1,2-Diphenylanthra[*b*]cyclobutadiene

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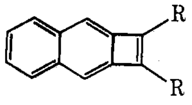
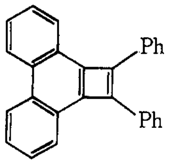
Received October 30, 1973

1,2-Diphenylanthra[*b*]cyclobutadiene (4) has been synthesized by two different routes, one starting from 2,3-naphthalenedicarboxaldehyde and the other starting from diphenylcyclobutadienequinone. The red crystalline 4 undergoes addition reactions (reduction, oxidation, bromination) at the 1,2 double bond preferentially; it does not form isolable adducts with the active diene 1,3-diphenylisobenzofuran (19) or with the active dienophiles tetracyanoethylene and 4-phenyltriazoline-3,5-dione.

The degree of stability of an aromatic system constructed by the terminal fusion of a cyclobutadiene ring to a polynuclear benzenoid hydrocarbon is strongly dependent upon the substitution pattern of the four-membered ring and on the nature of the condensed benzenoid portion of the molecule. Thus, naphtho[*b*]cyclobutadiene (1) is a highly reactive intermediate[2] in contrast to the stable crystalline 1,2-diphenylnaphtho[*b*]cyclobutadiene (2).[3] On the other hand, 1,2-diphenylphenanthro[*b*]cyclobutadiene (3) is a highly reactive species which can be trapped but not isolated.[4,5]



1, R = H
2, R = Ph



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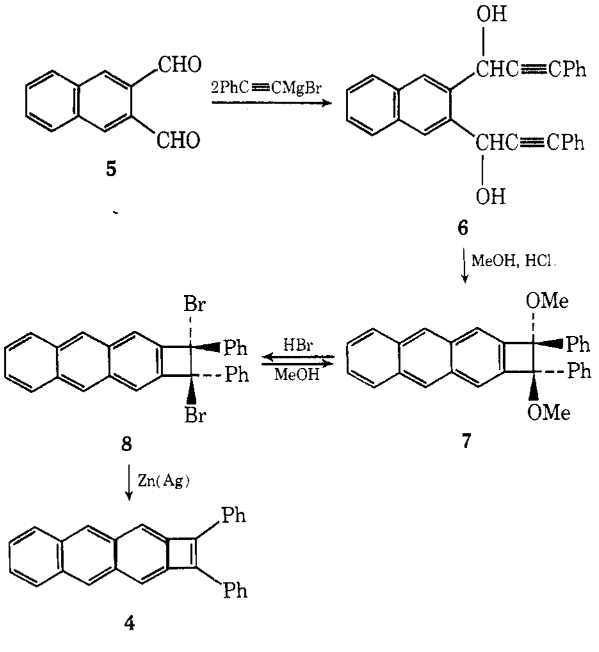
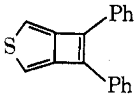
In this paper we report the synthesis and some properties of the stable linear isomer of 3, namely 1,2-diphenylanthra[*b*]cyclobutadiene (4). Compound 4 represents the first known anthracyclobutadiene.[6]

Results

Synthesis of 1,2-Diphenylanthra[*b*]cyclobutadiene. Two entirely unrelated syntheses of 1,2-diphenylanthra[*b*]cyclobutadiene (4) were achieved. The first was patterned after our earlier synthesis of 1,2-diphenylnaphtho[*b*]cyclobutadiene (2).[3] Thus, addition of phenylethynylmagnesium bromide to 2,3-naphthalenedicarboxaldehyde (5)[7] gave diol 6, which was converted by hydrogen chloride in dry methanol to *trans*-1,2-dimethoxy-1,2-diphenylanthra[*b*]cyclobutene (7). Reaction of ether 7 with hydrogen bromide gave the corresponding dibromide 8, methanolysis of which regenerated ether 7. Reaction of dibromide 8 with zinc–silver couple afforded hydrocarbon 4. The overall yield of 4 from dialdehyde 5 was 10%.



