# Synthesis and Chemistry of 1*H*-Cyclobuta[*de*]naphthalenes, 1-Alkylidene-1*H*-cyclobuta[*de*]naphthalenes, and 1*H*-Cyclobuta[*de*]naphthalen-1-one

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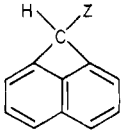
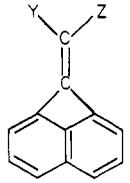
**Abstract:** Grignard and lithium reagents from 1-bromo-1*H*-cyclobuta[*de*]naphthalene (**1a**) are converted by protonic acids, trimethylsilyl chloride, methyl iodide, carbon dioxide, acetyl chloride, and ethylene oxide to the corresponding 1*H*-cyclobuta[*de*]naphthalene derivatives. Further, displacements of **1a** by various nucleophiles (aluminohydrides, iodide, chloride, cyanide, azide, methoxide and thiophenoxide, triphenylphosphine, silver nitrate, acetate, and tosylate, respectively; lithium cuprates) give 1-substituted 1*H*-cyclobuta[*de*]naphthalenes. Reactions however of (1) **1a** with piperidine or aniline, (2) 1-methoxy-1*H*-cyclobuta[*de*]naphthalene (**1o**) with sodium methoxide, and (3) **1a**, 1-acetoxy-1*H*-cyclobuta[*de*]naphthalene (**1p**), and 1*H*-cyclobuta[*de*]naphthalene (**1b**), respectively, with silver acetate/acetic acid result in cleavage of the four-membered ring moieties to yield naphthalene derivatives. 1-Hydroxy-1*H*-cyclobuta[*de*]naphthalene (**1n**) also converts rapidly to 1-naphthaldehyde (**5c**). 1*H*-Cyclobuta[*de*]naphthalen-1-yl radicals (**4**), cations, and carbanions are generated readily; formation of these intermediates is resisted in part however by the strains in their cyclobuta[*de*]naphthylen-1-yl moieties. (1*H*-Cyclobuta[*de*]naphthalen-1-ylidene)triphenylphosphorane (**36**) reacts efficiently with aldehydes and ketones to give 1-alkylidene-1*H*-cyclobuta[*de*]naphthalenes (**2a–e, 38**). The strained alkylidenes undergo normal directed ionic and free radical additions of hydrogen bromide. 1-Benzhydrylidene-1*H*-cyclobuta[*de*]naphthalene (**2e**) is isomerized however to 1,2-diphenylacenaphthylene (**21**) by acids. 3′-Methylspiro[1*H*-cyclobuta[*de*]naphthalene-1,2′-oxirane] (**22**) rearranges similarly to 1-acetyl-1*H*-cyclobuta[*de*]naphthalene (**1i**). At 430–550 °C 1-alkyl-1*H*-cyclobuta[*de*]naphthalenes and 1-alkylidene-1*H*-cyclobuta[*de*]naphthalenes (**2b–d**) convert to their corresponding 1-(1-alkenyl)naphthalenes and 1-(1-alkynyl)naphthalenes (**40**), apparently via 1,4-diradical intermediates. 1*H*-Cyclobuta[*de*]naphthalen-1-one (**3a**) is preparable by (1) ozonolysis of 1-(2-propylidene)-1*H*-cyclobuta[*de*]naphthalene (**2a**) and (2) hydrolysis of 1-chloro-1-(thiophenoxy)-1*H*-cyclobuta[*de*]naphthalene (**41**). Water, methanol, nitrogen nucleophiles, and Wittig reagents effect rapid ring opening of **3a**.

The present report summarizes synthesis and varied reactions of 1*H*-cyclobuta[*de*]naphthalenes (**1**), 1-alkylidene-1*H*-cyclobuta[*de*]naphthalenes (**2**), and 1*H*-cyclobuta[*de*]naphthalen-1-one (**3a**). This study reveals that 1*H*-cyclobuta[*de*]naphthalen-1-yl and 1*H*-cyclobuta[*de*]naphthalen-1-ylidene derivatives, though highly strained, are readily prepared and exhibit interesting preparative and physical-organic chemistry.

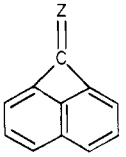


1a-w

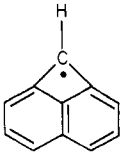
1a, Z = Br
b, Z = H
c, Z = MgBr
d, Z = Li
e, Z = D
f, Z = $Si(CH_3)_3$
g, Z = $CH_3$
h, Z = $CO_2H$
i, Z = $COCH_3$
j, Z = $CH_2CH_2OH$
k, Z = I
l, Z = Cl
m, Z = CN
n, Z = OH
o, Z = $OCH_3$
p, Z = $OCOCH_3$
q, Z = $NR_2$
r, Z = $N_3$
s, Z = $O_3SC_6H_4CH_3$-*p*
t, Z = $C_6H_5$
u, Z = $^+P(C_6H_5)_3$, $Br^-$
v, Z = $CH{=}CH_2$
w, Z = $SC_6H_5$



2a, Y = Z = $CH_3$
b, Y = Z = H
c, Y = $CH_3$, Z = H
d, Y = $C_6H_5$, Z = H
e, Y = Z = $C_6H_5$
f, Y = OH, Z = $CH_3$
g, Y = H, Z = $CH_2D$



3a, Z = O
b, Z = NH
c, Z = $P(C_6H_5)_3$



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## Results and Discussion

1-Bromo-1*H*-cyclobuta[*de*]naphthalene (**1a**) is preparable by photolysis of 8-bromo-1-naphthyldiazomethane or its precursor, the sodium salt of 8-bromo-1-naphthaldehyde *p*-tosylhydrazone in ethyl ether.[1-3] Bromide **1a** is now satisfactorily obtainable from 1*H*-cyclobuta[*de*]naphthalene (**1b**, 40% conversion, 91% yield) and *N*-bromosuccinimide in the presence of benzyl peroxide in refluxing carbon tetrachloride. Also, photolysis of bromide **1a** in cumene results in hydrogen abstraction and formation of **1b**. These latter experiments are thus of further interest in that the 1*H*-cyclobuta[*de*]naphthalen-1-yl radical (**4**) is an intermediate that can be readily generated.[4]

Bromide **1a** reacts efficiently with magnesium in refluxing tetrahydrofuran and with *tert*-butyllithium at −78 °C to form organometallics **1c** and **1d**, respectively. Hydrolysis of **1c** then yields 1*H*-cyclobuta[*de*]naphthalene (**1b**, 100%). Deuterium oxide converts **1c** to 1-deuterio-1*H*-cyclobuta[*de*]naphthalene (**1e**, ~76%) in which the deuterium content and location indicate that production of **1c** is at least 94% without exchange into naphthalene ring positions.[5]

Functionalization at C-1 in the 1*H*-cyclobuta[*de*]naphthalene system is readily accomplished with organometallics **1c** and **1d**.

(1) (a) Bailey, R. J.; Shechter, H. *J. Am. Chem. Soc.* **1974**, *96*, 8116. (b) Bailey, R. J.; Card, P.; Shechter, H. *Ibid.* **1983**, 105.

(2) (a) Becker, J.; Wentrup, C. *J. Chem. Soc., Chem. Commun.* **1980**, 190 have prepared **1b** by pyrolysis ($10^{-1}$–$10^{-4}$ torr) of 1- or 2-naphthyldiazomethanes at 400–500 °C generated in situ from sodium salts of 1- and 2-naphthaldehyde *p*-tosylhydrazones. (b) Engler, T. A.; Shechter, H. *Tetrahedron Lett.* **1982**, 2715 described **1b** as obtained by thermolysis of [methoxy(1- or 2-naphthyl)methyl]trimethylsilanes at 525–650 °C.

(3) Chapman, O.; *Chem. Eng. News* **1978**, Sept 18, 1978 has reported that photolysis (in matrix) of (1) 2-diazoacenaphthenone at 8 K yields 1,8-naphthyleneketene and (2) (8-hydroxy-1-naphthyl)glyoxylic acid at −195 °C results in carbon dioxide and 1*H*-cyclobuta[*de*]naphthalen-1-one (**3a**).

(4) For discussion of the mechanisms of bromination by *N*-bromosuccinimide see: (a) Dauben, H. V., Jr.; McCoy, L. L. *J. Am. Chem. Soc.* **1959**, *81*, 4863. (b) Incremona, J. H.; Martin, J .E. *Ibid.* **1970**, *92*, 627. (c) Day, J. D.; Lindstrom, M. H.; Skell, P. S. *Ibid.* **1974**, *96*, 5616. (d) References in **4a–c**.

(5) The Grignard reagent of 4-bromo-1*H*-cyclobuta[*de*]naphthalene also undergoes time-dependent isomerization to **1c**, decomposition of which with deuterium oxide yields **1e**.

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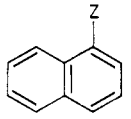
Grignard reagent **1c** effects displacement of trimethylchlorosilane and of methyl iodide to yield 1-(trimethylsilyl)-1*H*-cyclobuta[*de*]naphthalene (**1f**, 66%) and 1-methyl-1*H*-cyclobuta[*de*]naphthalene (**1g**, 60%), respectively. Carbon dioxide and acetyl chloride react normally with **1c** to give, after workup, 1*H*-cyclobuta[*de*]naphthalene-1-carboxylic acid (**1h**) and 1-acetyl-1*H*-cyclobuta[*de*]naphthalene (**1i**), respectively. Similarly, lithium reagent **1d** converts ethylene oxide to 1-(2-hydroxyethyl)-1*H*-cyclobuta[*de*]naphthalene (**1j**).

Bridged hydrocabron **1b** and derivatives **1f–j** are well-behaved thermally and can be separated and purified by usual techniques. The strain in 1*H*-cyclobuta[*de*]naphthalenes is revealed however by the ease of cleavage of their cyclobutyl moieties by catalytic hydrogenation. Thus, hydrogenation of **1d** in methanol over 10% palladium on carbon occurs rapidly at atmospheric pressure to yield 1-methylnaphthalene (**5a**, 94%). Similarly, **1f** is reduced at 40 psi to 1-[(trimethylsilyl)methyl]naphthalene (**5b**, 80%).



