Registry No. 1, 6651-43-0; 2, 76430-25-6; 3, 76430-26-7; 4, 76430-27-8; 5, 76430-28-9; 6, 76446-94-1; 7, 76430-29-0; 8, 63559-16-0; 9, 76430-30-3; 10, 76430-31-4; 11, 76430-32-5; 12, 76430-33-6; 13, 76430-34-7; 14 (isomer 1), 76430-35-8; 14 (isomer 2), 76496-33-8; 15, 76430-36-9; dichloroacetyl chloride, 79-36-7; methanol, 67-56-1; 2-chloro-2-methyl-3-[2-(trimethylsiloxy)ethenyl]cyclobutanone, 76430-37-0; 2-chloropropanoyl chloride, 7623-09-8; 2-chloro-2-methyl-3-(2,2-dimethoxyethyl)cyclobutanone, 76430-38-1; 2-chloro-2,3-dimethyl-3-(2-oxo-4-methylcyclohexyl)cyclobutanone, 76430-39-2; 7-chloro-7-methyl-1-(trimethylsiloxy)bicyclo[3.2.0]hept-2-en-6-one (isomer 1), 76430-40-5; 7-chloro-7-methyl-1-(trimethylsiloxy)bicyclo[3.2.0]hept-2-en-6-one (isomer 2), 76496-34-9; 7-chloro-1-hydroxy-7-methylbicyclo[3.2.0]hept-2-en-6-one (isomer 1), 76430-41-6; 7-chloro-1-hydroxy-7-methylbicyclo[3.2.0]hept-2-en-6-one (isomer 2), 76496-35-0; 2-cyclohexenone silyl enol ether, 54781-19-0; 6-(2,2-dichloroacetyl)cyclohex-2-enone, 76430-42-7.

Generation of Bicyclo[4.1.0]heptatrienes

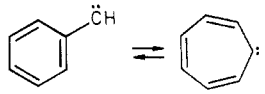
W. E. Billups,* Larry E. Reed, Edward W. Casserly, and L. P. Lin

Department of Chemistry, Rice University, Houston, Texas 77001

Received February 25, 1980

Derivatives of bicyclo[4.1.0]heptatriene have been generated in solution by the base-induced dehydrochlorination of *gem*-dichlorocyclopropanes. Reaction of 7,7-dichlorodibenzo[*a*,*c*]bicyclo[4.1.0]heptane with potassium *tert*-butoxide in tetrahydrofuran at 0 °C gives mainly products derived from solvent incorporation by carbene insertion. Evidence that the carbene results from rearrangement of the bicycloheptatriene derives from the successful interception of the bicycloheptatriene with nucleophile (MeS^-). *endo*-7-Chlorodibenzo[*a*,*c*]bicyclo[4.1.0]heptane failed to react with potassium *tert*-butoxide in tetrahydrofuran. Generation of benzobicyclo[4.1.0]heptatrienes was also accomplished via the base-induced dehydrochlorination of *gem*-dichlorocyclopropanes. 1-Methylbenzobicyclo[4.1.0]heptatriene gives products derived from multiple carbene–carbene rearrangements. In contrast, nonannelated methylbicycloheptatrienes generated by the dehydrochlorination route give only carbene-derived products resulting from the initially produced bicycloheptatriene.

The interconversion of phenyl carbene and its derivatives with bicycloheptatrienylidenes (eq 1) was first pos-



(1)

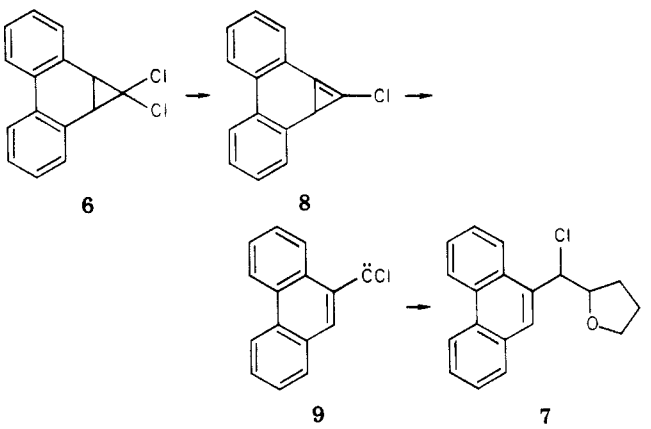
tulated by Shechter and Vander Stouw[1,2] to account for the formation of styrene in the gas-phase pyrolysis of *o*-tolylidiazomethane. On the basis of analogy with the well-known interconversion of vinylcarbene and cyclopropene,[2b] these workers suggested that the rearrangement depicted in eq 1 probably proceeds via bicyclo[4.1.0]heptatriene (1) as a reactive intermediate. Although other

1

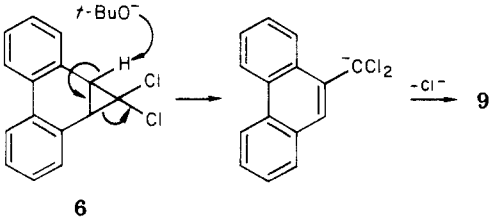
intermediates have been considered,[2-12] only 1 seems to be consistent with all of the experimental observations.

The discrete existence of bicyclo[4.1.0]heptatrienes 2 and 3 as intermediates in solution was established by their

Scheme I



Scheme II



(1) (a) G. G. Vander Stouw, *Diss. Abstr.*, **25**, 6974 (1965); (b) G. G. Vander Stouw, A. R. Kraska, and H. Shechter, *J. Am. Chem. Soc.*, **94**, 1655 (1972).

(2) (a) C. Wentrup, *Top. Curr. Chem.*, **62**, 173 (1976); (b) W. M. Jones and U. H. Brinker in "Pericyclic Reactions", A. P. Marchand and R. E. Lehr, Eds., Academic Press, New York, 1977, p 109; (c) W. M. Jones, *Acc. Chem. Res.*, **10**, 353 (1977), and numerous references therein.

(3) R. C. Joines, A. B. Turner, and W. M. Jones, *J. Am. Chem. Soc.*, **91**, 7754 (1969).

(4) P. Schissel, M. E. Kent, D. J. McAdoo, and E. Hedaya, *J. Am. Chem. Soc.*, **92**, 2147 (1970).

(5) C. Wentrup and K. Wilczek, *Helv. Chim. Acta*, **53**, 1459 (1970).

(6) J. A. Myers, R. C. Joines, and W. M. Jones, *J. Am. Chem. Soc.*, **92**, 4740 (1970).

(7) (a) T. Barton, J. Kilgour, R. Gallucci, A. Rothschild, J. Slertsky, A. Wolf, and M. T. Jones, Jr., *J. Am. Chem. Soc.*, **97**, 657 (1975); (b) W. Ando, A. Sekiguchi, A. Rothschild, R. Gallucci, M. T. Jones, T. Barton, and J. Kilgour, *ibid.*, **99**, 6995 (1977).

(8) W. J. Baron, M. T. Jones, and P. P. Gaspar, *J. Am. Chem. Soc.*, **92**, 4739 (1970).

(9) E. Hedaya and M. E. Kent, *J. Am. Chem. Soc.*, **93**, 3283 (1971).

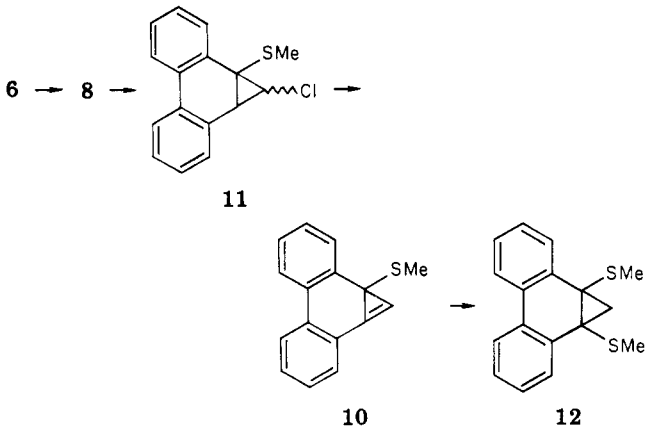
(10) W. M. Jones, R. C. Joines, J. A. Myers, T. Mitsuhashi, K. E. Krajca, E. E. Walli, T. L. Davis, and A. B. Turner, *J. Am. Chem. Soc.*, **95**, 826 (1973).