The second synthesis of 4 involves the use of the Wittig reaction for the construction of one of the benzenoid rings of 4. It is related to the reported synthesis of the thienocyclobutadiene 9, in which the heterocyclic ring was similarly constructed.[8] Thus, the ylide 10[2] derived from 2,3-bis(bromomethyl)naphthalene (11) reacted with diphenylcyclobutadienequinone (12) in warm dimethylformamide to give hydrocarbon 4 directly in 16% yield. The major reaction product was a yellow, crystalline material to which structure 13 has been assigned.



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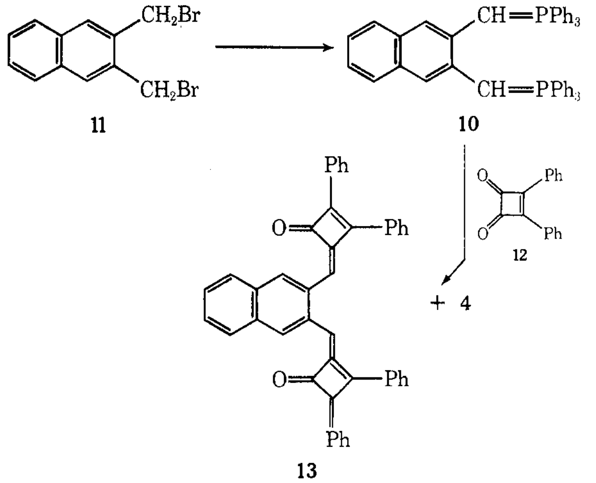
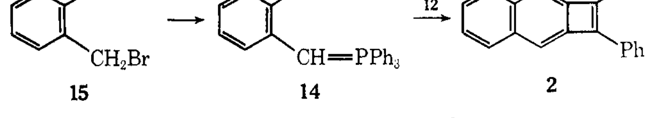
The Wittig synthesis of 4 suggested that a new short synthesis of the naphthocyclobutadiene 2 could be carried out in a similar manner, and this proved to be the case. Reaction of dione 12 with the ylide 14[9] derived from *o*-xylylene dibromide (15) afforded 2 directly in 20% yield.





Properties of 1,2-Diphenylanthra[*b*]cyclobutadiene. 1,2-Diphenylanthra[*b*]cyclobutadiene (4) forms bright red plates, mp 199–202°, which appear to be stable indefinitely. Its ultraviolet–visible spectrum is shown in Figure 1, along with that of its naphtho analog 2.

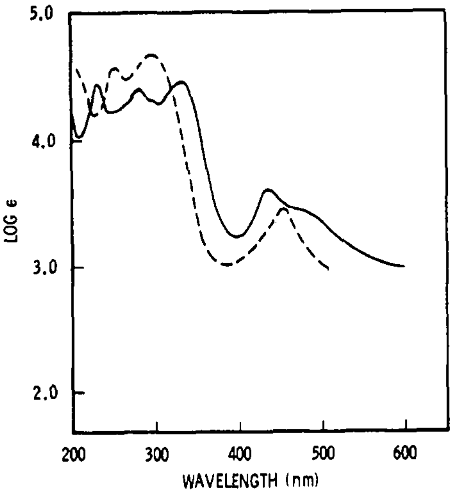
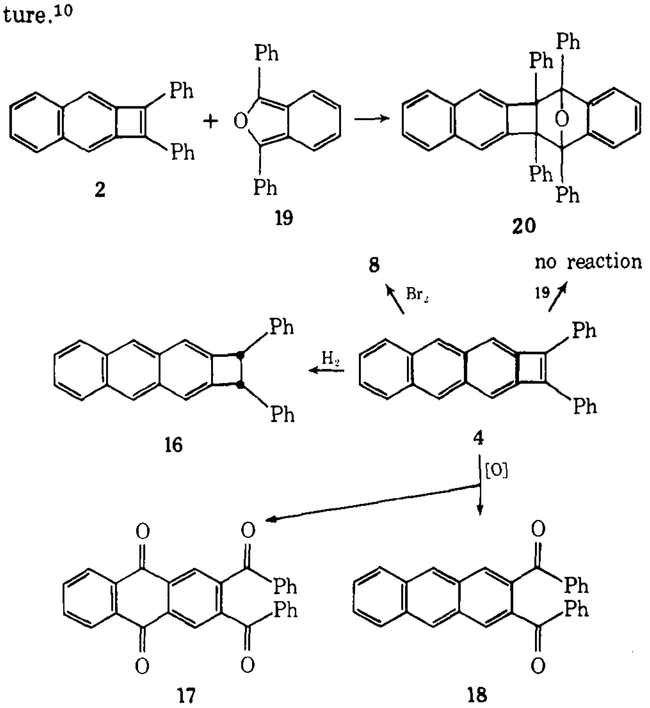


