mmoles) of the acid chloride in 20 ml of benzene. After the addition was complete, the reaction mixture was stirred for 4 hr at 25° and then poured into cold, aqueous HCl. The organic layer was combined with the ethyl acetate extract of the aqueous phase and the combined organic solutions were washed with aqueous $NaHCO_3$, dried, and concentrated. Chromatography of the residual oil (2.36 g) on silicic acid separated 1.35 g (40%) of the phenyl ketone **14** (mp 62–63°) in the early fractions eluted with hexane–ether mixtures and 469 mg (21%) of the indanone **15** in the later fractions eluted with the same solvent mixture. The pure **phenyl ketone 14** crystallized from cyclohexane as white needles: mp 62–63°; infrared (CCl_4), 1680 cm^{-1} (conjugated C=O); ultraviolet maxima, 228 $m\mu$ (ϵ 13,300), 242 (13,200), 278 (2810), and 284 (shoulder, ϵ 2380); nmr ($CDCl_3$), δ 7.3–8.0 (5 H multiplet, phenyl C–H), 7.10 (2 H doublet, J = 9 cps, aryl CH), 6.77 (2 H doublet, J = 9 cps, aryl CH), 3.73 (3 H singlet, $O{-}CH_3$), and 2.8–3.4 (4 H multiplet, aliphatic CH).

Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.79; H, 6.68.

The pure **indanone 15** crystallized from cyclohexane solution as white needles: mp 108–109° (lit.[3] mp 108–108.5°); infrared (CCl_4), 1715 cm^{-1} (conjugated C=O in a five-membered ring); ultraviolet maxima, 217 $m\mu$ (ϵ 23,500), 248 (9950), and 319 (4480); nmr ($CDCl_3$), δ 7.2–7.6 (3 H multiplet, aryl CH), 3.92 (3 H singlet, $O{-}CH_3$), and 2.5–3.4 (4 H multiplet, aliphatic CH).

In an effort to learn why our reaction in benzene solution yielded both the indanone **15** and the phenyl ketone **14** whereas similar reaction conditions had been reported earlier[3] to form the indanone **15** in high yield, we attempted to duplicate exactly the early reaction conditions.[3a,b] Reaction of 1.00 g (5.5 mmoles) of the acid **13a** with 1.27 g (6.1 mmoles) of phosphorus pentachloride in 10 ml of benzene was effected as previously described.[3a,b] From a solution of the crude product in 15 ml of benzene, a 1.5-ml aliquot was separated and distilled in a short-path still. The distillate (34 mg) was identified as the previously described acid chloride **13c** by comparison of infrared spectra. The crude residue, 61 mg of a high-boiling liquid, had infrared absorption (CCl_4) at 1820 and 1760 cm^{-1}, suggesting that the residue was the crude anhydride derived from acid **13a**. The remaining benzene solution (13.5 ml equivalent to 5.0 mmoles of acid chloride **13c**) was added to 0.96 g (7.2 mmoles) of aluminum chloride as previously described. A solution of this crude product in ethyl acetate was washed successively with aqueous HCl, aqueous NaOH, and water and then dried and concentrated to leave 385 mg of crude neutral product, mp 70–78°. Chromatography on silicic acid separated 105 mg (9%) of the pure phenyl ketone **14**, mp 60–62°, and 134 mg (17%) of the indanone **15**, mp 105–108°. After recrystallization the products melted at 61–62 and 107–108°, respectively. Each material was identified with the previously described sample by comparison of infrared spectra.

B. In Methylene Chloride Solution.—To a cold (0°) suspension of 3.10 g (23 mmoles) of aluminum chloride in 20 ml of methylene chloride was added, dropwise and with stirring, a solution of 3.12 g (15.8 mmoles) of the acid chloride **13c** in 20 ml of methylene chloride. The resulting mixture was stirred for 4 hr at room temperature and then subjected to the previously described isolation procedure. The crude neutral product was chromatographed on silicic acid to separate the crude indanone **15** (975 mg or 38%) in fractions eluted with an ether–hexane mixture. Recrystallization from cyclohexane separated 465 mg (18%) of the pure **indanone 15**, mp 107–108°, identified with the previously described sample by a mixture melting point determination and comparison of infrared spectra.