5a–o

5a, Z = $CH_3$
b, Z = $CH_2Si(CH_3)_3$
c, Z = CH=O
d, Z = $CH(OCH_3)_2$
e, Z = $CH(OCOCH_3)_2$
f, Z = $CH_2OCOCH_3$
g, Z = $CH_2OH$
h, Z = $CH(NR_2)_2$
i, Z = $CH_2CH(CH_3)_2$
j, Z = $CO_2CH_3$
k, Z = $CO_2K$
l, Z = $CONHC_6H_5$
m, Z = $CONHNHC_6H_3$-2,4-$(NO_2)_2$
n, Z = $CH=CH_2$
o, Z = $COCH_3$

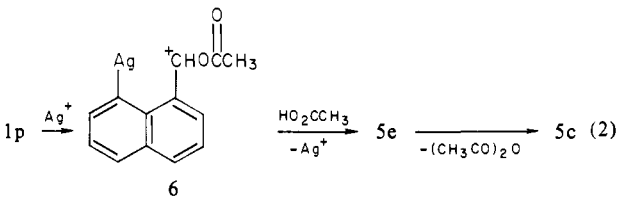
Bromide **1a** undergoes effective nucleophilic displacement at C-1. Lithium aluminum hydride and sodium bis(2-methoxyethoxy)aluminum hydride, respectively, in ethyl ether convert **1a** to **1b** near quantitatively. Analogously, potassium iodide and potassium chloride react with **1a** in acetonitrile containing traces of 18-crown-6 to form 1-halo-1*H*-cyclobuta[*de*]naphthalenes **1k** (91%) and **1l** (89%), respectively. 1-Cyano-1*H*-cyclobuta[*de*]naphthalene (**1m**, 85%) results from **1a**, potassium cyanide, and 18-crown-6 (1 equiv) in acetonitrile at ~25 °C (12 days).[6] Nitrile **1m** is an alternate entree to (1) carboxylic acid **1h** upon saponification and acidification and (2) ketone **1i** by reaction with methylmagnesium bromide and hydrolysis.

Oxygen-containing nucleophiles also effect displacement of **1a**. The initial products formed however may undergo profound change. As previously reported,[1a] solvolysis of **1a** in aqueous silver nitrate yields 1-naphthaldehyde (**5c**) as a major product presumably upon collapse of 1-hydroxy-1*H*-cyclobuta[*de*]naphthalene (**1n**). Further, sodium methoxide and **1a** in refluxing methanol and aqueous workup give 1-methoxy-1*H*-cyclobuta[*de*]naphthalene (**1o**, 18%; eq 1), the expected displacement product; 1-naphthaldehyde dimethyl acetal (**5d**) and **5c** are also formed however in 39:61 ratio in 65% yield (eq 1). Similarly, **5d** (60%)

$$\mathbf{1a} \xrightarrow[-NaBr]{NaOCH_3} \mathbf{1o} \xrightarrow[CH_3OH]{NaOCH_3} \mathbf{5d} \xrightarrow[-CH_3OH]{H_2O} \mathbf{5c} \qquad (1)$$

is obtained from sodium methoxide and **1a** in hexamethylphosphoric triamide at 75 °C (40 h) followed by aqueous workup. Acetal **5d** (and then **5c** by hydrolysis) has its origin in methoxide attack on C-1 in **1o** with ring cleavage and then protonation at C-8 (eq 1). The vulnerability of **1o** to ring opening by nucleophilic attack must be reflecting the strain in the forward section of the bridged ether.

Silver acetate in hexamethylphosphoric triamide at 75 °C converts **1a** cleanly to 1-acetoxy-1*H*-cyclobuta[*de*]naphthalene (**1p**, 93%). Silver acetate and **1a** in acetic acid at 75 °C however give α,α-diacetoxy-1-methylnaphthalene (**5e**, 65%) and aldehyde **5c** (35%). Presumably **1p** is formed from **1a** and silver acetate in hexamethylphosphoric triamide or acetic acid by processes having considerable $S_N1$ character. In acetic acid silver ion is apparently relatively poorly coordinated and thus silver ion catalyzed ring opening of **1p** possibly via **6** and solvent incorporation

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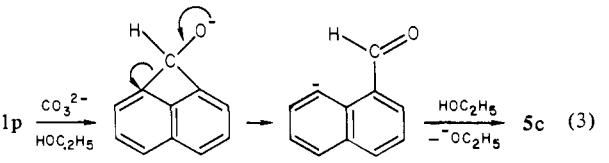
give **5e** and (thence) **5c**. The sensitivity of the 1*H*-cyclobuta[*de*]naphthalene system to silver acetate in acetic acid is revealed further by reaction of bridged hydrocarbon **1b** at 75 °C to yield 1-naphthylmethyl acetate (**5f**, 85%).[7]

Acetate **1p** is a possible precursor to cyclobutanol **1n** by hydrolysis or reductive methodology. Potassium carbonate in ethanol at 20–25 °C however converts **1p** to aldehyde **5c** (eq 3); similar

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results are obtained in acidic or other basic protic environments. Reduction of **1p** with lithium aluminum hydride in ethyl ether yields 1-naphthylmethanol (**5g**, 98%). In none of these experiments was **1n** detected. Presumably under the above conditions cyclobutoxide ion **7** collapses to **8** (eq 3) which then protonates to 1-naphthaldehyde (**5c**); in the presence of lithium aluminum hydride, **5c** is reduced to **5g**.

Ring-opened products are also formed in displacement of **1a** by amines (eq 4). Thus reaction of **1a** with piperidine at 20–25

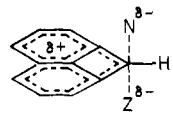
$$\mathbf{1a} \xrightarrow{HNR_2} \mathbf{1q} \xrightarrow[R_2NH_2Br]{R_2NH} \mathbf{5h} \xrightarrow{H_2O} \mathbf{5c} + HNR_2 \qquad (4)$$

°C, addition of water, and chromatography yield 1-naphthaldehyde (**5c**, 64%) and piperidine hydrobromide. Similarly, aniline and **1a** in hexamethylphosphoric triamide (90 °C, 7 days), aqueous dilution, and product isolation give **5c** and anilinium bromide. Displacement, ring opening, and hydrolysis schemes as in eq 4 rationalize the above transformations. An important feature of displacements of **1a** by methoxide, acetate, piperidine, and aniline therefore is that ring opening of the alkylation products is so facile. Such cleavage processes limit the use of nucleophilic substitution for synthesis of 1*H*-cyclobuta[*de*]naphthalenes containing highly electron-donating groups at C-1.

Azide ion is an effective nitrogen-containing nucleophile for displacement of **1a**. Thus, sodium azide in hexamethylphosphoric triamide at 20–25 °C converts **1a** to 1-azido-1*H*-cyclobuta[*de*]naphthalene (**1r**, 94%), a storable solid at −20 °C that decomposes slowly in light or at room temperature. Of note is that **1a** is 49% converted to **1r** in 20 min by sodium azide/hexamethylphosphoric triamide at 25 °C, whereas, under comparable conditions, reaction of 9-bromofluorene is 100% complete in <4 min. It is thus apparent that displacement reactions of 1*H*-cyclobuta[*de*]naphthalenes containing leaving groups at C-1 will be slowed because of the small C(1a)–C(1)–C(7a) bond angles available to its $S_N2$ (**9**) transition states.

(6) The relative reactivities for base-catalyzed deuterium exchange (triethylamine/*tert*-butyl alcohol-*d*) into the following nitriles are 9-cyanofluorene > diphenylacetonitrile > **1m** (see Experimental Section). It is apparent that steric effects lower the acidities of **1b** at C-1 because of strain increase during ionization.[7d]

(7) (a) Acetate **1p** has been demonstrated in a separate experiment to undergo slow ring opening in acetic acid at 75 °C to give **5e**. (b) Hydrocarbon **1b** is essentially inert in warm glacial acetic acid.[7d] (c) Ring opening of **1b** by perdeuterioacetic acid containing silver nitrate can be followed conveniently by NMR methods. (d) Private communication, Engler, T. A., Chemistry Department, The Ohio State University, Columbus, OH. The present authors wish to thank T. A. Engler for his contributions to the present report.



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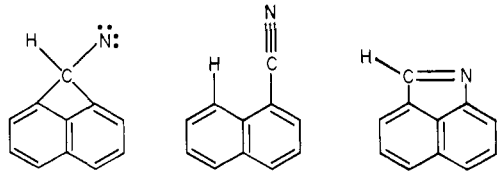
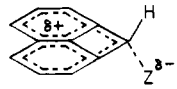
Study was then made of the decomposition reactions of **1r**. At 150 °C (0.5 h) **1r** decomposes in anhydrous hexamethylphosphoric triamide with loss of nitrogen possibly via nitrene **10** to give 1-cyanonaphthalene (**11**, 67%). Photolysis of **1r** in pentane also yields **11** (14%) along with intractables. No 1*H*-cyclobuta[*de*]-naphthalen-1-one imine (**3b**) nor benz[*ed*]indole (**12**), as yet unreported molecules, nor assignable products therefrom are observed in either experiment.



10 11 12

In a continuing effort to develop methods for forming carbon–carbon bonds at C-1 in 1*H*-cyclobuta[*de*]naphthalenes, the reactions of lithium dimethylcuprate with the 1-halo-1*H*-cyclobuta[*de*]naphthalenes **1a**, **1k**, and **1i** were investigated. The conversions to **1g** are poor however, ranging from 6 to 13%. Bromide **1a** is converted readily by silver *p*-toluenesulfonate in hexamethylphosphoric triamide at 75 °C to 1*H*-cyclobuta[*de*]-naphthalen-1-yl *p*-toluenesulfonate (**1s**, 60%) along with **5c** (17%). Displacement of **1s** by lithium dimethylcuprate then works quite well in that methylation to **1g** occurs in 71% yield. Further, **1s** and lithium diphenylcuprate at 25 °C yield 1-phenyl-1*H*-cyclobuta[*de*]naphthalene (**1t**, 56%). These latter results indicate promise for reactions of **1s** with other cuprate reagents.[8]

*p*-Toluenesulfonate **1s** is also revealing in that it is only 18% solvolyzed in acetic acid in 5 days at 75 °C to **1p** (15%) and **5c** (3%), whereas at 25 °C acetic acid converts 9-fluorenyl *p*-toluenesulfonate rapidly (53% in 5.2 min)[9a] and benzhydryl *p*-toluenesulfonate[9b] essentially instantly (too fast to measure) to their acetates. Analogously, **1a** reacts slowly with warm ethanolic silver nitrate, whereas 9-bromofluorene gives an instantaneous silver bromide precipitate. $S_N1$ reactions of 1*H*-cyclobuta[*de*]-naphthalenes with leaving groups at C-1 are thus retarded because of angle restrictions during ionization (**13**).



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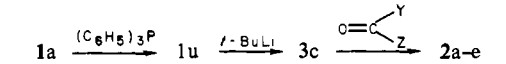
Of particular interest is that **1a** reacts efficiently with triphenylphosphine in refluxing xylenes to give 1-(triphenylphosphonio)-1*H*-cyclobuta[*de*]naphthalene bromide (**1u**, 97%, eq 5). Phosphonium salt **1u**, a white crystalline salt (mp 263–264 °C) assignable from its combustion, IR, and NMR analyses, is important because of its conversion by strong bases to (1*H*-cyclobuta[*de*]naphthalen-1-ylidene)triphenylphosphorane (**3c**, eq 5), a highly reactive phosphorous ylide. In initial study of generation of **3c**, reaction of **1u** at 20–25 °C with sodium dimsylate in dimethyl sulfoxide and then acetone produces 1-isopropylidene-1*H*-cyclobuta[*de*]naphthalene (**2a**, 48%) and **1d** (32%). Similarly, treatment of **1u** with *n*-butyllithium and then acetone yields **2a** (36%) and **1b** (44%). The origin of **2a** is obviously conversion of **1u** to **3c** and subsequent Wittig reaction with acetone (eq 5). Formation of **1b** is rationalized by nucleophilic attack of sodium dimsylate or *n*-butyllithium at phosphorous in **1u** with displacement and then protonation of the 1*H*-cyclobuta[*de*]naphthalen-1-yl carbanion. Use of a stronger less nucleophilic base should increase the yield of **2a**. Indeed, addition of *tert*-butyllithium to a suspension of **1u** in tetrahydrofuran at 0 °C and then acetone gives **2a** in 80% yield; no **1b** is observed. *tert*-Butyllithium was subsequently the base of choice for preparing **3c** as in eq 5.



