[CONTRIBUTION FROM NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Free Radical Rearrangements in the Decarbonylation of Aldehydes[1]

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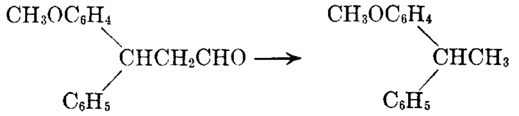
The reaction of β-deutero-β-(*p*-anisyl)-β-phenylpropionaldehyde with di-*t*-butyl peroxide has been found to give decarbonylation without rearrangement of the deuterium atom. A reinvestigation of the decarbonylation of β,β,β-triphenylpropionaldehyde has shown that in addition to the 1,1,2-triphenylethane previously reported there are present lesser amounts of triphenylethylene and 3,3-diphenyl-1-indanone. Decarbonylation of β-(*p*-nitrophenyl)-β,β-diphenylpropionaldehyde proceeded to only a small extent and led to the rearranged olefin, 2-(*p*-nitrophenyl)-1,1-diphenylethylene, as the only product which could be characterized.

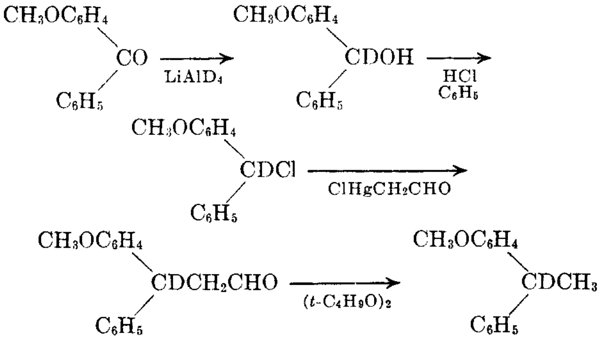
In a previous investigation[3] β,β,β-triphenylpropionaldehyde (I) was found to undergo decarbonylation on treatment with di-*t*-butyl peroxide to yield 1,1,2-triphenylethane (II) with migration of a phenyl group as the only reaction path detected. On the other hand, β-(*p*-anisyl)-β-phenylpropionaldehyde yielded only the unrearranged hydrocarbon, 1-(*p*-anisyl)-1-phenylethane. The present study was initiated to clarify several features of these two reactions.

$$\underset{\text{I}}{(C_6H_5)_3CCH_2CHO} \longrightarrow \underset{\text{II}}{(C_6H_5)_2CHCH_2C_6H_5}$$



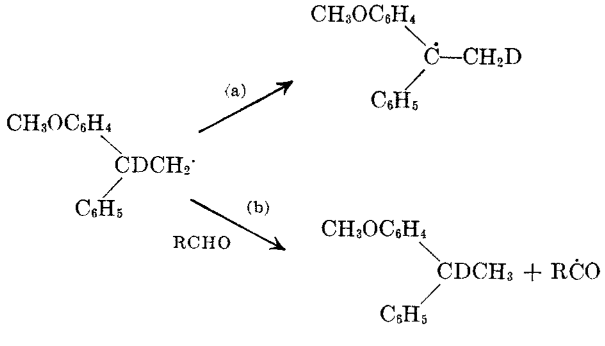
III IV

In view of the observed rearrangement of the triphenylaldehyde I it seemed quite possible that the aldehyde III was also undergoing rearrangement but with the migration of a hydrogen atom. The structure of the product does not distinguish between this possibility and a reaction without rearrangement. The aldehyde III-d was therefore synthesized with a deuterium atom on the β-carbon atom by the same general route employed previously[3] for the undeuterated compound. The steps in the synthesis are shown below. Treatment of the deuterated aldehyde III-d with 10 mole % of di-*t*-butyl peroxide at 140° resulted in the evolution of 40% of the theoretical amount of carbon monoxide. The infrared spectrum of the product mixture indicated that unchanged aldehyde was present to the extent of 50–55% and 46% of it was actually recovered. The only other component found was the hydrocarbon 1-deutero-1-(*p*-anisyl)-1-phenylethane (IV-d), formed without rearrangement of either a phenyl ring or a deuterium atom.



III-d IV-d

The position of the deuterium atom was established with the aid of infrared and nuclear magnetic resonance absorption spectroscopy.[4] It is estimated that within the limits of the method employed not more than 5% of the aldehyde molecules being decarbonylated could have undergone rearrangement of a deuterium atom. However, the extent of rearrangement is probably determined by the relative rates of the two processes shown. It will be seen that path (b) leading to nonrearrangement but not (a) leading to rearrangement should depend



on the aldehyde concentration. Such dependence has been demonstrated experimentally in the decarbonylation leading to the neophyl radical by Seubold.[5] The failure of deuterium to undergo migration is here demonstrated for a medium con-

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[1] Taken from the Ph.D. thesis of James C. Kauer, University of Illinois, 1955.

[2] We are indebted to the Rohm and Haas Co. for a Fellowship held by J. C. K. in 1953–54 and to the E. I. du Pont de Nemours & Co., Inc., for a Grant-in-Aid which supported a part of this work.

[3] D. Y. Curtin and M. J. Hurwitz, *J. Am. Chem. Soc.*, **74,** 5381 (1952).