Preparation of the Diels–Alder Adduct 17.—A solution of 20.0 g (0.072 mole) of the arylidenemalonate **11**, 15 ml of 1,3-butadiene, and 1.0 g of 2,5-di-*t*-butyl-1,4-hydroquinone (as inhibitor) in 80 ml of benzene was heated in an autoclave to 200° for 50 hr and then cooled, concentrated, and distilled. The distillate, 14.5 g collected at 145–165° (0.25 mm), contained[16] approximately equal amounts of the starting conjugated ester **11** (eluted first) and the adduct **17** (eluted second). A solution of this material in 50 ml of ether was stirred with excess aqueous 10% NaOH to effect selective saponification of the starting ester **11**. The ether solution (containing[16] *ca.* 8% of **11** and *ca.* 92% of **17**) was dried, concentrated, and distilled in a short-path still, 155–165° (0.3 mm), to separate 2.12 g (8.9%) of the adduct **17** as a colorless liquid which crystallized on standing, mp 53–56°. Recrystallization from a benzene–petroleum ether (bp 30–60°) mixture afforded the adduct **17** as white prisms: mp 53–56°; infrared ($CHCl_3$), 1735 cm^{-1} (ester C=O); ultraviolet maxima, 226 $m\mu$ (ϵ 12,700), 276 (1650), 283 (1490), and 312 (224); nmr ($CDCl_3$), δ 7.21 (2 H doublet, J = 9 cps, aryl CH), 6.81 (2 H doublet, J = 9 cps, aryl CH), 5.85 (2 H broad singlet, vinyl, CH), 4.17 and 4.07 (4 H overlapping quadruplets, J = 7 cps, $CH_2{-}O$), 3.78 (3 H singlet, $O{-}CH_3$), 3.6–3.8 (1 H multiplet, benzylic CH), 2.1–3.0 (4 H multiplet, aliphatic CH), and 1.17 (6 H triplet, J = 7 cps, $CH_3{-}C$).

Anal. Calcd for $C_{19}H_{24}O_5$: C, 68.65; H, 7.28. Found: C, 68.53; H, 7.03.

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[16] A gas chromatography column packed with silicone gum, no. SE-30, suspended on Chromosorb P was employed for this analysis.

Thermolysis Reactions of Biphenylene

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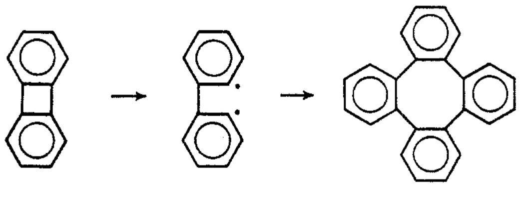
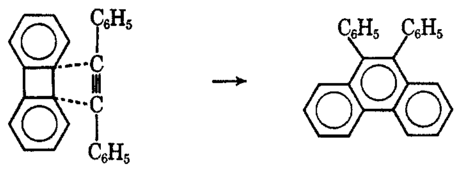
The question of biphenylene "inner ring" chemistry was discussed in 1959 by Baker and McOmie,[1] but attempts at experimental verification were unsuccessful. Thus it had been concluded that even though the biphenylene "inner ring" may be highly strained, it is very stable and, in general, unreactive. This present work shows that biphenylene "inner ring" chemistry does, in fact, exist.[2]

Previous work in this laboratory[3] has shown that under thermolytic conditions biphenylene undergoes bond fission which can lead to dimerization and the formation of tetraphenylene. The present study examines the thermolysis of biphenylene in the presence of other acceptors.



When biphenylene was heated to 350–375° (under N_2) in the presence of a fivefold excess of diphenylacetylene, 9,10-diphenylphenanthrene was formed in about 50% yield (gas chromatography) based on biphenylene.



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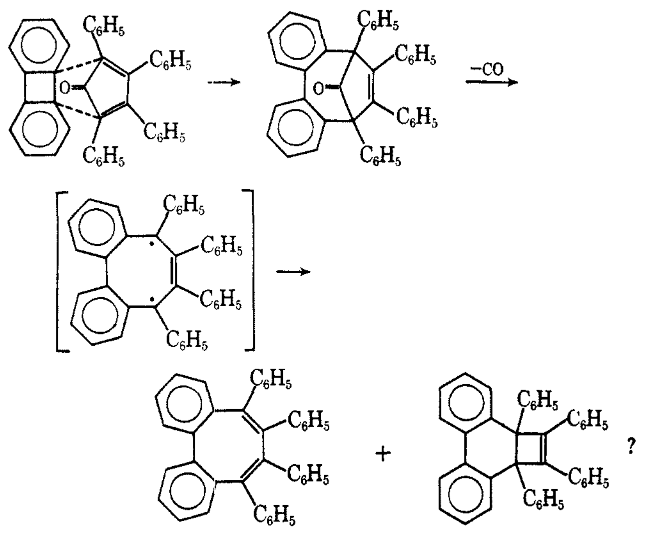
[1] D. Ginsburg, "Non-Benzenoid Aromatic Compounds," Interscience Publishers, Inc., New York, N. Y., 1959, p 78.

