X = Br), and 9,9-dichlorobicyclo[6.1.0]nonane (22, X = Cl) were all commercially available (Aldrich Chemical Co.).

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Naphtho[*b*]cyclobutadiene

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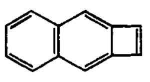
Abstract: Reaction of naphtho[*b*]cyclobutene (**6**) with 1 equiv of NBS gives crude 1-bromonaphtho[*b*]cyclobutene (**7**), which could be purified only chemically by hydrolysis to naphtho[*b*]cyclobuten-1-ol (**8**) followed by treatment of the latter with hydrogen bromide. Reaction of bromide **7** with potassium *tert*-butoxide generates the unstable naphtho[*b*]cyclobutadiene (**1**). The observed reactions of **1** include (a) addition of *tert*-butyl alcohol to give 1-*tert*-butoxynaphtho[*b*]cyclobutene (**12**), (b) formation of the dimer 1,2:5,6-dinaphtho[*b*]cycloctatetraene (**19**), and (c) addition of 1,3-diphenylisobenzofuran to give a mixture of endo and exo adducts **14** and **15**. The reactions of naphtho[*b*]cyclobutadiene are contrasted with those of benzocyclobutadiene (**11**).

Naphtho[*b*]cyclobutadiene (**1**) is a molecule of considerable theoretical interest. It is a closely related isomer of the much studied biphenylene (**2**) and is one of the simplest of all possible fully unsaturated condensed benzenoid systems.[1,2] The 1,2-diphenyl and 1,2-dibromo-3,8-diphenyl derivatives (**3** and **4**) have been isolated and characterized,[3,4] but attempts to isolate 3,8-diphenylnaphtho[*b*]cyclobutadiene (**5**) were unsuccessful.[5,6]



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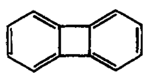

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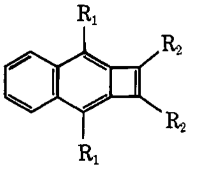

3, $R_1 = H; R_2 = Ph$
4, $R_1 = Ph; R_2 = Br$
5, $R_1 = Ph; R_2 = H$

In this paper, we report a method of generation of the parent naphtho[*b*]cyclobutadiene (**1**), as well as some simple chemical reactions of this hydrocarbon.

Results

Naphtho[*b*]cyclobutene (**6**)[7] reacts readily with 1 equiv of *N*-bromosuccinimide to give a crude product which was shown by nmr analysis to consist of about 35% unchanged hydrocarbon **6**, 60% 1-bromonaphtho[*b*]cyclobutene (**7**), and 5% of dibrominated derivatives of **6**. Attempts to separate pure bromide **7** from this mixture chromatographically were unsuccessful, but pure **7** was obtained indirectly in the following manner. Treatment of the bromination mixture with silver trifluoroacetate in aqueous acetonitrile gives the readily purified naphtho[*b*]cyclobuten-1-ol (**8**); reaction of **8** with hydrogen bromide affords pure **7**, mp 82–83.5°. In practice, impure **7** obtained by the bromination of **6** was satisfactory for further transformations.

The reaction of 1-bromobenzocyclobutene (**9**) with an excess of potassium *tert*-butoxide is known to afford a high yield of 6a,10b-dihydrobenzo[*a*]biphenylene (**10**), a product derived from benzocyclobutadiene (**11**) by angular dimerization.[8] Under similar conditions, dehydrobromination of 1-bromonaphtho[*b*]cyclobutene (**7**) gave no isolable hydrocarbon product. There was formed instead, in 72% yield, a crystalline product assigned the structure of 1-*tert*-butoxynaphtho[*b*]cyclobutene (**12**) on the basis of spectral and analytical data.

It seemed mechanistically unlikely that ether **12** was the product of a displacement reaction involving *tert*-butoxide ion; a mechanism involving dehydrobromination of **7** to napththo[*b*]cyclobutadiene (**1**), followed by addition of *tert*-butoxide ion to the cyclobutadienoid 1,2 bond of **1**, appeared more likely. Indeed, treatment of bromide **7** with excess potassium *tert*-butoxide in the presence of 1,3-diphenylisobenzofuran (**13**) gave a product consisting of ether **12** and the endo and exo adducts **14** and **15** in the ratio 2:2:5. It was found, however, that adducts **14** and **15** were not formed when a solution of ether **12** was refluxed with furan **13** and potassium *tert*-butoxide, showing that the alkoxide-catalyzed addition of *tert*-butyl alcohol to naphtho[*b*]cyclobutadiene is not a reversible process.