(11) T. T. Coburn and W. M. Jones, *J. Am. Chem. Soc.*, **96**, 5218 (1974).

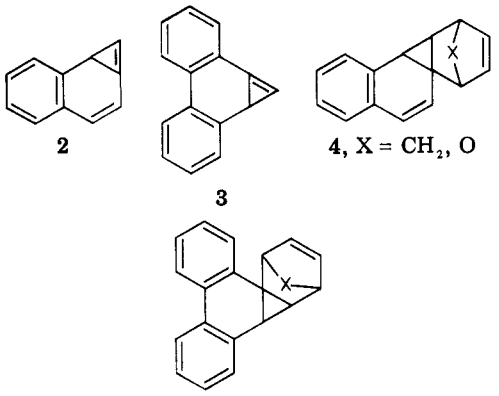
(12) E. E. Waali, J. M. Lewis, D. E. Lee, E. W. Allen, III, and A. K. Chappell, *J. Org. Chem.*, **42**, 3460 (1977).

0022-3263/81/1946-1326$01.25/0

Scheme III



interception with furan and cyclopentadiene to give **4** and **5**, respectively.[11]



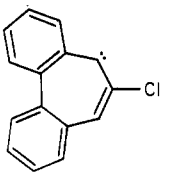
Simultaneously, work in our laboratory demonstrated that the dehydrochlorination of suitably substituted halocyclopropanes provides a direct entry into the bicyclo[4.1.0]heptatriene ring system.[13,14] The dehydrohalogenation route is attractive since the bicycloheptatriene can be generated at or below room temperature in solution and in the absence of radiation, which assures that excited states are not involved. In addition, the method promises to provide simple nonannelated derivatives which, heretofore, have not been generated in solution.

The adduct of dichlorocarbene and phenanthrene, 7,7-dichlorodibenzo[*a*,*c*]bicyclo[4.1.0]heptane (**6**)[15] was chosen for our initial studies. Treatment of **6** with a suspension of potassium *tert*-butoxide (2 equiv) in tetrahydrofuran at 0 °C gives a viscous oil identified as **7** (mixture of diastereomers).

The formation of **7** can be rationalized by invoking bicycloheptatriene **8** as a reactive intermediate, which rearranges to carbene **9** followed by insertion into the solvent (Scheme I). In principle, however, the carbene could be derived directly from **6** as shown in Scheme II. The formation of solvent-insertion product can, of course, be taken as evidence for the carbene.

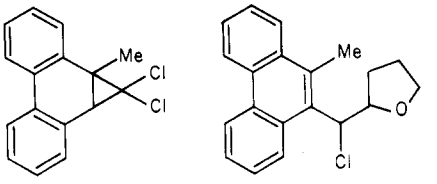
Fortunately, nucleophilic trapping experiments such as those employed by Shields and Gardner[16] provide a method to trap **8**. The result of an experiment in which methyl mercaptide is used as the trapping reagent is illustrated in Scheme III. It is interesting that in addition to the expected bicycloheptatriene **8**, one must also invoke **10**, which arises from elimination of HCl from the intermediate adduct **11**. Both bicycloheptatrienes must be sufficiently long lived to experience addition of the nucleophile. On the other hand, bicycloheptatriene **8**, in the absence of a trapping reagent, rearranges at 0 °C to give the arylcarbene, a species normally considered to be a high-energy one. The strain in **8** and the increase in resonance energy upon ring opening are probably sufficient to place the carbene at lower energy than the cyclopropene. These observations are consistent with other examples of low-temperature arylcarbene → bicycloheptatriene rearrangements.[11]

We did not observe insertion products arising from cycloheptatrienylidene **13**, but this is not surprising since the bicycloheptatriene → cycloheptatrienylidene rearrangement normally occurs at a much higher temperature (250–600 °C).[2b]



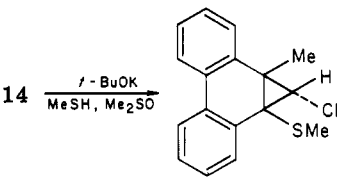
13

Experiments with **14**, prepared from 9-methylphenanthrene and dichlorocarbene, afforded none of the expected solvent insertion product **15** but only an amorphous solid which failed to yield characterizable products despite extensive efforts with column and thin-layer chromatography.



14 15

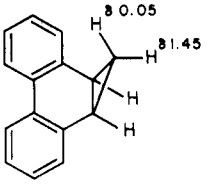
Evidence for the expected bicycloheptatriene is found, however, in the reaction of **14** with potassium *tert*-butoxide in the presence of methyl mercaptide which yields adduct **16** in 92% yield, eq 2. Although two stereoisomers of **16**



(2)

16

are possible, a single set of three signals at δ 1.87 (3 H), 2.04 (3 H), and 3.52 (1 H) in the nonaromatic region of the ^{1}H NMR spectrum suggested that only one isomer was produced. Using **17** as a model, one can reasonably assume



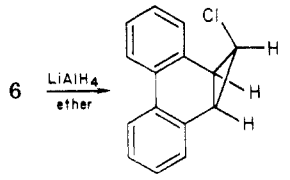
17

that the single cyclopropyl hydrogen resides in the exo

(13) W. E. Billups, L. P. Lin, and W. Y. Chow, *J. Am. Chem. Soc.*, **96**, 4026 (1974).
(14) W. E. Billups and L. E. Reed, *Tetrahedron Lett.*, 2239 (1977).
(15) G. C. Joshi, N. Singh, and L. M. Pande, *Synthesis*, 317 (1972).
(16) T. C. Shields and P. D. Gardner, *J. Am. Chem. Soc.*, **89**, 5427 (1967).

position since the *endo*-hydrogen of **17** is strongly shielded by overlap with the two aromatic rings.[17] This stereochemical assignment is also consistent with previous observations that nucleophiles add syn to cyclopropenyl double bonds.[16]

The lithium aluminum hydride reduction of **6** afforded a single isomer (eq 3) identified as **18** (60% yield) by the NMR chemical shift and coupling constant of the cyclopropyl hydrogens: δ 2.87 (d, J = 8.0 Hz, 2 H), 3.66 (t, J = 8.0 Hz, 1 H).

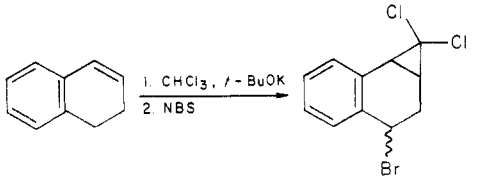


(3)

18

Surprisingly, compound **18** fails to react even after 1 week with potassium *tert*-butoxide in either tetrahydrofuran or dimethyl sulfoxide. Apparently, dehydrochlorination of **18**, as in other rigid cyclic and bicyclic systems in which an antiperiplanar relationship of leaving groups cannot be adopted, proceeds via syn periplanar transition states.[18]

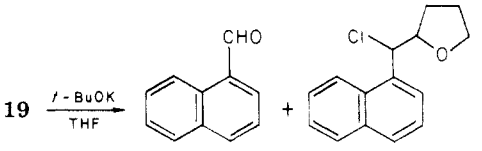
A second example illustrating the dehydrochlorination route to bicycloheptatrienes is found in the naphthalene system. Our initial studies were carried out with **19** which was prepared in the straightforward approach shown in eq 4.



