Carbenes and the O–H Bond: Benzoannelated Cycloheptatrienylidenes

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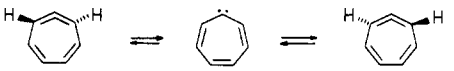
Received July 10, 1987

Various benzo- and dibenzoannelated cycloheptatrienylidenes (cycloheptatetraenes) have been generated in methanol and ethanol by alkoxide-induced dehydrochlorination of chlorocycloheptatrienes and, where applicable, by photolysis of tosylhydrazone sodium salts. 1,2- and 3,4-benzoannelated systems (**19**, **20** and **28**, **29**) give identical mixtures of allyl ethers (**23**, **25**) arising from the benzotropylium ion **24**. Formation of **24** and of vinyl ether **36** compete in the 2,3-benzoannelated case (**34**, **37**). The 2,3:4,5-dibenzoannelated intermediate **40** yields the vinyl ether **41** exclusively. Obviously, ethers arise by two distinct routes: either the hydrogen or the OR group of alcohols may be attached to the dicoordinate carbon of the intermediate(s). The protonation route, leading to tropylium ions, is attributed to cycloheptatrienylidenes. When the carbene is destabilized and the tetraene stabilized, by appropriate benzoannelation, vinyl ethers are formed by addition of ROH to cycloheptatetraenes (in analogy to the behavior of strained cyclic allenes).

The relationship between cycloheptatetraene (**1**) and cycloheptatrienylidene (**2**) has attracted much attention. Theory, spectroscopy, and trapping experiments have all been brought to bear on the question of structure and reactivity of C_7H_6 intermediates.[1] Several computational methods predict **1** to be more stable than singlet **2**.[2] Moreover, at the MNDO level, planar **2** is not an energy minimum but rather a transition state for the interconversion of nonplanar, chiral **1** and its enantiomer **1'**.[2f] MNDO and (uncorrected) ab initio calculations place triplet **2** 11–17 kcal/mol lower than singlet **2**.[2c,f]

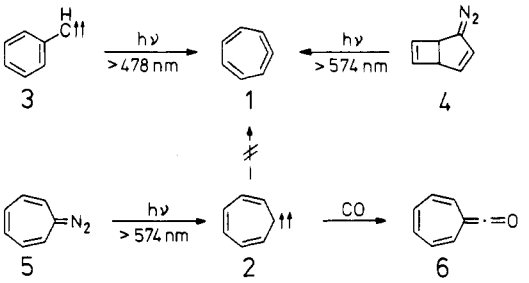


1 **2** **1'**

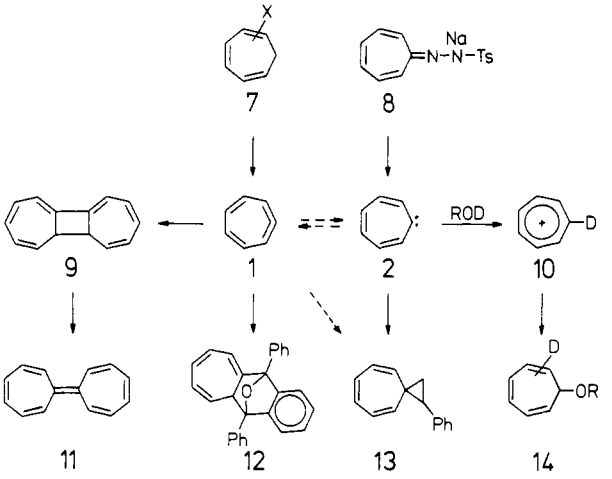
Spectroscopic evidence confirms most of these predictions. Chapman and his co-workers showed that the photoproduct of matrix-isolated phenylcarbene (**3**)[3,4] and of 4-diazobicyclo[3.2.0]hepta-2,6-diene (**4**) was the cyclic allene **1**.[4,5] On the other hand, photolysis of diazocycloheptatriene (**5**) (Ar, 15–21 K) generated triplet cycloheptatrienylidene.[6,7] According to its ESR spectrum, triplet **2** must be planar or nearly so. While triplet **2** readily accepts carbon monoxide to give the analogous ketene (**6**), it does not convert to cycloheptatetraene (**1**) photochemically or thermally[6] (Scheme I).

