Reaction of an Unsymmetrical π Anion with Methylene Chloride/ n-Butyllithium. Preparation of Several $C_{18}H_{12}$ Hydrocarbons[1]

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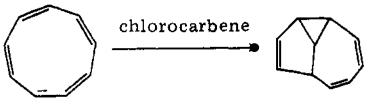
The reaction of the benz[*de*]anthracenyl anion (**17**) with methylene chloride/*n*-butyllithium is reported. The products of the reaction were shown to be 4,5-benzocyclohepta[1,2,3-*de*]naphthalene (**18**), 1,10-phenanthrotricyclo[4.1.0.$0^{2,7}$]heptene (**19**), and cyclohepta[*jk*]phenanthrene (**20**) in a ratio of 3:6:1, respectively; the overall yield was about 35%. The bicyclobutane **19** was converted into **20** and 1,10-phenanthrobicyclo[3.2.0]hepta-2,6-diene (**21**) by methods previously used for the bicyclobutane **11**. A qualitative scheme based on the total π-electron densities on the carbon atoms of **17** is used to rationalize the product distribution of the carbene reaction.

Ever since Katz and his co-workers prepared isobullvalene (**2**) by the reaction of the cyclononatetraenyl anion (**1**) with methylene chloride and strong base,[3,4] the reaction of cyclic π anions with chlorocarbene[5] has received increasing attention,[6-9] because many interesting compounds can be made by this procedure that have proven difficult or impossible to make by more traditional approaches. Without doubt the most well-known compound that has been prepared by this procedure is benzvalene (**5**), it resulting from the reaction of the cyclopentadienyl anion (**3**) with CH_2Cl_2/CH_3Li.[6] Another notable feature of the chlorocarbene procedure is that many of the highly strained molecules produced in these reactions can be converted into other interesting compounds. Benzvalene (**5**), for example, has been converted into prismane (**6**),[10] a compound not known from any other route.



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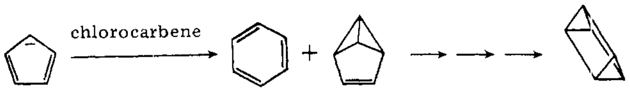
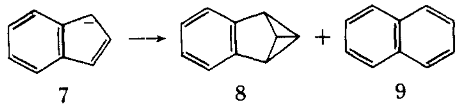


3 4 5 6

In a sense one can predict the products expected when the cyclic π anions, **1**,[3] **3**,[6] **7**,[6] **10**,[7,8] and **13**,[9] the ones which have been studied to date, are treated with methylene chloride and strong base. For the anions, **1**, **3**, and **10**, which possess high symmetry, there are a limited number of unique sites where the carbene can attack. For the anions, **7** and **13**, which lack high symmetry, there are still few plausible sites of attack for the carbene because the aromaticity of the anion would be destroyed in most of these attacks.



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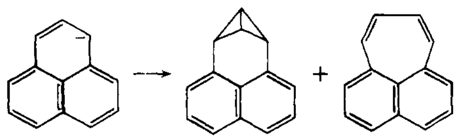

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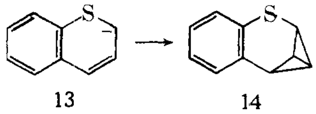
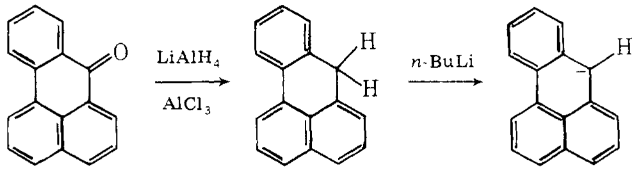


