tions at 100° and 30-p.s.i. helium inlet pressure at a flow rate of 200 ml./min. Only the front half of the myrcene peak was trapped, and 5 ml. of material was thus collected which contained approximately 60% α-myrcene, and 40% β-myrcene. Retrapping of this material in the same manner yielded α-myrcene which was 90% pure by analytical g.l.c.

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Attempted Synthesis of Hexaphenylcyclopropane

B. S. Gorton

Research Division, Electrochemicals Department,
E. I. du Pont de Nemours and Company, Inc.,
Wilmington, Delaware

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Korshak[1] has reported the synthesis of polydiphenylmethylene. The polymer was derived by a polyrecombination reaction in which diphenylmethane was treated with a stoichiometric amount of *t*-butyl peroxide, and was reported to have molecular weights of from 10,000 to 900,000. The high degree of steric hindrance in the chain and the possibility of hydrogen abstraction from the benzene ring during synthesis suggest that structures other than a linear one may be formed, although infrared spectra did not indicate the presence of any disubstituted benzene rings. To study this question, an attempt was made to prepare the polymer by an alternate route.

It has been reported that cyclopropanes can be polymerized either by heat and pressure[2] or by titanium coordination catalysts.[3] The results suggested that, if hexaphenylcyclopropane could be prepared, it might undergo ring opening to form polydiphenylmethylene.

The synthesis of hexaphenylcyclopropane was attempted by two techniques. One was the addition of diphenylmethylene to tetraphenylethylene; the other, the synthesis of hexaphenyl-1,3-propylene glycol.

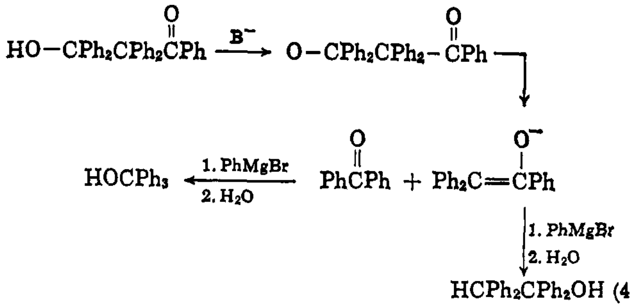
In planning the addition reaction, the series of tri-, tetra-, and pentaphenylcyclopropanes leading up to hexaphenylcyclopropanes were tried as models. The tri- and tetrasubstituted compounds, 1,1,2,2-tetraphenylcyclopropane and 1,1,2-triphenylcyclopropane, were made, but both the penta- and hexasubstituted ones failed. Only hexaphenylpyrazoline was isolated in the latter case.

The other planned route to hexaphenylcyclopropane is shown by eq. 1–3. However, our first step to hexaphenylpropylene glycol failed. Instead, 2-benzoyl-1,1,2,2-tetraphenylethanol was isolated. When this compound was treated further with phenylmagnesium bromide, the products isolated were triphenylmethanol, tetraphenylethanol, and biphenyl. These products correspond to a decomposition by the mechanism shown in eq. 4. The biphenyl is believed to be a by-product from the Grignard reagent and not a decomposition product of 2-benzyl-1,1,2,2-tetraphenylethanol.

$$Ph_2C(COOC_2H_5)_2 \xrightarrow[2.\ H_2O]{1.\ PhMgBr} HO[Ph_2]_3OH \tag{1}$$

$$HO[CPh_2]_3OH \xrightarrow{PBr_3} Br[CPh_2]_3Br \tag{2}$$

$$Br[CPh_2]_3Br \xrightarrow{Zn} C_3Ph_6 \tag{3}$$



(4)

Experimental

1,1,2-Triphenylcyclopropane.—A solution of 0.033 mole of diphenyldiazomethane[4] in 6 ml. of ethyl ether was added to 25 ml. of styrene. After the solution was irradiated for 2 hr. with a G. E. ultraviolet sun lamp (RS275-R-40), the red color of the diphenyldiazomethane was discharged and a yellow color had formed.