The stereochemistry of adducts **14** and **15** was assigned on the basis of their nmr spectra. The benzylic hydrogens of the endo adduct **14** appear at δ 4.63, compared with the value 4.30 for the corresponding hydrogens of the exo adduct **15**. This effect is attributable to a deshielding of these hydrogens in **14** by the

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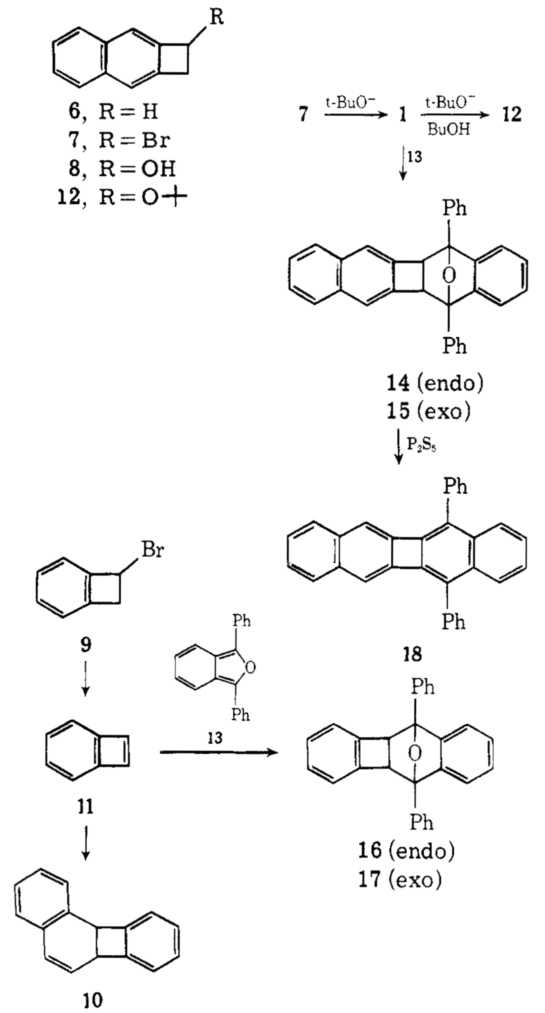
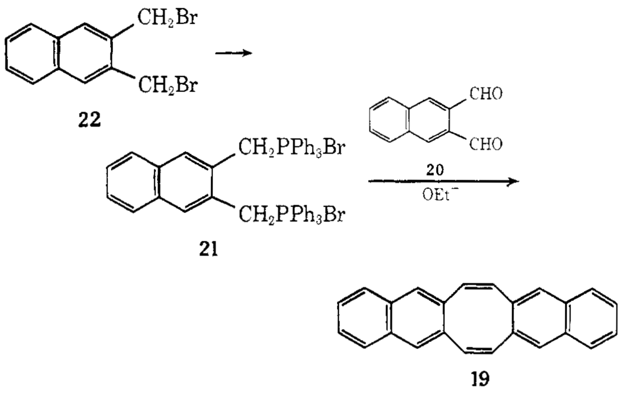


oxido bridge. A similar but even greater difference (0.55 ppm) has been recorded for the corresponding hydrogen pairs of the endo and exo adducts of furan **13** with 3-chlorocyclopropene.^{9}

It has been reported that the trapping of benzocyclobutadiene (**11**) by furan **13** affords a single adduct, mp 200–202°.^{10} Reinvestigation of this reaction showed that the product was in fact a mixture of this high melting adduct and a lower melting isomer, mp 128–130°, in a ratio of about 3:2. The benzylic hydrogens of the 200° isomer appeared at δ 4.03, while those of the 128° isomer appeared further downfield at 4.49. The latter isomer is therefore assigned the endo structure **16** and the former is assigned the exo structure **17**.

Dehydration of the benzocyclobutadiene adduct **17** takes place cleanly and without skeletal rearrangement on treatment with phosphorus pentasulfide.^{11} Similarly, both naphtho[*b*]cyclobutadiene adducts **14** and **15** were found to react with phosphorus pentasulfide to give 5,10-diphenyldibenzo[*b*,*h*]biphenylene (**18**).

