloride was added dropwise, with stirring, to the mixture which became warm and darkened. After one hour stirring, during which time the mixture cooled to room temperature, 200 ml. of water was added slowly and the layers separated. The benzene solution was then washed and distilled as above. The residue from the reaction was a dark oil which was twice distilled under vacuum. The yield of colorless liquid, b.p. 141-144° (1.4 mm.), from 61 g. (0.3 mole) of benzhydryl chloride and 84 g. (0.3 mole) of (I, R = H), was 23.5 g. (37%), $n^{20}D$ 1.5830. The aldehyde crystallized in the refrigerator but remelted when brought to room temperature.

Anal. Calcd. for $C_{15}H_{14}O$: C, 85.7; H, 6.7. Found: C, 85.9; H, 6.7.

The 2,4-dinitrophenylhydrazone[15] was bright orange-yellow and melted at 177-178°.

Anal. Calcd. for $C_{21}H_{18}O_4N_4$: C, 64.6; H, 4.6; N, 14.4. Found: C, 64.8; H, 4.7; N, 14.3.

(d) α-Methyl-β,β,β-triphenylpropionaldehyde (II, R = CH₃).—The reaction color in this case was a bright yellow which persisted throughout the stirring period. The resi-

due from the reaction was an impure solid which contained the aldehyde, as determined by the 2,4-dinitrophenylhydrazone, but which also contained large amounts of triphenylcarbinol which could not be removed by crystallization. The semicarbazone derivative also could not be obtained pure. An attempt to employ the procedure of Djerassi[17] to regenerate the aldehyde from its 2,4-dinitrophenylhydrazone using pyruvic acid was unsuccessful. The procedure of Lederer and Nachmias for the quantitative regeneration of aldehydes from their derivatives with Girard reagent[18] was successfully employed. Successive 20-g. portions of the crude residue were refluxed for one hour in 200 ml. of absolute ethanol with 20 g. (0.12 mole) of Girard T reagent, m.p. 188-190°. The clear solution was cooled and poured into 2 l. of ice-water and the water solution extracted repeatedly with ether until clear. To this solution was added 100 ml. of concentrated hydrochloric acid. There was immediate separation of the aldehyde. The solution was allowed to stand overnight, after which time it was extracted with ether. The ether extract was washed with 10% sodium carbonate solution, then with water, and dried over magnesium sulfate and the ether removed. The residue crystallized in the flask and was recrystallized from hexane and then from methanol. The yield of material, m.p. 89-90°, from 84 g. (0.3 mole) of trityl chloride and on 88 g. (0.3 mole) of (I, R = CH₃), was 29 g. (32%).

Anal. Calcd. for $C_{22}H_{20}O$: C, 88.0; H, 6.7. Found: C, 88.1; H, 6.9.

The 2,4-dinitrophenylhydrazone[15] was yellow-orange and melted at 190-191°.

Anal. Calcd. for $C_{28}H_{24}O_4N_4$: C, 70.0; H, 5.0; N, 11.7. Found: C, 70.0; H, 5.4; N, 12.1.

(e) α-Ethyl-β,β,β-triphenylpropionaldehyde (II, R = C₂H₅).—The reaction color in this case was a bright yellow which persisted throughout the stirring period. The aldehyde was isolated from the crude residue using Girard reagent as described in the previous synthesis. The yield of material, m.p. 101-102.5°, from 84 g. (0.3 mole) of trityl chloride and 92 g. (0.3 mole) of (I, R = C₂H₅), was 19 g. (20%).

Anal. Calcd. for $C_{23}H_{22}O$: C, 87.9; H, 7.0. Found: C, 88.0; H, 7.1.

The 2,4-dinitrophenylhydrazone[15] was yellow-orange and melted at 199-200°.

Anal. Calcd. for $C_{29}H_{26}O_4N_4$: C, 70.4; H, 5.3; N, 11.3. Found: C, 70.6; H, 5.3; N, 11.3.

