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).

URBANA, ILL.

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[32] Ref. 24, p. 225.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

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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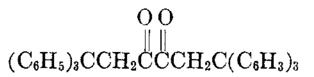
In a search for other methods of preparing the 2,2,2-triphenylethyl radical the thermal decomposition of di(3,3,3-triphenylpropionyl)diimide (I), and methylazo-2,2,2-triphenylethane (II) and the air oxidation of 2,2,2-triphenylethylhydrazine (III) were investigated. Decomposition of I at temperatures 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

$$(C_6H_5)_3CCH_2N{=}NCH_3 \quad (C_6H_5)_3CCH_2NHNH_2$$
II III



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

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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[1] Supported in part by a grant (G-4467) from the National Science Foundation. This work is taken from the Ph.D. thesis submitted by T. C. M. to the University of Illinois, 1959. It will be available from Univ. Microfilms, Ann Arbor, Mich.

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

[3] (a) W. H. Urry and M. S. Kharasch, *J. Am. Chem. Soc.*, **66**, 1438 (1944); (b) S. Winstein and F. H. Seubold, *J. Am. Chem. Soc.*, **69**, 2916 (1947); (c) F. H. Seubold, *J. Am. Chem. Soc.*, **75**, 2532 (1952); (d) W. H. Urry, 12th National Organic Symposium, ACS, Abstracts, p. 30.

[4] (a) D. Y. Curtin and M. J. Hurwitz, *J. Am. Chem. Soc.*, **74**, 5381 (1952); (b) D. Y. Curtin and J. C. Kauer, *J. Org. Chem.*, **25**, 880 (1960); H. Meislich and J. Costanza, Abstracts of the 132nd Meeting, ACS, New York, N. Y., 1957, p. 9P.

[5] (a) W. H. Urry and N. Nicolaides, *J. Am. Chem. Soc.*, **74**, 5163 (1952); (b) S. Winstein, R. Heck, S. Lapporte, and R. Baird, *Experientia*, **12**, 138 (1954); (c) J. Weinstock and S. N. Lewis, *J. Am. Chem. Soc.*, **79**, 6243 (1957); (d) W. D. Smith and J. D. Anderson, *J. Am. Chem. Soc.*, **82**, 656 (1960); (e) L. H. Slaugh and J. H. Raley, *J. Am. Chem. Soc.*, **82**, 1259 (1960).

[6] R. Stollé, *Ber.*, **45**, 273 (1912).

[7] J. E. Leffler and W. B. Bond, *J. Am. Chem. Soc.*, **78**, 335 (1956).

[8] H. H. Inhoffen, H. Pommer, and F. Bohlmann, *Ber.*, **81**, 507 (1948).

synthetic utility of the conversion of diacyldiimides to diketones. They were able to convert, *N,N'*-dipropionyl- and *N,N'*-dibutyrylhydrazine by way of the diimide, which was not isolated, to diacetyl, dipropionyl, and dibutyroyl (isolated as the bis-phenylhydrazone or bis-*p*-nitrophenylhydrazone) in over-all yields of 0.5 to 1.4%. Cramer[9] has shown that such decompositions lead to radicals which catalyze polymerization.

In spite of these discouraging reports it seemed worth-while to examine the decomposition of the diacyldiimide (I), particularly in dilute solution and at elevated temperatures. The diimide I was prepared by oxidation with iodine of the mercury salt of the corresponding hydrazine, a method previously employed[6] for the preparation of other diacyldiimides. The structure of I was confirmed by its infrared, visible, and NMR spectra as described in the Experimental section and by its ready reduction to the diacylhydrazine from which it had been obtained. It is of interest that the carbonyl stretching frequency in the infrared was 1780 cm.$^{-1}$ Since, apparently, there have been no previous reports of the spectra of compounds with the —CON=NCO—functional group, the spectra of diacetyl- and dibenzoyldiimide were also obtained. These showed strong absorption attributed to the carbonyl group at 1770 and 1730 cm.,$^{-1}$ respectively, in reasonable agreement with the value obtained with I. The diimide I was found to melt with gas evolution which was noticeable even when the sample was heated at 160°. When the solid was heated to 175° for one hour, 70% of the theoretical amount of nitrogen was evolved and treatment of the residue with boiling acetone gave a 45% yield of 1,1,1,6,6,6-hexaphenyl-3,4-hexanedione (IV). No other product could be identified and no hydrocarbon portion was obtained on chromatography. The structure of IV was established by its cleavage to 3,3,3-triphenylpropionic acid with alkaline hydrogen peroxide and by the following spectral evidence. There was strong carbonyl absorption at 1723 cm.$^{-1}$ (chloroform solution). Biacetyl has absorption at 1718 cm.$^{-1}$ in carbon tetrachloride solution.[10] The absorption maximum of a chloroform solution at 440 mμ (ϵ 29) is in fair agreement with λ_{max} 420 mμ (ϵ 10) reported for biacetyl in ethanol.[11] The NMR spectrum of a 20% solution in deuterochloroform showed a singlet at -238 p.p. 10^8 (rel. to water) due to the aromatic protons and another singlet at $+88$ p.p. 10^8 due to the methylene group.