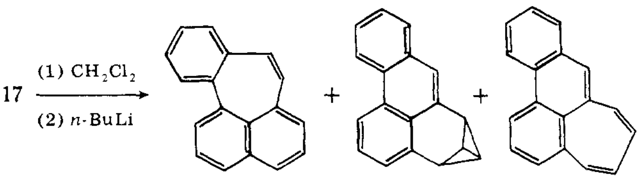
13 14

To make the reaction more useful it would be desirable to understand it in greater detail, thus transforming an intuitive approach to product prediction into a rational one. Although there are several ways one might do this, our initial endeavor was to look at an unsymmetrical anion where the carbene had several plausible points of attack. The benz[*de*]anthracenyl anion (**17**) was chosen because, in addition to fulfilling these criteria, it is easily prepared from the commercially available benzanthrone (**15**).[11]



15 16 17

The crude product resulting from the treatment of a solution of **17** in ether at dry ice–acetone temperature first with methylene chloride and then with *n*-butyllithium was shown to contain five products by thin layer chromatography. Three of these products, 4,5-benzocyclohepta[1,2,3-*de*]naphthalene (**18**), 1,10-phenanthrotricyclo[4.1.0.$0^{2,7}$]heptene (**19**), and cyclohepta[*jk*]phenanthrene (**20**), were formed in sufficient quantity to detect by NMR; two of these, **18** and **19**, could be separated by column chromatography on magnesium oxide[12,13] and isolated in sufficient quantity for spectral and analytical characterization.



	18	19	20
NMR ratio	3	6	1

4,5-Benzocyclohepta[1,2,3-*de*]naphthalene (**18**), the minor of the two isolated products, consistently was formed in 10 to 12% yield. If one had an interest in preparing this nonbenzenoid aromatic hydrocarbon, the chlorocarbene route might not appear to be the synthetic method of choice. Considering the large number of steps which were required in previous syntheses of this compound,[14] however, this rapid two-step synthesis seems very attractive.

The major product formed in about 23% yield was shown to be the bicyclobutane **19**, first on the basis of its NMR spectrum (see Experimental Section) which is characteristic of phenanthrene derivatives[15] and then definitively by X-ray crystallography.[16]

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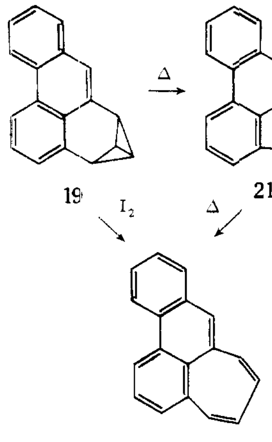
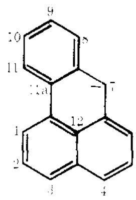
As was the case for the naphthobicyclobutane (**11**),[7,17] the phenanthrobicyclobutane (**19**) could be converted into isomeric hydrocarbons. Thermolysis, for example, led to the formation of 1,10-phenanthrobicyclo[3.2.0]hepta-2,6-diene (**21**), which, in turn, was converted into cyclohepta[*jk*]phenanthrene (**20**) on further heating. This latter compound could more conveniently be prepared by treating **19** with a catalytic amount of iodine. It should be noted that both **20** and **21** had not previously been reported in the literature.



Returning to the chlorocarbene reaction itself, can one explain the regioselectivity that has been observed? Note that **18** results from the attack of the carbene on C-7 of the anion **17**, while **19** and **20** result from the attack on C-4 and/or C-6. Qualitatively, one can indeed explain these results, although a quantitative treatment is not possible because the overall yield is far less than 100%. Shown below are the Hückel total π electron densities for the various carbons of **17**; C-7 has the largest value and C-4,6 have the next largest values. Thus, the electrophilic carbene has attacked the sites of highest electron density.



17

carbon[a]	total π electron density
7	1.247
4, 6	1.171
1, 3	1.110
8, 10, 11a	1.062
12	1.007

[a] Every other carbon has a value of 1.

The above analysis may seem surprising because π-electron densities are usually poor guides to regioselectivity in electrophilic reactions such as electrophilic aromatic substitution. The reaction of an electrophile such as a proton with an aromatic substrate to form a σ complex is normally endothermic, which means that the σ complex is a better model for the transition state than is the reactant aromatic substrate.