(4)

19

Treatment of **19** with potassium *tert*-butoxide in tetrahydrofuran afforded a tarlike substance which was subjected to column chromatography (silica gel, hexane) to yield 1-naphthaldehyde (**20**) in 10% yield and a diastereomeric mixture of solvent insertion products **21** in 20–45% yield, eq 5. We have assigned structure **21** as the



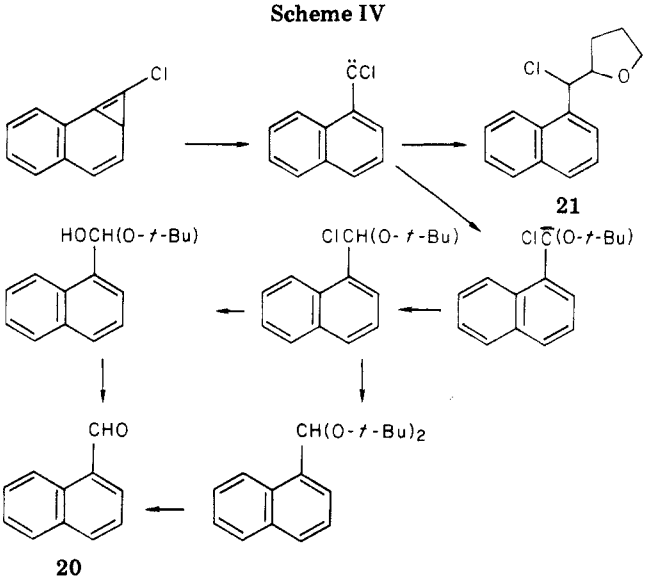
(5)

20 **21**

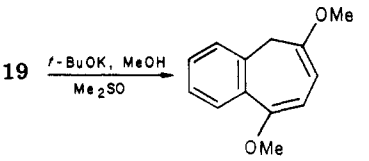
1-substituted naphthalene (rather than substitution in the 2-position) on the basis of the following observations: (1) compound **20** probably arises from the same carbene that gives the solvent insertion product (Scheme IV); (2) the NMR spectrum of the ether reveals that one of the aromatic protons is deshielded more than the remaining six, typical of 1-substituted naphthalenes.

We were not able to characterize products from the reaction of **19** with potassium *tert*-butoxide and methyl mercaptide. However, when methoxide was used as nucleophile, adduct **22** was isolated in 41% yield, eq 6. The

Scheme IV



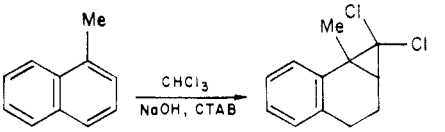
mechanism of formation of **22** is puzzling, and rationalization in terms of a bicycloheptatriene is difficult.



(6)

22

Precursor **23** was prepared in 85% yield from 1-methyl-3,4-dihydronaphthalene and dichlorocarbene, eq 7. The methyl group in **23** serves a dual purpose, first,

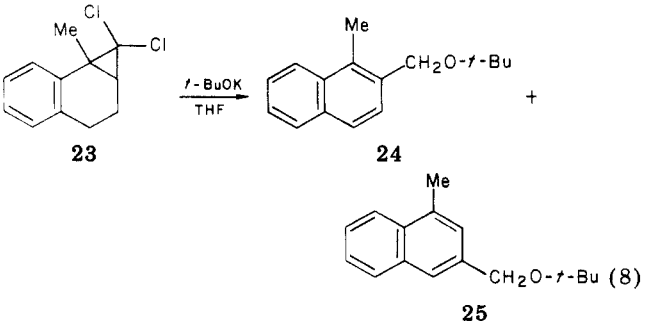


(7)

23

to act as a label to detect rearrangement and second to simplify the base-induced elimination sequence by replacement of the more acidic benzylic hydrogen.

Treatment of **23** as shown in eq 8 afforded, after preparative TLC, unreacted starting material (39%) and *tert*-butyl ethers **24** and **25** (eluting together, 43% com-



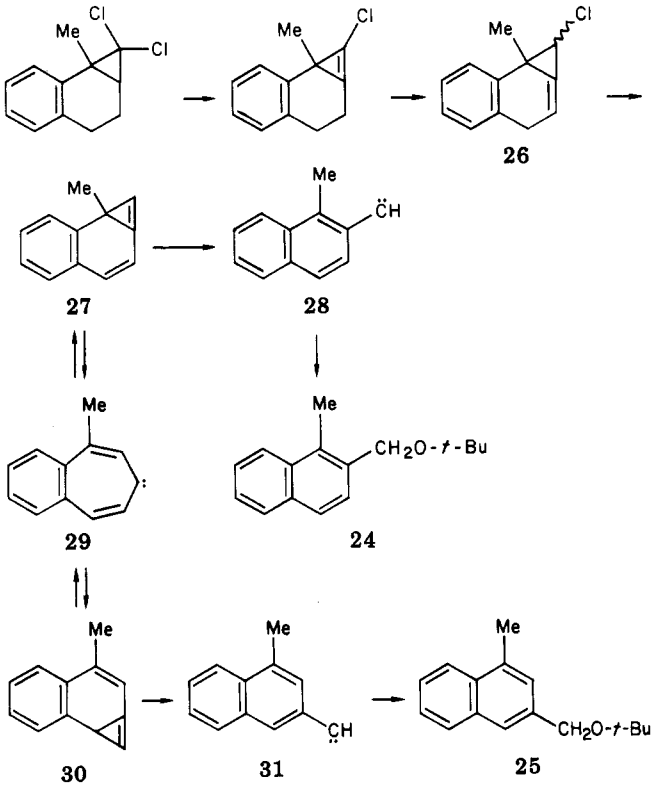
(8)

23 **24** **25**

bined yield) in a ratio of 3:2, respectively. Ethers **24** and **25** were separated by preparative GLC, and **24** was identified by comparison of its spectral and chromatographic properties with those of an authentic sample (see Experimental Section). The spectral properties of **25** reveal that it is an isomer of **24**, but an unambiguous synthetic route to **25**, as a structure proof, was not obvious. However, the formation of isomers other than **24** and **25** can be pre-

(17) E. Muller, H. Kessler, and H. Suhr, *Tetrahedron Lett.*, 423 (1965).
(18) H. Kwart, T. Takeshita, and J. L. Nyce, *J. Am. Chem. Soc.*, **86**, 2606 (1964).

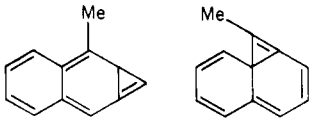
Scheme V



cluded with some confidence on mechanistic grounds (vide infra).

A sequence of steps which leads to **24** and **25** is illustrated in Scheme V. Dehydrochlorination of **23** followed by base-catalyzed isomerization of the cyclopropenyl double bond to the exocyclic position yields **26** which affords bicycloheptatriene **27** in subsequent steps by vinylogous β elimination or by isomerization and then β elimination.[19,20] Rearrangement of **27** to the naphthylcarbene **28** and subsequent trapping with nucleophile (t-BuO$^-$) gives **24**. Alternatively, **27** may undergo ring expansion to give benzocycloheptatrienylidene **29**, leading to ether **25** via bicycloheptatriene **30** and naphthylcarbene **31**.

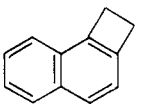
The formation of isomeric ethers other than **24** or **25** (or 1-vinylnaphthalene) would require not only that arylcarbenes **28** and **31** survive the reactions conditions but also that they rearrange to give bicycloheptatrienes **32** and **33** which are apparently not formed even in the gas phase



32 33

at 350 °C.[21] Formation of **32** and **33** would, of course, be energetically unfavorable since bond delocalization is lost in both rings.

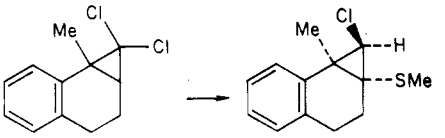
The reaction of naphthylcarbenes **28** and **31** with *tert*-butoxide to afford the *tert*-butyl ethers is expected, since electrophilic carbenes are known to react readily with alkoxides.[22] The failure of **29** to react with *tert*-butoxide is attributed to the nucleophilicity of this species.[23,24] It is interesting that naphtho[*a*]cyclobutene (**34**) was not formed, although it is the only product detected when **28** is generated in the gas phase.[23,25]



34

In contrast to the arylchlorocarbenes, solvent-insertion products were not observed. We have found that, in general, arylchlorocarbenes usually give solvent insertion products, whereas arylcarbenes react with nucleophile.

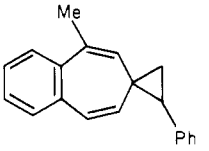
An attempt to trap **27** (or **30**) by dehydrochlorination in the presence of nucleophile (MeS$^-$) afforded only **35** (~100%), derived from the initially formed cyclopropene (eq 9). The stereochemistry (syn addition) was assigned from the chemical shift of the cyclopropyl proton (δ 3.38) by using compounds **16** and **17** as models.