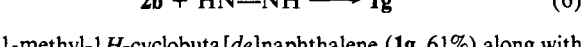
(5)

Table I. Ultraviolet Absorption Spectra of 2a–d and 1b in 95% Ethanol

| compd | $\lambda_{max}^{EtOH}$, nm (ε) | | | |
|---|---|---|---|---|
| 2b | 323 (1381) | 311 (1214) | 257 (12456) | 221 (62500) |
| 2c | 321 (932) | 309 (1619) | 258 (16621) | 218 (74324) |
| 2a | | 309 (1856) | 262 (17900) | 222 (81700) |
| 2d | 322 (13410) | 397 (22988) | 287 (25862) | 222 (79510) |
| | | | 277 (22030) | |
| 1b | | 312 (341) | 272 (4640) | 224 (69500) |

Ylide **3c** is an excellent Wittig reagent. Thus **3c** reacts smoothly with paraformaldehyde, acetaldehyde, benzaldehyde, and benzophenone to form 1-alkylidene-1*H*-cyclobuta[*de*]naphthalenes **2b–e** in yields of >70–85% (eq 5). Though highly strained, **2a–e** are quite stable, readily isolated, and satisfactorily purifiable by conventional laboratory methods. Structural assignments of **2a–e** were made from analytical and spectral (IR, NMR, and MS) data, upon consideration of the product origins and by chemical transformations to be described. Further, the increased absorptions of the transverse bands in the ultraviolet spectra of **2a–d** as compared to **1b** (Table I) indicate significant electronic interaction between the carbon–carbon double bonds and the naphthalene moieties in the 1-alkylidene-1*H*-cyclobuta[*de*]naphthalene systems.[10]

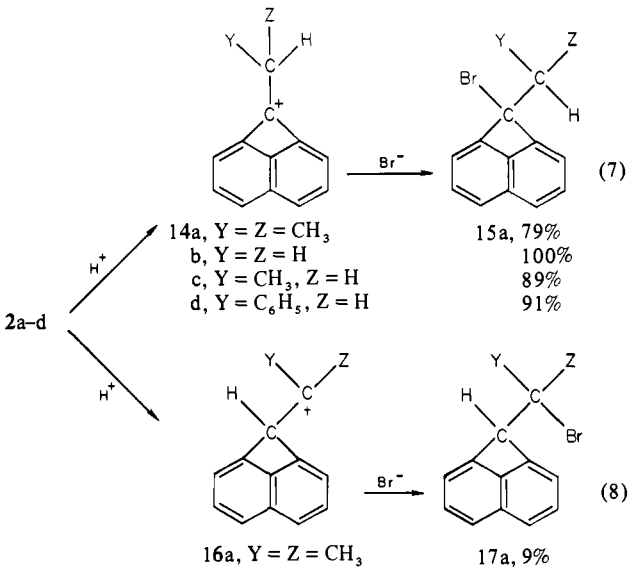
Study was then made of reduction of select 1-alkylidene-1*H*-cyclobuta[*de*]naphthalenes. Thus hydrogenation of **2a** in methanol at atmospheric pressure over 10% palladium on carbon results in saturation of the carbon–carbon double bond with reductive cleavage of the cyclobutyl ring to give 1-isobutylnaphthalene (**5i**, 96%) along with initial **2a**.[11] No 1-isopropyl-1*H*-cyclobuta-[*de*]naphthalene (**1v**) was detected under these conditions. Selective hydrogenation of the carbon-carbon double bond in **2b** (eq 6) does occur however with diimide in methanol at ~25 °C to yield 1-methyl-1*H*-cyclobuta[*de*]naphthalene (**1g**, 61%) along with recovered **2b**.[12] The method is not general since under the above conditions **2c** is unchanged. The reluctance of **2c** to undergo diimide reduction is presumably due to steric effects.



(6)

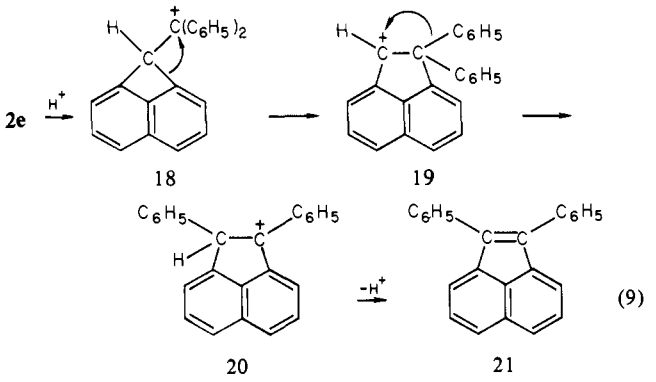
The direction of addition of hydrogen bromide to **2a–d** was then investigated as a probe of the ease of formation of carbonium ion intermediates (**14a–d**) at C-1 in the cyclobuta[*de*]naphthalene moieties as compared to the alternate primary, secondary, tertiary, and benzyl cations (**16**). The experiments were conducted by condensing hydrogen bromide into solutions of the olefin in methylene chloride at −78 °C wherein the reactions reached completion in several hours. The products appear to be of kinetic control since the compositions do not vary with reaction time and a temperature range of −78 to 25 °C. Equations 7 and 8 summarize the experimental results and illustrate that carbocations **14** are generated more rapidly and presumably are more stable than carbonium ions **16**. Only for olefin **2a** is a minor product

(8) Posner, G. H. *Org. React.* (*N.Y.*) **1975**, *22*, 253.
(9) (a) Corwell, G. W.; George, T. D.; Ledwith, A.; Morris, D. G. *J. Chem. Soc. B.* **1966**, 1169. (b) Corwell, G. W.; Ledwith, A.; Morris, D. G. *Ibid.* **1967**, 700.
(10) The chemical behavior of **2a–d** also reveals the conjugative interactions of their olefinic and naphthalenic systems.
(11) No attempt was made to find other experimental conditions or catalysts which allow hydrogenation of **2a** to **1v**.
(12) Synthesis of **1g** is effected advantageously from (1) **1s** and lithium dimethylcuprate and (2) **1c** and methyl iodide.



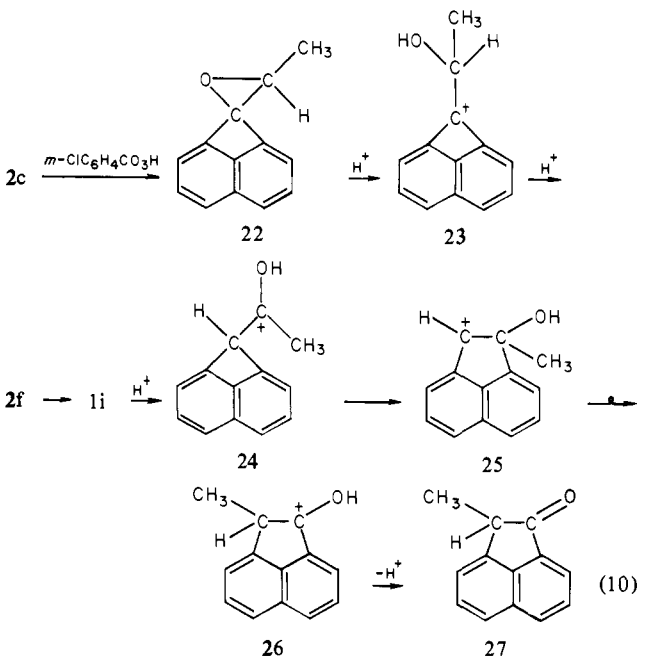

**17a** detectable, thus indicating that tertiary carbonium ion **16a** is closer in energy to C-1 cation **14a** than are the other examples. This result is also in general agreement with the known greater stabilities of tertiary over benzylic carbonium ions.

Electrophilic attack of hydrogen bromide on **2e** (eq 9) is of interest in that carbon skeleton rearrangement occurs to give 1,2-diphenylacenaphthylene (**21**)[13] almost quantitatively. The

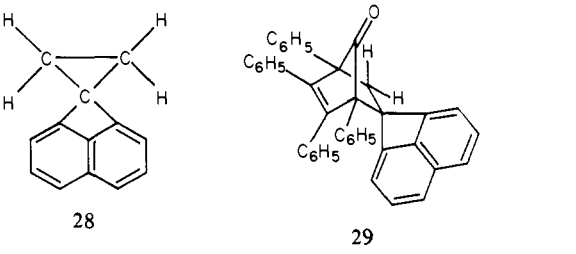



gross mechanism of rearrangement possibly involves protonation of **2e** at C-1, ring expansion of **18** to **19**, phenyl migration, and loss of a proton from **20**. Consistent with the mechanism proposal is that (1) the dark blue color of **20** persists until the hydrogen bromide is evaporated from the reaction mixture and (2) **21** does not add hydrogen bromide under the conditions for isomerization of **2e**.

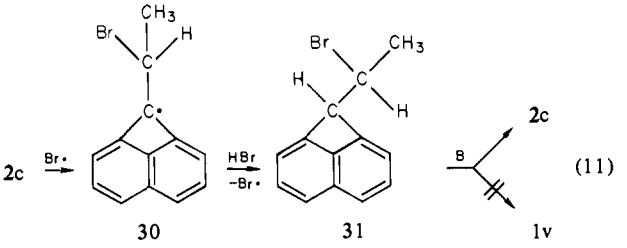
Of related interest is that epoxide **22** (3′-methylspiro[1*H*-cyclobuta[*de*]naphthalene-1,2′-oxirane]), prepared from **2c** and *m*-chloroperbenzoic acid (eq 10), is isomerized to 1-acetyl-1*H*-cyclobuta[*de*]naphthalene (**1i**) by boron trifluoride in ethyl ether at −30 °C. With precise control the rearrangement reaction is an excellent synthesis of **1i**;[14] if the reaction mixture is deliberately kept for a long period, **1i** rearranges to 2-methylacenaphthenone (**27**, 93%).[15] Further, reaction of **22** with excess boron trifluoride etherate at 25 °C in methylene chloride for 5 min yields **1i** and **27** in a ratio of 1:7. The direction of acid-catalyzed ring opening of **22** (eq 10) therefore is identical with that of electrophilic reaction of hydrogen bromide with **2c** (eq 7).




1-Alkylidene-1*H*-cyclobuta[*de*]naphthalenes (**2**) undergo other cycloaddition reactions. Thus, cyclopropanation of **2b** by methylene iodide and zinc/copper couple yields spiro[1*H*-cyclobuta[*de*]naphthalene-1,1′-cyclopropane] (**28**, 82%). Also, 1,4 addition of **2b** to tetraphenylcyclopentadienone occurs in refluxing xylenes to give 1′,4′,5′,6′-tetraphenylspiro[1*H*-cyclobuta[*de*]-naphthalene-1′,2′-[5]norbornen-7′-one] (**29**, 69%).[16] Ethylidene (**2c**) and isopropylidene (**2a**) analogues of **2b** fail however to react with tetraphenylcyclopentadienone in refluxing xylenes. Presumably steric factors in the latter systems prevent the Diels–Alder reactions from occurring.