[2] (a) The extraordinary stability of biphenylene (350°) has been noted previously: W. Baker and J. McOmie, Chemical Society Symposia, Bristol, 1958, Special Publication No. 12, The Chemical Society, London, pp 49–67. (b) Biphenylene has been treated with hexacarbonylchromium to provide fluorenone in low yield. This reaction, however, may not be mechanistically comparable to the present study; see E. Atkinson, P. Levins, and T. Dickelman, *Chem. Ind.* (London), 930 (1964).

[3] D. Lindow and L. Friedman, *J. Am. Chem. Soc.*, **89**, 1271 (1967); L. Friedman and D. Lindow, *ibid.*, in press.

When diphenylacetylene was heated alone under the reaction conditions, extensive polymerization resulted.

A second possible acceptor selected for study was tetracyclone (tetraphenylcyclopentadienone). When biphenylene and 1 equiv of tetracyclone (stable under the reaction conditions) were heated together, two isomeric hydrocarbons were formed (gas chromatography). Proposed structural assignments indicate the possibility of a common intermediate.



I 20-25%

II <5%

Chromatography afforded pure I along with a fraction containing I and II in almost equal amounts. Analysis of this mixture for carbon-hydrogen content and molecular weight support the hypothesis of two $C_{40}H_{28}$ isomers. Owing to lack of sufficient material and difficulties in isolation, no further attempt at analysis was made on compound II and a *tentative* structural assignment was made based on mechanistic considerations.

Spectral analysis of compound I is consistent with the proposed structure. Infrared analysis indicated monosubstitution and *ortho* disubstitution and nmr analysis showed aromatic protons consisting of a symmetrical multiplet and two singlets. Since the "dibenzo" protons might be expected to approach an A_2B_2-type system, this might account for the multiplet. Although incomplete separation of the multiplet inhibited exactness of integration, the relative areas approximated those expected for such an interpretation.

Mass spectral analysis gave a parent peak at *m/e* 508 along with major peaks at *m/e* 431 and 354 corresponding to loss of one and two phenyl groups, respectively.

Another potential acceptor selected for study was anthracene. When biphenylene and 6 equiv of anthracene were heated together at 375° for 1 hr, only starting material could be recovered. Since this is contrary to previous findings[3] that biphenylene dimerizes to tetraphenylene in either the presence or absence of anthracene (1 equiv), additional work was carried out. The results are summarized in Table I and, in fact, biphenylene does dimerize in the presence of 1 equiv of anthracene. The lack of tetraphenylene formation with 3 or more equiv seems to indicate a concentration effect with anthracene acting as a quenching agent. Since an increase in reaction time results in almost complete loss of biphenylene with only a minor amount of tetraphenylene being formed, the Scheme I is proposed whereby product formation is governed by diradical concentration. This is in agreement with Friedman and Lindow, who found that, with a decrease in temperature and an increase in reaction time (low radical concentration), a trend toward less tetraphenylene and more polymeric material develops.

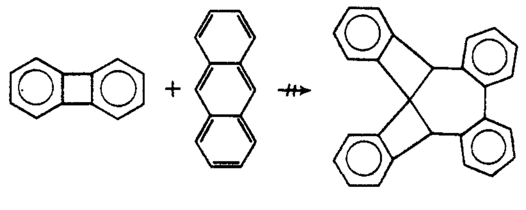


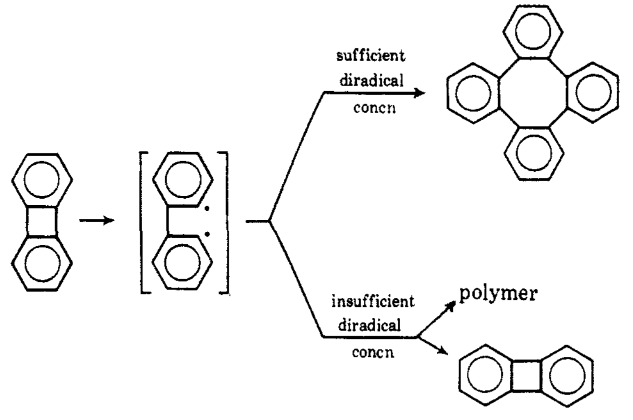
Table I

Thermolysis of Biphenylene in the Presence of Anthracene

Biphenylene, equiv	Anthracene,[a] equiv	Time,[b] hr	Recovered biphenylene, %	Tetraphenylene, %
1[c]	1[d]	1	. . .	100
1	1.5	1	75.8	24.2
1	2	1	98	2
1	3-6	1	100	. . .
1	3	6	Trace	11.5

[a] Complete recovery of anthracene. [b] 350-375°. [c] 0.5 g, 3.3 mmoles. [d] 0.59 g, 3.3 mmoles.