(9)

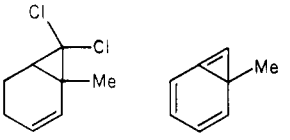
35

Several other experiments to trap the intermediates of Scheme V were also unsuccessful. Thus, no cycloadducts of **27** or **30** were isolated when 1,3-diphenylisobenzofuran[26,27] was added to the reaction medium. Furthermore, it was not possible to detect adduct **36** when styrene was added, although electrophilic olefins have been used previously to intercept cycloheptatrienylidenes.[23]



36

Generation of nonannelated bicyclo[4.1.0]heptatrienes via the elimination route is especially interesting since it has not been possible to prepare members of this series in solution. In analogy to the generation of **27** from **23**, compound **37** is attractive as a precursor to **38**. The methyl



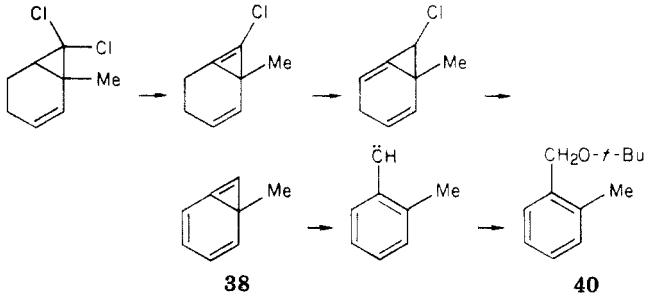
37 38

group is necessary since the dichlorocarbene adduct of 1,3-cyclohexadiene itself is known to give benzocyclopropene under the reaction conditions.[28]

The key step in the synthesis of **37** is the formation of 2-methyl-1,3-cyclohexadiene from the tosylhydrazone by the Shapiro modification[29] of the Bamford–Stevens reaction. The desired precursor, **37**, was produced in 14%

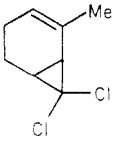
(19) T. C. Shields, B. Shoulders, J. Krause, C. Osboro, and P. Gardner, *J. Am. Chem. Soc.*, **87**, 3026 (1965).
(20) W. E. Billups, T. C. Shields, W. Y. Chow, and N. C. Deno, *J. Org. Chem.*, **37**, 3676 (1972).
(21) T. Mitsuhashi and W. J. Jones, *J. Am. Chem. Soc.*, **94**, 677 (1972).
(22) W. Kirmse, "Carbene Chemistry", 2nd ed., Academic Press, New York, 1971.
(23) W. M. Jones and C. L. Ennis, *J. Am. Chem. Soc.*, **91**, 6391 (1969).
(24) R. Gleiter and R. Hoffmann, *J. Am. Chem. Soc.*, **90**, 5457 (1968).
(25) We thank Professor R. Thummel for providing a sample of naphtho[*a*]cyclobutene.
(26) D. Longone and D. Stehouwer, *Tetrahedron Lett.*, 1017 (1970).
(27) T. Chan and D. Massuda, *Tetrahedron Lett.*, 3383 (1975).
(28) W. E. Billups, *Acc. Chem. Res.*, **11**, 245 (1978).
(29) R. Shapiro, *Org. React.*, **23**, 405 (1976).

Scheme VI



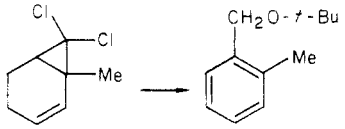
38 40

overall yield and free of its isomer **39**, as determined by gas chromatography.



39

Treatment of **37** with potassium *tert*-butoxide in tetrahydrofuran afforded, in addition to unreacted starting material (11.3%), *o*-methylbenzyl *tert*-butyl ether (**40**) in 40.5% yield, eq 10. A trace of what is probably a ben-

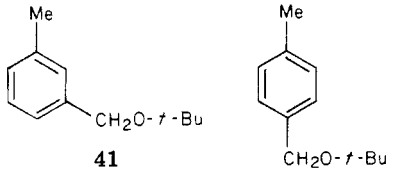


(10)

37 40

zocyclopropene derivative was also detected by the characteristic foul odor that is associated with benzocyclopropene and its derivatives.

In order to detect small amounts of the meta and para isomers that might have formed via rearrangement, authentic samples of xylyl *tert*-butyl ethers **41** and **42** were

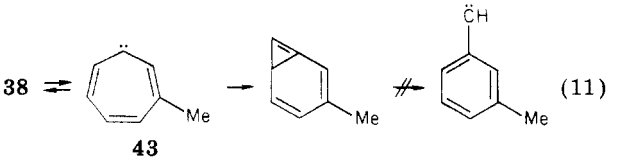


41 42

prepared by solvolysis of the respective methylbenzyl bromides. Surprisingly, it was not possible to resolve these isomers chromatographically. Even columns which resolved the three xylenes were ineffective for the separation of the ethers.

By use of nuclear magnetic resonance spectroscopy (EM-390, 50-fold expansion), the *tert*-butyl peaks could be resolved, but the methylene and methyl peaks remained unresolved. The product obtained from eq 10 showed only one *tert*-butyl resonance and had an infrared spectrum identical with authentic **40**, prepared from solvolysis of *o*-methylbenzyl bromide.

The formation of **40** can then be rationalized as shown in Scheme VI. The poor mass balance is perhaps an indication that some of the products are not stable to the reaction conditions. One might speculate that these could be derived from the aromatic carbene (perhaps dimers) and would most likely be unstable to the long reaction time required for the consumption of **37**. The absence of *m*-tolylcarbene-derived products (**41**, to a limit of detection of ca. 5% of **40**) indicates that rearrangement of **38** to **43** (if it occurs) is irreversible (eq 11).



(11)

43

Experimental Section

General Methods. Proton magnetic resonance spectra were recorded in $CDCl_3$ on a Varian Model EM-390 (90 MHz), XL-100 (100 MHz), or A56/60 (60 MHz) spectrometer. Chemical shifts (δ) are expressed in parts per million downfield from internal Me_4Si. Infrared spectra of liquids were taken on neat compounds held between sodium chloride plates with a Beckman IR8 spectrometer. High-resolution mass spectra were recorded on a double-focusing CEC 21-110 mass spectrometer operated at 70 eV. A Finnigan Model 3300 gas chromatograph/mass spectrometer was used to record low-resolution mass spectra. A Hewlett-Packard Model 700 gas chromatograph with a thermal-conductivity detector and operated with a flow rate of 60 mL/min was used for all analytical and preparative GLC. GLC column designations are as follows: (A) 4 ft × $^1/_4$ in., 20% OV-17 on Chromasorb WAW-DMCS; (B) 6 ft × $^1/_4$ in., 20% Apiezon L on Chromasorb WAW-DMCS; (C) 4 ft × $^1/_4$ in., 10% Carbowax 20M on Anakron ABS; (D) 4 ft × $^1/_4$ in., 10% SE-30 on Chromasorb WAW; (E) 6 ft × $^1/_4$ in., 20% SE-30 on Chromasorb PAW. All melting points and boiling points are uncorrected.

Tetrahydrofuran (THF) was distilled from sodium–benzophenone ketyl immediately before use. Dimethyl sulfoxide (Me_2SO) was distilled from calcium hydride under reduced pressure and stored over preconditioned 4A molecular sieves. Column chromatography was performed on Baker reagent grade silica gel (60–200 mesh). Merck precoated silica gel plates were used for analytical (100 × 50 × 0.25 mm) and preparative (200 × 200 × 2 mm) thin-layer chromatography. All other chemicals were of reagent quality and used as obtained from the suppliers.