With the objective of producing 3,3,3-triphenylpropionyl radicals under circumstances which would favor to the maximum extent their decarbonylation rather than their recombination to diketone, the diimide I dissolved in a small volume of chloroform was added very slowly to decalin at 180°. The concentration of diimide was estimated to have been very much less than 0.01*M* and perhaps as low as $10^{-5}M$, throughout the reaction. Again the diketone was formed in 43% yield but there were also significant amounts of hydrocarbons. These, when separated by chromatography and examined with the aid of ultraviolet and NMR spectroscopy were estimated to account for 11% of the initial triphenylethyl groups as 1,1,2-triphenylethane and 14% as triphenylethylene. No hydrocarbon products formed with an unrearranged carbon skeleton could be detected. There was also 4% of di(3,3,3-triphenylpropionyl)-hydrazine formed by reduction of the diimide I. A reaction carried out similarly except that the solvent temperature was 160° gave similar amounts of the two hydrocarbons and di(3,3,3)triphenylpropionyl)hydrazine, but only 31% of the diketone IV. Another experiment at 137° in xylene gave 29% of diketone IV and lesser amounts of rearranged hydrocarbons. At 111° 25% of diketone IV was formed but no hydrocarbon was isolated. The failure of the 3,3,3-triphenylpropionyl radicals to undergo decarbonylation under conditions more vigorous than are required for similar acyl radicals[9,12a] might be attributed to the rapid primary combination of the two acyl radicals produced together, behavior reminiscent of azobisisobutyronitrile decomposition.[12a,13] The activation energy for the decomposition of acetyl radical to methyl radical and carbon monoxide has been estimated to be about 17 kcal.[14] The failure of the relative amount of diketone produced to vary greatly over the temperature range investigated suggests that the diketone is being produced by a process which has an energy of activation not too different from that of decarbonylation. One possibility is the isomerization of the azo compound to the *cis* isomer followed by a simultaneous loss of nitrogen and formation of a carbon-carbon bond by a molecular mechanism similar to that previously proposed by Hammond, Sen, and Boozer[13] as a possibility for part of the azobisisobutyronitrile decomposition. The decomposition of the diimide I requires further study, however, before conclusions about the mechanism may be drawn with any assurance.

It appears that the utility of the thermal decomposition of diacyldiimides for the synthesis of 1,2-diketone is greater for more complex structures than would be anticipated from the earlier studies of structurally simple examples. In particular the tendency of the acyl radical first formed to attack

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[9] R. Cramer, *J. Am. Chem. Soc.*, **79**, 6215 (1957).

[10] R. S. Rasmussen, D. D. Tunnicliff, and R. R. Brattain, *J. Am. Chem. Soc.*, **71**, 1068 (1949).

[11] R. T. Holman, W. D. Lundberg, and G. O. Burr, *J. Am. Chem. Soc.*, **67**, 1669 (1945).

[12] See C. Walling, *Free Radicals in Solution*, John Wiley & Sons, N. Y., 1957, (a) pp. 278 ff., (b) pp. 76 ff., (c) p. 584 ff.

[13] G. S. Hammond, J. N. Sen, and C. E. Boozer, *J. Am. Chem. Soc.*, **77**, 3244 (1955).

[14] See T. L. Cottrell, *The Strengths of Chemical Bonds*, Butterworths Publications, Ltd., London, 1954, p. 204.

the starting diimide to give oxadiazole and triacylhydrazine which seems to be responsible to a considerable extent for the low yields of diketone, at least in the case of the diaroyldiimides,[7] appears to be greatly reduced in the decomposition of I. It should be noted in this connection that moderately good yields (40–55%) of diketone were obtained by Horner and Naumann[15] by the irradiation of the *p,p'*- or *o,o'*-dichlorodibenzoyldiimide but no diketone was obtained with dibenzoyldiimide or with its methyl and methoxyl substituted derivatives. The synthesis of the diketone IV by the thermal decomposition of I is of particular interest since the more conventional synthesis by the acyloin condensation fails in this case as will be discussed later in this paper.

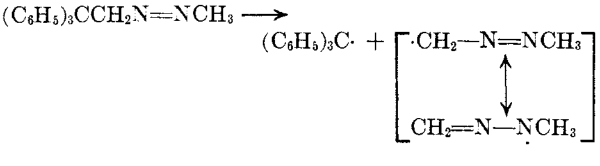
The second compound to be studied (II) was synthesized by the following route from triphenylacetaldehyde. The structure was confirmed by the

$$(C_6H_5)_3CCH{=}O \xrightarrow[CH_3NHNH_2]{}$$

$$(C_6H_5)_3CCH{=}NNHCH_3 \xrightarrow[CH_3COOH]{H_2/Pt}$$

$$[(C_6H_5)_3CCH_2NHNHCH_3] \xrightarrow[\substack{H_2O_2\\NaHCO_3}]{} II$$

infrared, ultraviolet, and NMR spectra described in the Experimental section. When the decomposition was carried out at 206° without a solvent the only identifiable products were triphenylmethane and benzophenone accounting for 23% and 6–10%, respectively, of the starting triphenylmethyl groups. It seems likely that the origin of the triphenylmethane is due to cleavage of the type shown.



$$(C_6H_5)_3CCH_2N{=}NCH_3 \longrightarrow (C_6H_5)_3C\cdot + \left[\begin{array}{c} \cdot CH_2{-}N{=}NCH_3 \\ \updownarrow \\ CH_2{=}N{-}\dot{N}CH_3 \end{array}\right]$$

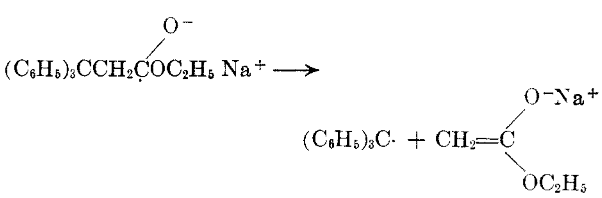
A radical chain version is also possible.

$$(C_6H_5)_3CCH_2N{=}NCH_3 + R\cdot \longrightarrow (C_6H_5)_3C\cdot + CH_2{=}NH{=}CH_2 + HR$$

The formation of isopropylbenzene in the decomposition of 2-azobis-3-methyl-3-phenylbutane reported by Overberger and Gainer[16] is suggestive of a similar cleavage in that case.