(f) β,β-Diphenylbutyraldehyde (VI).—Diphenylmethylcarbinol, m.p. 80-81°, was prepared in 90% yield by the method of Klages.[19] Since the corresponding chloride, α,α-diphenylethyl chloride, eliminates hydrogen chloride rapidly at room temperature, it was prepared in the cold by an adaptation of the procedure of Schoepfle and Ryan.[20] A mixture of 120 g. (0.6 mole) of the carbinol, 275 ml. of benzene, and 180 g. of calcium chloride was cooled in an ice-salt-bath and dry hydrogen chloride gas was bubbled through for several hours until a clear solution of the chloride in benzene resulted. The solution was then filtered into a flask immersed in an ice-salt-bath, and dry nitrogen was bubbled through it vigorously for several hours to remove the excess hydrogen chloride. The solution was then added directly to a mixture of 925 ml. of dry benzene and 280 g. (1.0 mole) of (I, R = H) which was stirred and cooled with an ice-salt-bath. A pale yellow color developed which soon faded. The mixture was allowed to warm to room temperature slowly and was stirred overnight. The reaction mixture was washed, the solvent distilled and the aldehyde was isolated from the crude residue using Girard reagent, all as described previously. The yield of colorless liquid, b.p. 133-135° (0.6 mm., under nitrogen), $n^{20}D$ 1.5769, was 10 g. (7.5%), based on the carbinol. The use of stannic chloride as a catalyst in this reaction resulted in a similar yield (8.0%).

(11) W. E. Bachmann, *Org. Syntheses*, **23**, 100 (1943).

(12) L. Hellerman and R. L. Garner, THIS JOURNAL, **68**, 819 (1946).

(13) We are indebted to Mr. Douglas Wiley for a gift of this substance.

(14) M. P. Montagne, *Rec. trav. chim.*, **25**, 403, 408 (1906).

(15) Shriner and Fuson, "Identification of Organic Compounds," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1940, p. 143.

(16) D. Y. Curtin and S. Leskowitz, THIS JOURNAL, **73**, 2632 (1951).

(17) C. Djerassi, *ibid.*, **71**, 1008 (1949).

(18) E. Lederer and G. Nachmias, *Bull. soc. chim. France*, [5] **16**, 400 (1949). Girard and Sandulesco, *Helv. Chim. Acta*, **19**, 1095 (1936), had previously erroneously stated that this reagent could not be used for the regeneration of aldehydes because of the difficulty in decomposing such derivatives.

(19) A. Klages, *Ber.*, **35**, 2646 (1902).

(20) C. S. Schoepfle and J. D. Ryan, THIS JOURNAL, **54**, 3692 (1932).

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.7; H, 7.1. Found: C, 85.7; H, 7.1.

The 2,4-dinitrophenylhydrazone[15] was yellow-orange and melted at 164–165°.

Anal. Calcd. for $C_{22}H_{20}N_4O_4$: C, 65.3; H, 5.0; N, 13.9. Found: C, 64.9; H, 4.8; N, 13.6.

The structure of this aldehyde was confirmed by oxidation with basic permanganate,[21] to the corresponding acid which melted at 98.5–101°, in agreement with that previously reported[22] for β,β-diphenylbutyric acid.

Decarbonylation of Aldehydes. (a) β,β,β-Triphenylpropionaldehyde (II, R = H).—Into a 250-ml. flask, equipped with a dropping funnel, a stirrer and a condenser, was placed 60 g. (0.21 mole) of (II, R = H). The system was flushed with a stream of dry nitrogen. The flask was immersed in a stirred oil-bath maintained at 140°. To the top of the condenser was connected a rubber tube leading to a graduated cylinder which was filled with water and inverted over a water trough. To the molten aldehyde was then added 3.50 g. (0.024 mole) of di-*t*-butyl peroxide, $n^{25.6}D$ 1.3864, $n^{21.4}D$ 1.3884, which had been purified by vacuum distillation. There was an almost immediate and rapid evolution of carbon monoxide gas which was collected in the cylinder. Over the course of the reaction there was a gradual diminution of the rate of gas evolution which was not affected by periodic addition of a total of 21.50 g. (0.216 mole) more of the peroxide catalyst. After 10 hours, 1300 ml. of gas had been collected, corresponding to approximately 26% completion, and the rate had decreased almost to zero. This procedure was repeated at a bath temperature of 110° and at 130°, with varying amounts of peroxide but the same decrease in rate was observed. The reaction flask was removed from the oil-bath and allowed to stand overnight. The presence of carbon monoxide in the collected gas was confirmed by its immediate reduction of a saturated palladous chloride solution to palladium black.