Experiments designed to trap the singlet species (**1** and/or **2**) are more difficult to interpret. Thermolysis or photolysis of the tosylhydrazone salt of tropone (**8**) in the presence of styrene gives the cyclopropane product **13**.[8] In

Scheme I



Scheme II



the presence of 1,3-diphenylisobenzofuran, thermolysis gives the adduct **12**.[9,10] Dehydrohalogenation of halocycloheptatrienes **7** (X = Cl, Br) with base in the presence of the same two acceptors gives the same products.[11] Definitive evidence for the origin of **12** was adduced by Harris and Jones,[12] taking advantage of the potential chirality of the cyclic allene **1** as opposed to the necessarily achiral nature of the carbene **2**. When the intermediate was generated from a chiral precursor, adduct **12** was obtained optically active. On the other hand, adduct **13** was not optically active. This is admittedly weak evidence for carbene **2** as the progenitor of **13**. The adduct **13** might be formed by an allowed ($\pi^2s + \pi^8s$) cycloaddition of **1**,[13]

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(2) (a) Tyner, R. L.; Jones, W. M.; Öhrn, Y.; Sabin, J. R. *J. Am. Chem. Soc.* **1974**, *96*, 3765. (b) Dewar, M. J. S., Landman, D. *Ibid.* **1977**, *99*, 6179. (c) Radom, L.; Schaefer, H. E., III; Vincent, M. A. *Nouv. J. Chim.* **1980**, *4*, 411. (d) Waali, E. E. *J. Am. Chem. Soc.* **1981**, *103*, 3604. (e) Glidewell, C.; Lloyd, D. *J. Chem. Res. Synop.* **1983**, 178. (f) Kassaee, M. Z.; Nimlos, M. R.; Downie, K. E.; Waali, E. E. *Tetrahedron* **1985**, *41*, 1579.

(3) West, P. R.; Chapman, O. L.; Le Roux, J. . *J. Am. Chem. Soc.* **1982**, *104*, 1779.

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(6) McMahon, R. J.; Chapman, O. L. *J. Am. Chem. Soc.* **1986**, *108*, 1713.

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(9) Saito, K.; Omura, Y.; Mukai, T. *Chem. Lett.* **1980**, 349.

(10) For analogous adducts with anthracenes, cf.: Saito, K.; Ishihara, I. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1095.

(11) Duell, B. L.; Jones, W. M. *J. Org. Chem.* **1978**, *43*, 4901.

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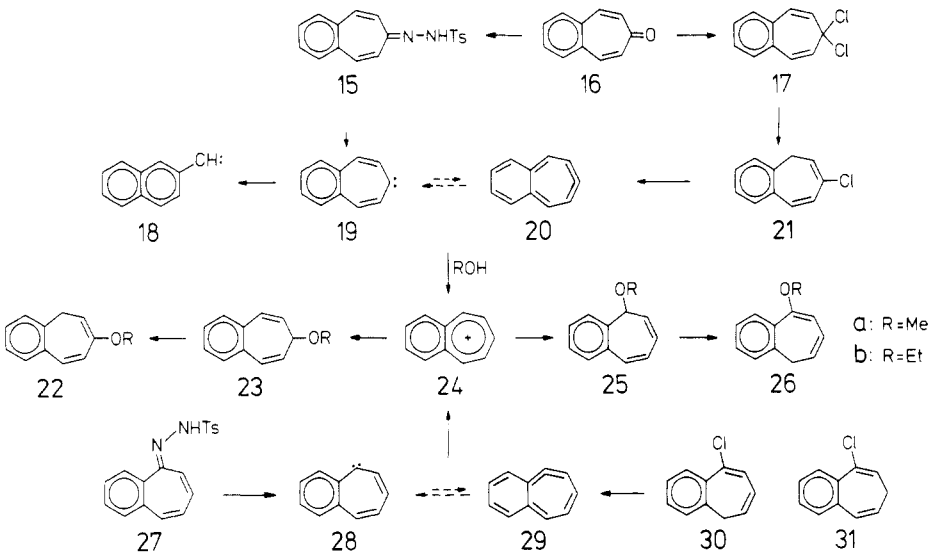
Scheme III



and its lack of optical activity might be fortuitous. Heptafulvalene (**11**), formerly viewed as a dimer of carbene **2**, is now thought to arise from **1**, presumably via **9**. Chapman has reported that warming of matrix-isolated **1** to room temperature does indeed give heptafulvalene.[4] (Scheme II)

Some years ago, we observed that the intermediate generated from either **7** or **8** is trapped by deuteriated alcohols to give 7-cycloheptatrienyl ethers **14** with the deuterium distributed equally between all positions of the seven-membered ring.[14] Intervention of the tropylium ion (**10**) is obvious. Available evidence indicated that cyclic allenes react with alcohols to give vinyl ethers.[15] Therefore, we postulated that the nucleophilic[11,16] carbene **2** is trapped from an unfavorable equilibrium with **1** by protonation.

Recently, Waali has questioned these views.[2f] He found that the HOMO of **1** is similar to that of **2**, having a large contribution of an atomic orbital which lies along the C_2 axis of symmetry. Waali feels that "the nature of the HOMO of **1** is consistent with the observed chemistry"[2f] (i.e., protonation to give **12**), and he concludes "that all of the chemistry once attributed to the singlet state of **2** should instead be explained in terms of the nonplanar allene **1**."[17]

For further insight, we have extended our studies to benzoannelated cycloheptatrienylidenes and cycloheptatetraenes. Inspection of resonance structures as well as INDO calculations[18] indicate that the relative energies of **1** and **2** are strongly affected by benzoannelation. We wish to report that the electronic properties of the intermediates correlate with their reactivity toward alcohols.