The previously reported observation[17] that 9-hydrazino-9,10-ethano-9,10-dihydroanthracene was oxidized by stirring in tetrahydrofuran solution for several days at room temperature to the corresponding hydrocarbon, 9,10-ethano-9,10-dihydroanthracene, in 60% yield suggested that the mild oxidation of the hydrazine III might be a further method of preparing the 2,2,2-triphenylethyl radical. Attempts to prepare the triphenylethylhydrazine III by reduction of triphenylacetaldehyde hydrazone failed because of the strong tendency of the hydrazone to be converted to triphenylacetaldehyde azine. However, the acetylhydrazone of triphenylacetaldehyde was readily reduced and hydrolyzed to the hydrazine III isolated as the hydrochloride. When the free hydrazine was liberated in benzene solution and air bubbled through the refluxing solution for eight hours the major product found was benzophenone, isolated as the 2,4-dinitrophenylhydrazone and estimated by the use of ultraviolet and infrared examination of the crude product to account for 30% of the triphenylmethyl groups initially present. Small amounts of hydrocarbons also obtained were not identified. It seems likely that the benzophenone was formed from the rearranged radical, $(C_6H_5)_2$-$CCH_2C_6H_5$, but a great deal more information about the mechanism of these reactions is desirable before any conclusions can be drawn as to the nature of the oxidation and possible radical rearrangement.

An attempt to prepare the hexaphenylhexandione IV during the course of the work just described led to an interesting example of a possible complication in the acyloin condensation. When ethyl 3,3,3-triphenylpropionate was treated with sodium in boiling xylene the only identifiable product was triphenylmethane in 42% yield. It is suggested that the ketyl supposed to be the first intermediate in the normal acyloin condensation[9c] lost triphenylmethyl radical (the reversal of the well known addition of a free radical to an olefin) to leave as the other product the sodium derivative of ethyl acetate. The reaction is thus apparently



similar to the cleavage of the azo compound II. The generalization can then be noted that there are two alternative reaction paths for the ketyl intermediate formed under the conditions of the acyloin reaction. The first, loss of carbon monoxide,[18] can be expected when the resulting radical is relatively stable and the second, cleavage with rupture of the α,β carbon-carbon bond, the choice being determined to a large extent by the relative stabilities of the radicals to be formed by these processes.

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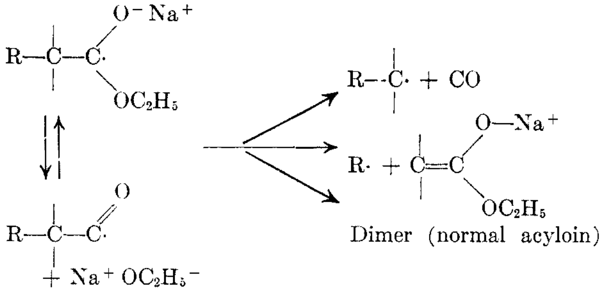
[15] L. Horner and W. Naumann, *Ann.*, **587**, 93 (1954).

[16] C. G. Overberger and H. Gainer, *J. Am. Chem. Soc.*, **80**, 4561 (1958).

[17] M. Wilhelm and D. Y. Curtin, *Helv. Chim. Acta*, **40**, 134 (1957).

[18] E. Van Heyningen, *J. Am. Chem. Soc.*, **74**, 4861 (1952); *J. Am. Chem. Soc.*, **77**, 4016 (1955).



The detailed ordering of the necessary steps and, in particular, the point at which the ethoxide ion is lost cannot be specified with certainty for any of these three reactions.

EXPERIMENTAL[19,20]

N,N'-Di(3,3,3-triphenylpropionyl)hydrazine. To a rapidly stirred mixture of hydrazine hydrate (3.25 g., 0.0650 mole) and 50 ml. of pyridine was added a solution of 3,3,3-triphenylpropionyl chloride[21,22] (40.2 g., 0.125 mole, m.p. 129–131°) in 200 ml. of pyridine. After 1 hr. of heating on a steam bath the pyridine was distilled under reduced pressure and the resulting brown solid was triturated with ether, 5% hydrochloric acid, and 1% sodium hydroxide solution. The tan solid remaining (37.5 g.) was recrystallized by heating under reflux with 500 ml. of glacial acetic acid (in which it dissolves only slowly) to give 22 g. (59%) of *N,N'*-di(3,3,3-triphenylpropionyl)hydrazine, m.p. 276–277°. The infrared spectrum (Nujol mull) showed N—H absorption at 3200 cm.$^{-1}$ and strong carbonyl absorption at 1620 cm.$^{-1}$

Anal. Calcd. for $C_{42}H_{36}N_2O_2$: C, 84.0; H, 6.0; N, 4.7. Found: C, 84.0; H, 6.3; N, 4.6.

Mercury N,N'-di(3,3,3-triphenylpripionyl)hydrazine. A solution of *N,N'*-di(3,3,3-triphenylpropionyl)hydrazine (21.9 g., 0.0365 mole) in 500 ml. of dioxane and yellow mercuric oxide (8.01 g., 0.0370 mole) was stirred for 12 hr. on the steam bath. The fine, white precipitate which resulted was filtered, washed with ether, and dried. The yield of product, m.p. 229–232°, was 25.7 g. (89%). An infrared spectrum (Nujol mull) showed no absorption in the 3200 cm.$^{-1}$-region. There was strong absorption at 1500 cm.,$^{-1}$ (shoulder at 1515 cm.$^{-1}$).

Anal. Calcd. for $C_{42}H_{34}HgN_2O_2$: C, 63.1; H, 4.3; N, 3.5. Found: C, 62.8; H, 4.4; N, 3.5.