The direction of addition of hydrogen bromide to **2c** at 24–29 °C in carbon tetrachloride containing azobis(isobutyronitrile) was then investigated. The sole product, 1-(1-bromoethyl)-1*H*-cyclobuta[*de*]naphthalene (**31**, eq 11) is assignable from its NMR

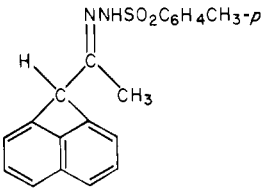



spectrum;[17] there is no evidence for the presence of **15c**. Formation of **31** may be rationalized by a homolytic mechanism as in eq 11 in which the 1-(1-bromoethyl)-1*H*-cyclobuta[*de*]naphthalen-1-yl (**30**) rather than the alternate secondary alkyl radical is formed. The orientation in initial attack on **2c** by a bromine atom parallels

(13) Richter, H. J.; Feist, W. C. *J. Org. Chem.* **1960**, *25*, 356.
(14) Prepared previously (21%) from acetyl chloride and **1c**.
(15) (a) In a separate experiment **1i** has been found to rearrange efficiently in the presence of boron trifluoride to **27**. (b) It is noted further that reactions of (1) **2d** with *m*-chloroperbenzoic acid/sodium phosphate buffer at 0 °C yields 3′-phenylspiro[1*H*-cyclobuta[*de*]naphthalene-1,2′-oxirane] (99%, mp 131–133 °C) and (2) **2e** and unbuffered *m*-chlorobenzoic acid at 0 °C results in 2,2-diphenylacenaphthenone (94%).
(16) Adduct **29** is assigned from its analysis and its IR, NMR, and MS properties.
(17) Bromide **31** displays a large doublet ($CH_3$) at $\delta$ 1.78, a doublet (bridge H) at $\delta$ 5.40 and a doublet of quartets ($H_\alpha$ to bromine) and is of proper IR absorption.

that of hydrogen ion (eq 7), thus implying that the stabilizations in **30** and **14c** are greater than in their secondary alkyl counterparts.

Bromide **31** is of interest as a source of 1-vinyl-1*H*-cyclobuta[*de*]naphthalene (**1v**, eq 11). Elimination of **31** with the highly hindered bases: 1,5-diazabicyclo[5.4.0]undec-5-ene, potassium triethylcarbinoxide, and lithium 2,2,6,6-tetramethylpiperidide, respectively, gives **2c** (eq 11) cleanly however. No **1y** was de-



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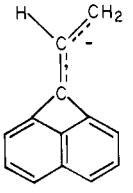

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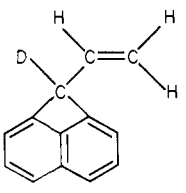
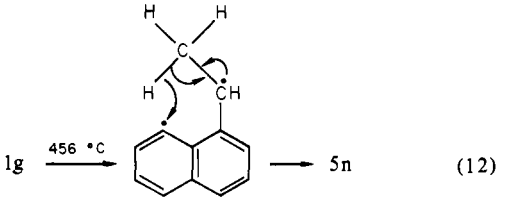


34

tected. Further, reaction of 1-acetyl-1*H*-cyclobuta[*de*]naphthalene *p*-tosylhydrazone (**32**) with *tert*-butyllithium (2 equiv) at −78 °C and then at 20–25 °C yields **2c** (21%).[18] Efforts to isomerize **2c** to **1y** were also unsuccessful. Thus, treatment of **2c** with *tert*-butyllithium at −78 °C generates the expected allyl anion **33** which when quenched with deuterium oxide gives only 1-(ethylidene-2-*d*)-1*H*-cyclobuta[*de*]naphthalene (**2g**). The alternate product 1-deuterio-1-vinyl-1*H*-cyclobuta[*de*]naphthalene (**34**) is not obtained. The absence of **1v** and **34** in these experiments reveals the dominance of naphthalene conjugation with the double bond of the bridging atom in **2c** even though the systems are highly strained.

Study was then made of the thermal behavior of varied 1*H*-cyclobuta[*de*]naphthalenes (**1**) and 1-alkylidene-1*H*-cyclobuta[*de*]naphthalenes (**2**). Passage of **1g** through a hot tube at 456 °C (0.1 mm) yields 1-vinylnaphthalene (**5n**, 80%, eq 12) quite



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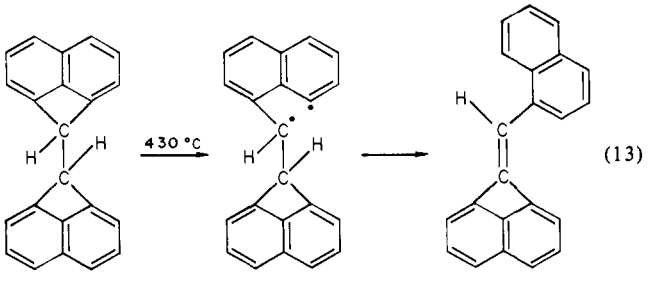
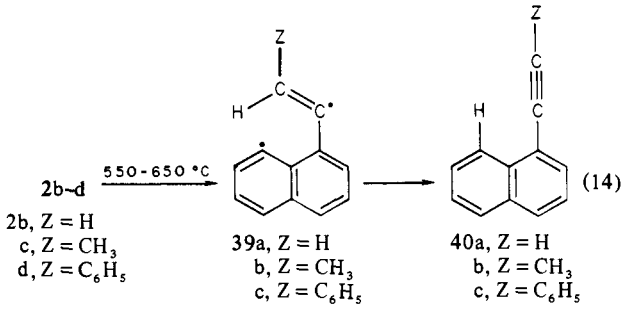
efficiently. The thermal rearrangement of **1g** possibly occurs via homolytic ring cleavage to 1,4-diradical **35** and subsequent hydrogen transfer through a six-membered cyclic transition state to give **5n**. Similarly, 1,1-bi-1*H*-cyclobuta[*de*]naphthalene (**36**), formed (60%) along with **1d** from **1a** and aqueous zinc-silver couple, isomerizes at 430 °C, possibly as in eq 13, to 1-(1-naphthylidene)-1*H*-cyclobuta[*de*]naphthalene (**38**, 64%).[19] Bridged olefin **38** is assigned upon preparation of an identical product by Wittig reaction of **3c** with **5c**.



36 37 38

1-Alkylidene-1*H*-cyclobuta[*de*]naphthalenes such as **2b–d**, though more stable thermally than their 1-alkyl analogues (**1b,g,f**), isomerize at sufficiently high temperatures to acetylenic naphthalenes. Thus, **2b** and **2c** rearrange at 550 °C (0.1 mm) to 1-ethynylnaphthalene (**40a**, 73%, eq 14) and 1-(1-propynyl)-naphthalene (**40b**, 100%, eq 14),[20] respectively. Similarly, **2d** converts at 650 °C (0.1 mm) to 1-(phenylethynyl)naphthalene (**40c**, 66%, eq 14). Homolytic collapse and (six-membered ring) transfer of hydrogen in 1,4-diradicals **39a–c** will account for the pyrolysis products.[21]



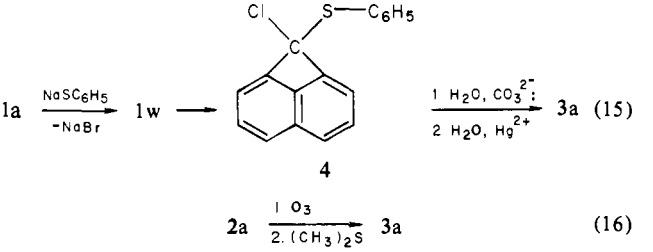
(14)

2b, Z = H
c, Z = $CH_3$
d, Z = $C_6H_5$

39a, Z = H
b, Z = $CH_3$
c, Z = $C_6H_5$

40a, Z = H
b, Z = $CH_3$
c, Z = $C_6H_5$

**Synthesis and Chemistry of 3a.** Synthesis and study of bridged ketone **3a** then became a major area of investigation. Ketone **3a** is obtainable, although in poor yields (~5–12%), by reaction of 1-(thiophenoxy)-1*H*-cyclobuta[*de*]naphthalene (**1w**, prepared in 90% yield from **1a** and sodium thiophenoxide) with *N*-chlorosuccinimide (NCS) and hydrolysis of the resulting 1-chloro-1-(thiophenoxy)-1*H*-cyclobuta[*de*]naphthalene (**41**, 93%, eq 15) with



(15)

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(16)

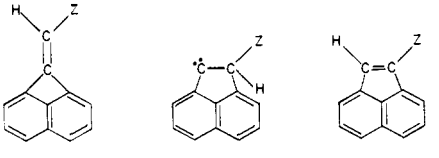
either aqueous sodium carbonate, aqueous mercuric chloride/cadmium carbonate, or chloramine-T (ClAm-T) in aqueous methanol. Ozonolysis of olefin **2a** in ethyl acetate and decomposition of the resulting ozonide with dimethyl sulfide[22] however give **3a** efficiently (71% conversion, eq 16) along with recovered **2a** (29%). Combustion analysis, mass spectroscopy (*m/e* 154), IR absorption at 1775 $cm^{-1}$ (C=O, four-membered ring), NMR absorptions at $\delta$ 7.34 (d of d, 2 H, ortho), and 7.5–7.9 (m, 4 H, meta and para), and a $^{13}C$ NMR spectrum consisting of seven lines confirm the structure of **3a**. Ketone **3a** exhibits a $^{13}C$ chemical shift of 178.2 ppm for C-1. Strained alicyclic ketones typically display carbonyl $^{13}C$ shifts in the range of 208–215 ppm;[23] the cyclobutanone $^{13}C$ carbonyl absorption shift is 208.2 ppm.[23] The large upfield shift (178.2 ppm) for C-1 in **3a** is probably the result of strain and of conjugative effects.

The strain in **3a** is also revealed by its rapid ring-opening reactions. Thus, methanol converts **3a** at 20–25 °C (1 h) to methyl 1-naphthoate (**5i**, 69%). Formation of **5i** is rationalized by addition of methanol to the carbonyl group of **1a** to form hemiketal **42**

(18) Much of the literature of this synthetic method has been summarized by: Shapiro, R. H. *Org. React. (N.Y.)* **1976**, *23*, 405.

(19) Bis(1-naphthyl)acetylene, as possibly produced by thermal rearrangement of **36** (an extension of the isomerizations of eq 12), is not found under the conditions indicated.

(20) Processes of the type shown below were not detected:

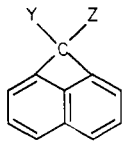


(21) To our knowledge the behavior of such 1,4-diradicals is novel.

(22) (a) Ozonolysis of **3c** also yields **3a**. (b) The method of Chang, C. W. J.; Iyer, K. N.; Pelletier, S. W. *J. Org. Chem.* **1970**, *35*, 3535.