The cooled reaction mixture consisted of a light yellow liquid from which had crystallized 25.0 g. (0.0875 mole) of unreacted aldehyde, m.p. 96–100° (mixed m.p. with pure aldehyde undepressed). The liquid was distilled under vacuum to remove the *t*-butyl alcohol and the excess peroxide. The oily residue was dissolved in a small volume of hexane and 7.3 g. (0.0255 mole) more of crystallized aldehyde was recovered (m.p. 96–101°, mixed melting point showed no depression).

After distilling off the hexane, the oily residue was distilled at 16 mm. and three cuts were collected: cut 1 consisted of 2.5 g. of an almost colorless oil, boiling at 216–219°; cut 2, 7.34 g. of a pale yellow oil boiling at 219–221°; cut 3, 4.5 g. of a viscous yellow oil boiling at 221–229°. (The reported boiling points of the expected hydrocarbons are: 1,1,2-triphenylethane, 216° at 14 mm.[23]; 1,1,1-triphenylethane, 205–210° at 18 mm.[24]; triphenylethylene, 220° at 14 mm.).[23] The oils failed to crystallize. Cut 1 gave a correct analysis for a triphenylethane.

Anal. Calcd. for $C_{20}H_{18}$: C, 93.0; H, 7.0. Found: C, 93.0; H, 6.8.

A one-gram aliquot of each distillation cut was then eluted with hexane through a three-inch long column of activated alumina. The elution was continued until the total weight of the material collected became constant. In each case the product was a colorless oil which crystallized upon standing overnight to a solid melting at 50–52°. After recrystallization from ethanol with 90% recovery, the melting point was 51–52.5°. (The reported melting points are: 1,1,2-triphenylethane, 54°; 1,1,1-triphenylethane, 95°; triphenylethylene, 70°.) Pure 1,1,2-triphenylethane, m.p. 52–54°, was prepared by the atmospheric pressure hydrogenation of triphenylethylene at room temperature using a 1/1 ether–ethanol solvent and a platinum catalyst, followed by recrystallization from ethanol. Mixed melting points with several compositions showed no depresson below 51°. By this method, cut 1 was found to contain 90.4% of 1,1,2-triphenylethane; cut 2, 96.0%; and cut 3, 67.6%, making a

total of 12.34 g. (0.0479 mole, 23 mole %) of the rearranged hydrocarbon.

The residue from the distillation was 15 g. of a yellow oil which crystallized on standing to a yellow solid, m.p. 95–110°. A one-gram aliquot portion of this was eluted on an alumina column using benzene. A yellow oil was obtained amounting to 88.0% of the residue, which crystallized to a yellowish solid, m.p. 99–104°; mixed with pure aldehyde showed no depression below 99°. The residue was thus estimated to contain 13.2 g. of aldehyde, making the total amount of recovered aldehyde 45.5 g. (76%). The amount of 1,1,2-triphenylethane based on unrecovered starting material was therefore 98 mole % and the total amount of starting material accounted for, 99%.

(b) α-Methyl-β,β,β-triphenylpropionaldehyde (II, R = CH_3).—The decarbonylation procedure was identical with the one previously described. In this reaction 29.0 g. (0.0967 mole) of (II, R = CH_3) and 3.03 g. (0.0208 mole) of di-*t*-butyl peroxide were used. After seven hours, 840 ml. of carbon monoxide had been collected, corresponding to 36% completion, and the rate of gas evolution had decreased almost to zero.

The cooled reaction flask consisted of a yellow oil which was distilled at 0.8–1.1 mm. Four cuts were collected: cut 1 consisted of 1.55 g. of an almost colorless liquid, b.p. 152–158°; cut 2, 2.4 g. of a b.p. 159–162°; cut 3, 0.85 g. of b.p. at 162–170°; and cut 4, 6.4 g. of a yellowish oil, b.p. 170–193°. A small amount of the oil from cut 2 was dissolved in ethanol from which it crystallized in the refrigerator. This solid was used to seed cuts 1, 2 and 3, which all crystallized rapidly. A one-gram aliquot portion of cut 4 was eluted on alumina as described previously and that cut was thus found to contain 4.0 g. of an oil which, when seeded with crystals from cut 2, crystallized rapidly. The entire solid material was recrystallized from ethanol with 98% recovery giving three fractions of crystals.