When 1-bromonaphtho[*b*]cyclobutene (**7**) and only 1 equiv of potassium *tert*-butoxide in *tert*-butyl alcohol were heated in refluxing *tert*-butyl alcohol, a hydrocarbon $C_{24}H_{16}$ was isolated in 22% yield. This compound, derived from two molecules of naphtho[*b*]cyclobutadiene (**1**), gave an nmr spectrum consisting only of signals in the δ 7.0–7.6 region. The absence of benzylic hydrogens in the dimer suggested the linear dinaphthocyclooctatetraene structure **19**. This structure was confirmed by an independent Wittig synthesis. Thus, **19** was formed when the bisphosphonium salt (**21**) derived from 2,3-bis(bromomethyl)naphthalene (**22**)^{12} was treated with 2,3-naphthalenedicarboxaldehyde (**20**)^{13} and lithium ethoxide in ethanol solution.



Discussion

The chemistry of naphtho[*b*]cyclobutadiene (**1**) contrasts in several ways with that of the closely related benzocyclobutadiene (**11**). One noteworthy difference is the ease with which **1** undergoes addition of *tert*-butoxide anion to give ether **12**. The analogous reaction product (**23**) from **11** could not be detected, even as a by-product, on repeating the reported reaction of potassium *tert*-butoxide with 1-bromobenzocyclobutene (**9**) to give dimer **10**. This difference in behavior may be attributed to a greater dimerization rate of the electronically less stabilized **11** compared to the electronically more stabilized naphtho compound **1**. In accord with this view, 1-bromo-1,2-di-*tert*-butylbenzocyclobutene (**24**) has been reported to react with potassium *tert*-butoxide to give the corresponding *tert*-butyl ether **25**.^{14} Dimerization of the presumed intermediate 1,2-di-*tert*-butylbenzocyclobutene (**26**) is here inhibited for steric reasons, and the competing addition of alkoxide to the 1,2-unsaturated center is therefore observed.

Another clear difference in the chemistry of naphtho[*b*]cyclobutadiene (**1**) compared to that of benzocyclobutadiene (**11**) is found in the dimerizationof these hydrocarbons. Generation of **11** by a variety of methods, such as by dehydrohalogenation of **9**, leads exclusively to the formation of the angular dimer **10**, by way of the initial transient intermediate **27**.^{1,2} Formation of a linear dimer (**28**) from **11** is observed only when **11** is generated in the presence of nickel carbonyl;^{15} an unstable red nickel complex of **11**, rather than **11** itself, is the intermediate in this process.^{16} By contrast, generation of naphtho[*b*]cyclobutadiene (**1**) in the absence of nickel derivatives leads to the cyclooctatetraene **19** as the only isolable dimeric hydrocarbon. The

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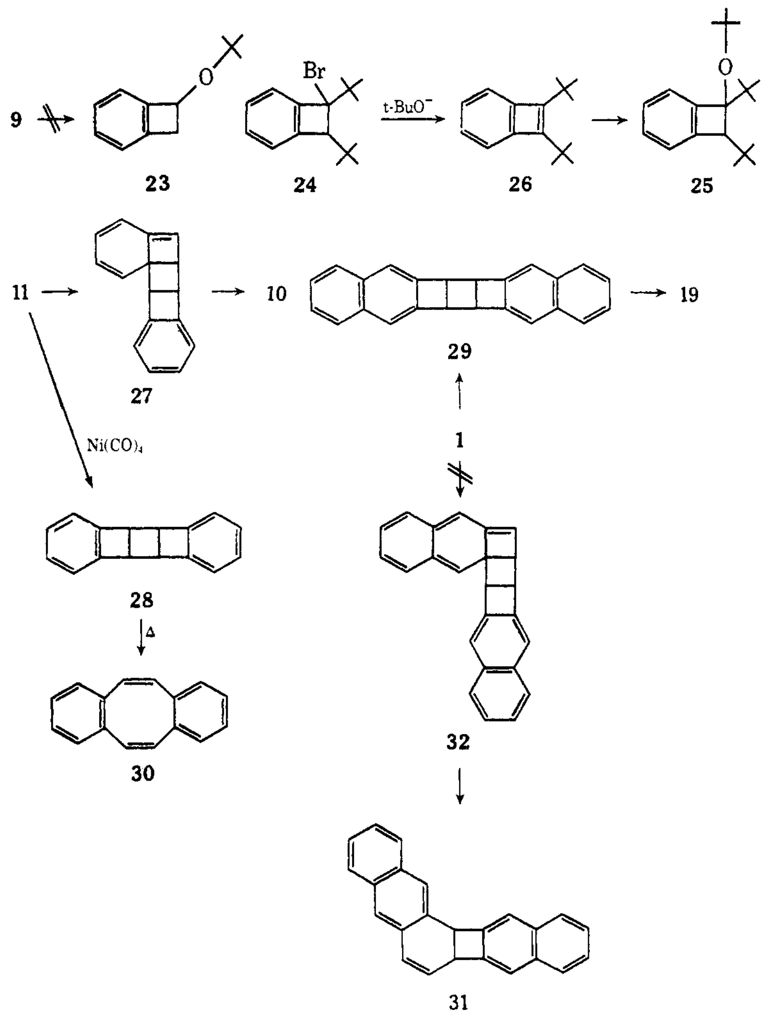
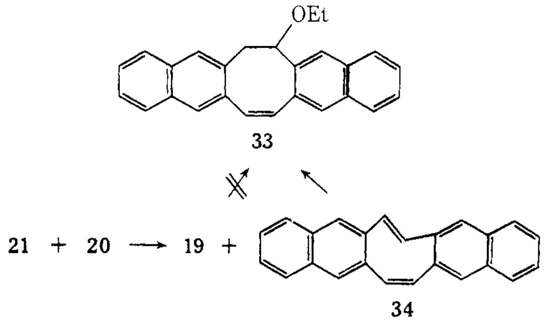