In the present case, the reaction of the electrophilic carbene with **17** may be exothermic, perhaps quite exothermic. If this is so, **17** should be a better model for the transition state than the resulting σ complex. In this event the π-electron densities at the various sites of **17** should reflect where the carbene will attack.

Even if this idea ultimately proves to be incorrect, at present it should be a useful guide in predicting where an unsymmetrical carbanion will be attacked by chlorocarbene.

Experimental Section

General Procedures. Melting points are uncorrected. NMR spectra were recorded on Varian A-60 and HA-100 spectrometers, while mass spectra were recorded on a Perkin-Elmer RMU-6E spectrometer. Elemental analyses were performed by Galbraith Labs, Knoxville, Tenn.

Reaction of Benz[*de*]anthracenyl Anion with Methylene Chloride/*n*-Butyllithium. To a solution of 6.92 g (32.1 mmol) of 7*H*-benz[*de*]anthracene[11] in 1 L of ether was added under nitrogen 22.5 mL of 1.6 *M* *n*-butyllithium (36.0 mmol). After stirring the purple solution at room temperature for 1 h and then cooling in a dry ice–acetone bath, 5.0 mL of methylene chloride was added over 0.5 h followed by an additional 24.0 mL of 1.6 M *n*-butyllithium (38.0 mmol) over 0.75 h. The dark green solution was warmed to room temperature, washed with water, and dried. Removal of the ether in vacuo gave an orange oil whose NMR spectrum showed the presence of 4,5-benzocyclohepta[1,2,3-*de*]naphthalene (**18**), 1,10-phenanthrotricyclo[4.1.0.0^{2,7}]heptene (**19**), and a barely perceptible amount of cyclohepta[*jk*]phenanthrene (**20**). After passage of a small amount of this oil through a Celite column (eluting with ligroine), sufficient polymeric material is removed so that the product ratio could be determined; the values were 3:6:1 for the products **18**, **19**, and **20**, respectively.

Attempted Separation of Products on Alumina. The crude product was chromatographed on alumina (Fisher, 80–200 mesh), eluting first with ligroine and then with increasing amounts of ether in ligroine. The first component off the column weighed 73.0 mg (blue fluorescence, aromatic absorption in NMR) and was not characterized. The second component was a green oil (682 mg) and was characterized as 4,5-benzocyclohepta[1,2,3-*de*]naphthalene (**18**). The third component, an orange solid weighing 1.09 g, was shown by NMR to be an admixture of 50% of 1,10-phenanthrotricyclo[4.1.0.0^{2,7}]heptene (**19**) and 50% of cyclohepta[*jk*]phenanthrene (**20**).

Characterization of 4,5-Benzocyclohepta[1,2,3-*de*]naphthalene (18). After carefully rechromatographing the green oil (second component above), the compound was induced to crystallize. An analytically pure sample was obtained after three recrystallizations from ligroine–ether and sublimation (100 °C (0.5 mm)). This afforded a yellow solid having: mp 66.0–66.5 °C (lit. mp 65 °C,[14a] 64–65 °C[14b]); mass spectrum, *m/e* 228 (parent peak); NMR (CCl_4) δ 6.98–7.70 (m, 10 H, benzo- and naphthoaromatic), and 6.45 (s, 2 H, vinyl). Anal. Calcd for $C_{18}H_{12}$: C, 94.70; H, 5.30. Found: C, 94.69; H, 5.18.

Separation of Products on Magnesium Oxide. A 3.5 × 75 cm column was prepared as follows. Approximately 40 mL of MgO, which had been dampened with ligroine, was added to the column and tamped down firmly. The process was repeated until the column was full. After saturating the column with ligroine, the crude product from the reaction of 5.93 g of 7*H*-benz[*de*]anthracene with methylene chloride/*n*-butyllithium was added to the top. The column, which was eluted with ligroine, was run in the usual manner except that air or nitrogen pressure ($\leq$10 psi) was applied to the top, while a partial vacuum ($\sim$50 mm) was applied to the bottom. This insured an acceptable flow rate.