Results

Benzoannelation of cycloheptatrienylidene at positions 4,5 or 2,3 narrows the energy gap between the carbene and allene structures, although even here, at the INDO level of computation, the allenes are more stable by ca. 4 kcal/mol.[18] 7*H*-Benzocycloheptenylidene (**19**) has been generated previously from 7*H*-benzocyclohepten-7-one tosylhydrazone (**15**).[19] A remarkable feature of **19** is its facile carbene–carbene rearrangement in solution.[19,20] When the sodium salt of **15** was thermolyzed or photolyzed in benzene or cyclohexane, the identified products were all derived from 2-naphthylcarbene (**18**).[19] The carbene–carbene rearrangement was completely quenched when we photolyzed **15** in ROH–RONa (R = Me, Et). 2-Naphthyl methyl ethers were seen in trace amounts, if at all. The major products were 7-alkoxy-7*H*-benzocycloheptenes **23** and 5-alkoxy-5*H*-benzocycloheptenes **25** in an approximate 1:1 ratio (Table I).

7-Chloro-5*H*-benzocycloheptene (**21**) is readily accessible from the ketone **16** (oxalyl chloride, followed by $LiAlH_4$ reduction).[21] On treatment of **21** with ROH–RONa, we obtained **23** and **25** as well as the vinyl ethers **22** and **26**.

Table I. Products Obtained from Benzocycloheptenylidenes 19 and 28 in ROH–RONa

precursor; conditions[a]	products, % 22	23	25	26
15; 0.04 M EtONa, *hν*, rt	0.5	53.0	39.6	
21; 2.5 M EtONa, 60 °C,				
14 h		12.8	11.9	
20 h	2.1	15.5	16.5	
38 h	7.9	20.1	26.6	
64 h	18.2	20.9	37.3	0.3
96 h	28.7	10.5	45.1	0.6
130 h	37.8	7.6	49.8	1.6
15; 0.03 M MeONa, *hν*, rt	0.9	48.3	46.5	
21; 3.5 M MeONa, 60 °C, 5 day	48.8	0.7	40.6	4.3
27; 0.16 M EtONa, *hν*, rt		23.8	22.7	
30, **31**; 2.5 M EtONa, 60 °C,				
17 h	9.1	18.6	31.2	
24 h	16.1	17.9	32.1	
27; 0.03 M MeONa, *hν*, rt		36.7	51.7	
30, **31**; 3.5 M MeONa, 60 °C,				
22 h	3.0	19.6	31.1	

[a] rt = room temperature.

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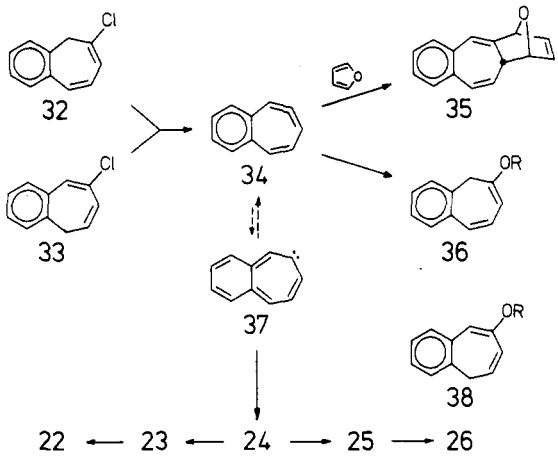
(19) Jones, W. M.; Joines, R. C.; Myers, J. A.; Mitsuhashi, T.; Krajca, K. E.; Waali, E. E.; Davis, T. L.; Turner, A. B. *J. Am. Chem. Soc.* **1973**, *95*, 826.
(20) Jones, W. M. *Acc. Chem. Res.* **1977**, *10*, 353.
(21) Föhlisch, B.; Fischer, C.; Widman, E.; Wolf, E. *Tetrahedron* **1978**, *34*, 533.

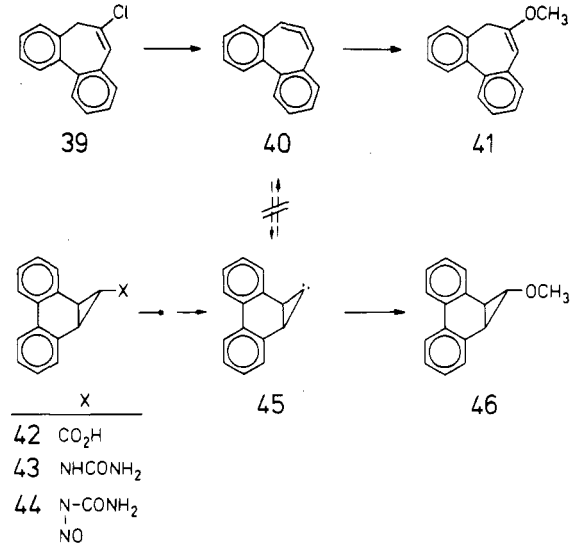
Table II. Products Obtained from Chlorobenzocycloheptenes 32 and 33 with ROH–RONa