initial linear dimerization product **29** would be expected to rearrange to **19** under the refluxing conditions employed; the analogous thermal conversion of the linear dimer **28** to 1,2:5,6-dibenzocyclooctatetraene (**30**) has been described.[15] The failure of **1** to undergo angular dimerization to a hydrocarbon of structure **31** may be attributed to the fact that the intermediate (**32**) in this reaction is a higher energy species than that (**27**) derived initially from benzocyclobutadiene (**11**). The reason for this is that formation of **32** as compared to **27** requires the loss of the delocalization energy of both rings of a naphthalene unit rather than a single benzene ring. A similar argument has been put forth to explain the greater thermal stability of naphtho[*b*]cyclobutene relative to benzocyclobutene.[7]



In the Wittig synthesis of the cyclooctatetraene **19**, the derived hydrocarbon was obtained in a yield of only about 3%. The major monomeric product, obtained in 23% yield, was assigned the ethoxycyclooctatriene structure **33** on the basis of analytical and spectral evdence. The remote possibility that **33** was a secondary product derived from **19** was eliminated by the finding that **19** could be recovered unchanged by subjecting it to lithium ethoxide in ethanol under the original reaction conditions. An intriguing alternative explanation is that the Wittig reaction may produce a considerable amount of cis,trans isomer (**34**) of **19**. Hydrocarbon **34** should be extremely reactive and could readily undergo a base-catalyzed addition of ethanol to the highly strained trans olefinic bond to give ether **33**.

Experimental Section

General. Melting points are uncorrected. Microanalyses were carried out by Midwest Microlab, Inc., Indianapolis, Ind. Spectra were recorded on a Perkin-Elmer Model 137 ir spectrophotometer, a Perkin-Elmer Model 202 uv-visible spectrophotomerer, a Varian A-60A nmr spectrometer, and a Perkin-Elmer Model 270B mass spectrometer.

1-Bromonaphtho[*b*]cyclobutene (7). A mixture of naphtho[*b*]cyclobutene[7] (**6**, 0.71 g), benzoyl peroxide (0.100 g), *N*-bromosuccinimide (0.837 g), and carbon tetrachloride (25 ml) was heated under reflux for 30 min. Evaporation of the cooled and filtered solution gave an oil which was chromatographed on neutral grade I alumina. Elution with cyclohexane gave a white solid (0.60 g), shown by spectral analysis (nmr and mass spectrometry) to consist of 35% **6**, 60% **7**, and 5% of dibromides. (The benzylic protons of **6** appear at δ 3.29; those of **7** form an ABX system with protons centered at 5.55, 3.91, and 3.70.) A pure sample of **7** was prepared by passing hydrogen bromide into a solution of naphtho[*b*]cyclobuten-1-ol (**8**, 0.020 g) in benzene for 3 hr, followed by tlc separation (silica) to give recovered **8** (0.010 g) and bromide **7** (0.005 g, 39% based on unrecovered **8**): mp 82.5–83.5°; *m/e* 234 (15%), 233 (8%), 232 (15%), 153 (100%), 154 (30%), 152 (5%), 151 (20%), 127 (25%), 105 (30%).