[4] We are indebted to Dr. H. S. Gutowsky and Dr. Jerry Heeschen for the NMR spectra and for assistance with their interpretation. See H. S. Gutowsky, "Physical Methods of Chemical Analysis," Edited by W. G. Berl, Academic Press, Inc., New York, N. Y., 1956, pp. 362, 363.

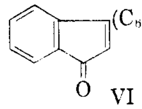
[5] F. H. Seubold, Jr., *J. Am. Chem. Soc.*, **75,** 2532 (1953).

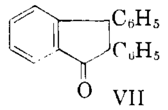
sisting of undiluted aldehyde, conditions less favorable to rearrangement than others which are attainable.[5] A second point to be considered is that path (a) but not (b) might be expected to be subject to a primary isotope effect.[6] It follows that hydrogen migration in the undeuterated radical obtained from the aldehyde (III) might be appreciably more important than deuterium migration in the corresponding deuterated radical. It is clear, however, that even with these complications hydrogen migration is not the dominant reaction of the intermediate radical from the aldehyde (III). An investigation of the behavior of the 2-phenylethyl-1-C^{14} radical has been reported by Slaugh[7] who found that in *o*-dichlorobenzene there was as much as 5% of phenyl migration but that there was no significant amount of hydrogen migration.

The reinvestigation of the decarbonylation of β,β,β-triphenylpropionaldehyde (I) previously reported[3] to give only 1,1,2-triphenylethane (II) was prompted by the failure to observe products of a termination step even though 10 mole % of di-*t*-butyl peroxide was employed as initiator. A second point was that the reaction went to only about 25% completion in contrast to the 90% of decarbonylation of β-phenylisobutyraldehyde observed by Winstein and Seubold[8] under otherwise comparable conditions. When the aldehyde (I) was treated with 20 mole % of di-*t*-butyl peroxide in a bath at 140° under reflux for twenty-eight hours, 32% of the theoretical amount of carbon monoxide was liberated, and in addition to 40% of recovered aldehyde there was obtained in agreement with the previous work[3] 20% of the rearranged triphenylethane (II). There were also formed 4% of triphenylethylene (V) and 3% of a ring-closed product, 3,3-diphenyl-1-indanone (VI). The indanone (VI) was identical with that prepared from triphenylpropionic acid and sulfuric acid by Moureu, Dufraisse, and Dean.[9] The infrared spectrum (in carbon tetrachloride) of triphenylethylene (V) is nearly superimposable on that of the triphenylethane (II), but the unsaturated hydrocarbon (V) could be readily determined quantitatively by the ultraviolet absorption at 298 mμ. The presence of weak absorption in the C-methyl deformation region suggested that as much as 10% of the hydrocarbon fraction might be the unrearranged hydrocarbon, 1,1,1-triphenylethane, but no more definite evidence for its presence was obtained.

The formation of the indanone (VI) is of interest since it apparently came from a radical version of the Friedel-Crafts acylation. Another example has been reported by Denny and Klemchuk.[10] Other related radical cyclizations have been described.[11] With the hope that the temperature dependence of the rates of cyclization and decarbonylation might be such that cyclization should be favored at lower temperatures, the aldehyde (I) was treated with dibenzoyl peroxide at 80°. Under conditions in which 35% of aldehyde failed to react about 13% decarbonylation and less than 9% indanone formation were observed.

$$\mathrm{I} \xrightarrow[(t\text{-}C_4H_9O)_2]{} \mathrm{II} + \underset{\mathrm{V}}{(C_6H_5)_2C{=}CHC_6H_5} +$$


VI


VII

It seemed possible that accumulation of acetone and *t*-butyl alcohol from the decomposition of di-*t*-butyl peroxide might be responsible for the decrease in rate after 25% reaction.[12] For this reason the decarbonylation of the aldehyde (I) was carried out as before except that a steam-jacketed condenser was used to permit the removal of low-boiling products as they were formed. A run carried out with 15 mole % of di-*t*-butyl peroxide for twenty-three hours gave 72% recovery of the aldehyde (I) together with 20 mole % of carbon monoxide. There were obtained 7 mole % of the triphenylethane (II), 3 mole % of triphenylethylene (V), and 3 mole % of the indanone (VI). Finally a reaction was carried out with a full mole of di-*t*-butyl peroxide per mole of aldehyde over a five-day period with a steam-jacketed condenser. No aldehyde was recovered. Only 50 mole % of carbon monoxide was obtained, together with 29 mole % of the triphenylethane (I), 12 mole % of triphenylethylene (V), and 25 mole % of the indanone (VI). In addition, there was a small amount of a substance believed to be 2,3-diphenyl-2-indene-1-one (VII) which was not obtained in pure form but which had infrared and ultraviolet spectra very similar to the spectra of an authentic sample of this substance. It seems likely that the indenone (VII) came from a radical rearrangement of the indanone (VI). The indanone (VI) had previously been reported[13] to undergo a thermal rearrangement to VII. Furthermore, the rearrangement of 3,3,5,6-tetraphenylindanone to 2,3,5,6-tetraphenylindene-1-one on heating with sulfur had been observed.[14]

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[6] K. Wiberg, *Chem. Revs.*, **55**, 713 (1955).