Scheme I



It should be noted, however, that the reaction temperature necessary for biphenylene "inner ring" chemistry imposes requirements for the stability of acceptors and products. For instance, an attempted reaction with maleic anhydride resulted only in severe charring, and thermolysis in the presence of molten sulfur resulted in a black, polymeric material analyzing as $(C_{12}H_8 \cdot S_8)_n$.

Experimental Section

Biphenylene was prepared in 27% yield from the decomposition of benzenediazonium-2-carboxylate.[4]

9,10-Diphenylphenanthrene.—Biphenylene (1.0 g, 0.0066 mole) and diphenylacetylene (6.0 g, 0.034 mole) were placed into a 45-ml-capacity stainless steel autoclave which was then evacuated and filled with nitrogen (1 atm). The autoclave was then heated to 350-375° for about 1 hr. The crude brown product obtained was analyzed on a F & M programmed temperature

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(4) L. Friedman and A. Seitz, *J. Org. Chem.*, in press.

gas chromatograph with a 5-ft 20% silicone grease column at 225°. The peak was not completely resolved from a small shoulder representing an unidentified impurity (acetylene dimer?) but the yield could be estimated to about 50% based on biphenylene. Crystallization of the crude product from acetone and subsequent recrystallization from cyclohexane afforded white needles, mp 235–236° (lit. mp 235°, no spectral data given[5]).

Nmr analysis in CS$_2$ on a Varian A60-A spectrometer showed a singlet at τ 2.48, a multiplet at 2.18, and a small multiplet at 0.90. The ratio of signals approximated the predicted 2.0:6.0:10.0.

Infrared analysis was carried out in CS$_2$ on a Beckman IR-8 spectrometer, major absorbance appearing at 3060 (split), 760, 750, 725, 700, and 635 cm^{-1}.

Ultraviolet analysis was carried out in spectroquality cyclohexane on a Cary 15 spectrometer. Maxima were found at 250 mμ (ϵ 50,600), 258 (65,000), 271 (29,600), 281 (18,100), 290 (14,400), and 301 (15,300).

5,6,7,8-Tetraphenyldibenzo[*a,c*]cyclooctatetraene.—Biphenylene (1.0 g, 0.0066 mole) and tetraphenylcyclopentadienone (2.52 g, 0.0066 mole) were heated together for 1 hr at 350–375°. Analysis of the crude product by gas chromatography on a 3-ft, 10% GE-SF96 silicone oil column at 265° showed 20–25% I, 5% II, about 15% unreacted tetraphenylcyclopentadienone, a little biphenylene, and a few other trace components (*m*-quaterphenyl was used as an internal standard).

The product was dissolved in cyclohexane and chromatographed on a column of neutral alumina. The first five fractions (15 ml each) were evaporated and the combined residues were recrystallized from ethanol. This afforded 0.57 g of pure I (17% yield based on biphenylene), mp 195–197°. The sixth fraction contained a mixture of I and II in almost equal amounts and latter fractions contained more product along with substantial amounts of nonvolatile, reddish brown oils.

Anal. Calcd for $C_{40}H_{28}$: C, 94.49; H, 5.56. Found for compound I: C, 94.46; H, 5.60. Found for mixture of I and II: C, 94.35; H, 5.71; mol wt (osmometry), 512 (calcd 508 for isomers).

The nmr spectrum of compound I showed a symmetrical multiplet centered at 2.63, a singlet at 2.90, and a singlet at 3.28. The expected integration for eight "dibenzo" protons (multiplet) and 20 phenyl protons (singlets) was not fully realized with the measured values of 5.5:20. However, if both singlets are assumed to equal ten protons, then the over-all ratio of the multiplet and adjacent singlet (not completely separated) to the remaining singlet of 18:10 is approximated by the measured value of 16.5:10.

Infrared analysis in CS$_2$ showed major absorbance at 3050 (split), 1075, 1030, 765 (split), 745, 735, and 695 cm^{-1}, and ultraviolet analysis in cyclohexane showed maxima at 245 mμ (ϵ 54,400) and 295 (13,600).