Di(3,3,3-triphenylpropionyl)diimide (I). A suspension of mercury *N,N'*-di(3,3,3-triphenylpropionyl)hydrazine (5.00 g., 0.00625 mole) in 100 ml. of reagent ether was stirred for 12 hr. at 25° with iodine (1.59 g., 0.0125 mole). The resulting suspension of pale yellow solid was decanted from the denser mercuric iodide and collected by filtration. About 300 ml. of acetone was required to dissolve the diimide, leaving a small amount of unchanged starting material behind. On cooling the red-orange acetone solution in Dry Ice, 2.04–2.91 g. (54–78% yield) of tiny, pale yellow prisms, m.p. 169–170° with decomposition and gas evolution, was obtained. The infrared spectrum of a 10% solution in chloroform showed strong absorption at 1780 cm.$^{-1}$ The visible spectrum of a chloroform solution showed a broad maximum at 474 mμ (ε 56). The NMR spectrum (20% solution in deuterochloroform) showed a sharp singlet at −243 (phenyl absorption) and a singlet at +85 (methylene group) p.p. 10^8.[20]

Anal. Calcd. for $C_{42}H_{34}N_2O_2$: C, 84.3; H, 5.7; N, 4.7. Found: C, 84.4; H, 5.9; N, 4.6.

The diimide I (195 mg., 0.326 mole) in 20 ml. of benzene containing 9.7 mg. of platinum oxide was hydrogenated at 25° and 1 atm. to give 138 mg. (70% yield) of *N,N'*-di(3,3,3-triphenylpropionyl)hydrazine; the infrared spectrum was identical with that of an authentic sample.

Dibenzoyldiimide, m.p. 118.5–120° (lit.[23] m.p. 119.5–121.5°), was prepared in 40% yield by bubbling chlorine through an alkaline solution of *N,N'*-dibenzoylhydrazine. The infrared spectrum of a 5% solution in chloroform showed strong absorption at 1730 cm.$^{-1}$ The visible spectrum in chloroform showed a broad maximum at 463 mμ, ε 48.

Diacetyldiimide,[8] prepared for infrared spectral examination, was not isolated, but a carbon tetrachloride solution of the crude diimide showed intense infrared absorption at 1765 cm.$^{-1}$

Thermal decomposition of solid di(3,3,3-triphenylpropionyl)-diimide. 1,1,1,6,6,6-Hexaphenyl-3,4-hexandione (IV). Di(3,3,3-triphenylpropionyl)diimide (2.32 g., 0.00388 mole) was placed in a 50-ml. flask equipped with a gas-collection buret and the air in the flask was replaced by nitrogen. The flask was heated to 175° for 1 hr. Rapid evolution of gas began at about 160° and little evolution was observed thereafter. Assuming that the gas was exclusively nitrogen 68% of the theoretical amount was evolved. The crude product was dissolved in 30 ml. of boiling reagent acetone and the solution was filtered while hot. On standing 0.97 g. (45% yield) of the hexandione IV, m.p. 217–219°, crystallized. Recrystallization gave bright yellow prisms, m.p. 218–220°.

The infrared spectrum of a 10% chloroform solution showed carbonyl absorption at 1723 cm.$^{-1}$ The NMR spectrum (20% solution in deuterochloroform) showed singlets at −238 and +88 p.p. 10^8.[20] The visible spectrum of a chloroform solution showed a broad absorption maximum at 440 mμ, ε 29.

Anal. Calcd. for $C_{42}H_{34}O_2$: C, 88.4; H, 6.0. Found: C, 88.0; H, 6.1.

Chromatography of the remainder of the reaction mixture after removal of IV failed to give any hydrocarbon fraction or any other identifiable products.

Oxidation of IV with alkaline hydrogen peroxide. The procedure was similar to that of Geissman and Koelsch.[24] To a solution of diketone IV (102 mg., 0.179 mole) in 10 ml. of acetone were added 0.20 ml. of 30% hydrogen peroxide and 1 ml. of 20% sodium hydroxide. After the addition of 30 ml. of water and distillation of the acetone the solution was filtered to remove unchanged starting material. Acidification of the filtrate gave 57 mg. (53% yield) of 3,3,3-triphenylpropionic acid which after one recrystallization from

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[19] All melting points are corrected. Microanalyses were performed by Mr. J. Nemeth, Mrs. H. Stingl, Miss C. Higham, Mrs. F. Ju, and Miss J. Liu. Infrared spectra were measured in part by Mr. J. Brader, Mr. P. McMahon, Miss M. DeMott, and Miss C. Luebke, with a Perkin-Elmer Model 21 spectrophotometer using 0.1 mm. cells. Ultra violet spectra were measured with a Cary Model 14M spectrophotometer by Mr. M. Chao and Mr. J. Chiu. The NMR spectra were measured by Mr. B. Shoulders with a Varian Associates V-4300-C high resolution spectrophotometer equipped with a VK-3606 flux stabilizer and operated at 40 Mc. Audiofrequency side bands generated with a Hewlett-Packard 200-CD oscillator together with an external methylene chloride standard were used to determine positions of absorption maxima. Most of the pertinent spectra will be available in the Ph.D. thesis of T.C.M.[1]

[20] All NMR spectra are reported in parts per 10^8 relative to water.

[21] Triphenylpropionic acid, best prepared (in 80% yield) from malonic acid (20% excess) and triphenylcarbinol [C. Moureu, C. Dufraisse, and P. M. Dean, *Bull. soc. chim. France,* **43,** 1367 (1928)], was converted to the acid chloride with thionyl chloride.[22]

[22] L. Hellerman, *J. Am. Chem. Soc.,* **49,** 1735 (1927).

[23] L. Horner and W. Naumann, *Ann.,* **587,** 81 (1954).

[24] T. A. Geissman and C. F. Koelsch, *J. Org. Chem.,* **3,** 489 (1938).