(23) Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972.

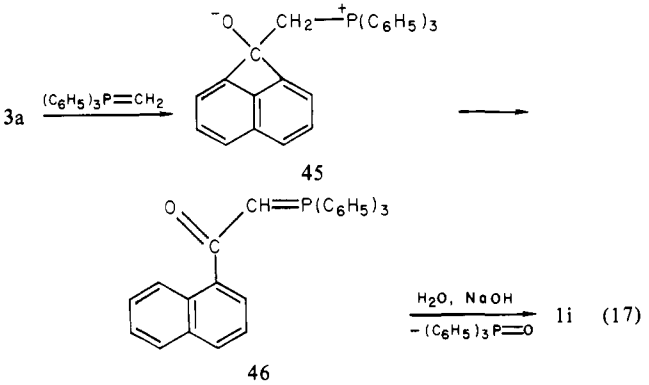
which then undergoes ring opening with proton transfer. Base-catalyzed hydrolysis of **3a** also results in ring cleavage in that reaction with potassium hydroxide in hexamethylphosphoric triamide at 20–25 °C gives potassium 1-naphthoate (**5k**, 88%), presumably via **43**.



42, Y = OH, Z = $OCH_3$
43, Y = OK, Z = $OCH_3$
44, Y = OH, Z = $NHC_6H_5$

The behavior of **3a** with nitrogen nucleophiles was then studied. Refluxing **3a** and aniline in benzene yields 1-naphthanilide (**51**, 81%). Formation of **51** possibly occurs via attack at C-1 in **3a** to give hemiaminal **44** which then rearranges. Attempts to prepare carbonyl derivatives of **3a** also lead to ring-opened products. Thus, **3a** reacts with (2,4-dinitrophenyl)hydrazine in ethanol or concentrated sulfuric acid to form 1-naphthoyl (2,4-dinitrophenyl)-hydrazide (**5m**).

Ketone **3a** is potentially useful for preparing bridged olefins such as **2** via Wittig reactions. Reaction of **3a** however with methylenetriphenylphosphorane in tetrahydrofuran results in ring opening and proton transfer yielding ylide **47** (eq 17). No **2b** was observed. The structure of **47** is established upon hydrolysis with sodium hydroxide to 1-acetonaphthalene (**1i**, eq 17).



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The photochemistry of **3a**[24] and various electrophilic substitution and addition reactions of **1b** will be reported subsequently.

## Experimental Section

**Reaction of 1b with *N*-Bromosuccinimide.** A suspension of *N*-bromosuccinimide (720 mg, 4 mmol) in carbon tetrachloride (15 mL) and **1b** (140 mg, 1 mmol) containing a small amount of benzoyl peroxide was refluxed 4.5 h under nitrogen, cooled, and filtered. The filtrate was extracted with saturated aqueous potassium carbonate and water, dried ($MgSO_4$), and concentrated. NMR revealed that the residue (147 mg), after purification on silica gel (hexane as eluent), contained bromide **1a**[1] (40% conversion) and initial **1b** (56% recovery).

**Photolysis of 1a in Cumene.** A solution of **1a** (55 mg, 0.25 mmol) in cumene (5 mL), after purging with nitrogen, was irradiated through quartz with a 450-W Hanovia high-pressure mercury arc lamp for 45 min. GC analysis (10% SF-96 on Chromosorb W) revealed that **1a** was completely consumed and **1b**[1] (60% relative to an internal standard) was the only volatile product.

**Reaction of 1a with *tert*-Butyllithium in Tetrahydrofuran.** *tert*-Butyllithium (1.6 mmol) in hexane was added to **1a** (52.5 mg, 0.375 mmol) in tetrahydrofuran (5 mL) at room temperature. The mixture was stirred 1 h and quenched with deuterium oxide. The hydrocarbon product isolated (40 mg, 76%) was a 94:6 mixture of 1-deuterio-1*H*-cyclobuta-[*de*]naphthalene (**1e**) and **1a** (NMR analysis). The **1e** is essentially identical with the hydrocarbon obtained by reduction of **1a** with lithium aluminum deuteride as described later.

**1-(Trimethylsilyl)-1*H*-cyclobuta[*de*]naphthalene (1f).** Chlorotrimethylsilane (6.9 g, 5.0 mL, 64 mmol) in tetrahydrofuran (25 mL) was added to Grignard reagent **1c** as prepared from sublimed magnesium (0.53 g, 22 mmol) and **1a** (4.38 g, 20 mmol) in refluxing tetrahydrofuran (75 mL).[25] After the resulting mixture had been refluxed 48 h, cooled, hydrolyzed with saturated aqueous ammonium chloride, and separated, the organic portion was washed with 10% hydrochloric acid and saturated aqueous sodium chloride, dried, and concentrated. Distillation of the oily residue (3.1 g) yielded a mixture (2.8 g) of **1f** and **1b**, bp 95–101 °C (1.15 mm).

Separation and isolation of the product by VPC (5% SE-30 on Chromosorb W) gave the following: (1) **1f** (66%)[26] as a semisolid: NMR ($CDCl_3$, $\delta$) 0.01 (s, 9 H, $Si(CH_3)_3$), 4.77 (s, 1 H, bridge), 6.94 (d of d, 2 H, $J$ = 5 and 2 Hz, ortho), 7.3–7.5 (m, 4 H, meta and para); $^{13}C$ NMR ($CDCl_3$, $\delta$) 54.52 (1 C, $C_1$, $J_{^{13}C-H}$ = 131.8 Hz), 116.7 (2 C, $C_{2,7}$), 120.88 (2 C, $C_{4,5}$), 124.98 (1 C, $C_9$), 130.37 (2 C, $C_{3,6}$), 143.81 (2 C, $C_{1a,7a}$), 146.33 (1 C, $C_8$), 2.50 (3 C, $Si(CH_3)_3$); exact mass, *m/e*(calcd) 212.1021, *m/e*(obsd) 212.1020. Anal. Calcd for $C_{14}H_{16}Si$: C, 79.18; H, 7.59. Found: C, 79.22; H, 7.59. (2) **1b** (15%): identical with an authentic sample.

**1-Methyl-1*H*-cyclobuta[*de*]naphthalene (1g).** Methyl iodide (4.54 g, 32 mmol) was syringed into **1c** prepared from **1a** (1.1 g, 5 mmol), magnesium (0.12 g, 5 mmol), and tetrahydrofuran (25 mL). The mixture was refluxed 48 h, cooled, hydrolyzed, and extracted with ethyl ether. Workup and concentration of the ether extract and molecular distillation of the residue gave a volatile colorless liquid mixture (650 mg) of **1g** (~60%) and **1b** (~15%) as determined by NMR ($CDCl_3$, $\delta$) methods: 1.67 (d, $J$ = 7 Hz, $CH_3$), 4.8 (s, bridge proton of **2**), 5.15 (q, $J$ = 7 Hz, bridge proton of **11**), 6.88–6.70 (d of d, ortho protons), and 7.1–7.5 (m, meta and para). Identification of **1g** was confirmed by comparison with the product from tosylate **1g** and lithium dimethylcuprate as subsequently described.

**1*H*-Cyclobuta[*de*]naphthalene-1-carboxylic Acid (1h).** Carbon dioxide was passed into **1c** prepared from **1a** (440 mg, 2 mmol) and magnesium (50 mg, 2 mmol) in ethyl ether. The mixture was acidified with hydrochloric acid (10%) and extracted with benzene. The benzene layer was washed with water and extracted with aqueous sodium hydroxide. Acidification of the alkaline extract with concentrated hydrochloric acid gave **1h** (110 mg, 30%): a colorless solid; mp 158.5–160 °C;[26] NMR (acetone-$d_6$, $\delta$) 5.97 (s, 1 H, bridge), 7.18 (d of d, 2 H, $J$ = 5 and 2 Hz, ortho) 7.35–7.68 (m, 4 H, aromatic); exact mass, *m/e*(calcd) 184.0524, *m/e*(osd) 184.0528. Anal. Calcd for $C_{12}H_8O_2$: C, 78.25; H, 4.38. Found: C, 77.62; H, 4.21.

Esterification of **1h** (40 mg, 0.217 mmol) in ethyl ether (20 mL) with excess alcoholic ethereal diazomethane, product workup, and chromatography on silica gel with hexane/ethyl ether as eluent yielded methyl 1*H*-cyclobuta[*de*]naphthalene-1-carboxylate (42 mg, 98%):[26] a water-white liquid; NMR ($CDCl_3$, $\delta$) 3.77 (s, 3 H, $CH_3$), 5.94 (s, 1 H, bridge), 7.19 (d of d, 2 H, $J$ = 5 and 2 Hz, ortho), 7.41–7.74 (m, 4 H, aromatic); exact mass, *m/e*(calcd) 198.0680, *m/e*(obsd) 198.0684.

**1-Acetyl-1*H*-cyclobuta[*de*]naphthalene (1i).** Grignard reagent **1c**, prepared from **1a** (110 mg, 0.5 mmol) and magnesium (13 mg, 0.5 mmol) in ethyl ether (15 mL), was syringed into acetyl chloride (1 mL) in ethyl ether (10 mL) at 0 °C. The mixture was stirred at 0 °C for 30 min and then overnight at 20–25 °C and poured into water, and the organic product was dried, concentrated, and chromatographed (VPC on 10% SF-96 on Chromosorb W) to give **1i** (21%) as separated from a six component mixture: NMR ($CDCl_3$, $\delta$) 23 (s, 3 H, $CH_3$), 5.88 (s, 1 H, bridge), 7.09–7.27 (d of d, 2 H, ortho), 7.34–7.76 (m, 4 H, aromatic); exact mass, *m/e*(calcd) 182.0731, *m/e*(obsd) 182.0734.[26,27] Anal. Calcd for $C_{13}H_{10}O$: C, 85.69; H, 5.53. Found: C, 85.70; H, 5.66.

**1-(2-Hydroxyethyl)-1*H*-cyclobuta[*de*]naphthalene (1j).** Ethylene oxide (5 mL) was added under nitrogen to a solution of **1d** at −78 °C prepared by syringing *tert*-butyllithium (1.1 equiv) to **1a** (220 mg, 1 mmol) in tetrahydrofuran (50 mL). After being stirred at −78 °C for 10 min, the mixture was warmed slowly to room temperature and concentrated. The residue, on chromatography on silica gel (hexane/benzene as eluent) gave the following: (1) **1b** (25 mg, 18%), identical with an authentic sample and (2) **1j**: 95 mg (51%),[27] NMR ($CDCl_3$, $\delta$) 1.96 (br s, 1 H, OH), 2.30 (q, 2 H, $J$ = 6 Hz, $CH_2$ attached to bridge), 3.85 (t, 2 H, $J$ = 6 Hz, $CH_2$ near hydroxyl), 5.32 (t, 1 H, $J$ = 6 Hz, bridge), 7.07 (d of d, 2 H, $J$ = 2 and 4 Hz, ortho), 7.2–7.7 (m, 4 H, meta and para); exact mass for $C_{13}H_{12}O$, *m/e*(calcd) 183.0810, *m/e*(obsd) 183.0815. Anal. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.57. Found: C, 84.38; H, 6.51.