The solution was diluted with *ca.* 500 ml. of petroleum ether. A precipitate of polystyrene was filtered off and discarded. The petroleum ether filtrate was evaporated under vacuum to an oil which was diluted with methanol. Some more polystyrene precipitated and was filtered off. The filtrate was once again evaporated to an oil and allowed to stand for several days. Crystals formed which were soluble in petroleum ether and moderately soluble in methanol. Recrystallization from methanol gave about 4 g. of white needles, m.p. 51–52°.

Anal. Calcd. for $C_{21}H_{18}$: C, 93.37; H, 6.63. Found: C, 93.39; H, 6.75.

The infrared spectrum of the compound (KBr pellet) shows peaks at 2.90 (s), 3.30 (s), 6.23 (s), 6.68 (s), 6.90 (s), 9.27 (m), 9.67 (m), 10.3 (m), 12.8 (s), 13.05 (s), 13.3 (m), 13.55 (m), and 14.2–14.4 (broad, strong) μ.

The n.m.r. spectrum of the sample in CCl_4 (Varian S-60A, 60 Mc., with tetramethylsilane as standard) was more complex than expected. The aromatic frequency was split unequally to −420 and −429 c.p.s. in ratio of 2:1, respectively. The $H\alpha$ line was split twice equally to −175, −168, −166, and −159 c.p.s. as expected. However, $H\beta^1$ and $H\beta^2$ showed seven lines instead of the expected eight: −120, −114, −115, −109, −104, −100, and −95 c.p.s. The ratio of the sum of areas of $H\alpha$, $H\beta^1$, and $H\beta^2$ to the aromatic hydrogen was 1:5 as expected. No propene structure was present.

1,1,2,2-Tetraphenylcyclopropane.—Approximately 0.05 mole of solid diphenyldiazomethane was prepared by evaporation of a petroleum ether solution under vacuum (see above). The solid was dissolved in 100 g. of 1,1-diphenylethylene[5] and the mixture was irradiated under a G.E. ultraviolet sun lamp for 2 days. The white crystals which formed were filtered off and washed with small amounts of petroleum ether to give about 8 g. of a product with m.p. 167–170°. Skell[6] has reported the reaction of diphenyldiazomethane with 1,1-diphenylethylene, but no details or properties of the product were given.

Anal. Calcd. for $C_{27}H_{22}$: C, 93.65; H, 6.35. Found: C, 93.65; H, 6.48.

The infrared spectrum (in KBr) was 2.95 (s), 3.30 (s), 6.25 (s), 6.70 (s), 6.90 (s), 9.25 (m), 9.65 (m), 9.85 (m), 10.95 (m), 12.52 (s), 13.2 (s), 13.9 (s), and 14.3 (s) μ.

The n.m.r. spectrum of the sample (as above) had one peak at −417 and one at −148 c.p.s.; the ratio of their areas was

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[1] (a) V. V. Korshak, S. L. Sosin, *Proc. Acad. Sci. USSR, Chem. Sec., Eng. Transl.*, **132**, 517 (1960); (b) V. V. Korshak, S. L. Sosin, *Vysokomolekul. Soedin.*, **3**, 1332 (1961).

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[3] M. Yamada, M. Yanagita, S. Makoto, *Rept. Inst. Phys. Chem. Res.* (Tokyo), **37**, 429 (1961).

[4] L. I. Smith and K. L. Howard "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 351.

[5] C. F. H. Allen and S. Converse "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 226.

[6] R. M. Etter, H. S. Skovronek, and P. S. Skell, *J. Am. Chem. Soc.*, **81**, 1008 (1959).

10:1, respectively. No peaks were present which could be assigned to a propene struckture.

Attempted Preparation of Pentaphenylcyclopropane. A. Ultraviolet Catalyzed.—A saturated solution of triphenylethylene[7] in petroleum ether was prepared. The solution formed by adding 0.05 mole of solid diphenyldiazomethane to the solution was irradiated for 4 days using the G.E. sun lamp, by which time the color was discharged. Fractional crystallization of the mixture from a large excess of petroleum ether yielded only crude diphenylketazine, m.p. 141–152° (identified by infrared spectra), unchanged triphenylethylene, and slight amount of unidentified oil.

