

similar manner, except that the dichloride was added dropwise into the vaporization coil.

Pyrolysis of 2-Iodomethyl-3-iodopropene. 2-Iodomethyl-3-iodopropene (2 g) was placed in a 25-ml distilling flask, and the flask was heated to 210°. Nothing volatile was observed. Iodine and a black polymeric material remained in the flask.

Reaction of 2-Iodomethyl-3-iodopropene with NaK in the Presence of Ethene. The reaction was carried out as above (3.1 g, 0.010 mole of 2-iodomethyl-3-iodopropene) except that ethene (0.20 mole) was added to the helium stream over the duration of the 18-min reaction period. Analysis of products was the same as above.

Preparation of 1,3-Diiodo-2-methylpropane. Attempts to prepare this compound by the Finkelstein exchange from 1-bromo-3-chloro-2-methylpropane under the usual conditions of refluxing acetone or 2-butanone resulted in replacement of the bromine alone. 1-Iodo-3-chloro-2-methylpropane, bp 45–47° (5 mm), was obtained in 74% yield. The mass spectrum had a parent peak at *m/e* 218. The nmr spectrum consisted of doublets at 1.12, 3.30, and 3.54 ppm, and a multiplet at 1.83 ppm in a ratio of 3:2:2:1.

The diiodide was obtained in 20% yield by carrying out the exchange reaction in a 100° acetone solution for 68 hr, employing a high-pressure bomb. The pure diiodide was isolated by distillation, bp 56–57° (1 mm). The nmr spectrum showed two doublets at 1.16 and 3.27 ppm, and a multiplet at 1.60 ppm in a ratio of 3:4:1.

Reaction of 1,3-Diiodo-2-methylpropane. The diiodide (2.47 g, 0.00797 mole) was vaporized from the 95° coil over a period of 12 min and was carried into the 227–228° reaction zone. The products were distilled through a –78° trap into a –196° trap on a vacuum line. Nothing was collected in the –78° trap. The gas in the –196° trap (0.00640 mole, 80.3% yield) was analyzed by vpc.

Simultaneous Reaction of Allene and Dibromomethane with NaK. Dibromomethane (8.8 g, 0.051 mole) was added dropwise to the vaporization coil of the NaK apparatus, and allene (0.34 mole) was added simultaneously to the helium carrier stream. The temperature of the vaporization coil was 74° and that of the reaction zone varied between 200 and 230°. The reaction time was 25 min.

The product was distilled through a –78° trap into a –196° trap on the vacuum line. The product in the –78° trap (0.1 g) consisted of six unidentified liquids with retention times less than those of 1,4-dimethylencyclohexane and *p*-xylene. The gas in the –196° trap (0.125 mole) consisted of (mole ratios) propane (5), propene (55), allene (33), 1-butene (3), and methylenecyclopropane (4). From a reaction at 270–280° none of the allene was recovered.

Reaction of 2-Iodomethyl-3-iodopropene with Excess Diiodomethane and NaK. 2-Iodomethyl-3-iodopropene (2.7 g, 0.0087 mole) and diiodomethane (12.2 g, 0.046 mole) were mixed and added dropwise to the vaporization coil of the NaK apparatus. The temperature of the vaporization coil was 100° and that of the reaction zone varied between 235 and 240°. The reaction was conducted over a period of 20 min.

The product was distilled through a –78° trap into a –196° trap on the vacuum line. A liquid, weighing 0.12 g, remained in the –78° trap. Analysis by vpc (Carbowax, 63°; and dipropylene glycol dibenzoate, 118°) showed that the liquid consisted of (mole ratios) benzene (2), 1,4-dimethylencyclohexane (20), *p*-xylene (33), and 17 unidentified components (45). The gas (0.00945 mole) was analyzed by vpc (dipropylene glycol dibenzoate, 25°; and 2,5-hexanedione, 0°). The products probably derived only from CH₂I₂ consisted (mole ratio) of ethane (9.8), ethene (80.0), propane (1.9), propene (6.7), and cyclopropane (1.7), the remainder of the gases being derived from trimethylencmethane (see Table III