TABLE I

THERMAL DECOMPOSITION OF DI(3,3,3-TRIPHENYLPROPIONYL)DIIMIDE (I)

		Max.	Percent Yields of Products Based on Diimide[a]				
Temp., °	Time, hr.	Initial concn., mole/l.	Di(3,3,3)triphenylpropionyl)hydrazine	1,1,1,6,6,6-Hexaphenyl-3,4-hexandione (IV)	1,1,2-Triphenylethane	Triphenylethylene	Total
175[b]	1	<1.7	None	45	None	None	45
111[c]	7	0.019	2	25	None	None	27
137[d]	3	0.015	None	29	<17[f]	8	37–54
160[e]	2	<0.01	6	31	10	13	60
180[e]	1.3	<0.01	4	43	11	14	72

[a] For 1,1,2-triphenylethane and triphenylethylene, % yield = (100) (moles of hydrocarbon) ÷ (2) (moles of diimide). [b] No solvent. [c] Solvent toluene. [d] Solvent xylene. [e] Solvent decalin. [f] The NMR spectrum of this fraction showed contamination by unidentified hydrocarbon impurities.

methanol melted at 178–180° and showed no melting point depression when mixed with an authentic sample.

Decomposition of di(3,3,3-triphenylpropionyl)diimide in solution. (a) *Decalin at 160°.* The solvent, *cis*-decalin (Eastman Kodak practical grade) was purified by washing with concd. sulfuric acid, then with 5% sodium bicarbonate solution, and finally with distilled water, drying over calcium chloride, and distilling under reduced pressure. A solution of diimide I (0.93 g., 0.0016 mole) in 20 ml. of reagent chloroform was added over a period of 2 hr. to 30 ml. of initially refluxing decalin at such a rate that the temperature of the solution did not drop below 160°. The chloroform was flashed into a Dry Ice trap. A dense black precipitate of palladium was observed as the nitrogen used to sweep the reaction mixture was passed through a dilute aqueous solution of palladous chloride, indicating the presence of carbon monoxide.[25] When the yellow decalin solution was cooled, a voluminous white precipitate was observed. Suction filtration afforded 0.06 g. (6%) of the *N,N'*-di(3,3,3)triphenylpropionyl)hydrazine, which was recrystallized from acetic acid, m.p. 270–273°. Its infrared spectrum was identical with that of authentic material. Most of the decalin was then removed by distillation under reduced pressure. The residue was taken up in boiling acetone, from which the hexandione IV (0.23 g., 31%, m.p. 218–220°) crystallized on cooling. The acetone was removed on the steam bath, finally under reduced pressure, and the residue was chromatographed on ethyl acetate–washed alumina, previously activated 24 hr. at 130°. The first fraction (eluent, hexane) was decalin. An infrared spectrum indicated the absence of phenyl group bands at 1600 cm.$^{-1}$, 1500 cm.$^{-1}$, and 700 cm.$^{-1}$ An ultraviolet spectrum indicated the absence of triphenylethylene. The second fraction (0.19 g.; eluent, hexane) contained 0.11 g. (13% yield based on diimide) of triphenylethylene, as determined by examination of the absorption intensity at 298 mμ (ϵ of the pure compound taken as 19,500)[4b] in the ultraviolet spectrum in ethanol. The NMR spectrum of a 20% solution in carbon tetrachloride showed absorption at −238, −215 and −205 p.p. 10^8 characteristic of triphenylethylene and also at −228, +63 (triplet) and +155 (doublet) due to 1,1,2-triphenylethane. The crude hydrocarbon fraction was submitted for carbon and hydrogen microanalyses after removal of low-boiling solvents by heating 1.5 hr. at 78° at 1 mm.

Anal. Calcd. for a mixture of 63.8% $C_{20}H_{16}$ and 36.2% $C_{20}H_{18}$: C, 93.5; H, 6.6. Found: C, 93.0; H, 6.6.

(b) *Decalin at 180°.* The decomposition of diimide I was repeated as above except that with stronger heating the temperature of the solution was maintained at 180–185° while the diimide (1.491 g., 0.00249 mole) in 25 ml. of reagent chloroform was added to 30 ml. of decalin. Isolation of the products as described above gave 0.055 g. (4% yield) of *N,N'*-di(3,3,3-triphenylpropionyl)hydrazine, 0.603 g. (43% yield) of dione IV, m.p. 214–219°, and 0.333 g. of a hydrocarbon mixture containing 55% of triphenylethylene (14% yield) and 45% 1,1,2-triphenylethane (11% yield) as estimated from the ultraviolet and NMR spectra.

(c) *Decompositions in toluene and xylene* were carried out similarly. The results of these decompositions together with those described in detail above are presented in Table I.

Triphenylethylene, kindly supplied by Mr. J. A. Kampmeier, melted at 68–70° after recrystallization from ethanol (lit.,[26] m.p. 67–68°). The ultraviolet maximum in carbon tetrachloride was at 298 mμ, ϵ 19,500. The NMR spectrum (20% in carbon tetrachloride) showed aromatic resonance at −243 and −220. A maximum at −208 is believed to be due to the olefinic hydrogen atom.

1,1,1-Triphenylethane, prepared from methylmagnesium iodide and triphenylmethyl chloride,[27] melted at 94.5–95.5° (lit.[28] m.p. 94–95°). The infrared spectrum (10% in carbon tetrachloride) showed a sharp moderately intense C-methyl absorption at 1378 cm.$^{-1}$, a region which was completely clear in both the spectra of 1,1,2-triphenylethane and triphenylethylene. The NMR spectrum (20% in carbon tetrachloride) showed sharp singlets at −225 and +263 p.p. 10^8 due to the phenyl and methyl group protons, respectively.[20]

1,1,2-Triphenylethane, kindly supplied by Mr. H. Gruen, melted at 54.5–55°, after recrystallization from 95% ethanol (lit.,[29] m.p. 54°). The NMR spectrum (20% solution in carbon tetrachloride) showed aromatic proton absorption at −233 and −220. The CH group gave rise to a triplet at +63 and the CH_2 to a doublet at +155. (J was 8 c.p.s.).