conditions	products, %						
	32	**33**	**22**	**23**	**25**	**26**	**36**
2.5 M EtONa, 60 °C,							
18 h	34.6	14.7	1.4	6.2	5.9		22.3
40 h	9.7	4.1	4.7	5.3	11.2	0.1	46.7
100 h	0.2		11.7	3.3	12.1	0.6	61.9
3.5 M MeONa, 60 °C,							
67 h	12.3	4.8	5.3	12.8	16.5	2.1	33.3

Scheme IV



Scheme V



The reluctant dehydrochlorination of **21**[22] requires high concentrations of base and elevated temperatures, which lead to base-catalyzed isomerization of **23** and **25**. The time-dependent product distributions (Table I) indicate that **22** and **26** do not arise directly from **21**. On the other hand, the **22** + **23**:**25** + **26** ratios are nearly independent of conversion, ranging from 1.1 to 0.9. Ether **23** is more readily isomerized than **25** (Scheme III).

Benzotropylium tetrafluoroborate (**24**·BF_4) has been reported to react with aqueous sodium carbonate[23] and with sodium methoxide–methanol[24] to give 1:1 mixtures of **23** and **25** (R = H, Me). Thus our results are most reasonably attributed to the intervention of **24**. For further support, we have generated 5*H*-benzocycloheptenylidene (**28**), which should also be protonated to give **24**. Neutral conditions were mandatory for the preparation of the tosylhydrazone **27** from 5*H*-benzocyclohept-5-one.[25] Treatment of the ketone, as reported for **16**, yielded a mixture of 5-chlorobenzocycloheptenes (**30**:**31** = 42:58). The isomers interconverted under the conditions of dehydrochlorination. Both **27** and **30**, **31** gave product ratios which were similar to those obtained from **15** and **21**. We hesitate to comment on small variations since acid-catalyzed and thermal conversion of **23** to **25** is known to occur with ease[24,26] and causes major analytical problems.

2,3-Benzoannelation of cycloheptatrienylidene destabilizes the carbene **37** and favors the tetraene **34**.[18] No diazo precursor to **37** is available, but dehydrohalogenation (potassium *tert*-butoxide–THF) of the chlorides **32**, **33** was used to generate the tetraene **34**.[13a] In the presence of furan, the [4 + 2] adduct **35** (21%) was obtained while styrene afforded a [2 + 2] adduct (35%)[13a] (Scheme IV). When we treated a mixture of **32** and **33** (67:33) with ROH–RONa, the isomeric chlorides reacted at similar rates. The ethers **22**, **23**, **25**, and **26** derived from benzotropylium ion **25** accounted for 35% (EtOH) to 50% (MeOH) of the product mixture; as before, the ratio **22** + **23**:**25** + **26** was close to unity (Table II). The major products, however, were 6-alkoxy-5*H*-benzocycloheptenes (**36**). Spectral evidence suggested the presence of minor quantities of 8-alkoxy-5*H*-benzocycloheptenes (**38**), but these products were not isolated in a pure state and apparently isomerized to **36** on prolonged treatment with base. Structures were assigned to **36** and (tentatively) to **38** on the basis of their NMR spectra which conform with those of the analogous chlorides **32** and **33**, respectively. Thus, for the first time, we observe the vinyl ethers expected from the addition of alcohols to strained cyclic allenes,[15] although the allyl ethers derived from the benzotropylium ion **24** are formed competitively.

In order to enlarge the energy gap between cycloheptatrienylidene and cycloheptatetraene even further, a second benzene ring was annelated. The dehydrochlorination of 6-chloro-5*H*-dibenzo[*a*,*c*]cycloheptene (**39**) has been mentioned in a review,[27] but no details have been published. In aprotic media, a dimer of **40** was obtained. A platinum complex of **40** was prepared from the bromo analogue of **39**.[28] With sodium methoxide (3.7 M) in methanol at 60 °C, we achieved 94% conversion of **39** within 24 h, the only (>99%) product being **41**. Experiments run in MeOD revealed rapid H–D exchange of recovered **39**, indicative of an E1cB mechanism. We have also explored whether the tetraene **40** might be accessible by way of a cyclopropylidene–allene rearrangement.[29] However, base-induced cleavage of the nitrosourea **44** afforded exclusively the cyclopropyl ether **46**, with no trace of **41**. Although cationic and carbenic pathways are not readily distinguished in the present case, there is ample