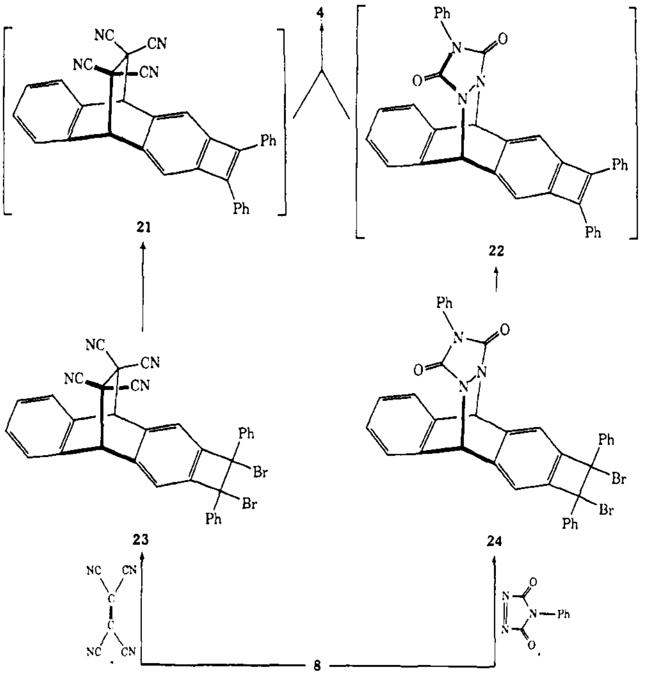
Figure 1. Uv spectrum of 1,2-diphenylnaphtho[*b*]cyclobutadiene (- - - -) and of 1,2-diphenylanthra[*b*]cyclobutadiene (——).

The two most reactive centers in hydrocarbon 4 would be expected to be the central ring of the anthracene portion and the 1,2-unsaturated bond of the four-membered ring. The latter center was found to be the one which is most prone to addition reactions. Thus, bromine adds selectively and quantitatively to the four-membered ring to give dibromide 8. Similarly, absorption of 1 molar equiv of hydrogen in the presence of palladium affords *cis*-1,2-diphenylanthra[*b*]cyclobutene (16). Chromic acid in warm acetic acid oxidizes both reactive centers of 4, giving 2,3-dibenzoyl-9,10-anthraquinone (17). On the other hand, permanganate oxidation of 4 can be controlled to give 2,3-dibenzoylanthracene (18); diketone 18 is also produced when a benzene solution of 4 is irradiated in the presence of oxygen.

1,2-Diphenylnaphtho[*b*]cyclobutadiene (2) undergoes addition of 1,3-diphenylisobenzofuran (19) to give the Diels–Alder adduct 20;[3] this addition takes place readily on heating, or more slowly even at room temperature. In contrast, addition of furan 19 to the anthracyclobutadiene 4 did not take place either on heating or at room temperature.[10]