Triphenylacetaldehyde. Triphenylacetaldehyde was prepared by the acid-catalyzed dehydration of triphenylethylene glycol.[30] Triphenylethylene glycol,[31] m.p. 166–167°, (128 g., 0.441 mole) was heated with stirring at reflux 24 hr. with 2.6 l. of 20% sulfuric acid. The resulting lumps of white crystals were filtered, crushed, washed with water, and dried to give 117 g. (97% yield). Comparison of the infrared absorption of the crude product with pure benzhydryl phenyl ketone and pure triphenylacetaldehyde at 1720 cm.$^{-1}$ (aldehyde carbonyl group) and 1685 cm.$^{-1}$ (ketone carbonyl group) indicated that the mixture consisted of 60 per cent of ketone and 40 per cent of aldehyde. In another preparation, using similar amounts of starting materials and a creased flask for more efficient stirring, and allowing refluxing to continue for 8 hr. instead of 24 hr., a dehydration product

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(25) V. J. Altieri, *Gas Analysis and Testing of Gaseous Materials,* American Gas Association, Inc., New York, 1945, p. 257.

(26) J. van de Kamp and M. Sletzinger, *J. Am. Chem. Soc.*, **63** 1880 (1941).

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

(28) E. Spath, *Monatsch*, **34**, 2013 (1913).

(29) A. Klages and B. Heilmann, *Ber.*, **37**, 1455 (1904).

(30) (a) C. J. Collins, *J. Am. Chem. Soc.*, **77**, 5517 (1955). (b) S. Danilov, *J. Russ. Phys. Chem. Soc.*, **49**, 282 (1917).

(31) S. F. Acree, *Ber.*, **37**, 2762 (1905).

whose infrared spectrum indicated the presence of 55% of ketone and 40% of aldehyde was obtained.

Benzhydryl phenyl ketone crystallized much more rapidly from 95% ethanol than did triphenylacetaldehyde. Advantage was taken of this phenomenon in separating the two compounds. Thus, pure triphenylacetaldehyde (white prisms, 32.9 g., 27.4% yield based on triphenylethylene glycol) was obtained; m.p. 105–105.5°; reported[30b] m.p. 105°.

Triphenylacetaldehyde methylhydrazone. A solution of methylhydrazine sulfate (Eastman Kodak White Label, m.p. 141.5–142.5°, 5.300 g., 0.0368 mole) in 10 ml. of distilled water was neutralized with 3.895 g. (0.0368 mole) of reagent sodium carbonate. Absolute ethanol (10 ml.) was added and the supernatant liquid was filtered into a solution of 5.00 g. (0.0184 mole) of triphenylacetaldehyde in 50 ml. of absolute ethanol. The resulting solution was heated 12 hr. on the steam bath. The white, crystalline product which precipitated on cooling was filtered and recrystallized from 95% ethanol; 4.62 g., 84% yield, m.p. 108–133°. Apparently decomposition occurred during melting.

Anal. Calcd. for $C_{21}H_{20}N_2$: C, 84.0; H, 6.7; N, 9.3. Found: C, 83.9; H, 6.9; N, 9.5. C, 83.7; H, 7.0; N, 9.1.

Methylazo-2,2,2-triphenylethane. A solution of triphenylacetaldehyde methylhydrazone (4.62 g., 0.0154 mole) in 50 ml. of glacial acetic acid containing 50 mg. of platinum oxide (estimated uptake of hydrogen, 24 ml., 27°/703 mm.) was shaken for 3.5 hr. with hydrogen supplied to the reaction flask from a water-filled buret equipped with a leveling bulb. The total uptake of hydrogen was 414 ml. (27°/703 mm.; 95%, corrected for temperature, atmospheric pressure, vapor pressure of water and acetic acid, and catalyst uptake). The catalyst was filtered and the solvent was distilled on the steam bath under reduced pressure, leaving a pale yellow oil containing some solid. The hydrazine was not isolated but was oxidized as follows by a modification of the procedure employed by Overberger and Gainer[16] for the preparation of 2,2′-azobis-2-methyl-2-phenylbutane. A solution of the pale yellow oil from the hydrogenation in 50 ml. of reagent ether was stirred for 4.5 hr. with a solution of 10 ml. of 30% hydrogen peroxide (*ca.* 0.1 mole) and 6 g. of sodium bicarbonate in 50 ml. of distilled water. The ether layer was washed with distilled water and dried over sodium sulfate. The ether was removed carefully on the steam bath, then overnight in vacuum at room temperature, leaving 4.41 g. of a viscous pale yellow oil, much of which crystallized on standing for 72 hr. Pure product, m.p. 70–72°, was obtained by recrystallization from methanol. The recrystallization was greatly hampered by the separation of the product as an oil. Therefore, the yield of pure product was low (1.62 g., 36% yield based on triphenylacetaldehyde methylhydrazone). The infrared spectrum measured in carbon tetrachloride showed no absorption maximum above 3100 cm.$^{-1}$ The NMR spectrum of a 20% solution in carbon tetrachloride showed three sharp singlets at −233 (aromatic), 0 (methylene group), and +130 (methyl group).[20]

Anal. Calcd. for $C_{21}H_{20}N_2$: C, 84.0; H, 6.7; N, 9.3. Found: C, 84.0; H, 6.6; N, 9.4.