The reported melting points for the expected products are: 1,1,1-triphenylpropane, 51°[25]; 1,1,2-triphenylpropane,[26] 73–75°; and 1,1,2-triphenyl-1-propene 92–93°.[25] These three possible hydrocarbons were prepared as described later.

Fraction 1, 0.4 g., m.p. 91–92°, was shown by m.p., mixed m.p. and its infrared spectrum (Fig. 1, curve E) to be 1,1,2-triphenylpropene (Fig. 1, curve B).

Fraction 2, 6.55 g., m.p. 71–72.5°, when mixed with authentic 1,1,2-triphenylpropane showed a slight m.p. depression (m.p. 68–72°). Comparison of its infrared spectrum (Fig. 1, curve F) with those of 1,1,2-triphenylpropane (Fig. 1, curve A) and 1,1,2-triphenylpropene (Fig. 1, curve B) indicated that it was a mixture containing approximately 40% of the triphenylpropane and 60% of the triphenylpropene. For example, the carbon–hydrogen bending region in curve F has both the 6.89 (1451 cm.$^{-1}$) absorption of curve A and the 6.95 (1439 cm.$^{-1}$) absorption of curve B as well developed shoulder. In a known 50–50 mixture of the two hydrocarbons the two bands appeared to be of nearly equal heights.

Fraction 3, 1.65 g., m.p. 71.5–74°, showed a m.p. depression (m.p. 68–72°) with 1,1,2-triphenylpropane and its infrared spectrum (curve D) indicated that it contained about 70% of this hydrocarbon together with 30% of 1,1,2-triphenylpropene.

Since it was desirable to determine if the unrearranged hydrocarbon, 1,1,1-triphenylpropane was present, its spectrum (Fig. 1, curve C) was also obtained. Unfortunately the spectrum has no large absorption where the two rearranged hydrocarbons do not absorb. However, a comparison of the relative heights of the two bands present in curves A and B at 9.74 affords information on this point since the first of these bands is intensified in curve C while the second is absent. An approximate calculation using these ratios indicated that there was no appreciable amount of 1,1,1-triphenylpropane in any of the three fractions.

Thus the total amount of hydrocarbon obtained was 0.0324 mole (33% yield), of which *ca.* 50% was the rearranged hydrocarbon and the other 50% its corresponding olefin. By means of the 2,4-dinitrophenylhydrazone, cut 3 and the residue from the distillation were found to contain a total of 0.050 mole (56% recovery) of the starting aldehyde. The yield based on unrecovered starting material is, there-

(21) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 170.

(22) E. Bergmann, H. Taubadel and H. Weiss, *Ber.*, **64B**, 1493 (1931).

(23) A. Klages and S. Heilmann, *ibid.*, **37**, 1455 (1904).

(24) L. F. Fieser and H. Heymann, THIS JOURNAL, **64**, 376 (1942).

(25) M. Gomberg and L. Cone, *Ber.*, **39**, 2961 (1906).

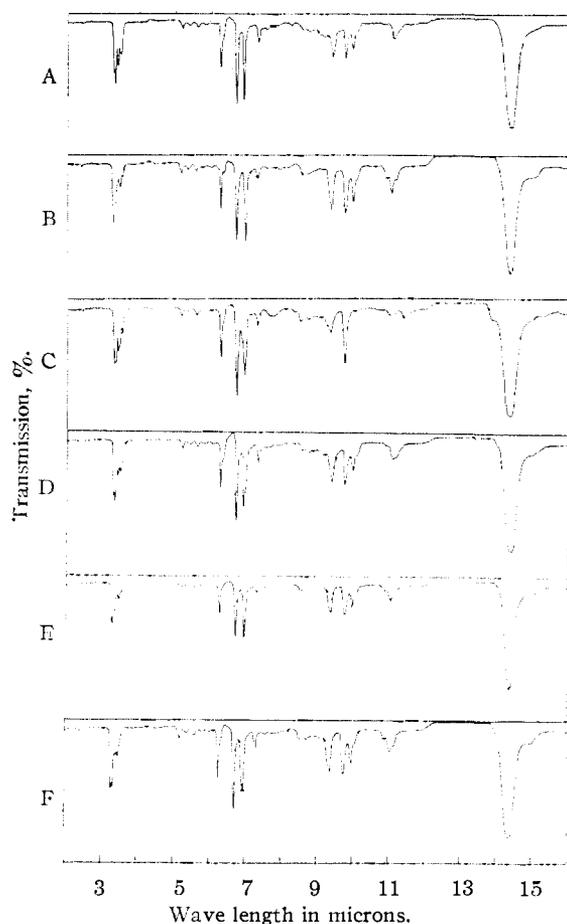(26) W. Schlenk and E. Bergmann, *Ann.*, **463**, 45 (1928).