[7] L. H. Slaugh, *J. Am. Chem. Soc.*, **81**, 2262 (1959).

[8] S. Winstein and F. H. Seubold, Jr., *J. Am. Chem. Soc.*, **69**, 2916 (1947).

[9] C. Moureu, C. Dufraisse, and P. M. Dean, *Bull. soc. chim. France*, **43**, 1367 (1928).

[10] D. B. Denny and P. P. Klemchuk, *J. Am. Chem. Soc.*, **80**, 3289 (1958).

[11] S. Winstein, R. Heck, S. Lapporte, and R. Baird, *Experientia*, **12**, 141 (1956); D. F. DeTar and C. Weis, *J. Am. Chem. Soc.*, **78**, 4297, 4302 (1956); J. W. Wilt and D. D. Oathoudt, *J. Org. Chem.*, **21**, 1550 (1956); *J. Org. Chem.*, **23**, 218 (1958).

[12] We are indebted to Professor W. H. Urry for this suggestion.

[13] C. Moureu, C. Dufraisse, and F. Baylocq, *Bull. soc. chim., France*, **43**, 1371 (1928).

[14] C. F. H. Allen and J. A. Van Allen, *J. Org. Chem.*, **20**, 315 (1955).

To determine whether one of the products had a marked inhibiting effect on the reaction, di-*t*-butyl peroxide was decomposed with the aldehyde (I) in mixtures containing the triphenylethane (II), the diphenylindanone (VI), and triphenylethylene (V). None of these substances showed any large effect on the rate of carbon monoxide evolution.

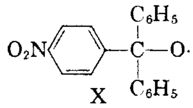
With the objective of obtaining information about the migration ratio of the *p*-nitrophenyl group in a radical carbon-carbon rearrangement it was desired to prepare and submit to the rearrangement conditions β-(*p*-nitrophenyl)-β,β-diphenylpropionaldehyde (VIII). The synthesis of this compound had been previously attempted unsuccessfully by Bartlett and Cotman.[15] It was prepared by the reaction of *p*-nitrotriphenylmethyl bromide with chloromercuriacetaldehyde in benzene with stannic chloride as a catalyst, a modification[3] of a reaction employed by Nesmeyanov, Lutsenko, and Tumanova.[16] The structure of the aldehyde (VIII) was confirmed by the infrared spectrum which showed absorption at 700 cm.$^{-1}$ (monosubstituted phenyl), 850 cm.$^{-1}$ (*p*-disubstituted phenyl), 1355 and 1530 cm.$^{-1}$ (nitro), and 1720 and 2730 cm.$^{-1}$ (aldehyde). When the aldehyde (VIII) was heated at 140° with 19 mole % of di-*t*-butyl peroxide only about 10% of the theoretical amount of carbon monoxide had been evolved although the infrared spectrum of the total product suggested that about 50% of the aldehyde (VIII) had been destroyed. Chromatography gave a nitrohydrocarbon fraction, 65% of which crystallized and was characterized as 2-(*p*-nitrophenyl)-1,1-diphenylethylene (IX) (3.3% over-all yield). There was also present an unidentified nitrohydrocarbon (17% of the chromatographic fraction) and a nonnitro-containing liquid ketone. If it is assumed that all of the *p*-nitrotriphenylethyl radicals formed in the decarbonylation ultimately ended in the nitrohydrocarbon fraction (a rather uncertain assumption) then, making a statistical correction for the two phenyl groups, the *p*-nitrophenyl/phenyl migration ratio is at least as great as 8. The happy agreement of this number with the factor of 8 found by Bartlett and Cotman[15] in the rearrangement of the radical X and with the partial rate factor of 6.6 for attack in the *p*-position of nitrobenzene by a phenyl radical[17] can only be regarded as coincidental.[18]

$$\substack{NO_2C_6H_4\\(C_6H_5)_2}CBr + ClHgCH_2CHO \xrightarrow[SnCl_4]{} \substack{NO_2C_6H_4\\(C_6H_5)_2}CCH_2CHO$$

VIII

$$\text{VIII} \xrightarrow[(t\text{-}C_4H_9O)_2]{} (C_6H_5)_2C{=}CHC_6H_4NO_2$$

IX



X

EXPERIMENTAL[19]

α-Deutero-p-methoxybenzhydrol. p-Methoxybenzophenone[22] (40 g., 0.20 mole) was reduced in 200 ml. of dry diethyl ether with 5.0 g. of lithium aluminum deuteride (93% D) and 2.0 g. of lithium aluminum deuteride (98% D), a total of 0.16 mole, in 300 ml. of dry ether. After 8 days water was added followed by 5% aqueous sulfuric acid. The ether layer was separated, dried, and the ether was distilled. Crystallization of the resulting oil from 1500 ml. of hexane gave 36 g. (82%) of the deuterobenzhydrol, m.p. 66.5–67.5°. Evaporation of the filtrate to a volume of 150 ml. gave 2.5 g. (6%) of additional benzhydrol, m.p. 65.5–66.5°.

Anal. Calcd. for $C_{14}H_{13}DO_2$: D, 7.1 atom %. Found: D, 8.5.

(The presence of residual O-deuterated material from incomplete exchange with water during the workup in a two-phase system probably accounts for the high deuterium analysis. The excess deuterium is then lost in the next step.)