Acknowledgment.—This investigation was supported by Public Health Service Research Grant No. Ca-7909 from the National Cancer Institute.

[5] C. Schoepfle and J. Ryan, *J. Am. Chem. Soc.*, **54**, 3692 (1932).

A Ring-Enlargement Procedure. I. The Decomposition of the Magnesium Salts of 1-(α-Bromobenzyl)-1-cycloalkanols

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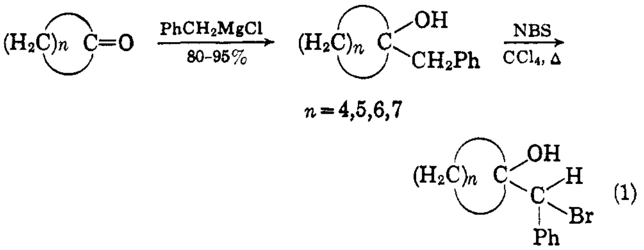
The ring expansion of alicyclic systems has been generally effected by a variety of methods involving the generation of a cationic center directly attached to a ring.[1] Among the various methods generally employed are the Demjanov[2] and Tiffeneau–Demjanov,[2] the acid-catalyzed dehydration of alcohols,[1] the reaction of carbonyl compounds with diazo compounds[1,3] (more recently the use of N-nitrosolactams with cycloalkanones[4]), the solvolysis of sulfonates,[5] and the electrolytic[6] and lead tetraacetate[7] decarboxylation of β-hydroxy acids. Two relatively recent examples of the generation of a carbonium ion directly attached to a ring are the reactions of 1-vinylcycloalkanols with *t*-butyl hypochlorite[8] and 1-isopropenylcycloalkanol epoxides with acidic alumina.[9] A major factor accounting for the success of the aforementioned ring-enlargement reactions is the generation of a more stable carbonium ion; generally, in the absence of this driving force little or no expansion occurs.[2]

I wish to report a method for ring enlargement superior to those previously described. The rearrangement of the magnesium salts of halohydrins to ketones has long been known. Over the past years its application to synthesis has been well established.[10–12] For example, the reaction of 2-chlorotetralone and 2-chloroindanone with aryl magnesium halides produced the corresponding 2-aryl-substituted derivatives in excellent yields.[12] It should be mentioned that the reactions of α-halo ketones with Grignard reagents producing α-substituted ketones proceed *via* the magnesium salt of the initially formed halohydrin.[12] As yet the rearrangment has not been synthetically exploited in order to accomplish a ring enlargement procedure. One of the attractive features of the method lies in the fact that little or no epoxide is formed.[11] Another is the experimental conditions under which the reaction may be conducted, anhydrous ether, benzene, *n*-butyl ether or the pyrolysis of the magnesium salts in the absence of any solvent.[11,12] The synthesis of compounds of the type depicted in 1 was undertaken and accomplished by conventional procedures (eq 1). The



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halohydrins, **1**, were dissolved in benzene and subsequently treated with an equivalent of isopropyl magnesium bromide at 0°. The resultant magnesium salt was refluxed for a period of 1–3 hr producing the cor-

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[1] R. A. Raphael, "The Chemistry of Carbon Compounds," Vol. II A, E. N. Rodd, Ed., Elsevier Press Inc., New York, N. Y., 1953, p 11.

[2] P. A. S. Smith and D. R. Baer, *Org. Reactions*, **11**, 157 (1960).

[3] L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1962, p 451.

[4] C. D. Gutsche and I. Y. C. Tao, *J. Org. Chem.*, **32**, 1778 (1967).

[5] E. J. Corey, M. Ohno, P. A. Vatakencherry, and R. B. Mitra, *J. Am. Chem. Soc.*, **83**, 1251 (1961).

[6] E. J. Corey, N. L. Bauld, R. T. LaLonde, J. Casanova, Jr., and E. T. Kaiser, *ibid.*, **82**, 2645 (1960).

[7] E. J. Corey and J. Casanova, Jr., *ibid.*, **85**, 165 (1963).

[8] C. R. Johnson, C. J. Cheer, and D. J. Goldsmith, *J. Org. Chem.*, **29**, 3320 (1964).

[9] C. J. Cheer, *ibid.*, **32**, 428 (1967).

[10] M. Tiffeneau and B. Tchoubar, *Compt. Rend.*, **198**, 941 (1934).

[11] T. A. Geissman and R. I. Akawie, *J. Am. Chem. Soc.*, **73**, 1993 (1951).

[12] A. S. Hussey and R. R. Herr, *J. Org. Chem.*, **24**, 843 (1959).