Fig. 1.—Infrared spectra of approximately 10% solutions in carbon tetrachloride taken with a Baird double beam spectrophotometer with a sodium chloride prism: A, 1,1,2-triphenylpropane; B, 1,1,2-triphenyl-1-propene; C, 1,1,1-triphenylpropane; D, rearrangement product fraction 3; E, product fraction 1; product fraction 2.
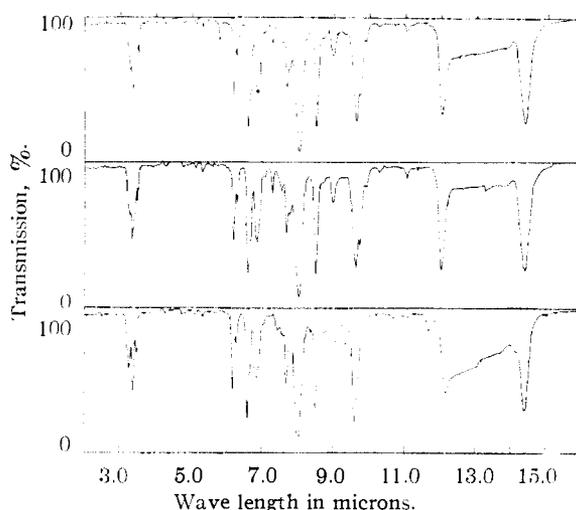

Fig. 2.—Infrared spectra of 10% solutions in carbon tetrachloride taken with a Baird double beam spectrophotometer with a sodium chloride prism: upper curve, 1-p-anisyl-1-phenylethane from the decarbonylation reaction; middle curve, authentic 1-p-anisyl-1-phenylethane; lower curve, 1-p-anisyl-2-phenylethane.

fore, 69% and the total amount of starting material accounted for is 85%.

(c) β-p-Anisyl-β-phenylpropionaldehyde (IV, X = CH$_3$O). —The decarbonylation procedure was identical with those previously described. In this reaction 41.0 g. (0.171 mole) of (IV, X = CH$_3$O) and 2.92 g. (0.020 mole) of di-t-butyl peroxide were used. After seven hours, 1670 ml. of gas had been collected, corresponding to approximately 40% completion and the rate of evolution had decreased almost to zero.

The cooled reaction flask consisted of a light yellow liquid which was distilled at 17–18 mm. Three cuts were collected: cut 1 consisted of 2.16 g. of a colorless liquid, boiling at 182–184°, $n^{24.8}$D 1.5698; cut 2, 11.25 g. of a colorless liquid, boiling at 184–185°, $n^{24.7}$D 1.5700; and cut 3, 17.17 g. of a yellow oil boiling mostly between 219 and 222°. The residue was a small amount of tarry material. Cuts 1 and 2 were combined and redistilled with no significant loss, and the distillate, n^{26}D 1.5690, gave the correct analysis for the isomeric anisylphenylethanes.

Anal. Calcd. for C$_{15}$H$_{16}$O: C, 85.0; H, 7.6. Found: C, 85.0; H, 7.7.