α-Deutero-p-methoxybenzhydryl chloride. The benzhydrol (39 g., 0.19 mole) in 50 ml. of benzene was treated with dry

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(15) P. D. Bartlett and J. D. Cotman, Jr., *J. Am. Chem. Soc.*, **72**, 3095 (1950).

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

(17) Chang Shih, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 4403 (1958). A summary of partial rate factors in the phenylation of monosubstituted benzenes is given by C. S. Rondestvedt, Jr., and H. S. Blanchard, *J. Org. Chem.* **21**, 229 (1956).

(18) For other studies of migration ratios in carbon-to-oxygen rearrangements see M. S. Kharasch, A. C. Poshkus, A. Fono, and W. Nudenberg, *J. Org. Chem.*, **16**, 1458 (1951); W. H. Urry, *Abstracts of the 12th National Organic Chemistry Symposium*, Denver, Colo., 1951. Bartlett and Cotman (Ref. 15) have a particularly rewarding discussion of migration ratios.

(19) All melting points are corrected. Microanalyses were carried out by Mr. Josef Nemeth, Mrs. Katherine Pih, Mrs. Esther Fett, and Mrs. Lucy Chang. Deuterium analyses were performed by the falling-drop method and are reported as absolute atom per cent deuterium $= \frac{D}{D + H} \times$ 100% where D and H refer to the numbers of deuterium and hydrogen atoms, respectively, in the molecule.[20] Unless otherwise specified the infrared spectra were obtained with 10% solutions in carbon tetrachloride in 0.1-mm. matched cells in a Perkin-Elmer Model 21 Double Beam Spectrophotometer by Miss Helen Miklas, Mrs. Beverly Thomas, Mr. James J. Brader, and Mrs. Louise Griffing. The ultraviolet spectra were obtained in 95% ethanol in 1-cm. cells with a Cary Double Beam Spectrophotometer by Miss Geraldine Meerman. The NMR spectra were obtained on a high resolution spectrophotometer[21] at an adjustable field strength of 4170 gauss with a maximum resolution of about one milligauss by Dr. Jerry Heeschen. Many traces were observed and visually averaged in drawing the conclusions described herein.

Most of the spectra are included in the thesis of JCK[1] which is available on microfilm as Univ. Microfilms Publ. No. 13, 505 [*Chem. Abstr.*, **50**, 2419*b* (1956)] Univ. Microfilms, Ann Arbor, Mich.

(20) A. S. Keston, D. Rittenberg, and R. Schoenheimer, *J. Biol. Chem.* **122**, 227 (1937).

(21) H. S. Gutowsky, L. H. Meyer, and R. E. McClure, *Rev. Sci. Instr.*, **24**, 644 (1953).

(22) P. P. Peterson, *Am. Chem. J.*, **46**, 335 (1911).

hydrogen chloride for 1 hr. Solvent was distilled, and the resulting oil was crystallized from benzene to yield 30 g. (65%) of the deuterobenzhydryl chloride, m.p. 64–64.5°. The absence of absorption at 1218 cm.$^{-1}$ in the infrared, characteristic of the undeuterated benzhydryl chloride indicated that the product was at least 90% deuterated.

Anal. Calcd. for $C_{14}H_{12}DClO$: D, 7.7. Found, D, 7.1.

β-Deutero-β-(p-anisyl)-β-phenylpropionaldehyde (III-d), b.p. 154–155.5° at 0.28 mm., n_D^{20} 1.5808, m.p. 17–19°, was prepared in 75% yield by the method previously reported[3] for the undeuterated compound. The aldehyde was stored under nitrogen since it undergoes air oxidation.

Anal. Calcd. for $C_{16}H_{15}DO_2$: D, 6.3. Found: D, 6.5.

p-Nitrotriphenylmethane. This modification of the procedure of Baeyer and Löhr[23] led to a product which was easier to purify. A solution of 102 g. of *p*-nitrobenzaldehyde in 1500 ml. of dry benzene was stirred for 6 days with 170 g. of phosphorus pentoxide and was then heated to reflux for 1 hr. The solution was cooled, and the benzene layer was decanted and washed thoroughly with 10% sodium carbonate, 5% sodium bisulfite, and water. Solvent was distilled, and the residue was crystallized from 500 ml. of ethanol to yield 75 g. m.p. 90–92°. Treatment of the brown phosphoric acid residue with water and benzene followed by the above treatment of the benzene layer yielded an additional 37 g., m.p. 89.5–91.5°. Recrystallization of both crops from 1 l. of hexane yielded 97.2 g. (50%) of *p*-nitrotriphenylmethane, m.p. 92–93° (lit., m.p. 93°).