(22) The analogous bromide failed to react with potassium *tert*-butoxide under a variety of conditions.[13b]
(25) Buchanan, G. L.; Lockhart, D. R. *J. Chem. Soc.* **1959**, 3586.
(26) Bertelli, D. J.; Rossiter, W. J. *Tertahedron* **1968**, *24*, 609.
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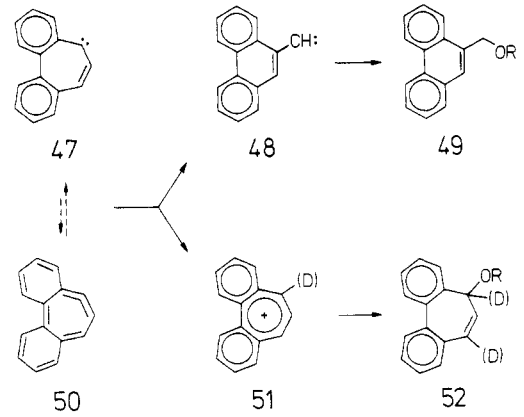
(28) Winchester, W. R.; Jones, W. M. *Organometallics* **1985**, *4*, 2228.
(29) For a review, see ref 1a, Section VI.

Scheme VI



precedent that cyclopropyl ethers arise from cyclopropylidenes under analogous conditions.[30] Obviously, the barrier separating **40** and **45** is too high to be passed in either direction, at least in the presence of methanol as a reactant (Scheme V).

Discussion

All reactions used in this study have previously been shown to generate cycloheptatetraenes, as confirmed by the characterization of cycloadducts or dimers. However, in the presence of alcohols, ethers arise by two distinct routes: either the hydrogen or the alkoxy group of ROH may be attached to the dicoordinate carbon of the intermediate(s). For the carbene–allene pairs **19**, **20** and **28**, **29** (Scheme III), this distinction is partly clouded by formal O–H insertion (**19** → **23**, **28** → **25**) and by base-induced isomerization of allyl ethers to vinyl ethers. However, the close agreement of isomer ratios (**22** + **23**:**25** + **26**) observed with both pairs of intermediates virtually excludes initial bonding of OR to the dicoordinate carbon. The two pathways outlined above compete in the case of **34**, **37** (Scheme IV) to give products which are not interconvertible by base-induced isomerization. The dehydrochlorination of **39** (Scheme V) yields a single vinyl ether (**41**) which is not accessible from the dibenzotropylium ion. Preliminary studies of the isomeric carbene–allene pair **47**, **50** (generated from the analogous tosylhydrazone) indicate that the rapid rearrangement to 9-phenanthrylcarbene (**48**)[31] is not quenched by methanol, the only product being **49** (R = CH_3).[32] The more acidic trifluoroethanol, on the other hand, afforded a mixture of **49** and **52** (R = CH_2CF_3); with CF_3CH_2OD, the deuterium was distributed equally between positions 5 and 7 of **52** (Scheme VI). Thus, once generated, the dibenzotropylium ion **51** behaves as expected. Obviously, **51** does not intervene in the dehydrochlorination of **39**.

As we have seen, the reactivity of benzoannelated cycloheptatetraenes (cycloheptatrienylidenes) ranges from exclusive protonation (**19**, **20** and **28**, **29**) to exclusive attack at oxygen (**40**), the pair **34**, **37** assuming an intermediate position. The reactions of **40** conform with those of nonconjugated cyclic allenes.[15] These observations are difficult to rationalize if cycloheptatetraenes are the only intermediates. Why should the reactivity of the dicoordinate carbon change from nucleophilic to electrophilic, depending on the site and number of annelated benzene rings? Alternatively, we may invoke two intermediates whose relative contributions depend on benzoannelation while their philicities do not. In fact, the product patterns correlate nicely with the stabilizing (destabilizing) effect of benzoannelation on cycloheptatetraene (cycloheptatrienylidene). Our only concern is the quantitation of these relative energies by MNDO/INDO computations.[2,18] Thus, the tetraene **34** is placed 79 kcal/mol below the singlet carbene **37** although both species appear to contribute about equally to the reaction with alcohols. Even an extreme difference in reaction rates could not compensate for such a huge difference in energy. More sophisticated theory may be helpful but will not eliminate the problem of solvation. The energy of cycloheptatrienylidenes is minimized by delocalization, as opposed to the twisting of cycloheptatetraenes. Therefore, preferential stabilization of cycloheptatrienylidenes by polar solvents is a reasonable assumption.

Conclusion

Our experience with benzoannelated systems leads us to reiterate our previous conclusion that tropylium ions arise by protonation of cycloheptatrienylidenes, rather than cycloheptatetraenes. Destabilization of the carbene, with concomitant stabilization of the tetraene, by appropriate benzoannelation restores the "normal" reactivity of strained cyclic allenes, i.e., the formation of vinyl ethers.