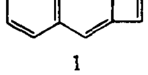


Attempted Conversion of 1,2-Diphenylanthra[*b*]cyclobutadiene to a Benzocyclobutadiene Derivative. Not only does hydrocarbon 4 fail to react as a dienophile with furan 19, but it also fails to react as an anthracene-type diene with the powerful dienophiles tetracyanoethylene (TCNE) and 4-phenyltriazoline-3,5-dione (PTD).[11] The hypothetical adducts (21 and 22) from the latter additions would be of considerable interest as derivatives of benzocyclobutadiene. In an attempt to synthesize 21 and 22 indirectly, dibromide 8 was found to add normally to TCNE and to PTD to give adducts 23 and 24, respectively. Debromination of 23 and 24 took place at room temperature, using zinc–silver couple. The initially formed dehalogenation products 21 and 22 were not stable, however, and underwent a spontaneous reverse Diels–Alder reaction with the formation of anthracyclobutadiene 4.



Discussion

Molecular orbital calculations have been reported which predict a delocalization energy (DE) of 5.88 β for the unsubstituted anthra[*b*]cyclobutadiene (25) as compared to a DE of 4.20 β for naphtho[*b*]cyclobutadiene (1).[12] Sub-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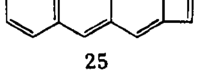
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stracting the accepted DE values for anthracene (5.31 β) and naphthalene (3.68 β) from these figures, we may predict that linear fusion of a cyclobutadiene ring to anthracene will result in slightly more stabilization than a similar fusion to naphthalene. The observation in the phenylated series that furan 19 adds to 2 but not to 4 offers experimental confirmation for this prediction.

Tetracyanoethylene (TCNE) and 4-phenyltriazoline-3,5-dione (PTD) are two of the most reactive dienophiles known. The great ease with which the adducts 21 and 22 break down to these dienophiles and 4 attests to the far greater stability of the anthracyclobutadiene of 4 as compared to the benzocyclobutadiene system present in the adducts.[13]

Experimental Section

General. Melting points are uncorrected. Ultraviolet-visible spectra were determined in dioxane unless otherwise noted. Spectra were recorded on a Perkin-Elmer Model 137 ir spectrophotometer, a Perkin-Elmer Model 202 uv-visible spectrophotometer, a Varian A-60A nmr spectrometer, and a Perkin-Elmer Model 270B mass spectrometer.

1,2-Diphenylnaphtho[*b*]cyclobutadiene (2). A solution of *o*-xylylene bis(triphenylphosphonium bromide) (0.304 g, 0.5 mmol) and diphenylcyclobutadienequinone (**12**, 0.117 g, 0.5 mmol) in dry dimethylformamide (40 ml) was stirred (nitrogen) for 4 hr at 90-95°, while a solution of sodium ethoxide (from 0.023 g of sodium) in ethanol was added dropwise. The cooled reaction mixture was diluted with water (250 ml) and extracted with ether. Evaporation of the washed and dried ether phase gave a red solid. Purification by chromatography (neutral I alumina, benzene eluent) and crystallization from chloroform-*n*-hexane gave red needles of **2** (0.030 g, 20%), mp 134-135° (lit.[3] mp 137-138°).

1,2-Diphenylanthra[*b*]cyclobutadiene (4). A solution of the phosphonium bromide precursor[2] of **10** (2.549 g, 3 mmol) and **12** (0.702 g, 3 mmol) in dry dimethylformamide (200 ml) was stirred (nitrogen) for 4 hr at 90-95° (absence of light), while a solution of sodium ethoxide (from 0.138 g of sodium) in absolute ethanol (25 ml) was added dropwise. The cooled reaction mixture was concentrated to 50 ml, diluted with water (500 ml), and extracted with ether. Evaporation of the washed and dried ether phase gave, on trituration with chloroform (10 ml), red plates of **4** (0.180 g, 16%). Recrystallization (chloroform-ether) gave the analytical sample, uv-visible spectrum λ_{max} (EtOH) 230 nm ($\log \epsilon$ 4.50), 283 (4.57), 335 (6.75), 430 (3.62).

Anal. Calcd for $C_{28}H_{18}$: C, 94.88; H, 5.12. Found: C, 94.78; H, 5.12.