β-(p-Nitrophenyl)-β,β-diphenylpropionaldehyde (VIII). A suspension of 65 g. (0.23 mole) of chloromercuriacetaldehyde[15] in dry benzene was added to a solution of 85 g. (0.23 mole) of *p*-nitrotriphenylmethyl bromide[24] in 400 ml. of dry benzene and 90 ml. of hexane cooled with an ice bath. The reaction mixture was protected from moisture with a calcium chloride tube and purged with nitrogen. Anhydrous stannic chloride (60 g., 0.23 mole) was added dropwise, and the mixture was stirred at 0° for 30 hr. and then at 25° for 10 hr. It was then stirred with water and with 10% sodium carbonate solution, and after filtration the benzene layer was washed with 5% sulfuric acid, water, 10% sodium carbonate and water. Solvent was distilled to a volume of 130 ml., and the brown solution was chromatographed on a column of Merck alumina which had been activated at 300° for 1 hr. at 25 mm. pressure. Elution with benzene-hexane (1:1) yielded a 300-ml. forerun followed by a 200-ml. fraction from which solvent was removed by distillation. The resulting solid was washed with 10 ml. of cold carbon tetrachloride and recrystallized from 25 ml. of carbon tetrachloride to yield 13 g. of aldehyde (VIII), m.p. 119–121°. Further elution yielded an additional 5.5 g. The crystalline products were dissolved in 100 ml. of hot ethyl acetate, and 100 ml. of hexane was added. The white crystalline aldehyde (m.p. 122.5–124°) weighed 14 g. (18%).

Anal. Calcd. for $C_{21}H_{17}NO_3$: C, 76.1; H, 5.2; N, 4.2. Found: C, 75.9; H, 5.0; N, 4.1.

β-(p-Nitrophenyl)-β,β-diphenylpropionaldehyde 2,4-dinitrophenylhydrazone,[25] bright yellow crystals, melted at 227–228°.

Anal. Calcd. for $C_{27}H_{21}N_5O_6$: N, 13.7. Found: N, 13.4.

Decarbonylation of the β-deutero aldehyde (III-d). In a flask maintained at 140° ± 1°, the aldehyde III-d (7.0 g., 0.029 mole) was allowed to react with 0.60 g. (0.0041 mole) of freshly distilled di-*t*-butyl peroxide for 11.8 hr. during which time 280 ml. (0.0109 mole, 38%) of gas was liberated.[26] The infrared spectrum of the product indicated by the absorption at 1730 and 2725 cm.$^{-1}$ that 50–55% of unchanged aldehyde III-d was present. Distillation through a 30-cm. spiral wire column[27] gave 1.8 g. of colorless liquid, b.p. 115–122° at 0.55 mm., m.p. −1.5–(+)2° whose infrared spectrum indicated that it contained 2.5% of starting aldehyde but was otherwise identical with that of 1-deutero-1-*p*-anisyl-1-phenylethane (IV-d), prepared as described below. Comparison (using an expanded scale) of the C-D stretching absorption of a solution 510 mg./ml. in carbon tetrachloride at 2119 cm.$^{-1}$ (characteristic of the tertiary C-D of IV-d) and at 2178 cm.$^{-1}$ (where the primary C-D of β-deuteroethylbenzene described below absorbed) confirms the presence only of tertiary C-D. The NMR spectrum[4] showed no splitting of the methyl absorption to be expected if there were coupling with a proton on an adjacent carbon atom. This splitting is prominent in the undeuterated hydrocarbon (IV). Allowing for the small amount of aldehyde (III-d) there was 29% of the deuteroethane (IV-d).

Anal. Calcd. for $C_{15}H_{15}DO$: D, 6.3. Found: D, 6.3.

Recovered aldehyde (III-d) obtained by continuing the distillation above amounted to 2.6 g., b.p. 145–152° at 0.55 mm. and an estimated 0.55 g. in the residue or a total of 46% of the starting material.

1-Deutero-1-(p-anisyl)-1-phenylethane (IV-d). The procedure used was an adaptation of that used by Gomberg and Cone[28] for 1,1,1-triphenylethane. α-Deutero-*p*-methoxybenzhydryl chloride (4.4 g., 0.019 mole) in 150 ml. of dry ether was added dropwise over a period of 1.5 hr. with stirring to a solution of methylmagnesium iodide prepared from 25 g. (0.18 mole) of methyl iodide and 4.3 g. (0.18 mole) of magnesium in 150 ml. of ether. After 0.5 hr. at 0° under a nitrogen atmosphere the solution was allowed to warm to 25° and then heated under reflux for 10 min. Addition of 5% aqueous hydrochloric acid, separation of the ether layer and distillation through a 30-cm. spiral wire column[27] gave 0.8 g. (20%) of IV-d, b.p. 102–103° at 0.3 mm., m.p. 5–6°.

Anal. Calcd. for $C_{15}H_{15}DO$: D, 6.3. Found: D, 6.3.

β-Deuteroethylbenzene was prepared by an adaptation of the method of Turkevich, McKenzie, Friedman, and Spurr[29] for α-deuterotoluene. In an atmosphere of dry nitrogen 20 g. (0.15 mole) of freshly distilled β-phenylethyl chloride in 150 ml. of dry ether was added to 3.6 g. (0.15 mole) of magnesium in 50 ml. of dry ether. After no further reaction was apparent the mixture was refluxed for 2 hr. and then cooled in a Dry Ice–acetone bath and 8 g. of 99.8% deuterium oxide was added dropwise. After 3 hr. 150 ml. of 5% aqueous hydrochloric acid was added, and the ether layer was separated and washed with sodium bicarbonate solution and water. After drying over sodium sulfate and removal of the solvent the residue was distilled through a 30-cm. spiral wire column.[27] The β-deuteroethylbenzene, b.p. 135–136.5°, $n_D^{20.3}$ 1.4950 amounted to 7.7 g. (52%).