Reaction of Triphenylmethyl with Diazomethane

Donald B. Denney and Neil F. Newman

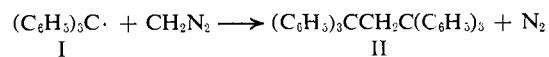
Contribution from the School of Chemistry, Rutgers, The State University, New Brunswick, New Jersey 08903. Received February 25, 1967

Abstract: The reaction of triphenylmethyl with diazomethane has been studied under several sets of conditions. The major products are 1,1,1,3,3,3-hexaphenylpropane, triphenylmethane, triphenylethylene, and 1,1,2-triphenylethane. The yields of products are strongly dependent on the concentration of reactants with the hexaphenylpropane being formed in greatest amount under more concentrated conditions. The results of these experiments are most easily explained by a mechanism which involves formation of a 2,2,2-triphenylethyl radical by reaction of a triphenylmethyl radical with diazomethane. This radical can then rearrange or react with triphenylmethyl to give 1,1,1,3,3,3-hexaphenylpropane. It has been found that this substance decomposes quantitatively at 250° to triphenylmethane and triphenylethylene.

Although diazomethane most commonly reacts by ionic or carbene pathways, it is also susceptible to attack by free radicals. The presence of radical intermediates in diazomethane reactions has been demonstrated by Urry and co-workers¹ who observed a high quantum yield in photoinitiated reactions of diazomethane with polyhalomethanes. They proposed that a radical chain reaction was involved.

More recently Müller and co-workers² have investigated the reaction of diazomethane with aryloxy radicals. The products are methylene acetals and these can be most easily explained by a free radical mechanism. These workers also reinvestigated the reaction of triphenylmethyl with diazomethane which was

originally described by Schlenk.³ Schlenk reported that 1,1,1,3,3,3-hexaphenylpropane (II) was formed as the product of this reaction.



The structural assignment was based on molecular weight and analytical data. Müller, *et al.*, isolated the same compound and reported its nmr spectrum which showed a single absorption at 4.13 ppm and aromatic protons at 6.86 ppm in the ratio of 1:15. This spectrum is certainly in agreement with the structural assignment except perhaps for the position of the –CH₂– absorption which is downfield from the normal region where this is found. This downfield shift could be due to deshielding by the aromatic rings.

(1) W. H. Urry, J. R. Eiszner, and J. W. Wilt, *J. Am. Chem. Soc.*, **79**, 918 (1957).

(2) E. Müller, A. Moosmayer, and A. Rieker, *Z. Naturforsch.*, **18b**, 982 (1963).

(3) W. Schlenk and C. Bornhardt, *Ann.*, **394**, 183 (1912).

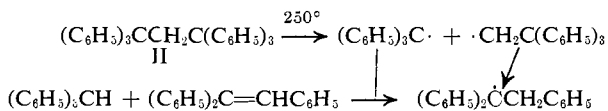
These observations are of particular interest because the most reasonable mechanism for the reaction of triphenylmethyl with diazomethane would involve the 2,2,2-triphenylethyl radical as an intermediate. At the time of the inception of this present study all attempts but one to prepare this radical and trap it before it rearranged had been unsuccessful.^{4,5} The only indication that a 2,2,2-triphenylethyl radical had any stability arose from the finding of 1,1,1,4,4,4-hexaphenylbutane as a product of the decomposition of 3,3,3-triphenylpropanoyl peroxide.⁶ The yield of this material was very small; however, this could have been due to factors other than the instability of the 2,2,2-triphenylethyl radical.

Quite recently Kaplan⁷ has studied the reduction of 2,2,2-triphenylethyl chloride by triphenyltin hydride. He has found that 1,1,1-triphenylethane can be obtained in yields as high as 90% by using suitable reaction conditions. He concluded that the 2,2,2-triphenylethyl radical was formed and was efficiently trapped before rearrangement.

It was the purpose of this work to (1) investigate the mechanism of the triphenylmethyl-diazomethane reaction, (2) to add further structural proof for the 1,1,1,3,3,3-hexaphenylpropane, and (3) if 2,2,2-triphenylethyl radicals were involved to try and learn more about their stability.