Anal. Calcd for $C_{12}H_9Br$: C, 61.80; H, 3.86. Found: C, 62.04; H, 4.11.

Naphtho[*b*]cyclobuten-1-ol (8). A mixture of crude bromide **7** (0.495 g, 63% pure), silver trifluoroacetate (3.0 g), acetonitrile (30 ml), and water (10 ml) was heated to reflux with stirring for 5 hr in the absence of light. Evaporation of the filtered solution gave a residue which was dissolved in chloroform. After washing well with water, evaporation of the solvent gave an oil which was chromatographed on silica using benzene as eluent. Crystallization from benzene–hexane gave pure alcohol **8** (0.143 g, 62% based on pure **7**): mp 131–132°; ultraviolet spectrum λ_{max}^{EtOH} 233 mμ (log ϵ 4.71), 268 (3.64), 278 (3.71), 291 (3.58), 319 (3.14), 232 (3.21).

Anal. Calcd for $C_{12}H_{10}O$: C, 84.70; H, 5.92. Found: C, 84.41; H, 6.10.

1-*tert*-Butoxynaphtho[*b*]cyclobutene (12). Bromide **7** (0.940 g, 63% pure) was added to 90 ml of 1 *M* potassium *tert*-butoxide in *tert*-butyl alcohol. After refluxing for 7 hr, water (360 ml) was added and the neutral product was recovered by chloroform extraction. Purification by plc (silica, benzene) followed by sublimation afforded ether **12** (0.415 g, 72% based on pure **7**): mp 71–72°; *m/e* 266 (1%), 170 (100%), 169 (60%), 141 (40%), 115 (15%). The nmr spectrum of **12** qualitatively resembled that of **7** except for the presence of the *tert*-butyl singlet at δ 1.4.

Anal. Calcd for $C_{16}H_{18}O$: C, 84.93; H, 7.97. Found: C, 84.76; H, 8.20.

Ether **12** was recovered quantitatively after a mixture of **12** (55.4 mg) and 1,3-diphenylisobenzofuran (**13**, 36.1 mg) was refluxed for 20 hr in 15 ml of 1 *M* potassium *tert*-butoxide in *tert*-butyl alcohol.

Adducts 14 and 15 of Naphtho[*b*]cyclobutadiene (1) with 1,3-Diphenylisobenzofuran. To a solution of bromide **7** (0.448 g, 63% pure) in benzene (15 ml) was added 1,3-diphenylisobenzofuran (**13**, 0.336 g) and 15 ml of a 1 *M* solution of potassium *tert*-butoxide in *tert*-butyl alcohol. After refluxing with stirring under nitrogen for 10 hr, the solution was evaporated to dryness and the products were isolated by chromatography on silica (1:1 benzene–cyclohexane eluent). Fractional crystallization (benzene–hexane) gave adducts **14** and **15**. The less soluble isomer was exo adduct **15** (0.206 g, 40%): mp 199.5–200°.

Anal. Calcd for $C_{32}H_{20}O$: C, 90.43; H, 5.55. Found: C, 90.66; H, 5.25.

The more soluble isomer was endo adduct **14** (0.040 g, 8%): mp 217.5–219.5°.

Anal. Calcd for $C_{32}H_{20}O$: C, 90.43; H, 5.55. Found: C, 90.54; H, 5.35.

A similar reaction of **7** and **13** was run (5 hr refluxing) using three times as much potassium *tert*-butoxide. The product was shown (nmr) to contain **12**, **14**, and **15** in the ratio 2:2:5.

Adducts 16 and 17 of Benzocyclobutadiene (11) with 1,3-Diphenylisobenzofuran. A solution of *trans*-1,2-dibromobenzocyclobutene (1.399 g) in benzene (25 ml) was added slowly to a stirred and refluxing mixture (nitrogen atmosphere) of zinc dust (5 g, NH_4Cl activated), furan **13** (1.42 g), *tert*-butyl alcohol (50 ml), and benzene (25 ml). After refluxing for 10 hr, the usual work-up gave an oil which was chromatographed on silica (benzene–cyclohexane eluent). Fractional crystallization (benzene–hexane) gave adducts **16** and **17**. The less soluble isomer was exo adduct **17** (0.630 g, 32%), mp 198–200° (lit.[10] mp 200–202°), identical with the previously reported adduct.[10] The more soluble isomer was endo adduct **16** (0.420 g, 22%): mp 128–130°.