B. Thermal Decomposition.—To a melt of 100 g. of triphenylethylene was slowly added a saturated solution of 0.1 mole of diphenyldiazomethane in petroleum ether. The mixture was heated for 2 days at 100°. Only unchanged triphenylethylene could be identified in the reaction mixture.

3,3,4,4,5,5-Hexaphenylpyrazoline.—To a solution of 0.2 mole of diphenyldiazomethane in 250 ml. of benzene was added 28.5 g. of tetraphenylethylene (Columbia Organic Chemicals, Columbia, S. C.). The mixture was refluxed on a steam bath for 3 days to give an orange-colored solution. The solution on cooling deposited crystalline tetraphenylethylene. The solution was concentrated further and crystals were removed at intervals. Diphenylketazine, identified by infrared spectrum, came out next, and finally several fractions of crystals melting from 90–130° were obtained. The crude crystals were purified by vacuum sublimation to give about 12 g. of a yellow, waxy material which was recrystallized from ethanol to give crystals, m.p. 123–131°.

Anal. Calcd. for $C_{39}H_{30}N_2$: C, 89.0; H, 5.70; N, 5.32. Found: C, 88.44; H, 5.94; N, 5.44.

The infrared spectrum of the compound (KBr pellet) shows peaks at 2.90 (m), 3.30 (m), 6.20 (s), 6.30 (m), 6.40 (m), 6.72 (s), 6.95 (s), 7.60 (s), 7.82 (m), 8.50 (m), 9.30 (m), 9.72 (s), 10.45 (m), 10.75 (w, shoulder), 10.95 (m), 12.83 (s), 13.05 (s), 13.42 (s), 13.75 (m), and 14.2–14.4 μ (broad, strong).

Decomposition of Hexaphenylpyrazoline. A.—A 1-g. sample of hexaphenylpyrazoline was heated in an oil bath at 240–250° at atmospheric pressure for 48 hr. in a vessel attached to an ice trap for collecting products and a nitrogen stream to remove volatiles. The batch was cooled slowly for 2 days to yield a black mass of crystals. When the mass was washed with ethanol, the color was removed leaving a cluster of cream-colored fine needles, m.p. 216–222°. The infrared spectrum of a sample of the needles confirmed that it was tetraphenylethylene.

B.—A second 1-g. sample (as a fine, powdery film) of the hexaphenylpyrazoline was irradiated with the G.E. ultraviolet sun lamp for 4 days. No change was detected in the infrared spectrum of the material.

2-Benzoyl-1,1,2,2-tetraphenylethanol.— Asolution of 0.8 mole of phenylmagnesium bromide (Arapahoe Chemical Company, Boulder, Colo.) in 1000 ml. of absolute ethyl ether was refluxed for 5 days with 60 g. of ethyl diphenylmalonate.[8] The solution was poured into an ice–ammonium chloride mixture and the mixture was extracted with ether. The ether layer was dried and evaporated to yield 79 g. of yellow-orange crystals, m.p. 84°. The crude crystals were crystallized from ethanol to give light orange crystals, m.p. 118°.

Anal. Calcd. for $C_{33}H_{26}O_2$: C, 87.20; H, 5.72; O, 7.05. Found: C, 87.07; H, 5.86; O, 6.53.

The infrared spectrum showed a carbonyl absorption at 5.95 μ. The complete spectrum (KBr pellet) was 2.90 (s), 3.30 (m), 5.95 (s), 6.28 (m), 6.70 (m), 6.92 (s), 7.55 (m), 7.65 (m), 7.85 (m), 8.29 (m), 8.48 (w), 8.62 (m), 9.68 (m), 9.87 (m), 13.15 (s), 13.50 (m), and 14.2–14.4 (s, broad) μ.