Thermal decomposition of methylazo-2,2,2-triphenylethane (II). The azo compound II (202 mg., 0.672 mmole) was placed in a tube which was evacuated to 0.1 mm. and filled with nitrogen several times and then heated for 12 hr. at 205 ± 5° in refluxing tetralin vapor. Effluent gases were collected over silicone oil. The theoretical amount of nitrogen is 16.5 ml. but only 4 ml. of gas was evolved. The crude product was dissolved in chloroform to effect its transfer and the chloroform was then removed under reduced pressure to give 171 mg. of dark brown oil with an amine-like odor. Chromatography on ethyl acetate-washed alumina with pentane gave 38 mg. (23% yield) of triphenylmethane, m.p. 89–92°, as shown by comparison of its infrared and NMR spectra with those of an authentic sample and by the fact that a mixed melting point showed no depression. Further elution with pentane-ether (9/1) gave 66 mg. of yellow oil of which the infrared spectrum showed all the bands present in the spectrum of benzophenone. Using the bands at 1320 cm.$^{-1}$ and 1310 cm.$^{-1}$ it was estimated that the fraction contained 11–18% benzophenone (6–10% of the initial triphenylmethyl groups). Further elution with increasing amounts of ether and finally with methanol gave 69 mg. of additional red and brown oils which could not be identified.

Triphenylacetaldehyde acetylhydrazone. To a solution of triphenylacetaldehyde hydrazone[32] (112 mg., 0.390 mmole, m.p. 138–140°) in 2 ml. of reagent pyridine was added *ca.* 0.2 ml. of reagent acetyl chloride. Excess distilled water was added and the resulting white solid was filtered and washed with distilled water. Two recrystallizations from 95% ethanol gave 57 mg. (45% yield) of white platelets, m.p. 238.5–239°.

Anal. Calcd. for $C_{22}H_{20}N_2O$: C, 80.5; H, 6.1; N, 8.5. Found: C, 80.1; H, 6.2; N, 8.3.

The compound could also be prepared from triphenylacetaldehyde (5.00 g., 0.0184 mole) and acetylhydrazide (1.63 g., 0.0220 mole) which were heated overnight at reflux in 75 ml. of 95% ethanol, during which time white crystals separated from the hot solution. The mixture was chilled and filtered and the product was washed with generous quantities of 95% ethanol. The yield of product, m.p. 237–239°, after drying was 5.50 g., 91.2% yield. Admixture with the product prepared from triphenylacetaldehyde hydrazone and acetyl chloride gave no depression of the melting point. The infrared spectra of the two products were identical.

N-(2,2,2-Triphenylethyl)-N′-acetylhydrazine. A solution of triphenylacetaldehyde acetylhydrazone (3.572 g., 0.01087 mole) in 150 ml. of glacial acetic acid containing 201 mg. of platinum oxide (estimated uptake of hydrogen, 99 ml., 24°/697 mm.) was shaken for 6.3 hr. with hydrogen at 1 atm. The total uptake of hydrogen was 395 ml. (24°/697 mm.; 102%, corrected for temperature, atmospheric pressure, vapor pressure of water and acetic acid, and catalyst uptake). The catalyst was filtered and the solvent was distilled under reduced pressure, leaving a white solid, which on drying weighed 3.513 g. (97.8% yield) and whose infrared spectrum was identical with that of the product recrystallized once from 95% ethanol. Repeated recrystallizations caused air oxidation with formation of triphenylacetaldehyde acetylhydrazone, the appearance of whose strong infrared bands at 1385 cm.$^{-1}$ and 1330 cm.$^{-1}$ was noted. The melting point was dramatically dependent on the rate of heating. When heated at 1–2°/min. at 140–150°, the product began to melt at 151°, while when heated rapidly the melting point was around 170°.

Anal. Calcd. for $C_{22}H_{22}N_2O$: C, 80.0; H, 6.7; N, 8.5. Found: C, 80.3; H, 6.9; N, 8.4.

2,2,2-Triphenylethylhydrazine hydrochloride. A solution of *N*-(2,2,2-triphenylethyl)-*N*′-acetylhydrazine (508 mg., 1.54 mmoles) in 18 ml. of 95% ethanol and 2 ml. of concd. hydrochloric acid was heated for 12 hr. under reflux. The solvents were distilled at reduced pressure, leaving a white solid which was washed exhaustively with ether and dried (78°/1 mm.) over potassium hydroxide; 463 mg. (92.7% yield), m.p. 197–199° dec. The hydrochloride could be sublimed slowly under high vacuum (150°/0.2 mm.), but sublimation did not raise the melting point.

Anal. Calcd. for $C_{20}H_{21}ClN_2$: C, 73.9; H, 6.5; N, 8.6. Found: C, 73.5; H, 6.4; N, 8.4.

Attempted isolation of 2,2,2-triphenylethylhydrazine. 2,2,2-Triphenylethylhydrazine hydrochloride (198 mg., 0.610 mmole) was shaken in a 50-ml. of reagent ether. During this step, no matter how finely ground beforehand, some of the hydrochloride formed lumps which were neutralized slowly. Thus, the next step was carried out before the neutralization was complete. The ether layer was washed with distilled water until the washings were neutral (three or four times), dried over sodium sulfate, and filtered. The solvent

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(32) L. Hellerman and R. L. Garner, *J. Am. Chem. Soc.*, **57**, 139 (1935).

was removed in a stream of nitrogen, leaving fine, white needles, which were dried overnight under high vacuum at room temperature; 111 mg. (76.1% yield), m.p. 86–88° with decomposition and gas evolution. An accurate elemental analysis could not be made because the compound lost weight on the analytical balance. Thus, the decomposition in air is very rapid, with apparent loss of nitrogen. On standing in air the white crystals reverted to a pale yellow gum with entrained gas bubbles. An infrared spectrum run after 2 days' standing exhibited bands characteristic of the infrared spectrum of benzophenone. A calculation using the carbonyl group stretching frequency at 1655 cm.$^{-1}$ indicated the presence of 4.5–7.5% benzophenone.