7,7-Dichlorodibenzo[*a*,*c*]bicyclo[4.1.0]heptane (6). Saturated aqueous sodium hydroxide (100 g, 2.5 mol) was added over 2 h to a stirred mixture of phenanthrene (89 g, 0.50 mol), triethylbenzylammonium chloride (TBAC; 1.138 g, 5 mmol), and chloroform (800 mL, 10 mol) which was maintained at 50 °C. The reaction mixture was refluxed 5 h and then poured into water. The organic layer was separated and neutralized with dilute hydrochloric acid. The crude product was then dried over sodium sulfate and decolorized with charcoal. Purification was achieved by recrystallization several times from acetone to give 58.7 g of **6**: mp 142 °C (lit.[15] mp 141.2 °C); colorless long silky needles; 45% yield; NMR δ 3.27 (s, 2 H), 7.3 (m, 6 H), 7.9 (m, 2 H); IR (KBr) 1430 (s), 830 (s), 750 (s), 720 (s) cm^{-1}.

Reaction of 7,7-Dichlorodibenzo[*a*,*c*]bicyclo[4.1.0]heptane (6) with Potassium *tert*-Butoxide in Tetrahydrofuran. A solution of **6** (2.61 g, 0.01 mol) in 20 mL of tetrahydrofuran was added under nitrogen to a chilled suspension of potassium *tert*-butoxide (2.26 g, 0.02 mol) in tetrahydrofuran (50 mL). The mixture was stirred at 0 °C for 18 h and then worked up by adding 500 mL of water and 50 mL of chloroform. The organic layer was separated, washed several times with water, and dried over sodium sulfate, and the solvent was removed in vacuo. Purification by column chromatography (silica gel, chloroform) gave 2.36 g of **7** (3:1 mixture of diastereomers by NMR). Further purification was achieved by preparative thin-layer chromatography (silica gel, chloroform): NMR δ 1.70–2.20 (m, 4 H), 3.50–4.10 (m, 2 H), 4.40–4.80 (m, 1 H), 5.50–5.70 [the major diastereomer exhibits a doublet at 5.53 (1 H, J = 5 Hz) while the remaining diastereomer exhibits the doublet at 5.63 (1 H, J = 5 Hz)], 7.30–8.80 (m, 9 H); IR 1690 (s), 1498 (m), 1450 (s), 1060 (s), 745 (s) cm^{-1}; mass spectrum, m/e 296.0984 (M^+, calcd 296.0967).

Reaction of 7,7-Dichlorodibenzo[*a*,*c*]bicyclo[4.1.0]heptane (6) with Potassium *tert*-butoxide and Methyl Mercaptan in Dimethyl Sulfoxide. Methyl mercaptan (1.92 g, 0.04 mol) was added to a cooled solution of potassium *tert*-butoxide (10 g, 0.09 mol) in 50 mL of dry dimethyl sulfoxide. The mixture was stirred for 30 min followed by the dropwise addition of a solution

of 6 (2.61 g, 0.01 mol) in 50 mL of dimethyl sulfoxide. The mixture was stirred at room temperature for 3 h and then poured into water. The resulting solution was extracted with chloroform, washed with water, and dried over sodium sulfate. After removal of solvent, 12 was isolated as a yellow solid. Decoloration with charcoal and recrystallization from pentane gave 2.36 g (83% yield) of colorless material: mp 149–149.5 °C; NMR δ 1.21 and 1.81 (AB q, J_{AB} = 5.50 Hz, 2 H cyclopropyl), 2.1 (s, 6 H, SMe), 7.1–7.6 (m, 4 H, aromatic), 7.9–8.7 (m, 4 H, aromatic); IR 308 (m, br), 3010 (s), 294 (m), 1480 (s), 1430 (s, br); mass spectrum, *m/e* 284.0688 (M^+, calcd 284.0692). Oxidation of 12 with hydrogen peroxide in acetic acid gave the disulfone: mp 233 °C (sublimes); NMR δ 1.62 and 3.40 (AB q, J_{AB} = 6 Hz, 2 H cyclopropyl), 3.30 (s, 6 H, SO_2Me), 7.23–7.47 (m, 4 H, aromatic), 7.80–8.23 (m, 4 H, aromatic). Anal. Calcd for $C_{12}H_{10}O_4S_2$: C, 58.60; H, 4.63. Found: C, 58.80; H, 4.69.

7,7-Dichloro-1-methyldibenzo[*a*,*c*]bicyclo[4.1.0]heptane (14). A solution of 50% aqueous sodium hydroxide (16 mL, 0.2 mol) was added dropwise at 0 °C to a stirred solution of 9-methylphenanthrene (4.0 g, 14.6 mmol) and cetyltrimethylammonium bromide (0.07 g, 0.2 mmol) in chloroform (16 mL). The resulting mixture was stirred for 23 h at room temperature and then poured into 100 mL of water and extracted twice with 50-mL portions of chloroform. The chloroform extracts were combined, washed with brine (100 mL), and dried over Na_2SO_4. Solvent removal in vacuo gave a black oil which was filtered through a pad of silica gel and recrystallized from ethyl acetate to afford 3.38 g of 14 (62%) as white crystals: mp 84–85 °C; NMR δ 1.90 (s, 3 H), 2.90 (s, 1 H), 7.17–7.47 (m, 5 H), 7.50–7.70 (m, 1 H), 7.90–8.07 (m, 2 H); mass spectrum, *m/e* 274.0314 (M^+, calcd 274.0316). Anal. Calcd for $C_{16}H_{12}Cl_2$: C, 69.84; H, 4.40. Found: C, 69.54; H, 4.49.

Reaction of 7,7-Dichloro-1-methyldibenzo[*a*,*c*]bicyclo[4.1.0]heptane (14) with Potassium *tert*-Butoxide in Tetrahydrofuran. Compound 14 (1.2 equiv) was treated with *tert*-BuOK (16 equiv) in THF at 0 °C. Workup by thin-layer chromatography failed to provide characterizable products.

Reaction of 7,7-Dichloro-1-methyldibenzo[*a*,*c*]bicyclo[4.1.0]heptane (14) with Potassium *tert*-Butoxide and Methyl Mercaptan in Dimethyl Sulfoxide. Previously condensed methyl mercaptan (0.80 g, 16.6 mmol) was allowed to distill under nitrogen into a stirred suspension of potassium *tert*-butoxide (3.72 g, 33.2 mmol) in dry dimethyl sulfoxide (20 mL). After the mixture was stirred an additional 10–15 min, 14 (433.3 mg, 1.58 mmol) in Me_2SO (5 mL) was added dropwise. The mixture was then stirred for 3 h, added to water (100 mL) and extracted with chloroform (100 mL). The chloroform extract was washed with water (100 mL), 10% sodium bicarbonate solution (100 mL), and brine (100 mL) and dried over $MgSO_4$. Solvent removal in vacuo afforded a pale yellow solid. Rapid elution through silica gel ($CHCl_3$) gave 417 mg (92%) of 16 as pale yellow crystals: mp 128–129.5 °C; NMR δ 1.87 (s, 3 H), 2.04 (s, 3 H), 3.52 (s, 1 H), 7.2–7.4 (m, 4 H), 7.5–7.7 (m, 1 H), 7.9–8.1 (m, 2 H), 8.2–8.4 (m, 1 H); mass spectrum, *m/e* 286.0593 (M^+, calcd 286.0583).

Reduction of 7,7-Dichlorodibenzo[*a*,*c*]bicyclo[4.1.0]heptane (6) with Lithium Aluminum Hydride. A solution of 6 (2.71 g, 10.4 mmol) in dry ether (80 mL) was added dropwise to a suspension of lithium aluminum hydride (4.8 g, 0.13 mol) in ether (40 mL). The mixture was refluxed 21 h and then worked up by the dropwise addition of water (2.7 mL), 15% sodium hydroxide (2.7 mL), and then water (8.1 mL). The inorganic salts were then removed by filtration, and the filtrate was concentrated in vacuo to yield 1.41 g (60%) of 18: mp 142–144 °C (after recrystallization from chloroform); NMR δ 2.81 (d, J = 8.0 Hz, 2 H), 3.66 (t, J = 8.0 Hz, 1 H), 7.1–7.5 (m, 4 H), 7.9–8.1 (m, 2 H); mass spectrum, *m/e* 226 (M^+, calcd 226). Anal. Calcd for $C_{15}H_{11}Cl$: C, 79.47; H, 4.89. Found: C, 79.31; H, 4.99.