The hydrocarbon fraction was shown to be largely 1-p-anisyl-1-phenylethane by comparison of its infrared spectrum with those of the authentic hydrocarbon and authentic 1-p-anisyl-2-phenylethane (both prepared as described below) (Fig. 2). Inspection of the curves shows that the spectrum of the hydrocarbon product is virtually superimposable on that of the 1-p-anisyl-1-phenyl. Close examination however, shows that the two bands at 9.35 and 11.69 µ which are present in 1-anisyl-2-phenylethane but

absent in spectrum of the unrearranged isomer are present in an embryonic stage in the product curve. It is possible that rearranged hydrocarbon is present to the extent of as much as 15%. The small carbonyl peak present at 5.89 (1700 cm.$^{-1}$) in the decarbonylation product is probably due to traces of unreacted aldehyde.

The amount of 1,1-diarylethane (13 g.) corresponds to a 36% yield. Cut 3 in the distillation above was shown, by treatment with 2,4-dinitrophenylhydrazine, to contain about 95% starting aldehyde (0.068 mole, 40% of aldehyde originally employed) which makes the yield 60% based on unrecovered starting material and the total amount of starting aldehyde accounted for 76%.

(d) β,β-Diphenylbutyraldehyde (IV).—The decarbonylation procedure was the same as above. In this reaction 25.8 g. (0.115 mole) of (IV) and 3.94 g. (0.027 mole) of di-t-butyl peroxide were used. After 8 hours, 850 ml. of carbon monoxide had been collected, corresponding to approximately 31% completion, and the rate of evolution had decreased almost to zero.

When the flask was removed from the oil-bath crystalline material was observed which had remained solid at 140°. The cooled reaction flask was filtered with suction and a high-melting solid was obtained. This solid was recrystallized by dissolving it in a minimum of benzene and adding an equal volume of low-boiling petroleum ether, and 4.5 g. of material, m.p. 223–224°, was thus obtained. The solid gave the correct analysis for a hydrocarbon dimer of the decarbonylated radical.

Anal. Calcd. for C$_{30}$H$_{30}$: C, 92.3; H, 7.7. Found: C, 92.6; H, 8.1.

The material was found by the Rast method to have a molecular weight corresponding to that of a dimeric hydrocarbon.

Anal. Calcd. for C$_{30}$H$_{30}$: mol. wt., 390. Found: mol. wt., 379 ± 14.

(The reported melting points for the possible dimeric hydrocarbons are: 2,2,5,5-tetraphenylhexane, 110°[27]; 3,3,-4,4-tetraphenylhexane, 85–86°.[26,28] Neither of the two possible diastereoisomeric 2,3-dibenzyl-2,3-diphenylbutanes has been reported. The possible monomeric hydrocarbons are all liquids.) This compound was found to be resistant to oxidation either by nitric acid or by potassium permanganate, since a large part of the starting material was recovered unchanged after treatment with either reagent.

The same 2,3-dibenzyl-2,3-diphenylbutane was synthe-

(27) W. Schlenk, J. Appenrodt, A. Michael and A. Thal, *Ber.*, **47**, 478 (1914).

(28) K. Ziegler and B. Schnell, *Ann.*, **437**, 247 (1924).

sized unequivocally (see next section). Mixed melting points of several different compositions with the product of the decarbonylation reaction gave no depression. Infrared spectra of the two materials, taken in Nujol mull, showed them to be identical.

The filtrate from the suction filtration was distilled under nitrogen (0.8–0.9 mm.), yielding 17.1 g. of liquid, b.p. 130–135°, $n^{19.5}$D 1.5775, which was found, from its 2,4-dinitrophenylhydrazone, to be virtually 100% aldehyde (0.076 mole, 66% recovery). The distillation residue was recrystallized from benzene–petroleum ether and 3.0 g. more of the dimeric hydrocarbon was isolated. Thus the total amount of dimer of the rearranged radical obtained was 0.019 mole, which was formed from 0.039 mole of starting aldehyde (34% yield). The yield based on unrecovered starting material is therefore 100% and the total amount of starting material either recovered or rearranged and then dimerized is also 100%.

Preparation of 1,1,2-Triphenyl-1-propene. (a) Phenyldesoxybenzoin.[29]—Benzoin (212 g., 1 mole), 780 g. of dry benzene and 100 g. of 98% sulfuric acid were refluxed for 48 hours with stirring with continuous removal of water formed during the reaction (18 g. collected in all). The mixture was washed with 10% sodium carbonate solution and water and the benzene distilled off. The brown residual solid was extracted with 500 cc. of methanol which removed dark impurities. Recrystallization of the remainder gave 150 g. (55% yield) of white solid, m.p. 133–135°, mixed m.p. with benzoin depressed.

