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.

---

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

[8] A. C. Cope and S. M. McElvain, *J. Am. Chem. Soc.*, **54**, 4322 (1932).

[9] A. McKenzie and J. S. W. Boyle, *J. Chem. Soc.*, **119**, 1139 (1921).

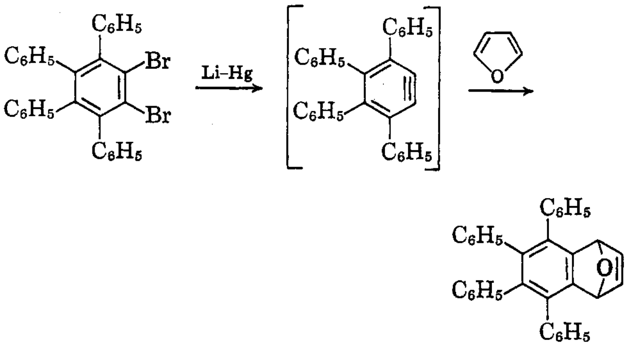
Tetraphenylbenzyne

Dietmar Seyferth and Horst H. A. Menzel

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

Received September 11, 1964

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

---

[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).

benzyne itself. Stabilization through conjugation of the tetraphenylbenzyne is not deemed likely in view of probability that the adjacent phenyl rings are not coplanar with the central ring. A comparison of the relative reactivities of tetraphenylbenzyne and the structurally related 9,10-phenanthryne toward a diene or of phenyllithium and lithium piperidide toward tetraphenylbenzyne[2b] should shed more light on this question.

Experimental

Preparation of 1,4-Dihydro-5,6,7,8-tetraphenylnaphthalene 1,4-Endoxide.—Lithium amalgam was prepared[2] from 45 g. (0.225 g.-atom) of mercury and 0.12 g. (0.018 g.-atom) of lithium in a Schlenk tube under argon. To the amalgam then was added 3.2 g. (5.3 mmoles) of 1,2-dibromotetraphenylbenzene, 35 ml. of dry diethyl ether, and 35 ml. of dry furan. The resulting suspension (maintained under an argon atmosphere) was shaken using a mechanical shaker for 6 days at room temperature. During this time the liquid phase became light yellow in color.

The Schlenk tube was cooled and opened, and benzene and methylene chloride were added to effect solution of all organic components. The filtered, yellow organic solution was evaporated at reduced pressure, leaving 2.8 g. of crystalline residue, m.p. 78–86°. The latter was recrystallized from carbon tetrachloride–petroleum ether to give a solid with m.p. 182–184°. Further recrystallization gave 1.9 g. (66%) of the desired product, m.p. 214–217° (decomposition with gas evolution).

Anal.[3] Calcd. for $C_{34}H_{24}O$: C, 91.04; H, 5.39; O, 3.57. Found: C, 90.44; H, 5.41; O, 3.52.

The n.m.r. spectrum[4] showed a triplet at 5.55 and a singlet at 6.75 followed by a multiplet from 6.9–7.2 p.p.m. The integrated area ratio of the triplet to the singlet plus multiplet was 1:11. The triplet is assigned to the bridgehead protons at the 1,4-positions, and the olefinic protons appear to overlap with the aromatic protons. A similar situation has been observed in the case of benzonorbornadiene.[5]

Attempted purification of the product by column chromatography (Woelm alumina, neutral) was unsuccessful. Green-violet coloration was observed, and elution with 1:1 benzene–cyclohexane gave a product which did not contain oxygen. Its m.p. 203–205° and its analysis suggest that it is 1,2,3,4-tetraphenylnaphthalene (lit.[6] m.p. 201–203°,[6a] 198–200°[6b]).

Anal. Calcd. for $C_{34}H_{24}$: C, 94.41; H, 5.59. Found: C, 94.28; H, 5.90.

Analysis of the crude product of the tetraphenylbenzyne–furan reaction by thin layer chromatography showed that tetraphenylnaphthalene was not present.

---

[3] Analyses were performed by the Galbraith Laboratories, Knoxville, Tenn.

[4] Measured in carbon tetrachloride solution using a Varian Associates A60 n.m.r. spectrometer. Chemical shifts are given in parts per million downfield from tetramethylsilane.

[5] H. Menzel, Dissertation, Universität Heidelberg, 1963.

[6] (a) W. Herwig, W. Metlesics, and H. Zeiss, *J. Am. Chem. Soc.*, **81**, 6203 (1959); (b) H. Gilman, S. G. Cottis, and W. H. Atwell, *ibid.*, **86**, 1596 (1964).