Chromatography (silica gel, benzene eluent) of the residues from **4** gave, on crystallization from benzene, yellow needles of **13** (0.32 g, 40%): mp 223-225°; *m/e* 588 (M^+); ir (KBr) 5.70 μ (C=O); uv spectrum λ_{max} 212 nm ($\log \epsilon$ 4.60), 265 (4.68), 325 (4.63), 350 (4.60).

Anal. Calcd for $C_{44}H_{28}O_2$: C, 89.79; H, 4.76. Found: C, 89.55; H, 5.00.

Oxidation of 1,2-Diphenylanthra[*b*]cyclobutadiene (4). A. By Oxygen and Light. Oxygen was passed through a solution of **4** (0.050 g, 0.143 mmol) in benzene (8 ml) which was irradiated with a high-pressure Hanovia lamp (Pyrex filter). After 1 hr, the reaction mixture had become yellow. Evaporation of the solvent and crystallization from ethanol gave 2,3-dibenzoylanthracene (**18**, 0.025 g, 45%): mp 170-171°; *m/e* 386 (M^+); ir (KBr) 6.1 μ (C=O); uv spectrum λ_{max} 215 nm ($\log \epsilon$ 4.41), 273 (4.73), 345 (3.77).

Anal. Calcd for $C_{28}H_{18}O_2$: C, 87.02; H, 4.69. Found: C, 86.73; H, 4.68.

B. By Potassium Permanganate. Saturated potassium permanganate solution in acetone (1 ml) was added to a solution of **4** (0.030 g, 0.116 mmol) in acetone (3 ml). Dilute hydrochloric acid (15 drops) was added and the mixture was heated on the steam bath for 20 min. Evaporation of the mixture, extraction (benzene) of the residue, and crystallization from benzene-*n*-hexane gave **18** (0.055 g, 33%), mp 169-171°.

C. By Chromium Trioxide. A solution of **4** (0.050 g, 0.143 mmol) and finely ground chromium trioxide (0.080 g, 0.8 mmol) in acetic acid (5 ml) containing sulfuric acid (50%, 5 drops) was heated for 10 min on the steam bath. Dilution with water, followed by crystallization of the suspended solid from trichloroethylene-*n*-hexane, gave pure 2,3-dibenzoyl-9,10-anthraquinone (**17**, 40 mg, 70%): mp 244-245°; *m/e* 416 (M^+); ir (KBr) 6.0, 6.1, 6.3 μ (C=O); uv spectrum λ_{max} 215 nm ($\log \epsilon$ 4.49), 260 (4.81), 330 (3.90).

Anal. Calcd for $C_{28}H_{16}O_4$: C, 80.76; H, 3.87. Found: C, 80.89; H, 4.13.

Hydrogenation of 1,2-Diphenylanthra[*b*]cyclobutadiene (4). A solution of **4** (0.150 g, 0.43 mmol) in benzene (6 ml) and ethanol (5 ml) was shaken under hydrogen (atmospheric pressure, room temperature) in the presence of 5% palladium on charcoal (0.1 g) until the orange color vanished (*ca.* 30 min). Solvent evaporation, followed by crystallization from benzene-*n*-hexane, gave pure *cis*-1,2-diphenylanthra[*b*]cyclobutene (**16**, 100 mg, 70%): mp 175-176°; *m/e* 356 (M^+); nmr ($CDCl_3$) δ 5.42 (s); uv spectrum λ_{max} 214 nm ($\log \epsilon$ 5.81), 260 (5.93), 275 (5.94), 360 (4.30).

Anal. Calcd for $C_{28}H_{20}$: C, 94.38; H, 5.62. Found: C, 94.15; H, 5.88.

Bromination of 1,2-Diphenylanthra[*b*]cyclobutadiene (4). A bromine solution (25%) in tetrachloride was added dropwise (40 drops) to a stirred suspension of anthracyclobutadiene **4** (0.070 g, 0.2 mmol) in carbon tetrachloride at room temperature during 10 min. Solvent evaporation and crystallization from trichloroethylene-*n*-hexane gave *trans*-1,2-dibromo-1,2-diphenylanthra[*b*]cyclobutene (**8**, 0.080 g, 80%): mp 190° dec; *m/e* 512, 514, 516 (M^+); uv spectrum λ_{max} 210 nm ($\log \epsilon$ 5.71), 275 (6.08).