**Hydrogenation of 1d.** Hydrogenation (20 psi) of **1d** (48 mg, 0.34

(24) Decarbonylation of **3a** occurs at 180–350 °C and upon photolysis.

(25) All reaction solvents used in this research were dried and purified.
(26) The IR absorptions of all such compounds are recorded in the Ph.D. Thesis of Card, P. J., The Ohio State University, Columbus, OH.
(27) (a) From the Ph.D. Thesis of Frideli, F. E., The Ohio State University, Columbus, OH. (b) IR absorptions are recorded therein.

mmol) for 2 h in methanol (50 mL) containing 10% palladium on carbon as catalyst, filtration through Celite, and concentration of the mixture gave a colorless liquid (45 mg, 94%) which NMR revealed to be 1-methylnaphthalene (**5a**, >96%; compared with an authentic sample) and **4** (<4%).

**Hydrogenation of 1f.** A mixture of **1f** (160 mg, 0.75 mmol) and methanol (45 mL) containing 10% palladium on carbon was hydrogenated (Parr apparatus) at 40 psi for 3 h. Filtration (Celite), concentration, and preparative VPC (12.5% QF-1 on Chromosorb W) yielded 1-[(trimethylsilyl)methyl]naphthalene (**5b**):[26] 130 mg (80%); NMR ($CDCl_3$, $\delta$) 0.05 (s, 9 H, $Si(CH_3)_3$), 2.62 (s, 2 H, $CH_2$), 7.1–8.1 (m, 7 H, aromatic); exact mass, *m/e*(calcd) 214.1177, *m/e*(obsd) 214.1181. Anal. Calcd for $C_{14}H_{18}Si$: C, 78.44; H, 8.46. Found: C, 78.50; H, 8.57.

**Reduction of 1-Bromo-1*H*-cyclobuta[*de*]naphthalene (1a) with Sodium Bis(2-methoxyethoxy)aluminum Hydride.** Red-al (20 mL, a 70% solution of sodium bis(2-methoxyethoxy)aluminum hydride in benzene) in ethyl ether (30 mL) was added to **1a** (4.4 g, 20 mmol) in anhydrous ethyl ether (50 mL) at a rate to maintain reflux, and the solution was then refluxed overnight. The mixture was cooled and hydrolyzed with saturated sodium sulfate. The ethereal layer was extracted with water and saturated sodium chloride, dried, and concentrated to yield colorless 1*H*-cyclobuta[*de*]naphthalene (**1b**), 2.75 g (98%). Vacuum distillation gave **1b**, bp 62–63 °C (0.24 mm) whose NMR, IR, and VPC properties (QF-1 on Chromosorb W) are identical with an authentic sample.[26]

Addition of **1b** (440 mg, 2 mmol) in hot ethanol (10 mL) to picric acid (460 mg, 2 mmol) in hot ethanol (10 mL) and allowing the mixture to cool to room temperature, washing the precipitate (100%) formed with cold ethanol, and recrystallization of the product from ethyl ether at −78 °C yielded 1*H*-cyclobuta[*de*]naphthalene picrate as bright yellow needles, mp 151–153 °C. Anal. Calcd for $C_{17}H_{11}N_3O_7$: C, 55.29; H, 3.00. Found: C, 55.30; H, 2.92.

**1-Deuterio-1*H*-cyclobuta[*de*]naphthalene (1e).** Reaction of **2** (219 mg, 1.0 mmol) in ethyl ether (5 mL) with lithium aluminum deuteride (42 mg, 1 mmol) in ethyl ether (5 mL), hydrolysis of the mixture with aqueous sodium sulfate, and product isolation gave a yellow oil (101 mg) whose NMR spectrum revealed that 72% deuteride displacement had occurred. VPC of the product (as for **1b**) yielded pure **1e**:[26] NMR ($CDCl_3$, $\delta$) 4.80 (s, 1 H, bridge), 7.1 (d of d, 2 H, $J$ = 5 and 2 Hz), 7.25–7.65 (m, 4 H); mass spectrum for $C_{11}H_7D$, *m/e*(calcd) 141.0688, *m/e*(found) 141.0690.

**1-Iodo-1*H*-cyclobuta[*de*]naphthalene (1k).** A mixture of **1a** (640 mg, 2.9 mmol), potassium iodide (1.5 g, 9 mmol) and a catalytic amount of 18-crown-6 in acetonitrile (30 mL) was refluxed 60 h, concentrated, and taken up in pentane. Chromatography on silica gel using pentane as eluent gave **1k** (710 mg, 91%): a colorless solid; mp 101–104 °C;[26] NMR ($CDCl_3$, $\delta$) 6.76 (s, 1 H, bridge), 7.03 (d of d, 2 H, $J$ = 5 and 2 Hz, ortho), 7.32–7.66 (m, 4 H, meta and para); $^{13}C$ NMR ($CDCl_3$, $\delta$) 144.2 (2 C, $C_{1a,7a}$), 143.8 (1 C, $C_8$), 131.4 (2 C, $C_{3,6}$), 126.0 (1 C, $C_9$), 122.5 (2 C, $C_{4,5}$), 115.7 (2 C, $C_{2,7}$), 21.5 (1 C, $C_1$); exact mass, *m/e*(calcd) 265.9594, *m/e*(obsd) 265.9598. An analytical sample was obtained by sublimation at 75–80 °C (0.2 mm), mp 101–104 °C. Anal. Calcd for $C_{11}H_7I$: C, 49.65; H, 2.65. Found: C, 49.59; H, 2.70.

**1-Chloro-1*H*-cyclobuta[*de*]naphthalene (1l).** A solution of **1a** (220 mg, 1.0 mmol), acetonitrile (50 mL), potassium chloride (1 g), and 18-crown-6 ether (20 mg) was refluxed 10 days, then poured into water, and extracted with ether. The ethereal layer was dried ($MgSO_4$) and the solvent removed under reduced pressure to yield **1l**, 155 mg (89%).[26] Sublimation at 50 °C (0.3 mm) gave an analytical sample: mp 65–67 °C; NMR ($CDCl_3$, $\delta$) 6.77 (s, 1 H, bridge), 7.18 (d of d, 2 H, $J$ = 5 and 2 Hz, ortho), 7.3–7.7 (m, 4 H, meta and para); $^{13}C$ NMR ($CDCl_3$, $\delta$) 66.050 (1 C, $C_1$), 115.934 (2 C, $C_{2,7}$), 123.023 (2 C, $C_{4,5}$), 126.251 (1 C, $C_9$), 131.276 (2 C, $C_{3,6}$), 143.729 (2 C, $C_{1a,7a}$), 145.282 (1 C, $C_8$); exact mass for $C_{11}H_7Cl$, *m/e*(calcd) 174.0236, *m/e*(obsd) 174.0240. Anal. Calcd for $C_{11}H_7Cl$: C, 75.66; H, 4.04. Found: C, 75.57; H, 4.02.

**1-Cyano-1*H*-cyclobuta[*de*]naphthalene (1m).** Dry potassium cyanide (500 mg) was added to **1a** (220 mg, 1 mmol) and 18-crown-6 ether (300 mg) in acetonitrile (15 mL), and the mixture was stirred vigorously at room temperature for 12 days. The dark solution was poured into water and extracted with ethyl ether. After the ethereal layer was dried and the solvent was removed under reduced pressure, the residue was passed through silica gel while eluting with benzene to give **1m**: 140 mg (85%);[27] mp 127.5–129.5 °C; NMR ($CDCl_3$, $\delta$) 5.81 (s, 1 H, bridge), 7.25 (d of d, 2 H, $J$ = 2 and 5 Hz, ortho), 7.5–7.7 (m, 4 H, meta and para); $^{13}C$ NMR ($CDCl_3$, $\delta$) 45.684 (1 C, $C_1$), 117.342 (2 C, $C_{2,7}$), 123.314 (2 C, $C_{4,5}$), 126.130 (1 C, $C_9$), 131.130 (2 C, $C_{3,6}$), 137.005 (1 C, $C_8$), 146.423 (2 C, $C_{1a,7a}$); exact mass for $C_{12}H_7N$, *m/e*(calcd) 165.0578, *m/e*(obsd) 165.0582. Anal. Calcd for $C_{12}H_7N$: C, 87.25; H, 4.27. Found: C, 86.96; H, 4.39.

**Deuterium Exchange into 1m, Diphenylacetonitrile, and 9-Cyanofluorene.** Each nitrile (0.10 mmol) was dissolved in *tert*-butyl alcohol-*d* (0.50 mL) and placed in a NMR tube, and its reference spectrum was determined immediately. A standard solution (0.50 mL of a solution of 200 μL of triethylamine in 2.0 mL of *tert*-butyl alcohol-*d*) was then added to each of the sample solutions. The progress of each reaction at 20 °C was monitored by NMR at selected time intervals. The percentage deuterium exchange (%) into **1m** with time (h) is 4 (0.016), 17 (1.25), 19 (4), 25 (20), 30 (40), 44 (75), 57 (150), and 77 (190). The deuterium exchange (%) into diphenylacetonitrile with time (min) is 10 (1), 15 (3), 21 (5), 30 (10), 34 (25), 37 (40), 45 (75), 60 (240), 68 (360), 88 (1200), and 96 (2400). Deuterium incorporation (%) into 9-cyanofluorene as a function of time (min) is 33 (3), 52 (10), 60 (25), 71 (240), 94 (1200), and 100 (4500).[27]

**Hydrolysis of 1m.** A solution of **1m** (55 mg, 0.33 mol), sodium hydroxide (0.1 g), water (20 mL), and ethanol (20 mL) was refluxed 2.5 h, acidified, and extracted with ethyl ether. After the ethereal extract was dried and concentrated the residue was passed through silica gel (benzene as eluent) to yield, after solvent removal, carboxylic acid **1h** (>20 mg, >32%), identical with an authentic sample.[27]

**Reaction of 1m with Methylmagnesium Bromide.** Methylmagnesium bromide (2 mL of a 1.3 M solution in ethyl ether) was syringed into **1m** (250 mg, 1.5 mmol) in tetrahydrofuran (25 mL). After having been refluxed 12 h under nitrogen and 10% hydrochloric acid had been added, the mixture was refluxed 3 h, neutralized with sodium bicarbonate and extracted with ethyl ether. Workup of the organic extract and chromatography through silica gel (benzene as eluent) yielded methyl ketone **1i** (50 mg, 18%), identical with the previous sample.[27]

**Reaction of 1a with Sodium Methoxide. A.** A mixture of **1a** (1.1 g, 5 mmol) and sodium methoxide (1.35 g, 25 mmol) in methanol (50 mL) was refluxed 50 h, cooled, and concentrated. Upon solution of the residue in ethyl ether and drying and concentrating the organic extract, the residue was passed through silica gel (hexane as eluent) and separated by HLPC (30–60 °C petroleum ether as eluent) into the following fractions: (1) Recovered **1a** (88 mg, 8%): identical with initial material. (2) 1-Methoxy-1*H*-cyclobuta[*de*]naphthalene (**1o**):[26] 140 mg (18%),[28] a colorless oil; NMR ($CDCl_3$, $\delta$) 3.42 (s, 3 H, O-$CH_3$), 6.64 (s, 1 H, bridge), 7.2 (d of d, 2 H, $J$ = 5 and 2 Hz, ortho), 7.44–7.7 (m, 4 H, meta and para); exact mass, *m/e*(calcd) 170.0731, *m/e*(obsd) 170.0733. (3) An oil (500 mg) which NMR analysis revealed to be a 61:39 mixture of 1-naphthaldehyde (**5c**) and 1-naphthaldehyde dimethyl acetal (**5d**). Treatment of the mixture with (2,4-dinitrophenyl)hydrazine reagent yielded 1-naphthaldehyde (2,4-dinitrophenyl)hydrazone in 65% overall yield;[29] mp 250–253 °C.