Reaction of 2-Benzoyl-1,1,2,2-tetraphenylethanol with Phenylmagnesium Bromide.—A solution of 10 g. of 2-benzoyl-1,1,2,2-tetraphenylethanol together with 1.0 mole of phenylmagnesium bromide in 250 ml. of ethyl ether was refluxed for 4 days. The solution was then poured into an ice–ammonium chloride mixture and extracted with ether. The ether layer was separated, dried over anhydrous sodium sulfate, and then concentrated to yield two fractions of crystals: A, m.p. 155–240°, and B, 55–62°.

Fraction A was fractionally sublimed at 140° (0.2 mm.) and 210° (0.5 mm.) to yield two sets of crystals.

The infrared spectrum of an authentic sample of triphenylmethanol, m.p. 161–163°, was identical with that of the lower subliming material, m.p. 155–164°.

Anal. Calcd.: C, 87.7; H, 6.16; O, 6.16; mol. wt., 260. Found: C, 87.33; H, 6.39; O, 6.30; mol. wt., 258, 254 (in ethylene chloride).

The higher subliming material, m.p. 213–236°, analyzed for tetraphenylethanol (lit.[9] m.p. 232–236).

Anal. Calcd.: C, 89.0; H, 6.33; mol. wt., 350.3. Found: C, 88.33; H, 6.50; mol. wt., 344, 352.

The fraction B was sublimed at 100° (0.25 mm.) to give crystals, m.p. 68–71°, which analyzed for biphenyl (m.p. 69–71°). The infrared spectrum of an authentic sample of biphenyl was found to be identical with that of the sublimed material.

Anal. Calcd.: C, 93.50; H, 6.50. Found: C, 92.52; H, 6.54.

Acknowledgment.—The author wishes to acknowledge the helpful suggestions by Dr. H. K. Sinclair on some of the mechanism interpretations.

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[7] H. Adkins and W. Zartman "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 606.

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Tetraphenylbenzyne

DIETMAR SEYFERTH AND HORST H. A. MENZEL

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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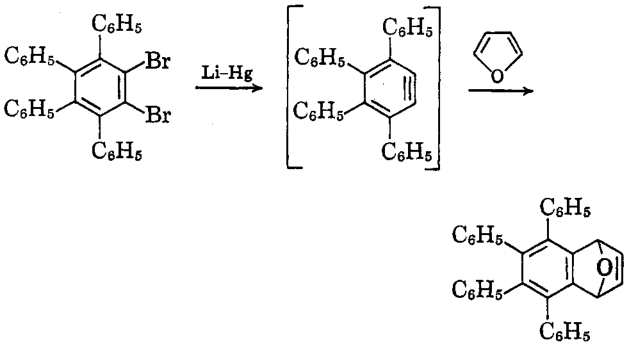
The availability of 1,2-dibromotetraphenylbenzene during the course of a recent study in these laboratories[1] has prompted this brief investigation of the possibility of generating tetraphenylbenzyne, previously unknown, *via* this precursor. The procedure chosen was that used by Wittig and Pohmer[2a] to generate benzyne itself from *o*-bromofluorobenzene in the presence of furan as a benzyne-trapping agent. This reaction, carried out under nitrogen at room temperature during 6 days, gave 1,4-dihydro-5,6,7,8-tetraphenylnaphthalene 1,4-endoxide in 66% recrystallized yield. Attempted column chromatographic purification of the endoxide on neutral alumina led to decomposition to 1,2,3,4-tetraphenylnaphthalene. Thin layer chromatographic analysis showed that the latter was not present in the original crude reaction product.



This brief study has shown that the four phenyl substituents in 1,2-dibromotetraphenylbenzene do not hinder benzyne formation, nor do they appear to make the benzyne intermediate significantly less stable than

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(1) D. Seyferth, C. Sarafidis, and A. B. Evnin, *J. Organometal. Chem.*, **2**, 417 (1964).

(2) (a) G. Wittig and L. Pohmer, *Chem. Ber.*, **89**, 1334 (1956). (b) See related experiments with benzyne, 1,2-naphthyne, and 9,10-phenanthryne: R. Huisgeu and J. Sauer, *Angew Chem.*, **72**, 91 (1960).