Anal. Calcd. for $C_{20}H_{20}N_2$: C, 83.3; H, 7.0; N, 9.7. Found: C, 79.6; H, 6.5; N, 4.7.

Air oxidation of 2,2,2-triphenylethylhydrazine. A solution of 2,2,2-triphenylethylhydrazine in 30 ml. of reagent benzene prepared by the neutralization of 2,2,2-triphenylethylhydrazine hydrochloride (535 mg., 1.62 mmoles) was heated for 10 hr. under reflux. The benzene was distilled at reduced pressure, leaving 320 mg. of a light yellow oil, whose infrared spectrum, when compared with that of benzophenone, revealed the presence of 12% (13% yield calculated for the stoichiometry in which 1 mole of benzophenone is formed from 1 mole of hydrazine and based on 2,2,2-triphenylethylhydrazine hydrochloride) of benzophenone. Chromatography of 285 mg. of the yellow-orange oil on 15 g. of ethyl acetate–washed alumina, activated overnight at 130°, gave 64 mg. of a hydrocarbon fraction shown by examination of the ultraviolet spectrum to contain no more than 9% (1% yield) of triphenylethylene. Absence of absorption in the infrared at 1380 cm.$^{-1}$ indicated that no significant amounts of 1,1,1-triphenylethane were present. The NMR spectrum gave no evidence of the presence of 1,1,2-triphenylethylene nor dibenzyl, although a maximum at +90 p.p. 10^8 indicated the possible presence of diphenylmethane. The second fraction obtained by elution with 600 ml. of benzene amounted to 145 mg. and the ultraviolet spectrum showed absorption at 252 mμ indicating that it consisted to the extent of about 33% of benzophenone. No other products were isolated. From another run carried out in a similar fashion, except that air was bubbled through the solution, benzophenone, estimated from the infrared to have been formed in about 20% yield, was isolated as the 2,4-dinitrophenylhydrazone, m.p. 236–238°, and a mixed melting point with an authentic sample, m.p. 240–241°, showed no depression.

Reaction of ethyl 3,3,3-triphenylpropionate and sodium in xylene. The procedure was similar to that used in the preparation of lauroin.[33] A solution of ethyl 3,3,3-triphenylpropionate[34] (5.00 g., 0.0151 mole, m.p. 79–80.5°) in 30 ml. of reagent xylene was added dropwise to a rapidly stirred suspension of 0.7 g. (0.03 g. atom) of freshly-cut sodium in 100 ml. of reagent xylene heated in an oil bath held at 119°. The addition required 5 min. and heating was continued for 30 min., while the reaction flask was constantly swept with nitrogen. The reaction mixture was then cooled to room temperature and 10 ml. of reagent methanol was added to decompose the excess sodium. The xylene solution was extracted with 5% hydrochloric acid and water. The xylene was distilled on the steam bath under reduced pressure, leaving 4.07 g. of a viscous light brown residue. The crude product was chromatographed on 200 g. of untreated alumina. Triphenylmethane (1.50 g., 42% yield, m.p. 89–93°) was eluted with 4:1 hexanebenzene. Several recrystallizations from absolute ethanol gave pure triphenylmethane; m.p. 93–93.5°, reported, m.p. 92.5–93°. An infrared spectrum was identical with a spectrum of authentic triphenylmethane. The NMR spectrum (50% solution in carbon tetrachloride) showed a singlet at −55 p.p. 10^8. The subsequent fractions of the chromatography were not examined.

Anal. Calcd. for $C_{19}H_{16}$: C, 93.4; H, 6.6. Found: C, 93.4; H, 6.9.

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[33] S. M. McElvain, *Org. Reactions*, IV, 256 (1948).

[34] A. T. Blomquist, R. W. Holley, and O. J. Sweeting, *J. Am. Chem. Soc.*, **69**, 2356 (1957).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF LOYOLA UNIVERSITY OF CHICAGO]

Ring Size Effects in the Neophyl Rearrangement[1,2]

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1-Phenylcyclopentylacetaldehyde (I) and 1-phenylcyclohexylacetaldehyde (II) have been prepared and characterized. The rearrangement percentages upon di-*t*-butyl peroxide-induced decarbonylation in the liquid phase under various conditions have been determined (Table V). The results indicate that the 1,2-phenyl shift is markedly more facile in II than in I. Arguments are presented that this ring size effect results from differences in steric interference with the formation of the requisite transition states and from differences in the hydrogen donor abilities of the aldehydes. The reactions follow the course of other neophyl-type rearrangements and do not appear to involve bridged radicals as intermediates.

The production of a radical site on the cyclohexane ring is generally rather difficult and, in some of the comparisons known, less ready than on the cyclopentane ring, a situation common also to carbonium ion and carbanion formation[4] on these rings. Cyclopentene, for instance, is three to seven times more reactive than cyclohexene toward addition of trichloromethyl radicals in the photochemical addition of bromotrichloromethane[5] while cyclopentaneazobisnitrile undergoes thermal decomposition at 80° about 11.5 times as fast as does the cyclohexane analog.[6] Commonly these ring size effects have been ascribed to conforma-

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[1] Abstracted from the thesis of Brother Herbert Philip (Hogan), F.S.C., presented to the faculty of the Graduate School of Loyola University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1959.

[2] A preliminary report of this work appeared in *J. Org. Chem.*, **24**, 441 (1959).

[3] An Arthur Schmidt Pre-doctoral Fellow, 1957–58.

[4] For a survey of much work in these areas, see E. L. Eliel in *Steric Effects in Organic Chemistry*, edited by M. S. Newman, John Wiley and Sons, New York, N.Y., 1956, pp. 121 ff.