Anal. Calcd for $C_{28}H_{18}Br_2$: C, 65.30; H, 3.50. Found: C, 65.56; H, 3.47.

Methanolysis of Dibromide 8. A solution of dibromide **8** (0.250 g, 0.5 mmol) in benzene (20 ml) and dry methanol was allowed to stand for 24 hr at room temperature. Solvent evaporation, followed by chromatography (silica gel, benzene eluent) gave, after crystallization from benzene-*n*-hexane, pure dimethoxy compound **7** (0.126 g, 60%): mp 142-143° dec; nmr ($CDCl_3$) δ 3.19 (s); uv spectrum λ_{max} 210 nm ($\log \epsilon$ 4.43), 260 (5.16), 343 (3.69), 362 (3.84), 382 (3.69).

Anal. Calcd for $C_{30}H_{24}O_2$: C, 86.53; H, 5.69. Found: C, 86.82; H, 5.88.

Addition of Dienophiles to Dibromide 8. A. Tetracyanoethylene. A solution of dibromide **8** (0.257 g, 0.5 mmol) and tetracyanoethylene (0.064 g, 0.5 mmol) in dry tetrahydrofuran was allowed to stand at room temperature for 3 hr. The reaction mixture was evaporated and the residue, after trituration with ether (4 ml), was filtered and crystallized from tetrahydrofuran-*n*-hexane to give adduct **23** (0.200 g, 62%): mp 195-197° dec; nmr ($CDCl_3$) δ 5.96 (s); uv spectrum λ_{max} 222 nm ($\log \epsilon$ 4.04), 236 (4.05), 282 (3.80); *m/e* 578 ($M^+ - 64$).

This adduct gave good analytical values for carbon, but rather erratic results for hydrogen and nitrogen.

Anal. Calcd for $C_{34}H_{18}Br_2N_4$: C, 63.55; H, 2.80; N, 8.72. Found: C, 63.56; H, 3.51; N, 8.03.

B. 4-Phenyltriazoline-3,5-dione. A solution of dibromide **8** (0.257 g, 0.5 mmol) and triazolinedione (0.088 g, 0.5 mmol) in benzene (10 ml) was allowed to stand for 24 hr at room temperature. The reaction mixture was evaporated and the residue, after trituration with ether (3 ml), was filtered and crystallized from dichloromethane-ether to give adduct **24** (0.240 g, 60%): mp 170° dec; nmr ($CDCl_3$) δ 6.40 (s); ir (KBr) 5.90 μ (C=O); uv spectrum λ_{max} 223 nm ($\log \epsilon$ 3.53), 234 (3.51), 280 (2.90); *m/e* 608 ($M^+ - 81$), 610 ($M^+ - 79$).

This adduct gave good analytical results for carbon, but rather erratic results for hydrogen and nitrogen.

Anal. Calcd for $C_{36}H_{23}Br_2N_3O_2$: C, 62.69; H, 3.33; N, 6.09. Found: C, 62.38; H, 4.30; N, 5.46.

Debromination of Adduct 23. A solution of adduct **23** (0.050 g, 0.079 mmol) in benzene (10 ml) was debrominated with zinc-silver couple[14] (0.5 g) at room temperature. The reaction mixture was filtered and purified by ptlc (basic silica, benzene) to give 1,2-diphenylanthra[*b*]cyclobutadiene (**4**, 0.020 g, 40%).

Debromination of Adduct 24. A solution of adduct **24** (0.020 g, 0.03 mmol) in acetone was debrominated with zinc-silver couple (0.5 g) at room temperature. After 2 min, a deep red color had developed. The uv-visible spectrum of this solution was identical with that of an equimolar acetone solution of **4** and 4-phenyltriazoline-3,5-dione, and showed only bands attributable to these components.