Anal. Calcd. for C_8H_9D: D, 10.0. Found: D, 9.7.

Decarbonylation of β,β,β-triphenylpropionaldehyde. (a) *Under partial reflux with excess peroxide.* In a flask maintained at 140 ± 1° and equipped with a steam-jacketed condenser followed by a Dry Ice trap and finally an inverted graduated cylinder arranged to collect noncondensable gases was placed 53 g. (0.18 mole) of the aldehyde I, and 28 g. (0.19 mole) of freshly distilled di-*t*-butyl peroxide was added in small portions over a period of 5 days. The gas liberated amounted to 3.0 l. (0.12 mole). The distillate (25 g.) in the Dry Ice trap was fractionated through a 30-cm. spiral wire column[27] and found to consist of acetone (1.4 g., 0.025 mole, b.p. 49.5–50.5°), *t*-butyl alcohol (22 g., 0.30 mole, b.p. 76–76.5°) and di-*t*-butyl peroxide (1.07 g., 0.007 mole, b.p. 100–106°, n_D^{20} 1.3882). The acetone was further

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(23) A. Baeyer and R. Löhr, *Ber.*, **23**, 1621 (1890).

(24) V. A. Izmail'skiĭ and D. K. Surkov, *J. Gen. Chem.* (U.S.S.R.) **13**, 848 (1943). [*C.A.* **39**, 1407 (1945)].

(25) R. L. Shriner and R. C. Fuson, *The Systematic Identification of Organic Compounds*, 3rd ed., John Wiley and Sons, Inc., New York, 1948, p. 171.

(26) Throughout this work the gas was collected over water, and the volume was corrected for the vapor pressure of water.

(27) C. W. Gould, Jr., G. Holzman, and C. Niemann, *Anal. Chem.* **20**, 361 (1948).

(28) M. Gomberg and L. H. Cone, *Ber.*, **39**, 2963 (1906).

(29) J. Turkevich, H. A. McKenzie, L. Friedman, and R. Spurr, *J. Am. Chem. Soc.*, **71**, 4045 (1949).

identified by its infrared spectrum and by the 2,4-dinitrophenylhydrazone, m.p. 124–125°. The *t*-butyl alcohol formed a phenylurethan, m.p. 133–134°. The noncondensable gas was not analyzed but was assumed to consist of methane and carbon monoxide,[30] the amount of methane being estimated from the amount of acetone to amount to 0.025 mole, thus leaving 0.092 mole (50%) as the amount of carbon monoxide. In other experiments the gas was analyzed by an Orsat volumetric gas apparatus and found to consist of carbon monoxide with traces of oxygen, carbon dioxide, and small amounts of an inflammable gas, presumably methane.

Chromatography of the thick orange oily product (a 2.2-g. aliquot) on a 300 × 17 mm. column of Harshaw Al-0109P activated alumina gave on elution with hexane a hydrocarbon fraction of 0.65 g. Further elution with 20% ether in hexane gave 0.11 g. of red oil with a strong infrared absorption maximum at 1715 cm.$^{-1}$ and an ultraviolet maximum at 258 mμ. Both the infrared and ultraviolet spectra were very similar to the spectra of the diphenylindenone (VII) but on rechromatography the compound still failed to crystallize. Finally 0.64 g. of oil was obtained which when triturated with hexane deposited crystals of the indanone (VI). The indanone was isolated in small amount as crystals, melting point and mixed melting point with an authentic sample, 130.5–131°, and the infrared spectrum was identical with that of the authentic sample. It was estimated from the intensity of the characteristic infrared absorptions of the indanone (VI) at 1240 and 1290 cm.$^{-1}$ in the crude reaction mixture that about 20% of the indanone (VI) was present. From the absence of absorption at 2740 cm.$^{-1}$ it was concluded that less than 5% of aldehyde remained.

Distillation of a 16.8-g. aliquot of the product through a 30-cm. spiral wire column[27] gave 6.3 g. of yellow liquid, b.p. 133–137° at 0.2 mm. which was purified by chromatography on Merck alumina (elution with 2500 ml. of hexane) to give with 98% recovery a clear colorless liquid whose infrared spectrum was almost identical with the rearranged triphenylethane (II). However, the ultraviolet absorption at 296 mμ indicated that it consisted to the extent of 29% of triphenylethylene. The infrared showed that no significant amount (less than 0.5%) of carbonyl-containing compounds could be present. A small absorption at 1380 cm.$^{-1}$ indicated that 1,1,1-triphenylethane might be present but not to an extent of more than 10%. The infrared spectrum of a mixture of 62% of the rearranged triphenylethane (II), 10% of 1,1,1-triphenylethane and 28% triphenylethylene (V) was nearly identical with the spectrum of the mixture except that the product had somewhat more intense absorption at 2980 cm.$^{-1}$ than did the known mixture. Continuation of the distillation gave, after an intermediate fraction of 0.16 g. (b.p. 140–168° at 0.25 mm.), 4.9 g. of viscous orange oil, b.p. 168° at 0.25 mm. which solidified on standing. Its absorption at 1240, 1290, and 1720 cm.$^{-1}$ showed that it consisted to the extent of about 80% of the indanone (VI). The nonvolatile residue was a brown, glassy solid amounting to 4.6 g. and estimated from its infrared spectrum to contain less than 3% of the aldehyde (I) and about 8% of the indanone (VI). The reaction mixture was thus concluded to contain about 0.022 mole (12%) of triphenylethylene, 0.047 mole (25%) of the indanone VI and 0.053 mole (29%) of triphenylethanes chiefly II with not more than 4% of the 1,1,1-isomer.