4,5-Benzocyclohepta[1,2,3-*de*]naphthalene (**18**) was collected until the NMR spectrum of the eluate showed bicyclobutane peaks. The column was continued until all the bicyclobutane had come off. The bicyclobutane fractions were combined and they partially crystallized on standing. After separating the crystals, the oily residue was rechromatographed on MgO and the entire process was repeated. A total of three columns was run and yielded 447 mg of 4,5-benzocyclohepta[1,2,3-*de*]naphthalene (**18**) and 1.47 g of a solid that was >80% bicyclobutane (**19**).

Characterization of 1,10-Phenanthrotricyclo[4.1.0.0^{2,7}]heptene (19). Repeated recrystallization from ligroine/methylene chloride of the enriched bicyclobutane sample above gave an analytically pure sample of **19** having: mp 99–100 °C; mass spectrum, parent peak at *m/e* 228; NMR (CCl_4) δ 8.28–8.72 (m, 2 H, H-4 and -5 of the phenanthrene ring), 7.18–7.95 (m, 6 H, remaining phenanthrene protons), 3.10–3.38 (two overlapping t, 2 H, bicyclobutane benzylic), and 2.45–2.58 (t, 2 H, remaining bicyclobutane protons, J = 3.0 Hz). Anal. Calcd for $C_{18}H_{12}$: C, 94.70; H, 5.30. Found: C, 94.84; H, 5.27.

Cyclohepta[*jk*]phenanthrene (20). A solution consisting of 10 mg of I_2 and 1.37 g of a mixture containing 40% of 4,5-benzocyclohepta[1,2,3-*de*]naphthalene (**18**) and 60% of 1,10-phenanthrotricyclo[4.1.0.0^{2,7}]heptene (**19**) in 50 mL of CCl_4 was stirred at room temperature for 18 h. After washing with aqueous $Na_2S_2O_3$, the CCl_4 was dried and removed in vacuo. NMR of the red oil showed that the bicyclobutane had all reacted and been converted into cyclohepta[*jk*]-phenanthrene (**20**). The two components were easily separated on an alumina column. The red **20** (568 mg) was recrystallized twice from ligroine/ether and sublimed to give analytically pure material having: mp 107–108 °C; mass spectrum, parent peak at *m/e* 228; NMR (CCl_4) δ 8.00–8.33 (m, 2 H, H-4 and H-5 of phenanthrene ring), 6.67–7.48 (m, 6 H, remaining aromatic), 5.87–6.32 (m, 2 H, vinyl adjacent to aromatic), and 5.18–5.62 (m, 2 H, remaining vinyl). Anal. Calcd for $C_{18}H_{12}$: C, 94.70; H, 5.30. Found: C, 94.58; H, 5.29.

1,10-Phenanthrobicyclo[3.2.0]hepta-2,6-diene (21). Two tubes, one containing 800 mg of a mixture of 80% 1,10-phenanthrotricyclo[4.1.0.0^{2,7}]heptene (**19**) and 20% 4,5-benzocyclohepta[1,2,3-*de*]naphthalene (**18**) in 500 mL of cyclohexane and the other containing 120 mg of the same mixture in 50 mL of cyclohexane, were sealed in vacuo and heated at 150 °C for 8 h. After removing the cyclohexane, the residue was chromatographed on alumina eluting with ligroine and increasing amounts of ether in ligroine. The first component (690 mg) off the column was a mixture of 1,10-phenanthrobicyclo[3.2.0]hepta-2,6-diene (**21**) (70%) and 4,5-benzocyclohepta[1,2,3-*de*]naphthalene (**18**) (30%). The second component (101 mg) was shown by NMR to be cyclohepta[*jk*]phenanthrene (**20**).