Results and Discussion

The reaction of triphenylmethyl with diazomethane in benzene at 25° affords the material reported to be 1,1,1,3,3,3-hexaphenylpropane. Further structural proof for this material has been obtained by studying its thermal decomposition. After 1 hr at 250° complete decomposition had occurred and a quantitative yield of triphenylmethane and triphenylethylene was obtained.



The products of this reaction can be easily rationalized if the starting material is in fact II and thus on this basis and the other evidence the structure seems firmly established.⁸

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

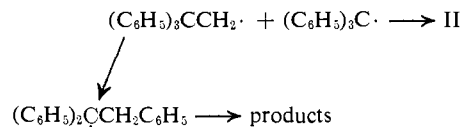
(5) D. Y. Curtin and T. C. Miller, *J. Org. Chem.*, **25**, 885 (1960).

(6) D. B. Denney, R. L. Ellsworth, and D. Z. Denney, *J. Am. Chem. Soc.*, **86**, 1116 (1964).

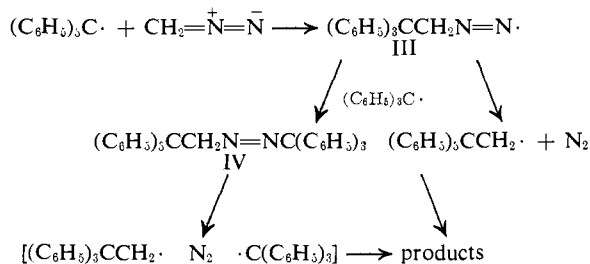
(7) L. Kaplan, *ibid.*, **88**, 4531 (1966).

(8) A referee has suggested that an alternate structure, $(\text{C}_6\text{H}_5)_3\text{C}-\text{C}(\text{C}_6\text{H}_5)_2\text{CH}_2\text{C}_6\text{H}_5$, should be considered for II. We had considered this as a possibility and discarded it for two reasons. The yield of II varies as a function of the concentration of starting materials. This is what is predicted for II if it is in fact 1,1,1,3,3,3-hexaphenylpropane. If it is 1,1,1,2,2,3-hexaphenylpropane then the yield should not vary as a function of concentration, nor should the relative amounts of products change. There is no report of the preparation of 1,1,1,2,2,3-hexaphenylpropane in the literature; however, one can predict from the stabilities of structurally similar materials that it will be quite unstable. Pentaphenylethane is known to react with oxygen quite rapidly, $t_{1/2} = 49$ min at 80°; see J. Coops, H. Galenkamp, J. Haantjes, H. L. Luirink, and W. Th. Nauta, *Rec. Trav. Chim.*, **67**, 469 (1948), and references therein. K. Ziegler, A. Seib, K. Knoevenagel, P. Herte, and F. Andreas, *Ann.*, **551**, 161 (1942), have studied the reactions of various compounds, $\text{RC}(\text{C}_6\text{H}_5)_2\text{C}(\text{C}_6\text{H}_5)_2\text{R}$, with oxygen. They find when $\text{R} = \text{C}_6\text{H}_5$, $t_{1/2} = 60$ min, and $\text{R} = n\text{-C}_3\text{H}_7$, $t_{1/2} = 1.3$ min at 20°. These data are relevant to our understanding of the influences of resonance and steric effects in promoting the dissociation of the carbon-carbon bond. It is quite apparent that 1,1,1,2,2,3-hexaphenylpropane has the ability to dissociate into a triphenylmethyl radical as does pentaphenylethane,

Investigation of the reaction mixture after the removal of II showed that triphenylmethane, triphenylethylene, and 1,1,2-triphenylethane were also products of the reaction. No evidence for the formation of 1,1,1-triphenylethane was obtained; however, trace amounts (<1-2%) could have escaped detection. The rearranged triphenylethyl compounds are indicative of the formation of a 2,2,2-triphenylethyl species and in this case the radical is by far the most likely candidate.⁹ Furthermore it was found that the ratio of rearranged material to II varied as a function of the concentration of starting material. For example, a solution whose initial concentration of hexaphenylethane was $8.5 \times 10^{-2} M$ and whose diazomethane concentration was $1.5 \times 10^{-1} M$ gave a 26.5% yield of II, 13.1% of triphenylmethane, 20.7% of triphenylethylene, and 8.1% of 1,1,2-triphenylethane. When the initial concentration of hexaphenylethane was $2.7 \times 10^{-3} M$ and the diazomethane concentration was $2.7 \times 10^{-2} M$ the yields were 5.4, 25.3, 32.7, and 7.3%, respectively. The changes in product ratios with changes in concentrations are indicative of competing processes with different kinetic orders. These data are satisfactorily accommodated if a 2,2,2-triphenylethyl radical is formed during the reaction sequence and it undergoes intramolecular rearrangement which is in competition with combination with triphenylmethyl to give II. The route by which