Attempted Reaction of *endo*-7-Chlorodibenzo[*a*,*c*]bicyclo[4.1.0]heptane (18) with Potassium *tert*-Butoxide in Tetrahydrofuran. A solution of 18 (505 mg, 2.2 mmol) in dry tetrahydrofuran (8 mL) was added dropwise under N_2 to a stirred suspension of potassium *tert*-butoxide (501 mg, 4.5 mmol) in tetrahydrofuran (10 mL). The temperature was maintained at 0 °C during the addition. The reaction mixture was stirred for 18 h at room temperature, poured into water (50 mL), extracted with ether (50 mL), dried over $MgSO_4$, and evaporated in vacuo to afford 500 mg of white solid which was shown to be starting material by comparison of NMR spectra and TLC properties. Starting material was also recovered when 18 was treated with 16 equiv of potassium *tert*-butoxide for 7 days.

Attempted Reaction of *endo*-7-Chlorodibenzo[*a*,*c*]bicyclo[4.1.0]heptane (18) with Potassium *tert*-Butoxide and Methyl Mercaptan in Dimethyl Sulfoxide. Compound 18 (665 mg, 2.9 mmol) in dimethyl sulfoxide (15 mL) was added dropwise to a solution of potassium *tert*-butoxide (2.74 g, 24.5 mmol) and methyl mercaptan (0.52 g, 10.8 mmol) in dimethyl sulfoxide (15 mL). After the mixture was stirred for 3 h, water was added and the solution was extracted with ether (3 × 50 mL). The combined extracts were washed with water and dried over $MgSO_4$. Solvent evaporation afforded 670 mg (100%) of starting material.

7,7-Dichloro-5-bromobenzo[*a*]bicyclo[4.1.0]heptane (19). 7,7-Dichloro-3,4-benzobicyclo[4.1.0]heptane[30] (42.6, 0.2 mol) was added to a solution of *N*-bromosuccinimide (35.6 g, 0.20 mol) in degassed CCl_4 along with a trace of benzoyl peroxide and the resulting mixture refluxed under nitrogen for 5 h. The reaction mixture was then washed with water and dried over Na_2SO_4. Compound 19 (mp 97 °C) was obtained in 73% yield (42.6 g) after recrystallization from pentane: NMR (CCl_4) δ 2.0–3.0 (m, 6 H), 5.01 (s, J = 3.0 Hz, 1 H), 7.0–7.5 (m, 4 H). This compound was used immediately in the following experiment.

Reaction of 7,7-Dichloro-5-bromobenzo[*a*]bicyclo[4.1.0]heptane (19) with Potassium *tert*-Butoxide in Tetrahydrofuran. A solution of 19 (2.11 g, 7.23 mmol) in tetrahydrofuran (5 mL) was added under nitrogen to a suspension of potassium *tert*-butoxide (2.44 g, 21.8 mmol) in tetrahydrofuran (25 mL). The temperature was maintained at 0 °C throughout the addition. The reaction mixture was stirred at 0 °C for 12 h, poured into water (300 mL), and extracted with dichloromethane (2 × 50 mL). The combined extracts were washed with brine (100 mL) and dried over $MgSO_4$. Solvent removal in vacuo gave a black tar which was subjected to column chromatography (silica gel, hexane) to yield 109.7 mg (10% yield) of 1-naphthaldehyde (20), one diastereomer of 21 (134.8 mg, 8% yield), and the remaining diastereomer of 21 (150.5 g, 10% yield). When the reaction was run on a larger scale, the yield of 21 was 45%: NMR (CCl_4) δ 1.60–2.10 (m, 4 H), 3.65–3.97 (m, 2 H), 4.30–4.68 (m, 1 H), 5.47–5.70 (2 d, 5.53 and 5.63, 1 H each, J = 5 Hz), 7.30–8.32 (m, 7 H); IR (neat) 3060 (s), 2900 (s), 2870 (s), 1595 (s), 1510 (s), 1600 (s, br), 745 (s) cm^{-1}.

Reaction of 7,7-Dichloro-5-bromobenzo[*a*]bicyclo[4.1.0]heptane (19) with Potassium *tert*-Butoxide and Methanol in Dimethyl Sulfoxide. Compound 19 (2.92 g, 10 mmol) was added to a mixture of potassium *tert*-butoxide (9.04 g, 0.08 mol) and methanol (0.96 g, 0.03 mol) in dimethyl sulfoxide (70 mL), and the mixture was stirred under nitrogen at room temperature for 18 h. Workup and purification by column chromatography provided 0.89 g (41% yield) of 22: NMR δ 3.04 (s, 2 H), 3.36 (s, 3 H), 3.60 (s, 3 H), 4.77 (AB q, J_{AB} = 6.6 Hz, 1 H), 5.43 (AB q, J = 6.6 Hz, 1 H), 6.70–7.70 (m, 4 H); IR 3055 (s), 3000 (s), 2940 (s), 2900 (s), 2830 (s), 1730 (m), 1635 (s), 1485 (s), 2940 (s), 2900 (s), 2830 (s), 1730 (m), 1635 (s), 1600 (s), 1485 (s), 1440 (s), 1355 (s), 1250 (s), 1135 (s), 1080 (s), 1015 (s) cm^{-1}; mass spectrum, *m/e* 202.998 (M^+, calcd 202.993).

1-Methyl-3,4-dihydronaphthalene. A solution of methyl iodide (72.4 g, 0.51 mol) in 50 mL of ether was added dropwise, so as to maintain reflux, to 12.0 g (0.5 mol) of magnesium turnings under 200 mL of ether. After the addition was completed, stirring was continued an additional 15 min. α-Tetralone (36.3 g, 0.25 mol) in 50 mL of ether was then added so as to maintain a reflux. The product was hydrolyzed by dropwise addition of 50 mL of saturated NH_4Cl solution. The supernatant was decanted, and the granular precipitate was washed with ether (2 × 100 mL). The ether extracts were combined, washed with brine, and dried over $MgSO_4$. Solvent evaporation in vacuo and vacuum distillation afforded 28.7 g (80% yield) of product, bp 43–46 °C (0.03 mmHg).

7,7-Dichloro-1-methylbenzo[*a*]bicyclo[4.1.0]heptane (23). A 50% aqueous sodium hydroxide solution (160 mL, 2 mol) was added dropwise with stirring to a solution of 1-methyl-3,4-dihydronaphthalene (28.7 g, 0.13 mol) and cetyltrimethylammonium

(30) M. G. Banwell, R. Blattner, A. R. Browne, J. T. Craig, and B. Halton, *J. Chem. Soc., Perkin Trans. 1*, 2165 (1977).

bromide (0.766 g, 2.1 mmol) in 80 mL of chloroform. After being stirred at room temperature for 64 h, the reaction mixture was poured into 400 mL of water and extracted with dichloromethane (3 × 150 mL). The dichloromethane extracts were combined, washed with water several times and with brine, and dried over $MgSO_4$. Vacuum distillation afforded 40.14 g (85% yield) of **23**: bp 73–76 °C (0.2 mmHg); NMR δ 1.64 (s, 3 H), 1.60–2.03 (m, 3 H), 2.11–2.98 (m, 2 H), 6.87–7.41 (m, 4 H); mass spectrum, *m/e* (relative intensity) 226 (1.7, M^+), 211 (31), 191 (12), 128 (100). Anal. Calcd for $C_6H_{12}Cl_2$: C, 63.46; H, 5.33. Found: C, 63.43; H, 5.41.