Anal. Calcd for $C_{28}H_{20}O$: C, 90.32; H, 5.38. Found: C, 90.28; H, 5.49.

5,10-Diphenyldibenzo[*b,h*]biphenylene (18). A mixture of exo adduct **17** (0.123 g), phosphorus pentasulfide (2.5 g), and carbon disulfide (30 ml) was stirred at room temperature for 3 days. The mixture was then evaporated and the product was extracted into benzene and purified by chromatography on grade I neutral alumina (benzene eluent). Crystallization from benzene–pentane afforded hydrocarbon **18** (0.059 g, 50%) as golden yellow needles; mp 225–226°; ultraviolet spectrum $\lambda_{max}^{dioxane}$ 240 mμ (log ϵ 4.39), 300 (5.00), 325 (4.32), 390 (3.86), 412 (3.99).

Anal. Calcd for $C_{32}H_{22}O$: C, 95.05; H, 4.95. Found: C, 94.83; H, 5.07.

Under the same conditions, **18** was obtained in 48% yield from endo adduct **16**.

1,2:5,6-Dinaphtho[*b*]cyclooctatraene (19). A. From Monobromide 7. A mixture of bromide **7** (0.140 g, 63% pure), potassium *tert*-butoxide (0.043 g), and dry *tert*-butyl alcohol (20 ml) was refluxed for 6 hr. Water was added and the product was extracted into chloroform. Purification by plc (neutral grade I alumina, *n*-hexane eluent) gave hydrocarbon **19** (0.014 g, 22% based on pure **7**), which crystallized from benzene as white needles: mp 244–244.5°; ultraviolet spectrum $\lambda_{max}^{CHCl_3}$ 233 mμ (log ϵ 3.96), 273 (4.45); *m/e* 304 (71%), 303 (61%), 302 (62%), 152 (22%), 151 (100%) 151.5 (43%), 150 (43%), 144.5 (22%), 138 (24%).

Anal. Calcd for $C_{24}H_{16}$: C, 94.73; H, 5.25. Found: C, 94.18; H, 5.63.

B. By a Wittig Synthesis. A mixture of 2,3-bis(bromomethyl)-naphthalene[12] (**22**, 2.48 g), triphenylphosphine (4.41 g), and dimethylformamide (30 ml) was refluxed for 4 hr and then concentrated under reduced pressure. The precipitate was filtered, washed with ether, and recrystallized from ethanol to give white needles (5.86 g, 87%) of bisphosphonium salt **21**: mp 316–320°.

Anal. Calcd for $C_{48}H_{40}Br_2P_2$: C, 68.75; H, 4.76; Br, 19.07. Found: C, 68.47; H, 5.01; Br, 18.78.

A mixture of salt **21** (14.0 g), 2,3-naphthalenedicarboxyaldehyde[13] (**20**, 2.50 g), and dry dimethylformamide was heated to 90–100° under N_2, and a solution of lithium ethoxide (from 1.96 g of lithium) in ethanol (80 ml) was added with stirring during 2 hr. After an additional 3 hr of heating, water (500 ml) was added and the products were extracted into ether. The usual work-up gave an oil which was chromatographed on neutral grade I alumina (benzene eluent). Crystallization from benzene yielded triphenylphosphine oxide (3.0 g). The benzene mother liquor was concentrated and subjected to plc on alumina (benzene developer) to give two major bands.

Band I gave hydrocarbon **19** (0.129 g, 3.1%), mp 245.5–246.5°, identical with material prepared from bromide **7**.

Band II crystallized from benzene–hexane to give 7-ethoxy-1,2:5,6-dibenzocyclooctatriene (**33**, 1.10 g, 23.4%): mp 128–129°; *m/e* 350 (100%), 321 (50%), 291 (50%), 279 (28%); nmr δ 1.19 (t, 3 H, J = 8 Hz), 3.14–3.85 (m, 4 H), 5.05 (t, 1 H, J = 7.5 Hz), 7.03 (s, 2 H), 7.2–7.78 (m, 12 H).

Anal. Calcd for $C_{26}H_{22}O$: C, 89.14; H, 6.28. Found: C, 89.16; H, 6.47.

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