the 2,2,2-triphenylethyl radical is formed is not defined in detail by these studies; however, an addition to diazomethane followed by loss of nitrogen seems most likely. The intermediate azo radical probably loses



nitrogen rapidly to give the 2,2,2-triphenylethyl radical which then reacts by rearrangement or reaction with triphenylmethyl. Reaction of III with triphenylmethyl to give the azo compound IV cannot be completely excluded. It cannot be the only mode of reaction for III because then decomposition of IV should yield essentially the same amounts of unrearranged *vs.* rearranged materials irrespective of the concentrations of reactants. Loss of nitrogen from III is probably ex-

and it also has steric interactions like those of the hexasubstituted ethanes. These two factors then should make this material less stable than either of the two kinds of ethanes and thus one predicts with a high degree of certainty that 1,1,1,2,2,3-hexaphenylpropane will be very unstable indeed. In fact the substance, II, showed no change in melting point after standing at 25° in the presence of air for 15 months.

(9) Rearrangement of the 2,2,2-triphenylethyl cation and carbanion are known and thus these intermediates cannot be absolutely excluded from consideration. There is, however, no obvious way in which they can be formed by reaction of triphenylmethyl with diazomethane and so they will not be given further consideration.

ceedingly fast¹⁰ and there seems to be very little reason for considering that IV can be formed in any appreciable quantity.

Unfortunately, the results of these experiments do not permit an accurate assessment of the rate of rearrangement of the 2,2,2-triphenylethyl radical; however, it must be a relatively fast process to be able to compete with hexaphenylpropane formation.

Experimental Section¹¹

Triphenylmethyl. Trityl chloride, 22.0 g, in 200 ml of dry benzene was stirred under nitrogen for 20 hr with 77.0 g of mercury. The resulting solution was filtered by forcing it under nitrogen pressure through a filter stick. The yield of triphenylmethyl was determined by allowing an aliquot of the solution to react with oxygen. Insoluble trityl peroxide is formed under these conditions. Yields of triphenylmethyl were 70–77%.

Reaction of Triphenylmethyl with Diazomethane in Benzene. Solutions of diazomethane in benzene were prepared by decomposing *p*-toluenesulfonylnitrosamide and entraining the liberated diazomethane in a stream of nitrogen. The diazomethane–nitrogen gas mixture was then allowed to bubble through cold benzene.

A solution of 1.3 g (0.031 mole) of diazomethane in 90 ml of benzene was added to a stirred solution of 7.1 g (0.029 mole) of triphenylmethyl in 250 ml of benzene. The resulting solution was stirred under nitrogen at 25° for 75 min. At that time a solution of 1.5 g (0.036 mole) of diazomethane in 100 ml of benzene was added. The orange-red color of the triphenylmethyl disappeared *ca.* 135 min after the initial addition of the diazomethane. The reaction mixture was allowed to stand under nitrogen at 25° for 24 hr.

In another experiment 7.5 g (0.031 mole) of triphenylmethyl in 250 ml of benzene was added dropwise over a period of 3 hr to a stirred solution of 1.3 g (0.031 mole) of diazomethane in 2.2 l. of benzene. After 75 min a solution of 1.5 g (0.036 mole) of diazomethane in 100 ml of benzene was added. The reaction mixture was allowed to stand under nitrogen for 20 hr.