Synthesis of Diol 6. A solution of phenylacetylene (2.04 g, 0.02 mmol) and ethynylmagnesium bromide in ether (6.66 ml of a 3 *M* solution) was refluxed for 1 hr. To the resulting reaction mixture a solution of 2,3-naphthalenedicarboxaldehyde (**5**, 1.84 g, 0.01 mol) in dry tetrahydrofuran (15 ml) was added. After refluxing for 30 min, the solution was diluted with water and ether. The dried organic phase was treated with charcoal (2 g), filtered, and evaporated. Crystallization from dichloromethane-*n*-hexane gave diol **6** (1.85 g, 48%): mp 157-159°; ir (KBr) 2.9 (OH), 4.5 μ (C≡C); uv spectrum λ_{max} 225 nm ($\log \epsilon$ 4.81), 243 (4.83), 253 (4.83), 270 (4.62); *m/e* 388 (M^+).

Anal. Calcd for $C_{28}H_{20}O_2$: C, 86.55; H, 5.15. Found: C, 86.30; H, 4.99.

1,2-Dimethoxy-1,2-diphenylanthra[*b*]cyclobutene (7). Hydrogen chloride gas was passed through a stirred solution of diol **6** (0.386 g, 1.007 mmol) in methanol until it became hot and saturated with the acid. The reaction mixture was concentrated, cooled, and filtered. The residue was crystallized from benzene-*n*-hexane to give dimethoxydiphenylanthracyclobutene compound **7** (0.450 g, 50%), mp 108-110° dec. Recrystallization gave material identical with that prepared from dibromide **8**.

Reaction of 7 with Hydrogen Bromide. Hydrogen bromide gas was passed through a stirred solution of ether **7** (dimethoxydiphenylanthracyclobutene, 0.050 g, 0.143 mmol) in a mixture of ether (5 ml) and *n*-hexane (5 ml) for 1 min. After standing at room temperature for 48 hr, the mixture was evaporated and the residue was crystallized from trichloroethylene-*n*-hexane to give dibromide **8** (0.025 g, 60%), mp 188-190° dec.

Reaction of 1,2-Diphenylnaphtho[*b*]cyclobutadiene (2) with 1,3-diphenylisobenzofuran (19). A solution of **2** (0.0152 g, 0.05 mmol) and furan **19** (0.0135 g, 0.05 mmol) in dichloromethane (0.5 ml) was allowed to stand at room temperature for 24 hr, during which time a crystalline adduct formed. The reaction mixture was evaporated to dryness and the residue was washed with ether to give the pure adduct **20** (0.022 g, 72%), mp 295–296° dec (lit.[3] mp 296–297°).

Reaction of 1,2-Diphenylanthra[*b*]cyclobutadiene (4) with 1,3-Diphenylisobenzofuran (19). A solution of **4** (0.0354 g, 0.1 mmol) and furan **19** (0.027 g, 0.1 mmol) in dichloromethane (1.5 ml) was allowed to stand at room temperature for 30 hr. The resulting mixture was chromatographed (neutral I alumina, benzene eluent) to give 0.025 g (70%) of hydrocarbon **4**, identical with an authentic sample.

Acknowledgment. We thank the National Science Foundation for a grant (GP 24057X) in support of this research.

Registry No. 2, 4023-74-9; **4,** 49626-41-7; **5,** 7149-49-7; **6,** 36229-72-8; **7,** 49626-44-0; **8,** 49626-45-1; **12,** 24234-76-2; **13,** 49626-46-2; **16,** 49626-47-3; **17,** 49626-48-4; **18,** 42189-19-5; **23,** 49626-50-8; **24,** 49626-51-9; *o*-xylylenebis(triphenylphosphonium bromide), 1519-46-6; [2,3-naphthalenediylbis(methylene)]bis(triphenylphosphonium bromide), 39013-98-4; tetracyanoethylene, 670-54-2; 4-phenyltriazoline-3,5-dione, 4233-33-4; phenylacetylene, 536-74-3.