(b) *Under partial reflux with a catalytic amount of peroxide.* The reaction of 15 g. (0.052 mole) of aldehyde 1 with 1.2 g. (0.0079 mole) of di-*t*-butyl peroxide added at once was carried out as above for 23 hr. after which gas evolution had ceased. There were obtained 274 ml. (0.011 mole) of carbon monoxide (21%) and 15.4 g. of a liquid product mixture which was found by the method outlined above to contain 11 g. (72%) of starting material (I), 0.0036 mole (6.9%) of saturated triphenylethanes [chiefly the rearrangement product (II)], 0.0017 mole (3.2%) of triphenylethylene, and 0.0018 mole (3.4% of the indanone (VI).

(c) *Under total reflux.* A reaction of 10.0 g. (0.035 mole) of aldehyde I with 0.98 g. (0.0067 mole) of di-*t*-butyl peroxide was carried out for 28 hr. when 290 ml. (0.11 mole) of gas had been liberated (corresponding to 32% decarbonylation if the gas were entirely carbon monoxide). The products estimated as before were 0.0068 g. (20%) of triphenylethane (I) (and any 1,1,1-triphenylethane, if formed), 0.0015 mole (4.3%) of triphenylethylene, and 0.0011 mole (3.2%) of the indanone (VI). The aldehyde (I) was recovered to the extent of 40%, and 0.06 g. of a compound with infrared absorption at 1677 cm.$^{-1}$ was obtained. A reaction was carried out as above with the exception that 0.0116 mole of the triphenylethane (II) was added initially. After 24 hr. 370 ml. (0.14 mole) of gas had been evolved corresponding to 39% decarbonylation. A similar experiment with 3.1 g. (0.011 mole) of the indanone (VI) gave 260 ml. (27% of the theoretical amount of carbon monoxide) after 6.3 hr. and 420 ml. (44%) after 21 hr. With the addition of 3.0 g. (0.012 mole) of triphenylethylene there was 125 ml. of gas (13%) after 4.75 hr. and 317 ml. (33%) after 23 hr. The addition of 1.6 g. (0.022 mole) of *t*-butyl alcohol retarded the reaction (by lowering the temperature) as shown by the fact that after 6 hr. only 90 ml. of gas had been evolved (10%) and 84% of the aldehyde (I) could be recovered.

3,3-Diphenyl-1-indanone (VI), prepared by the method of Moureu, Dufraisse, and Dean,[9] melted at 130–131°. The infrared spectrum[19] showed strong absorption at 1725 cm.$^{-1}$ and the ultraviolet spectrum[19] showed λ_{max} 297 ϵ 2230.

2,3-Diphenylindenone (VII), prepared by the method of Moureu, Dufraisse, and Baylocq,[13] melted at 151.5–152°, with infrared absorption[19] at 1712 cm.$^{-1}$ and a maximum in the ultraviolet at 258 mμ, ϵ 35,000.

Decarbonylation of β-(p-nitrophenyl)-β,β-diphenylpropionaldehyde (VIII). The reaction of 13.1 g. (0.040 mole) of the aldehyde (VIII) was carried out with 1.1 g. (0.0075 mole) of di-*t*-butyl peroxide at 140° for 22.5 hr. as described for the reactions under total reflux discussed above. A total of 112 ml. of gas was evolved corresponding to 11% decarbonylation. The residue of 13.5 g. had absorption at 2730 cm.$^{-1}$ the intensity of which, measured in a 20% carbon tetrachloride solution, indicated that 50% of the starting aldehyde (VIII) was unchanged. Chromatography of 11.8 g. of the product on a 350 × 43 mm. column of alumina activated for 1 hr. at 300° and 25 mm. with 5 l. of 1:1 hexane-benzene gave separation into a yellow band (100 mm. long) followed by two brown bands (each about 50 mm.). These were separated and the yellow band rechromatographed by elution with 1:1:1 hexane-benzene-ether. After elution with 1 l. of the solvent and evaporation of the solvent there was obtained 0.22 g. of 1,1-diphenyl-2-(*p*-nitrophenyl)ethylene (IX), m.p. 153.5–155°. Further elution with 1 l. of the same solvent gave 0.24 g. of yellow oil containing crystals, and further elution with 2.5 l. more of the same solvent gave 0.13 g. of yellow oil. Recrystallization of the solid from the second fraction from 2 ml. of carbon tetrachloride and 5 ml. of petroleum ether gave 0.02 g. of the nitroolefin (IX), m.p. 153–154°. Rechromatography of the combined noncrystalline portions of the eluate gave 0.11 g. more of the nitroolefin (IX) and 0.19 g. of orange oil. Thus, from an 11.8 g. aliquot a total of 0.35 g. (0.0012 mole, 3.3%) of the rearranged nitroolefin (IX) and 0.19 g. of unidentified orange oil were obtained. Further recrystallization of IX from hexane showed m.p. 156–156.5° (reported[31] for brown form, m.p. 148°, for yellow form, m.p. 158–160°). The nitroolefin (IX) was characterized by bromination in 60% yield to 1-bromo-2,2-diphenyl-1-(*p*-nitrophenyl)ethylene, m.p. 181–182° (reported,[31] m.p. 178°) when recrystallized from ethyl acetate-hexane. Oxidation of 100 mg. of IX in 7 ml.