The Chemistry of Carbanions. VIII. The Intramolecular Alkylation of Ketyl Radical Anions[1]

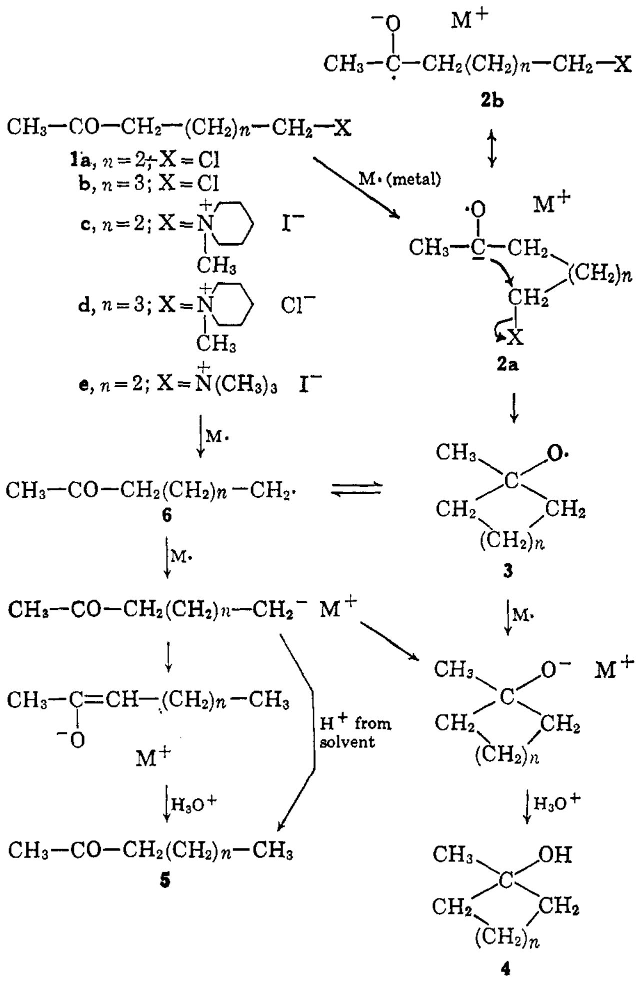
HERBERT O. HOUSE, JEAN-JACQUES RIEHL, AND
COLIN G. PITT

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

Received September 18, 1964

Several alkylation reactions have been described[2] which presumably involve either the intramolecular or the intermolecular alkylation of an intermediate radical anion. These intermediate radical anions have been derived from reduction of either aromatic nuclei or α,β-unsaturated ketones with metals. We wished to learn whether a comparable intramolecular alkylation of a simple ketyl anion radical might be effected since such a procedure might offer a useful synthetic route to bridgehead tertiary alcohols.[3] The accompanying equations illustrate the reaction of interest, namely 1 → 2 → 3 → 4 (see Scheme I).

SCHEME I



To examine this possibility the reactions of the ω-chloro ketones **1a** and **1b** with lithium in liquid ammonia, with the sodium–phenanthrene and sodium–naphthalene radical anions, and with chromium(II) ion [Cr(II)][4] were examined. Although treatment of the chloro ketone **1a** with chromium(II) acetate led to recovery of the starting material, the other two reducing systems did convert the chloro ketones **1a** and **1b** to mixtures of the desired cyclic carbinols **4**

---

[1] This research has been supported by Grant No. AF-AFOSR-573-64 from the U. S. Air Force Office of Scientific Research.

[2] (a) G. Stork and J. Tsuji, *J. Am. Chem. Soc.*, **83**, 2783 (1961); (b) S. Rakhit and M. Gut, *ibid.*, **86**, 1432 (1964); (c) J. Wiemann and F. Weisback, *Compt. rend.*, **257**, 1486 (1963); (d) D. R. Weyenberg and L. H. Torporcer, *J. Am. Chem. Soc.*, **84**, 2843 (1962); (e) D. Lipkin, F. R. Galiano, and R. W. Jordan, *Chem. Ind.* (London), 1657 (1963).

[3] The acylation of anion radicals derived from saturated carbonyl functions is exemplified by the acyloin reaction and by the cyclization of certain δ-keto esters. See C. D. Gutsche and I. Y. C. Tao, *J. Org. Chem.*, **28**, 883 (1963).

[4] The use of the chromium(II) ion was prompted by the observation of an intramolecular alkylation reaction when a suitably substituted α,β-unsaturated δ-bromo ketone was treated with chromium(II) chloride. D. H. R. Barton and C. H. Robinson, U. S. Patent 3,026,337 (March 20, 1962); *Chem. Abstr.*, **57**, 3532 (1962).