Product Isolation. The benzene solutions were evaporated to 30 ml and then treated with 20 ml of hexane. The resulting solutions were cooled for 2 hr in an ice bath. The mixtures were filtered to remove trityl peroxide, and then the solvents were removed *in vacuo* to give a dark oil which was treated with 40 ml of a solution of methanol–acetone, 3:1. A white crystalline material precipitated, mp 200–214°. A small amount of the same material was obtained as a residue after evaporatively distilling the oil obtained after removing the methanol and acetone. The melting points

(10) W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, Chapter 10.

(11) Infrared spectra were recorded on a Perkin-Elmer Model 21 spectrometer. The ultraviolet spectra were obtained with a Cary Model 14 spectrometer. The nmr spectra were measured with a Varian Associates Model A-60 spectrometer; absorptions are reported in parts per million relative to tetramethylsilane as an internal standard.

were raised to 218.5–219.8° (lit.^{2,3} 216°) after recrystallization from acetic acid. The yields were 1.91 (26.5%) and 0.42 g (5.4%). The nmr spectra were identical with that reported.² The molecular weight was found to be 496 (calcd for C₃₀H₃₂: 500), by the Rast method.

The oily distillate obtained above had a singlet at 5.45 ppm which is characteristic of the methine proton in triphenylmethane. Gas-liquid chromatography of the distillate on a silicone gum column at 180° showed that there was a material present whose retention time was identical with that of triphenylmethane. Triphenylmethane was isolated from a preliminary experiment by chromatographing the reaction mixture, after removal of excess solvent, on silica gel. Elution with benzene–hexane, 1:3, afforded triphenylmethane, mp 88–91°, with no depression on admixture with an authentic sample. The yields of triphenylmethane were obtained by glpc using dicumyl as an internal standard.

The molecular distillate had a maximum absorption in the ultraviolet at 300 m μ ; reported for triphenylethylene 300 m μ .⁵ Glpc analysis on a silicone gum column at 180° showed a material with a retention time identical with that of triphenylethylene. The yields of triphenylethylene were calculated from ultraviolet and glpc data. Good agreement was obtained between the two methods.

The nmr spectrum of the molecular distillate had a doublet at 3.2 ppm ($J = 8$ cps) and a triplet at 4.1 ppm ($J = 8$ cps). These absorptions were also found in an authentic sample of 1,1,2-triphenylethane. Glpc analysis on a silicone gum column at 180° showed that a material was present whose retention time was identical with that of 1,1,2-triphenylethane. The yields of this substance were calculated from glpc data using dicumyl as an internal standard.

Reaction of Triphenylmethyl with Diazomethane in Ether. Reactions entirely similar to those reported above were conducted in ether solution. In one experiment the initial concentrations of triphenylmethyl and diazomethane were $8.7 \times 10^{-2} M$ and $1.7 \times 10^{-1} M$, respectively. In this case the yields of products were: 1,1,1,3,3,3-hexaphenylpropane, 29.4%, triphenylmethane, 11.1%, triphenylethylene, 14.5%, and triphenylethane, 4.5%. In another experiment the initial concentration of triphenylmethyl was $1.6 \times 10^{-3} M$ and the diazomethane was $3.2 \times 10^{-2} M$. The yields of products were: 1,1,1,3,3,3-hexaphenylpropane, 7.4%, triphenylmethane, 15.6%, triphenylethylene, 24.2%, and 1,1,2-triphenylethane, 8.9%. The nmr spectra of the crude reaction mixtures, containing broad aliphatic proton resonances at 0.9 and 1.2 ppm, indicated that some reaction with the solvent had occurred; however, no identifiable products could be isolated.

Thermal Decomposition of 1,1,1,3,3,3-Hexaphenylpropane. A sample, 0.103 g, of the material believed to be 1,1,1,3,3,3-hexaphenylpropane was heated at 250° for 1 hr in a sealed glass ampoule. The cooled product, a colorless oil, weighed 0.103 g. Glpc analysis showed that only two materials, whose retention times were identical with those of triphenylmethane and triphenylethylene, were present. The nmr spectrum had, besides absorptions in the aromatic region, an absorption at 5.45 ppm identical with that of triphenylmethane. The ultraviolet spectrum showed a maximum at 300 m μ which confirmed the presence of triphenylethylene.