Experimental Section

General Methods. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. ^1H NMR spectra were obtained at 80 (Bruker WP 80) and 400 MHz (Bruker AM 400). Chemical shifts in $CDCl_3$ are reported in δ values (ppm) relative to tetramethylsilane as an internal standard, unless otherwise indicated. Gas chromatography (GC) was performed by the use of a Siemens Sichromat equipped with glass capillary columns. Varian Aerograph 920 instruments equipped with packed glass columns were used for preparative gas chromatography (PGC). High-pressure liquid chromatography (HPLC) was carried out with LDC (Milton Roy) chromatographs and refractrometric detection.

Starting Materials. 7*H*-Benzocyclohepten-7-one tosylhydrazone (**15**),[19] 7-chloro-5*H*-benzocycloheptene (**21**),[21] and 6-chloro- and 8-chloro-5*H*-benzo-cycloheptene (**32**, **33**)[13a] were prepared by the reported methods. 5*H*-Benzocyclohepten-5-one[25] (0.5 g, 3.2 mmol), dissolved in methanol (1.5 mL), was added at 60 °C to a solution of tosylhydrazide (0.59 g, 3.2 mmol) in methanol (5 mL). The reaction mixture was stirred at 60 °C for 45 min and then cooled to −15 °C for 2 weeks. Yellow crystals (0.52 g, 50%) of 5*H*-benzocyclohepten-5-one tosylhydrazone (**27**) were obtained by filtration and recrystallized from methanol, mp 134–135 °C: ^1H NMR δ 2.36 (s, 3 H), 6.1–6.5 (m, 3 H), 3.87 (br d, J = 11 Hz, 1 H), 7.15–7.65 (m, 5 H), 7.7–8.0 (m, 3 H). Anal. Calcd for $C_{18}H_{16}N_2O_2S$: C, 66.65; H, 4.97; N, 8.63. Found: C, 66,56; H, 5.05; N, 8.78.

To a stirred solution of 5*H*-benzocyclohepten-5-one[25] (1.0 g, 6.4 mmol) in dry methylene chloride (5 mL) at 0 °C was added dropwise oxalyl chloride (7.4 g, 58 mmol). After 2 h at room temperature solvent and excess oxalyl chloride were removed in vacuo. The residue was dissolved in dry ether (20 mL) and added to a suspension of lithium aluminum hydride (0.55 g, 13 mmol) in ether (10 mL). The mixture was heated at reflux for 1 h. After workup, the crude product (0.79 g, 70%, 89% pure) was purified by PGC (0.5 m silicone DC 200, 145 °C) to give a 42:58 mixture of 9-chloro-5*H*-benzocycloheptene (**30**) and 5-chloro-7*H*-benzocycloheptene (**31**): ^1H NMR δ 2.35 (td, J = 7 and 1 Hz, 7-H of **31**), 3.07 (d, J = 6 Hz, 5-H of **30**), 5.7–6.3 (m, 4 H), 6.5–6.9 m (2 H), 7.05–7.45 (m, 6 H), 7.75–8.0 m (2 H).

1,1-Dichloro-1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthrene[31,33] (3.1 g, 11.9 mmol) was heated in a sealed tube at 160 °C for 2 h

(30) Kirmse, W.; Hellwig, G. *Chem. Ber.* **1982**, *115*, 2744. Kirmse, W.; Rode, J.; Rode, K. *Chem. Ber.* **1986**, *119*, 3672.
(31) Coburn, T. T.; Jones, W. M. *J. Am. Chem. Soc.* **1974**, *96*, 5218.
(32) Gumbiowski, R., unpublished results. A full account, including derivatives of **47** and **48**, is in preparation.
(33) Müller, B.; Weyerstahl, P. *Liebigs Ann. Chem.* **1975**, 201.

to give 5,6-dichloro-5*H*-dibenzo[*a*,*c*]cycloheptene.[31,34] The crude product was dissolved in tetrahydrofuran (10 mL), added to lithium aluminum hydride (0.76 g, 18 mmol) in THF (30 mL), and heated at reflux for 2 h. Workup yielded 2.2 g (82%) of 6-chloro-5*H*-dibenzo[*a*,*c*]cycloheptene (**39**) (94% pure). Purification to 99.4% was achieved by HPLC (22-cm RP 18–10 μm; acetonitrile–H_2O, 7:3): ^1H NMR δ 3.44 (s, 2 H), 6.73 (s, 1 H), 7.2–7.8 m (8 H). Anal. Calcd for $C_{15}H_{11}Cl$: C, 79.47; H, 4.89. Found: C, 79.31; H, 5.10.

Solvolysis of Chlorobenzocycloheptenes. Product distributions were determined by GC (5-m Carbowax + KOH, 11.5-m polypropylene glycol + KOH, 51-m silicon oil OV 101) from runs with 0.1–0.5 g of the chloride in 10–15 mL of 2.5 M EtONa or 3.5 M MeONa (N_2, 60 °C, cf. Tables I and II). Reference samples were isolated from preparative runs or prepared independently (see below). The ratio of the major products (**23**, **25**) obtained from **21**, **30**, and **31** was confirmed by ^1H NMR.