Reaction of 7,7-Dichloro-1-methylbenzo[*a*]bicyclo[4.1.0]heptane (23) with Potassium *tert*-Butoxide in Tetrahydrofuran. A solution of **23** (646 mg, 2.7 mmol) in 2 mL of tetrahydrofuran was added dropwise under N_2 to a stirred suspension of potassium *tert*-butoxide (4.59 g, 41.0 mmol) in 48 mL of tetrahydrofuran at 15 °C. The mixture was stirred at 15 °C for 23 h followed by dilution with water (250 mL) and extraction into chloroform (2 × 40 mL). The chloroform extracts were combined, washed with water, and dried over $MgSO_4$. Solvent evaporation in vacuo and preparative TLC (pentane–dichloromethane, 4:1) afforded unreacted starting material (39%) and a mixture of *tert*-butyl ethers **24** and **25** (43%) in a ratio of 2:3, respectively, as determined by NMR. They were separated by preparative GLC (column B, 230 °C); **24** is an oil and **25** is a white solid, mp 62–63 °C. The spectral data are as follows. For **24**: NMR δ 1.30 (s, 9 H), 2.63 (s, 3 H), 4.59 (s, 2 H), 7.33–7.87 (m, 5 H), 7.95–8.13 (m, 1 H); mass spectrum, *m/e* (relative intensity) 228 (11, M^+), 172 (8), 154 (100), 143 (54), 57 (38). For **25**: NMR δ 1.36 (s, 9 H), 2.51 (s, 3 H), 4.79 (s, 2 H), 7.13–7.87 (m, 5 H), 8.00–8.20 (m, 1 H); mass spectrum, *m/e* (relative intensity) 228 (3, M^+), 172 (11), 155 (69), 154 (96), 143 (100), 128 (40), 115 (25), 57 (71). Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 81.18; H, 8.14 (loss of isobutylene).

1-Bromo-2-(bromomethyl)naphthalene. A solution of 1-bromo-2-methylnaphthalene[31] (22.60 g, 0.08 mol) and *N*-bromosuccinimide (14.25 g, 0.08 mol) in degassed CCl_4 (100 mL) was refluxed under nitrogen with a trace of benzoyl peroxide for 3 h. The hot reaction mixture was filtered and the solid washed with CCl_4. Solvent removal in vacuo afforded a yellow solid which was purified by recrystallization from ethanol to give 29.51 g (96% yield) of beige crystals: mp 104–105 °C (lit.[32] 103.5–105.5 °C); NMR δ 4.68 (s, 2 H), 7.17–7.73 (m, 5 H), 7.95–8.25 (m, 1 H).

1-Methyl-2-(*tert*-butoxymethyl)naphthalene (24). 1-Bromo-2-(bromomethyl)naphthalene[31] (10.0 g, 0.03 mol) and potassium *tert*-butoxide (15.5 g, 0.14 mol) in 100 mL of *tert*-butyl alcohol were refluxed for 17 h, followed by dilution with water (200 mL) and extraction into ether (3 × 200 mL). The combined ether extracts were washed with 4 N NaOH (3 × 200 mL) and brine (200 mL) and dried over Na_2SO_4. Solvent evaporation in vacuo and fractional distillation afforded 2.57 g (26% yield) of 1-bromo-2-(*tert*-butoxymethyl)naphthalene: bp 111–112 °C (0.15 mmHg); NMR δ 1.27 (s, 9 H), 4.66 (s, 2 H), 7.24–7.68 (m, 5 H), 8.08–8.26 (m, 1 H). A solution of *n*-BuLi in hexane (4.5 mL, 10.8 mmol) was then added dropwise under nitrogen to a stirred solution of 1-bromo-2-(*tert*-butoxymethyl)naphthalene (1.06 g, 3.6 mmol) at −78 °C. After the mixture was stirred an additional 15 min at −78 °C, 1.35 mL (21.7 mmol) of methyl iodide was added dropwise. After 5 min, the cooling bath was removed and stirring continued an additional 1 h followed by dilution with water (50 mL) and extraction into ether (50 mL). The ether extract was washed with brine (50 mL) and dried over $MgSO_4$. Solvent evaporation afforded 0.85 g of an orange oil. GLC (column B, 230 °C) indicated two components in the ratio 21:79. These were separated by preparative GLC, and the minor one (lower boiling) was identical with an authentic sample of 2-(*tert*-butoxymethyl)naphthalene by GLC coinjection and NMR, whereas the major one was identical with **24** obtained from **23**, as shown by its IR and NMR spectra and by GLC coinjection (column B, 230 °C, and column C, 220 °C).

Reaction of 7,7-Dichloro-1-methylbenzo[*a*]bicyclo[4.1.0]heptane (23) with Potassium *tert*-Butoxide and Methyl Mercaptan in Dimethyl Sulfoxide. Methyl mercaptan (previously condensed, 0.35 g, 7.3 mmol) was allowed to distill through a dip tube into a stirred suspension of potassium *tert*-butoxide (2.01 g, 17.9 mmol) in dimethyl sulfoxide (20 mL). The mixture was stirred for a few minutes followed by the dropwise addition of a solution of **23** (337 mg, 1.5 mmol) in dimethyl sulfoxide (5 mL). After 1 h, the black reaction mixture was diluted with water (200 mL) and extracted with ether (3 × 50 mL). The combined ether extracts were washed with water (3 × 100 mL) and dried over $MgSO_4$. Solvent removal gave 322 mg (ca. 90% yield) of essentially pure **35**: NMR δ 1.67 (s, 3 H), 2.18 (s, 3 H), 1.90–3.11 (m, 4 H), 3.38 (s, 1 H), 6.93–7.33 (m, 4 H); mass spectrum, *m/e* 238.0581 (M^+, calcd 238.0583).

Attempted Reaction of 7,7-Dichloro-1-methylbenzo[*a*]bicyclo[4.1.0]heptane (23) with Potassium *tert*-Butoxide and Diphenylisobenzofuran. A solution of **23** (177 mg, 0.74 mmol) in THF (2 mL) was added dropwise to a solution of diphenylisobenzofuran (401 mg, 1.5 mmol) and potassium *tert*-butoxide (1.27 g, 11.3 mmol) in THF (8 mL). After being stirred at room temperature for 23 h, the reaction mixture was diluted with water (100 mL) and extracted with ether (3 × 25 mL). The combined ether extracts were washed with water (2 × 100 mL) and brine (100 mL) and dried over Na_2SO_4. Solvent evaporation in vacuo afforded a yellow solid which had no olefinic signals in the NMR spectrum. Preparative TLC (hexane–CH_2Cl_2, 4:1) afforded unreacted starting material (196 mg, 49%), ethers **24** and **25** (37 mg, 22%), and diphenylisobenzofuran (329 mg, 82%).

Attempted Reaction of 7,7-Dichloro-1-methylbenzo[*a*]bicyclo[4.1.0]heptane (23) with Potassium *tert*-Butoxide and Styrene. Compound **23** (302 mg, 1.3 mmol) in 3 mL of THF was added dropwise to a solution of potassium *tert*-butoxide (2.15 g, 19.2 mmol) and styrene (784 mg, 7.5 mmol) in THF (17 mL) stirred at 0 °C. The mixture was stirred at 10–15 °C for 43 h, diluted with water (200 mL), and extracted with chloroform (100 mL). The chloroform extract was washed with water (100 mL) and brine (100 mL) and dried over $MgSO_4$. The solvent and traces of styrene were removed by pumping at 0.1 mm overnight. Preparative TLC (hexane–CH_2Cl_2, 4:1) afforded only unreacted starting material (145 mg, 51%) and *tert*-butyl ethers **24** and **25** (34 mg, 19%).

2-Methylcyclohexenone Tosylhydrazone. Freshly prepared 2-methylcyclohexenone[33] (5.42 g, 0.05 mol) was added all at once to a refluxing solution of tosylhydrazine (9.13 g, 0.057 mol) in 60% aqueous methanol (17 mL). The reaction mixture was placed immediately in a refrigerator and allowed to stand for 6 days. The resultant solid was collected by filtration and recrystallized from absolute ethanol to afford 10.64 g (76.5% yield) of the tosylhydrazone, mp 158–160 °C (lit.[34] 156.5–157 °C).

2-Methyl-1,3-cyclohexadiene.[34] Methyllithium (75 mL, 138 mmol) in ether was added dropwise with stirring under nitrogen to a solution of 2-methylcyclohexenone tosylhydrazone in 100 mL of ether at 0 °C. After the addition was complete, stirring was continued at room temperature until gas evolution had ceased (ca. 1 h). Following the cautious dropwise addition of water (60 mL), the two layers were separated. The ether layer was washed with water (100 mL) and brine (100 mL) and dried over Na_2SO_4. Removal of the ether in vacuo at 0 °C provided crude diene which was shown by GC (column E, 100 °C) to be homogeneous. The diene was used in subsequent experiments without further purification.