References and Notes

(1) To whom inquiries should be addressed: at the University of Pennsylvania.
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Cyclopropanols. XI. Acid-Catalyzed Ring Opening of Arylcyclopropanols

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Received September 4, 1973

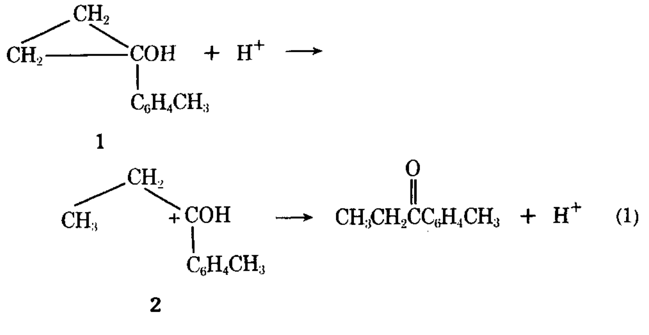
Rates of acid-catalyzed ring opening of a series of 1-arylcyclopropanols and of 1-phenyl-2-arylcyclopropanols and their acetates have been measured in several solvents. The effect of substituents on the rate for the former series is moderately large ($\rho = -1.5$) but substituents in the 2-aryl group have almost no effect on the acid-catalyzed cleavage of the 1,2 bond. Substituents in the 1-aryl ring have little effect on the rates of base-catalyzed cleavage of 1-arylcyclopropanols. The implication of these results on the mechanism of cyclopropane ring cleavage by acids and bases is briefly discussed.

The cleavage of the carbon–carbon single bond of a cyclopropane by electrophiles is a reaction of some mechanistic interest.[1] Stereochemical studies have shown that the ring-opening reaction with a proton can occur with either retention[2] or inversion[3] of configuration, and, while Markovnikov's rule is followed in a broad sense,[4] the tendency for a proton to add to the least substituted carbon atom of the ring is not great.[1] Even an example of complete anti-Markovnikov cleavage has been reported.[5]

Only a very few actual kinetic studies on electrophile ring openings of cyclopropanes have been reported,[6-8] and these have not been especially revealing about the nature of the transition state for the reaction. In this paper we report some studies on the rates and direction of ring opening of a series of aryl-substituted 1-phenyl- and 1,2-diphenylcyclopropanols.

Results and Discussion

Our initial studies were with 1-(*p*-tolyl)cyclopropanol (**1**), since this molecule is crystalline and undergoes ring opening (eq 1) at a convenient rate for study over a large range of acid concentrations. The reaction rate is easily followed by ultraviolet spectroscopy, since the propiophenone product absorbs strongly and the cyclopropanol does not.



1

2

(1)

The rate constants for the ring opening of **1** of 60:40 vol. % dioxane–water as a function of perchloric acid concentration are given in Table I. The most important conclusion is that the reaction is first order in both cyclopropanol and in acid. Bunton and coworkers[9] have determined values for the Hammett acidity function in this solvent system; a plot of log *k vs.* H_0 gives a slightly better straight line than a similar plot *vs.* pH. However, in view of the difficulties of drawing mechanistic conclusions from such plots, we will not comment further.

To determine something about the amount of charge which develops on the benzylic carbon in the transition state, the rate of ring opening of a series of 1-arylcyclopropanols was determined in 60:40 dioxane–water and 1.45 *M* $HClO_4$. The results are given in Table II. These rate data indicate that a positive charge is present in the transition state, although not a particularly large one. The correlation of rate with σ is better than with σ^+; ρ for the former is -1.46 and ρ^+ for the latter is -0.755. Stewart and Yates[10] have measured the pK_a's of 20 substituted acetophenones in H_2SO_4. The protonated forms of these ketones resemble **2**, which might have been suggested as a reasonable model for the transition state of the ring-opening reaction. Plotted against σ^+ these pK_a data gave $\rho^+ = -2.17$ and, slightly less satisfactorily, against σ, $\rho = -2.22$. Both values are significantly larger than those measured for the ring opening.