**B.** The solution from reaction of **1a** (220 mg, 1 mmol) and sodium methoxide (60 mg, 1 mmol) in hexamethylphosphoric triamide (5 mL) at 75 °C for 40 h was poured into water and extracted with ethyl ether. Workup, concentration, and chromatography (silica gel with 2:1 hexane/benzene as eluent) of the products yielded: (1) Recovered **1a** (55 mg, 25%) and (2) **5c** (93.5 mg, 60%): identified by comparison with an authentic sample.

**Reaction of 1a with Silver Acetate. A.** Silver acetate (900 mg, 5 mmol), **1a** (1.1 g, 5 mmol), and anhydrous sodium acetate (1.0 g, 12.5 mmol) were heated in hexamethylphosphoric triamide (40 mL) for 24 h at 75 °C. The mixture was poured into water and extracted with ethyl ether. The organic product was washed with water, dried ($MgSO_4$), concentrated (380 mg of residue), and separated on a silica gel column (2:1 hexane/benzene as eluent) as follows: (1) Unreacted **1a**: 80 mg (7.3%), compared with authentic **1a**. (2) 1-Acetoxy-1*H*-cyclobuta[*de*]-naphthalene (**1p**):[26] 850 mg (93%);[28] bp 85–90 °C (0.15 mm); NMR ($CDCl_3$, $\delta$) 2.05 (s, 3 H, $OCOCH_3$), 7.0–7.28 (m, 3 H, ortho and bridge), 7.34–7.67 (m, 4 H, meta and para); $^{13}C$ NMR ($CDCl_3$, $\delta$) 170.6 (1 C, C=O), 146.8 (1 C, $C_8$), 143.0 (2 C, $C_{1a,7a}$), 130.9 (2 C, $C_{3,6}$), 126.1 (1 C, $C_9$), 122.8 (2 C, $C_{4,5}$) 117.0 (2 C, $C_{2,7}$) 84.7 (1 C, $C_1$) 20.8 (1 C, $CH_3$); exact mass, *m/e*(calcd) 198.0680, *m/e*(obsd) 198.0684.

1-Acetoxy-1*H*-cyclobuta[*de*]naphthalene picrate was prepared as a derivative of **1p** as follows. Acetate **1p** (100 mg, 0.5 mmol) in benzene (2 mL) was added to picric acid (115 mg, 0.5 mmol) in benzene (3 mL), and the resulting green-yellow solution was evaporated overnight. The yellow precipitate (100%) that formed, on recrystallization from ethyl ether at −78 °C, melted at 113–115 °C. Anal. Calcd for $C_{19}H_{13}N_3O_9$: C, 53.40; H, 3.06. Found: C, 53.34; H, 3.10.

**B.** The mixture from **1a** (440 mg, 2 mmol) and silver acetate (340 mg, 2 mmol) in glacial acetic acid (20 mL) at 75 °C for 39 h was worked up as in the previous experiment. Column chromatography on silica gel (4:1 hexane/ethyl acetate as eluent) gave as follows: (1) initial **2** (70 mg, 16%), (2) aldehyde **5c** (90 mg, 35%;[28] identical with an authentic sam-

(28) The yield reported is based on the prime reagent which has reacted (initial reactant minus recovered reactant).

(29) Identical with an authentic sample.

ple), and (3) $\alpha,\alpha$-diacetoxy-1-methylnaphthalene (**5e**) [270 mg (65%);[28] mp 106–108.5 °C as purified by sublimation at 100 °C (0.2 mm); IR (KBr, $cm^{-1}$) 1760, 1740 (C=O), 1400, 1240, 1210 (C—O); NMR ($CDCl_3$, $\delta$) 2.09 (s, 6 H, $OCOCH_3$), 7.32–7.88 (m, 6 H, aromatic), 8.1–8.25 (m, 2 H, 1 aromatic and H—$C(OAc)_2$); exact mass, *m/e*(calcd) 258.0891, *m/e*(obsd) 258.0896]. Anal. Calcd for $C_{15}H_{14}O_4$: C, 69.75; H, 5.46. Found: C, 70.00; H, 5.44.

**Reaction of 1b with Silver Acetate in Acetic Acid.** Heating **1b** (70 mg, 0.5 mmol) and silver acetate (83 mg, 0.5 mmol) in glacial acetic acid (3 mL) at 75 °C for 16 h, addition of water, extraction with ethyl ether, and standard workup yielded 1-naphthylmethyl acetate (**5f**, 84.5 mg, 85%) as a colorless oil identical with an authentic sample: NMR ($CDCl_3$, $\delta$) 2.03 (s, 3 H, $CH_3$), 5.53 (s, 2 H, $CH_2$), 7.34–8.09 (m, 7 H, aromatic).

**Reaction of 1-Acetoxy-1*H*-cyclobuta[*de*]naphthalene (1p) with Potassium Carbonate in Ethanol.** A solution of **1p** (147 mg, 0.74 mmol), potassium carbonate (690 mg, 5 mmol), and ethanol (12 mL) was stirred at 20–25 °C for 6 h, poured into water, and extracted with ethyl ether. The organic product was washed with water, dried ($MgSO_4$), and concentrated to aldehyde **5c** (80 mg, 70%), identified by NMR and IR comparison with an authentic sample.

**Reaction of 1p with Lithium Aluminum Hydride.** Acetate **1p** (100 mg, 0.05 mmol) in ethyl ether (3 mL) was stirred in a slurry of lithium aluminum hydride (10 mg, 0.25 mmol) in ethyl ether (2 mL) for 10 min. After aqueous sodium sulfate was added, the organic layer was decanted and the salts were washed with ethyl ether. The combined ether extracts on drying, concentration, and chromatography on silica gel (hexane/ethyl acetate as eluent) yielded (1) initial **1p** (35 mg, 35%) and (2) 1-naphthylmethanol [**5g**, 50 mg, 98%;[28] NMR ($CDCl_3$, $\delta$) 2.33 (bis, 1 H, exchangeable, OH), 5.0 (s, 2 H, $CH_2$), 7.2–8.1 (m, 7 H, aromatic)].

**Reaction of 1p with Methanolic Hydrochloric Acid.** A methanolic (10 mL) solution of **1p** (128 mg, 0.65 mmol) and concentrated hydrochloric acid (4 drops) was refluxed 5.5 h, concentrated, poured into water, and extracted with ethyl ether. Workup and NMR analysis revealed the product to be **5c** (68% relative yield) and acetal **5d** (32% relative yield). The mixture of **5c** and **5d** was isolated in 82% overall yield and identified by its NMR absorptions at $\delta$ 3.3 (s, 6 H, $OCH_3$ of dimethyl acetal), 5.84 (s, 1 H, $CH(OCH_3)_2$), 7.34–8.0 (m, 12 H, aromatic), 8.3 (m, 1 H, peri proton of acetal), 9.15 (m, 1 H, peri proton of **5c**), and 10.02 (s, 1 H, CHO).

**Reaction of 1a and Piperidine.** A solution of **1a** (110 mg, 0.5 mmol) in piperidine (4 mL) was stirred at ~25 °C for 24 h, and the piperidine hydrobromide precipitated was filtered. After water was added to the filtrate and the mixture was extracted with ethyl ether, the ethereal solution was washed with 10% hydrochloric acid, dried ($MgSO_4$), concentrated, and chromatographed on silica gel (benzene as eluent) to yield **5c** (~50 mg, 64%) as the only product.

**Reaction of 1a and Aniline.** Aniline (46 mg, 0.5 mmol) and **1a** (110 mg, 0.5 mmol) in hexamethylphosphoric triamide (5 mL) was heated at 90 °C for 7 days. The mixture was poured into water and extracted with ethyl ether. The ether layer was washed with 10% hydrochloric acid, dried, concentrated, and chromatographed on silica gel (hexane/benzene as eluent), yielding (1) **1a** (40 mg, 37%) and (2) **5c** (20 mg, 41%),[28] identical with an authentic sample.

**1-Azido-1*H*-cyclobuta[*de*]naphthalene (1r).** Sodium azide (520 mg, 8 mmol) and **1a** (440 mg, 2 mmol) was stirred in hexamethylphosphoric triamide (30 mL) at 20–25 °C for 60 h. The mixture was poured into water and extracted with pentane. The pentane layer was washed with water, dried ($MgSO_4$), and concentrated to **1r**: 340 mg (94%); a colorless solid;[26] mp 45–46 °C upon recrystallization from pentane at −78 °C; NMR ($CDCl_3$, $\delta$) 6.17 (br s, 1 H, bridge), 7.17 (d of d, 2 H, $J$ = 5 and 2 Hz, ortho), 7.45–7.75 (m, 4 H, meta and para); $^{13}C$ NMR ($CDCl_3$, $\delta$) 74.8 (1 C, $C_1$), 116.9 (2 C, $C_{2,7}$), 122.9 (2 C, $C_{4,5}$), 125.8 (1 C, $C_9$), 130.8 (2 C, $C_{3,6}$), 142.0 (2 C, $C_{1a,7a}$), 146.0 (1 C, $C_8$); exact mass, *m/e*(calcd) 181.0639, *m/e*(obsd) 181.0642.

**Decomposition of 1r. A.** A solution of **1r** (700 mg, 3.9 mmol) in pentane (150 mL) was deoxygenated with nitrogen and irradiated through quartz with a 450-W Hanovia high-pressure mercury arc lamp for 140 min. Removal of the pentane under reduced pressure gave a black mass (630 mg) which upon column chromatography on silica gel yielded (1) **1r** (140 mg, 20%), (2) 1-cyanonaphthalene (**11**, 80 mg; 14%), and (3) intractables.

**B.** A mixture of **1r** (180 mg, 1 mmol) and hexamethylphosphoric triamide (3 mL) was heated for 150 °C for 25 min, poured into water, and extracted with ethyl ether. Product isolation and chromatography on silica gel (2:1 hexane/benzene as eluent) gave **11** (120 mg, 67%) as the principal product.