7-Chloro-5*H*-benzocycloheptene (**21**) (1.0 g, 43.5 mmol) was added to 3.7 M EtONa (14 mL) and heated for 4 days at 80 °C. The products were partitioned between water and ether. The ether extracts were dried over K_2CO_3 and evaporated in vacuo. Short-path distillation of the residue afforded 0.40 g (38%) of volatile material from which **22b**, **25b**, and **26b** were isolated by PGC (0.5-m Carbowax + KOH, 130 °C). 7-Ethoxy-5*H*-benzocycloheptene (**22b**): ^1H NMR δ 1.32 (t, J = 6.5 Hz, 3 H), 3.04 (d, J = 7 Hz, 2 H), 3.71 (q, J = 6.5 Hz, 2 H), 4.90 (td, J = 7 and 2 Hz, 1 H), 6.39 (dd, J = 11.5 and 2 Hz, 1 H), 7.09 (d, J = 11.5 Hz, 1 H), 7.1–7.5 (m, 4 H). Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.62; H, 7.45. 5-Ethoxy-5*H*-benzocycloheptene (**25b**): ^1H NMR δ 1.31 (t, J = 7 Hz, 3 H), 3.61 (q, J = 7 Hz, 2 H), 4.15 (d, J = 4 Hz, 1 H), 5.80 (dd, J = 10 and 4 Hz, 1 H), 6.08 (m, 1 H), 6.55 (dd, J = 11.5 and 5.5 Hz, 1 H), 7.17 (d, J = 11.5 Hz, 1 H), 7.25–7.6 (m, 4 H). Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.58; H, 7.65. 9-Ethoxy-5*H*-benzocycloheptene (**26b**): ^1H NMR δ 1.49 (t, J = 6 Hz, 3 H), 3.06 (d, J = 6.5 Hz, 2 H), 4.17 (q, J = 6 Hz, 2 H), 5.67 (dt, J = 10 and 6.5 Hz, 1 H), 5.73 (d, J = 6 Hz, 1 H), 6.08 (dd, J = 10 and 6 Hz, 1 H), 7.15–7.45 (m, 3 H), 7.78 (m, 1 H). Anal. Calcd for $C_{13}H_{14}O$: C, 83,83; H, 7.58. Found: C, 83.70; H, 7.72.

From an analogous solvolysis of **32**, **33** (2.5 M EtONa, 60 °C, 5.5 days), 6-ethoxy-5*H*-benzocycloheptene (**36b**) was isolated by HPLC (25-cm Lichrosorb-Merck Si 60, 7 μm; hexane–ether, 95:5): ^1H NMR δ 1.33 (t, J = 7 Hz, 3 H), 3.22 (s, 2 H), 3.81 (q, J = 7 Hz, 2 H), 5.16 (d, J = 6 Hz, 1 H), 6.41 (dd, J = 11 and 6 Hz, 1 H), 6.83 (d, J = 11 Hz, 1 H), 7.1–7.4 (m, 4 H). Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.55; H, 7.49. When **32**, **33** was treated with 3.6 M NaOMe (60 °C, 67 h), HPLC yielded a product fraction which contained predominantly 6-methoxy-5*H*-benzocycloheptene (**36a**); ^1H NMR δ 3.26 (s, 2 H), 3.62 (s, 3 H), 5.21 (d, J = 6 Hz, 1 H), 6.44 (dd, J = 11.5 and 6 Hz, 1 H), 6.88 (d, J = 11.5 Hz, 1 H), 7.1–7.4 (m, 4 H), but appeared to be comtaminated with some 8-methoxy-5*H*-benzocycloheptene (**38a**): ^1H NMR δ 2.69 (d, J = 6.5 Hz, 2 H), 3.73 (s, 3 H), (the signals of the olefinic and aromatic protons overlapped with those of **36a**). When this sample was heated for 24 h at 120 °C, **36a** increased at the expense of **38a**.

6-Chloro-5*H*-dibenzo[*a*,*c*]cycloheptene (**39**) (0.11 g, 0.5 mmol) and 3.5 M NaOMe (14 mL) were heated for 24 h at 60 °C. GC indicated 6.1% of unreacted **39** and 93.4% of 6-methoxy-5*H*-dibenzo[*a*,*c*]cycloheptene (**41**), which was purified by HPLC (22-cm RP 18-10 μm; acetonitrile–H_2O, 4:1): ^1H NMR δ 3.22 (s, 2 H), 3.68 (s, 3 H), 5.65 (s, 1 H), 7.1–7.8 (m, 8 H). Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.25; H, 6.30. An analogous run in MeOD (3 h) gave 66% of recovered **39** and 34% of **41**. The distribution of deuterium (^2H NMR) between positions 5 and 7 was 87:13 for **39** and 93:7 for **41**. The deuterium content of **39** was d_0 16%, d_1 50%, and d_2 34% (MS, 16 eV), while **41** gave no reliable MS data.