(b) 1,1,2-Triphenyl-2-propanol was prepared in 80% yield from phenyldesoxybenzoin with methylmagnesium iodide by the procedure of Levy.[30]

(c) 1,1,2-Triphenyl-1-propene, m.p. 86–89°, was prepared from the above alcohol in 90% yield by the procedure of Schlenk and Bergmann.[26]

1,1,2-Triphenylpropane, m.p. 72–74°, was prepared in 80% yield by treating benzhydryl sodium with α-phenylethyl chloride according to the method of Bergmann.[31]

1,1,1-Triphenylpropane was prepared in 80% yield by the coupling of triphenylmethyl chloride with ethylmagnesium bromide according to the procedure of Gomberg and Cone.[32] The liquid product, b.p. 178–181° (2.9 mm.), $n^{19.5}$D 1.6172, was used as such in the infrared product analysis of (II, R = CH_3).

Anal. Calcd. for $C_{21}H_{20}$: C, 92.6; H, 7.4. Found: C, 92.8; H, 7.2.

(29) R. Robinson and D. Mercer, U. S. Patent 2,298,169 (1943) [C. A., 37, 1450 (1943)].

(30) J. Levy, Bull. soc. chim., [4] 29, 892 (1921).

(31) E. Bergmann, J. Chem. Soc., 412 (1936).

(32) M. Gomberg and L. H. Cone, Ber., 39, 1466 (1906).

Upon standing, a portion of this oil crystallized. The solid had a melting point of 50–51°, in agreement with that previously reported.[25]

1-p-Anisyl-1-phenylethane which had not previously been reported was prepared by the low pressure reduction with Adams catalyst of 1-p-anisyl-1-phenylethylene.[33] The substance was obtained as a liquid, b.p. 183° (17 mm.), n^{28}D 1.5680.

Anal. Calcd. for $C_{15}H_{16}O$: C, 85.0; H, 7.6. Found: C, 84.8; H, 7.8.

1-p-Anisyl-2-phenylethane, m.p. 60–61°, was prepared by the catalytic hydrogenation with Adams catalyst of p-methoxystilbene.[33]

2,3-Dibenzyl-2,3-diphenylbutene. (a) Benzylmethylphenylcarbinol, m.p. 50–51°, was prepared from benzylmagnesium chloride and acetophenone in 56% yield according to the method of Hell.[34]

(b) α-Benzyl-α-phenylethyl Chloride.—This unstable compound was prepared in the cold by the treatment of 25 g. (0.118 mole) of the above carbinol with hydrogen chloride gas, using the procedure of Schoepfle and Ryan[20] for α,α-diphenylethyl chloride. It was obtained as an anhydrous oil.

(c) 2,3-Dibenzyl-2,3-diphenylbutane.—The chloride obtained from the above procedure was dissolved in 50 ml. of cold dry ether. This solution was added to a mixture of 1.35 g. (0.059 mole) of magnesium and 20 ml. of dry ether, maintained below 0° by means of an ice–salt-bath. The reaction mixture was allowed to warm to room temperature and a small amount of methylmagnesium iodide was added, after which there was a slow formation of a white precipitate. The mixture was stirred at room temperature for four hours, after which time there was a copious white precipitate and no apparent further slight bubbling of the ether solution. The reaction mixture was then decomposed with 10% sulfuric acid, and washed with a 10% sodium carbonate solution and then with water. An insoluble white solid collected between the ether and aqueous layers and was not rejected during the washings. The material was then filtered by suction. The solid material collected, after recrystallization from benzene–petroleum ether, was 7.0 g. (0.018 mole, 30% based on carbinol) of material, m.p. 223–224°. The analysis was in agreement with that for 2,3-dibenzyl-2,3-diphenylbutane.

Anal. Calcd. for $C_{30}H_{30}$: C, 92.3; H, 7.7. Found: C, 92.2; H, 7.7.

URBANA, ILLINOIS

(33) We are indebted to Mr. Arthur Bradley for these compounds.

(34) C. Hell, Ber., 37, 457 (1904).