Trituration of component 1 with ligroine/ether induced crystallization. Four recrystallizations of this solid from ligroine/ether afforded analytically pure 1,10-phenanthrobicyclo[3.2.0]hepta-2,6-diene (**21**) having: mp 133 °C; mass spectrum, *m/e* 228 (parent peak); NMR (CCl_4) δ 8.17–8.70 (m, 2 H, H-4 and -5 of phenanthrene ring), 7.26–7.93 (m, 6 H, remaining aromatic), 6.30 (s, 2 H, vinyl), and 4.63 (s, 2 H, benzylic). Anal. Calcd for $C_{18}H_{12}$: C, 94.70; H, 5.30. Found: C, 94.61; H, 5.27.

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Registry No.—**17**, 63264-00-6; **18**, 198-73-2; **19**, 63212-63-5; **20**, 199-85-9; **21**, 63241-09-8; 7*H*-benz[*de*]anthracene, 199-94-0; butyllithium, 109-72-8; methylene chloride, 75-09-2.

References and Notes

(1) A preliminary report of this work has appeared R. M. Pagni, M. Burnett, and A. C. Hazell, *Tetrahedron Lett.*, 163 (1977).

(2) (a) University of Tennessee; (b) Aarhus University.

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Oxidative Cyclization of 2-Allylphenols by Palladium(II) Acetate. Changes in Product Distribution

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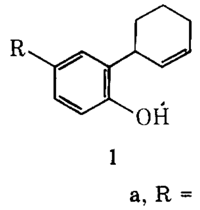
The cyclization of 2-allylphenols **1** having a cyclohexenyl moiety by an equimolar amount of $Pd(OAc)_2$ in air (MeOH, 25 °C) gives a mixture of *cis*-1,2,4a,9b- and *cis*-1,4,4a,9b-tetrahydrodibenzofurans **3** and **4** in nearly equal ratio, together with a small amount of 2,3-butanobenzofuran **5**. The addition of 9 equiv of cyclohexene to this reaction increases the proportion of **3** at the expense of those of **4** and **5**. Further, the distribution of these products changes with changing the substrate concentration. In the presence of excess substrate, the major product is again **3**. In the presence of O_2 (~1 atm), the cyclization proceeds catalytically with respect to Pd(II) without using another cooxidant such as Cu(II), and 0.5 molar equiv of O_2 is constantly consumed for the catalytic production of 1 mol of cyclized products (**3** + **4** + **5**). On the basis of these results, the observed change in product distribution is interpreted in terms of alternation of reacting Pd(II) species involved in the reactions and interaction of intermediate Pd(II) complexes with olefins. In relation to the stereochemistry of the intermediate oxypalladation adduct, the metal-exchange reaction of the trans oxymercurials I and II has been examined by using palladium(II) acetate.

The oxidative cyclization of 2-allylphenols by palladium(II) salts produces 2-substituted benzofurans or chromenes.[1,2] Cyclization of this type can be applicable to a variety of olefins bearing OH,[3] NOH,[4] COOH,[5] or NH_2[6] groups and provides a unique method for synthesizing heterocyclic compounds. The reaction is analogous to the oxidation of olefins by palladium(II),[7–9] and the isomer distribution of cyclized products is sensitively affected by small changes in the reaction conditions, the nature of ligands, and the structure of substrates. Thus, in the present study we have aimed to elucidate some of the fundamental factors controlling the distribution of isomeric benzofurans formed in the cyclization of 2-allylphenols by palladium(II) acetate. For this study, the allylphenols **1** and **2** (R = OMe or H) having cyclohexenyl and cyclopentenyl moieties were chosen since the product distri-



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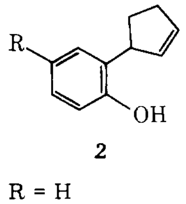

2

a, R = OMe; **b**, R = H