7,7-Dichloro-1-methylbicyclo[4.1.0]hept-2-ene (37). Chloroform (6.57 g, 55 mmol) was added dropwise over 45 min at 0 °C to a mixture of 2-methyl-1,3-cyclohexadiene (excess) and potassium *tert*-butoxide (4.93 g, 44 mmol) in 35 mL of *n*-pentane. After being stirred an additional 15 min, the reaction mixture was poured into 25 mL of water. The aqueous layer was then extracted with pentane (25 mL), combined with the original organic fraction, and dried over $MgSO_4$. Solvent evaporation in vacuo afforded a dark red liquid which was distilled through a short-path column to give 3.36 g of **37** (43% from the tosylhydrazone) as a clear liquid: bp 35–45 °C (3 mm); NMR δ 1.41 (s, 3 H), 1.50–2.17 (m, 5 H), 5.47–5.93 (m, 2 H); mass spectrum

(31) R. Adams and L. O. Binder, *J. Am. Chem. Soc.*, **63**, 2774 (1941).
(32) M. S. Newman and A. I. Kosak, *J. Org. Chem.*, **14**, 375 (1949).
(33) E. Warnhoff, D. Martin, and W. Johnson, "Organic Syntheses", Collect Vol. IV, Wiley, New York, 1975, p 162.
(34) R. L. Cargill, A. B. Sears, J. Boehm, and M. R. Willcott, *J. Am. Chem. Soc.*, **95**, 4346 (1973).

178 (m^+), calcd 178. Anal. Calcd for $C_8H_{10}Cl_2$: C, 54.26; H, 5.69. Found: C, 54.55; H, 5.72.

Reaction of 7,7-Dichloro-1-methylbicyclo[4.1.0]hept-2-ene (37) with Potassium *tert*-Butoxide in Tetrahydrofuran. A solution of **37** (581 mg, 3.3 mmol) in tetrahydrofuran (95 mL) was added dropwise under nitrogen to a solution of potassium *tert*-butoxide (5.51 g, 49.2 mmol) in dry tetrahydrofuran (30 mL) which was maintained at 0 °C by means of an ice bath. After being stirred at room temperature for 72 h, the reaction mixture was diluted with water (100 mL) and extracted with ether (100 mL). The ether extract was washed with brine (100 mL) and dried over $MgSO_4$. Solvent evaporation in vacuo afforded 567.6 mg of dark brown oil which was shown by GLC (column A, 170 °C) to contain starting material (11.3% yield) and *o*-xylyl *tert*-butyl ether (**40**, 40.5% yield). Compound **40** was isolated by preparative GLC and shown to be identical (IR and NMR) with an authentic sample: NMR δ 1.26 (s, 9 H), 2.30 (s, 3 H), 4.37 (s, 2 H), 7.03–7.20 (m, 3 H), 7.20–7.37 (m, 1 H); mass spectrum, 178 (M^+, calcd 178).

Synthesis of *o*-, *m*-, and *p*-Xylyl *tert*-Butyl Ethers (40–42). An authentic sample of each ether was prepared in >95% yield by reaction of the corresponding bromoxylene with potassium *tert*-butoxide in tetrahydrofuran for 12–20 h.

Acknowledgment. We gratefully acknowledge The Robert A. Welch Foundation for support of this work.

Registry No. **6**, 37608-29-0; **7** (isomer 1), 52688-71-8; **7** (isomer 2), 52688-68-3; **12**, 52688-72-9; **12** disulfone, 75948-99-1; **14**, 75949-00-7; **16**, 75949-01-8; **18**, 55831-21-5; **19**, 60096-40-4; **20**, 66-77-3; **21** (isomer 1), 75949-02-9; **21** (isomer 2), 76010-85-0; **22**, 75949-03-0; **23**, 65130-35-0; **24**, 65130-36-1; **25**, 65130-37-2; **35**, 75949-04-1; **37**, 75949-05-2; **40**, 56636-82-9; **41**, 40677-59-6; **42**, 75949-06-3; phenanthrene, 85-01-8; tetrahydrofuran, 109-99-9; methyl mercaptan, 74-93-1; 9-methylphenanthrene, 883-20-5; 7,7-dichloro-3,4-benzobicyclo[4.1.0]heptane, 60096-38-0; 1-methyl-3,4-dihydronaphthalene, 4373-13-1; α-tetralone, 529-34-0; methyl iodide, 74-88-4; 1-bromo-2-(bromomethyl)naphthalene, 37763-43-2; 1-bromo-2-methylnaphthalene, 2586-62-1; 2-methylcyclohexenone tosylhydrazone, 75949-07-4; 2-methylcyclohexenone, 1121-18-2; 2-methyl-1,3-cyclohexadiene, 1489-57-2; *o*-bromoxylene, 89-92-9; *m*-bromoxylene, 620-13-3; *p*-bromoxylene, 104-81-4.

S → N and N → S Reverse Rearrangement of *S*- and *N*-(2,4-Dinitrophenyl)cysteines[1]

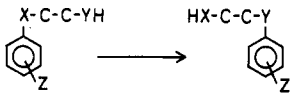
Hiroki Kondo, Fumio Moriuchi, and Junzo Sunamoto*

Department of Industrial Chemistry, Faculty of Engineering, Nagasaki University, Nagasaki 852, Japan

Received July 30, 1980

The reversible Smiles rearrangement between *S*-(2,4-dinitrophenyl)cysteine (**1a**) and *N*-(2,4-dinitrophenyl)cysteine (**2a**) has been kinetically studied in methanol, DMF, and Me_2SO containing an organic base such as imidazole or DBU. The overall reaction is composed of the spontaneous and base-catalyzed reactions. In methanol the rearrangement from **1a** to **2a** goes virtually to completion in most cases. In DMF containing DBU, the reverse rearrangement from **2a** to **1a** becomes observable to afford eventually an equilibrium mixture of **1a** and **2a**. During this transformation an intermediate was spectroscopically detected, which showed an absorption band around 500 nm. The amide derivative of **1a** (**1b**) failed to undergo a facile rearrangement except under much severer conditions. In this case the normal Smiles rearrangement was accompanied by some side reactions.

Intramolecular rearrangements shown in eq 1 are known



(1)

as Smiles rearrangements.[2] They may take place with various combinations of hetero atoms for X and Y (e.g., O, S, and N), when the migrating phenyl ring is activated by substituent Z. In addition to the synthetic utility the Smiles rearrangement provides a good opportunity to study the mechanism of aromatic nucleophilic substitution reactions, because the anionic σ complex intermediate (**4**)

4

observed in some of the Smiles rearrangements[3,4] appears to be common to the aromatic nucleophilic substitution reactions as well.[5] The stability of the σ complex, however, varies due to the substrate. Therefore when a stable complex is not detected by conventional means, the mechanism of the rearrangement remains unclear with regard to the involvement of such a complex. If the complex is extremely labile so as not to be detected readily, it is kinetically equivalent to having such a complex present only at the transition state. This situation occurred in the rearrangement of DL-2-aminododecanoic acid *N*-methyl-*p*-nitroanilide (**5**), where the reaction took place

5

without any stable intermediate under mild conditions.[6] Introducing another nitro group into the benzene ring would stabilize the complex and allow it to be detected readily, because the existence of similar anionic σ complexes has been previously confirmed.[3,4] Our current choice

(1) Abbreviations used in this article for bases are the following: Dabco, 1,4-diazabicyclo[2.2.0]octane; DBU, 1,5-diazabicyclo[5.4.0]undec-5-ene.

(2) W. E. Truce, E. M. Kreider, and W. W. Brand, *Org. React.*, 18, 99 (1970).

(3) C. F. Bernasconi, R. H. DeRossi, and C. L. Gehriger, *J. Org. Chem.*, 38, 2838 (1973).

(4) S. Sekiguchi and K. Okada, *J. Org. Chem.*, 40, 2782 (1975).

(5) J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, 49, 275 (1951).

(6) J. Sunamoto, H. Kondo, F. Yanase, and H. Okamoto, *Bull. Chem. Soc. Jpn.*, 53, 1361 (1980).

0022-3263/81/1946-1333$01.25/0