Photolysis of Tosylhydrazones. Dilute solutions of the tosylhydrazones (**15** or **27**) (0.21 g, 0.65 mmol) in 0.03–0.13 M NaOEt or NaOMe (50 mL, see Table I) were purged with nitrogen and irradiated for 23–26 h in a Rayonet-Photochemical Reactor (The Southern New England Ultraviolet Company). RPR 3500 A lamps (14 × 24 W) were used in combination with a bismuth chloride filter (4.5 cm of 1.2 M $BiCl_3$ in 14.8% aqueous hydrochloride acid, cutoff at 355 nm) to prevent photoisomerization of the products. The product distribution was estimated by GC and ^1H NMR, as described above.

Reference Samples. 7-Methoxy-5*H*-benzocycloheptene (**22a**),[24] 7-methoxy-7*H*-benzocycloheptene (**23a**),[26] and 5-methoxy-5*H*-benzocycloheptene (**25a**)[24] were prepared as reported. Reduction of **16** with lithium aluminum hydride, followed by ethylation (NaH, EtI, DMF; procedure of ref 26) gave 7-ethoxy-7*H*-benzocycloheptene (**23b**): ^1H NMR δ 1.15 (t, J = 7 Hz, 3 H), 3.43 (q, J = 7 Hz, 2 H), 3.77 (m, 1 H), 5.68 (dd, J = 10 and 4 Hz, 2 H), 6.35 (dd, J = 10 and 2 Hz, 2 H), 6.8–7.4 (m, 4 H). Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.75; H, 7.68. Compound **25a** (40 mg, 0.23 mmol) and 2.5 M NaOMe (0.6 mL) were heated at 100 °C for 10 days in a sealed ampule to give 9-methoxy-5*H*-benzocycloheptene (**26a**): ^1H NMR δ 3.06 (d, J = 6.5 Hz, 2 H), 3.86 (s, 3 H), 5.50–5.85 (m, 2 H), 6.11 (dd, J = 9 and 6 Hz, 1 H), 7.10–7.85 (m, 4 H).

***N*-Nitroso-*N*-(1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthr-1-yl)urea (44).** The carboxylic acid **42**[35] (5.0 g, 21.2 mmol) was subjected to Curtius degradation, following the procedure of Weinstock,[36] to give the urea **43** (3.05 g, 58%), mp 210–212 °C (from ethyl acetate). To a solution of **43** (0.4 g, 1.6 mmol) in acetic acid (5 mL) was slowly added sodium nitrite (0.12 g, 1.7 mmol). The mixture was stirred for 2 h at room temperature and then evaporated to dryness in vacuo. The residue was partitioned between water and methylene chloride. The crude product obtained by evaporation of the organic phase was recrystallized from methylene chloride–pentane to give 0.20 g (45%) of **44**, mp 189–192 °C (dec).

To 2 M $NaOCH_3$ (13 mL) was added with stirring the nitrosourea **44** (0.10 g, 0.36 mmol). After being stirred for 1 h at room temperature, the mixture was partitioned between water and ether. The major product (93% by GC), 1-methoxy-1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthrene (**46**), was purified by HPLC (22-cm RP 18–10 μm; acetonitrile–H_2O, 7:3): ^1H NMR δ 2.58 (t, J = 2.2 Hz, 1 H), 2.62 (d, J = 2.2 Hz, 2 H), 3.35 (s, 3 H), 7.15 (m, 4 H) 7.3 (m, 2 H), 7.8 (m, 2 H). Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.33; H, 6.40.

Registry No. **15**, 40154-60-7; **16**, 4443-91-8; **21**, 67730-14-7; **22a**, 65660-34-6; **22b**, 112270-49-2; **23a**, 17573-42-1; **23b**, 112270-50-5; **25a**, 17573-41-0; **25b**, 112270-51-6; **26a**, 112270-48-1; **26b**, 112296-49-8; **27**, 112270-52-7; **30**, 112270-53-8; **31**, 112270-54-9; **32**, 55665-43-5; **33**, 55831-13-5; **36a**, 112270-55-0; **36b**, 112270-47-0; **38a**, 112270-56-1; **39**, 112270-57-2; **41**, 112270-58-3; **42**, 891-58-7; **43**, 112270-59-4; **44**, 112270-60-7; **46**, 112270-61-8; 5*H*-benzocyclohepten-5-one, 485-46-1; tosylhydrazide, 1576-35-8; 1,1-dichloro-1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthrene, 37608-29-0; 5,6-dichloro-5*H*-dibenzo[*a*,*c*]cycloheptene, 100083-00-9.

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