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[30] See C. Walling, *Free Radicals in Solution*, John Wiley and Sons, New York, 1957, p. 470f.

[31] F. Bergmann, E. Dimant, and H. Japhe, *J. Am. Chem. Soc.*, **70**, 1618 (1948).

of acetone with 130 mg. of potassium permanganate in 1 ml. of water and 7 ml. of acetone gave on treatment with 2,4-dinitrophenylhydrazine after 18 hr. at 25°, 48 mg. (40%) of benzophenone 2,4-dinitrophenylhydrazone, m.p. 242–243° and undepressed when admixed with an authentic sample, and 20 mg. (36%) of *p*-nitrobenzoic acid, m.p. 240–241° (reported,[32] m.p. 241°).

The 0.19 g. of orange oil remaining after separation of IX was distilled in a microdistillation apparatus to give 0.10 g. of colorless oil, b.p. 140° at 5 mm. and 0.09 g. of brown residue. The colorless oil had strong infrared absorption at 1682 cm.$^{-1}$ and ultraviolet absorption at 253 mμ. The brown residue had strong peaks at 1350 and 1530 cm.$^{-1}$ (nitro group) and 850 cm.$^{-1}$ (*p*-disubstituted benzene derivative).

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[32] Ref. 24, p. 225.

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Free Radical Rearrangements. Di(3,3,3-triphenylpropionyl)diimide, Methylazo-2,2,2-triphenylethane, and 2,2,2,-Triphenylethylhydrazine as Radical Sources[1]

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In a search for other methods of preparing the 2,2,2-triphenylethyl radical the thermal decomposition of di(3,3,3-triphenylpropionyl)diimide (I), and methylazo-2,2,2-triphenylethane (II) and the air oxidation of 2,2,2-triphenylethylhydrazine (III) were investigated. Decomposition of I at temperatures between 110 and 180° in the melt or in nonpolar solvents gives 1,1,1,6,6,6-hexaphenyl-3,4-hexandione (IV) in yields of 25–45%. In addition at 160–180° there are formed 1,1,2-triphenylethane and triphenylethylene in nearly equal amounts (11 and 14%, respectively). The thermal decomposition of II leads to triphenylmethane (23% yield), presumably formed by a free radical cleavage reaction, and benzophenone (6–10%) as the only products thus far identified. Air oxidation of III in boiling benzene gives benzophenone in an amount which accounts for some 30% of the triphenylmethyl groups initially present. Attempts to prepare the diketone IV by the more conventional acyloin condensation have led to another cleavage (presumably free radical) resulting in triphenylmethane in 42% yield. Infrared spectra of the diacyldiimide I, diacetyldiimide, and dibenzoyldiimide show their carbonyl stretching absorptions at 1780, 1770, and 1730 cm.$^{-1}$, respectively.

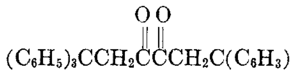
Although a number of studies of carbon-to-carbon free radical rearrangements of the neophyl radical,[3] the 2,2,2-triphenylethyl radical,[4] and other similar radicals[5] have been reported, none of these has been ideally suited to a detailed study of such rearrangements. The present work was undertaken with the hope that a survey of other methods of producing the 2,2,2-triphenylethyl radical might provide a system more amenable to such a study. To this end the syntheses and thermal decomposition of di(3,3,3-triphenylpropionyl)diimide (I) and methylazo-2,2,2-triphenylethane (II) and also the preparation and air oxidation of 2,2,2-triphenylethylhydrazine (III) were investigated.

$(C_6H_5)_3CCH_2CON{=}NCOCH_2C(C_6H_5)_3$

I

$(C_6H_5)_3CCH_2N{=}NCH_3$ $(C_6H_5)_3CCH_2NHNH_2$

II III



$$(C_6H_5)_3CCH_2\overset{\overset{\displaystyle O}{\|}}{C}\overset{\overset{\displaystyle O}{\|}}{C}CH_2C(C_6H_3)_3$$

IV

The thermal decomposition of diacyl- and diaroyldiimides had been investigated previously without very promising results. Thus Stollé[6] reported that dibenzoyldiimide when heated gave benzil in small but unspecified amounts and a more recent and careful study by Leffler and Bond[7] has demonstrated that in benzene solution the major products were 2,5-diphenyl-1,3,4-oxadiazole, biphenyl, dibenzoylhydrazine and a large amount of a mixture of what was presumably di- and tribenzoylhydrazines. In other solvents small amounts of benzil could be obtained. Inhoffen, Pommer, and Bohlmann[8] have investigated the possible

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[2] Standard Oil Company of California Fellow, 1957–58.

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