**1*H*-Cyclobuta[*de*]naphthalen-1-yl *p*-Toluenesulfonate (1s).** A heated mixture (75 °C, 50 h) of **1a** (1.1 g, 5 mmol), silver *p*-toluenesulfonate (1.4 g, 5 mmol), and hexamethylphosphoric triamide (25 mL) was poured into water and extracted with ethyl ether. The extract was dried ($MgSO_4$), concentrated under vacuum to a yellow solid, and chromatographed on silica gel to yield: (1) initial **1a** (280 mg, 25%), (2) **5c** (100 mg, 17%),[28] and (3) **1s**[26] (680 mg (60%);[28] recrystallized from petroleum ether (bp 30–60 °C) at −78 °C; NMR ($CDCl_3$, $\delta$) 243 (2, 3 H, $CH_3$), 6.83–8.03 (m, 11 H, aromatic and bridge); $^{13}C$ NMR ($CDCl_3$, $\delta$) 146.6 (1 C, quaternary), 145.2 (1 C, quaternary), 141.4 (2 C, $C_{1a,7a}$), 133.5 (1 C, $C_4'$), 131.0 (2 C, aromatic), 129.9 (2 C, aromatic), 128.3 (2 C, aromatic), 126.1 (1 C, $C_9$), 123.2 (2 C, $C_{4,5}$), 117.0 (2 C, $C_{2,7}$), 87.4 (1 C, $C_1$), 21.6 (1 C, $CH_3$); exact mass, *m/e*(calcd) 310.0663, *m/e*(obsd) 310.0668). Anal. Calcd for $C_{18}H_{14}O_3S$: C, 69.66; H, 4.54. Found: C, 69.27; H, 4.67.

**Reactions of Lithium Dimethylcuprate with 1s, 1a, 1k, and 1l, Respectively.** *p*-Toluenesulfonate **1s** (310 mg, 1 mmol) in ethyl ether (15 mL) was added slowly at 0 °C to lithium dimethylcuprate prepared by adding methyllithium (20 mmol) to a suspension of cuprous iodide (2 g, 10 mmol) in ethyl ether (30 mL). After the resulting mixture had been stirred 30 h at ~25 °C, decomposed with water, and extracted with ethyl ether, concentration of the ether extract gave **1g** (110 mg, 71%) identical by NMR and MS with the sample described earlier.

Lithium dimethylcuprate, generated as previously described, was reacted with halides **1a**, **1k**, and **1l**, respectively, on the same scale and by the same procedure and work up as for **1s**. The yields of **1g** were 10%, 6% and 13%, respectively; the remaining products were not identified.

**1-Phenyl-1*H*-cyclobuta[*de*]naphthalene (1t).** Phenyllithium (1.8 M, 11 mL, 20 mmol) was added to cuprous bromide (1.43 g, 10 mmol) suspended in dry ethyl ether (60 mL) cooled to 0 °C under argon. Tosylate **1s** (1.05 g, 3.4 mmol) was then added, and the mixture was refluxed overnight. The reaction mixture was washed with saturated aqueous ammonium chloride and water and dried ($MgSO_4$). Removal of solvent followed by preparative TLC on silica gel (hexane) yielded **1t** as a light yellow oil which crystallized slowly: 0.41 g (56%); mp 57–60 °C upon recrystallization from methanol; $^1H$ NMR ($CDCl_3$, $\delta$) 6.35 (s, 1 H, CH), 6.9–7.6 (m, 11 H aromatic); $^{13}C$ NMR ($CDCl_3$, $\delta$, 20.11 MHz) 66.61 (CH), 116.48 ($C_{2,7}$ of naphthyl), 121.66 ($C_{4,5}$ of naphthyl), 126.03 ($C_9$ of naphthyl), 127.00 ($C_4$ of phenyl), 127.2 and 128.51 ($C_{2,3}$ of phenyl), 130.07 ($C_{3,6}$ of naphthyl), 133.22 ($C_1$ of phenyl), 140.05 ($C_8$ of naphthyl), 145.65 ($C_{1a,7a}$ of naphthyl); exact mass, *m/e*(calcd) 216.0939, *m/e*(obsd) 216.0945. Anal. Calcd for $C_{17}H_{12}$: C, 94.41; H, 5.59. Found: C, 93.89; H, 5.62.

**Solvolysis of 1s in Acetic Acid. A.** *p*-Toluenesulfonate **1s** (102.6 mg, 0.33 mmol) in glacial acetic acid (3 mL) was heated at 75 °C for 5 days. When the mixture was poured in water and extracted with ethyl ether, the ether extract was washed with water and saturated aqueous sodium bicarbonate, dried, and concentrated. NMR analysis of the yellow oil (80 mg) indicated it to be a 82:15:3 mixture of **1s**, acetate **1p**, and aldehyde **5c**.

**B.** A similar experiment (100 mg of **1s**) for 27 days at 75 °C and chromatography of the product on silica gel (6:1 hexane/ether as eluent) resulted in isolation of **1s** (12.5 mg, 12.5%) and **5c** (41 mg, 82%).

**1-(Triphenylphosphonio)-1*H*-cyclobuta[*de*]naphthalene Bromide (1u).** A mixture of **1a** (3.1 g, 14 mmol), triphenylphosphine (13.1 g, 50 mmol), and xylene (150 mL) was refluxed 72 h, cooled, and filtered. The precipitate was washed with warm benzene and dried in vacuo to give **1u** (6.56 g, 97%): white platelets from ethanol/ethyl ether; mp 263–266 °C; NMR ($Me_2SO$-$d_6$, $\delta$) 7.23 (m, 2 H), 7.5–7.98 (m, 20 H).[26] Anal. Calcd for $C_{29}H_{22}BrP$: C, 72.36; H, 4.61. Found: C, 72.17; H, 4.72.

**1-Isopropylidene-1*H*-cyclobuta[*de*]naphthalene (2a).** A suspension of **1u** (1.44 g, 3 mmol) in anhydrous tetrahydrofuran (30 mL) was cooled to 0 °C and treated with *tert*-butyllithium (4.5 mmol) in pentane. The resulting red solution was stirred at room temperature until all of the **1u** dissolved (~45 min). Anhydrous acetone (3.0 mL) was added by syringe, and the resulting yellow solution was stirred for 1 h. The mixture on concentration and then separation on silica gel gave **2a** (430 mg, 80%):[26] NMR ($CDCl_3$, $\delta$) 2.02 (s, 6 H, $CH_3$), 7.04 (d of d, 2 H, $J$ = 5 and 2.5 Hz, ortho), 7.43 (m, 4 H, meta and para); $^{13}C$ NMR ($CDCl_3$, $\delta$) 146.4 (1 C, $C_1$), 145.9 (2 C, $C_{1a,7a}$), 140.2 (1 C, $C_8$), 130.4 (2 C, $C_{3,6}$), 126.0 (1 C), 125.3 (1 C), 121.2 (2 C, $C_{4,5}$), 144.1 (2 C, $C_{2,7}$), 20.77 (2 C, $CH_3$); exact mass, *m/e*(calcd) 180.0938, *m/e*(obsd) 180.0942. An analytical sample of **2a** was obtained by sublimation, 63–66 °C (0.45 mm). Anal. Calcd for $C_{14}H_{12}$: C, 93.29; H, 6.71. Found: C, 92.89; H, 6.79.

**1-Methylene-1*H*-cyclobuta[*de*]naphthalene (2b).** Paraformaldehyde (2.0 g, 22.2 mmol) was added to **3c** prepared from **1u** (5.62 g, 12 mmol), THF (120 mL), and *tert*-butyllithium (17.5 mmol) in pentane. The resulting solution was refluxed 2 h, concentrated, and chromatographed on silica gel (pentane as eluent). Vacuum distillation of the crude **2b** (1.55 g, 85%) afforded a colorless liquid: bp 70 °C (0.45 mm);[26] NMR ($CDCl_3$, $\delta$) 5.45 (s, 2 H, olefinic), 7.16 (d of d, 2 H, $J$ = 5 and 2 H, ortho), 7.52 (m, 4 H, meta and para); $^{13}C$ NMR ($CDCl_3$, $\delta$) 150.6 (2 C,

$C_{1a,7a}$), 149.6 (1 C, $C_1$), 145.8 (1 C, $C_8$), 130.6 (2 C, $C_{3,6}$), 125.7 (1 C, $C_9$), 121.9 (2 C, $C_{4,5}$), 114.2 (2 C, $C_{2,7}$), 104.1 (1 C, terminal olefin); exact mass, *m/e*(calcd) 152.0625, *m/e*(obsd) 152.0628. An analytical sample was obtained by VPC (12.5% QF-1 on Chromosorb W) at 115 °C. Anal. Calcd for $C_{12}H_8$: C, 94.70; H, 5.30. Found: C, 94.27; H, 5.54.

**1-Ethylidene-1*H*-cyclobuta[*de*]naphthalene (2c).** Purification of **2c**,[26] prepared (85%) from acetaldehyde and **3c** by extension of the above procedure, gave a colorless liquid upon vacuum distillation: bp 70–75 °C (0.22 mm); NMR ($CDCl_3$, δ) 2.0 (d, 3 H, *J* = 6.5 Hz, $CH_3$), 5.8 (q, 1 H, *J*= 6.5 Hz, olefinic), 6.93–7.27 (m, 2 H, ortho), 7.34–7.59 (m, 4 H, meta and para); exact mass, *m/e*(calcd) 166.0782, *m/e*(obsd) 166.0784. Anal. Calcd for $C_{13}H_{10}$: C, 93.94; H, 6.06. Found: C, 93.72; H, 6.24.

**1-Benzylidene-1*H*-cyclobuta[*de*]naphthalene (2d).** Reaction of benzaldehyde and **3c** (as above) yielded **2d** (85%): mp 54–56 °C (from hexane);[26] NMR ($CDCl_3$, δ) 6.74 (s, 1 H, olefinic), 7.06–7.77 (m, 11 H, aromatic); exact mass, *m/e*(calcd) 228.0938, *m/e*(obsd) 228.0943. Anal. Calcd for $C_{18}H_{12}$: C, 94.70; H, 5.30. Found: C, 94.89; H, 4.99.

**1-(Diphenylmethylene)-1*H*-cyclobuta[*de*]naphthalene (2e).** Ylide **3c** (red), prepared by adding *tert*-butyllithium (4 equiv) to **1u** (1.44 g, 3 mmol) in tetrahydrofuran (30 mL) at −78 °C, was quenched by slow addition of benzophenone (2 g) in tetrahydrofuran (10 mL). The mixture was refluxed 30 h, cooled, chromatographed on silica gel (hexane as eluent), and worked up to give **2e** (640 mg, 70%);[26] white needles; mp 144–146 °C; NMR ($CDCl_3$, δ) 6.95 (d of d, 2 H, *J* = 2 and 4 Hz, ortho on naphthalene ring), 7.15–7.8 (m, 14 H, aromatic); exact mass for $C_{24}H_{16}$, *m/e*(calcd) 304.1252, *m/e*(obsd) 304.1260. Anal. Calcd for $C_{24}H_{16}$: C, 94.70; H, 5.30. Found: C, 94.78; H, 5.33.

**Catalytic Hydrogenation of 2a.** Hydrogenation of **2a** (45 mg, 0.25 mol) in methanol (50 mL) over 10% palladium on carbon at atmospheric pressure (Parr apparatus) for 3 h, filtration, and concentration gave 1-isobutylnaphthalene (**5i**, 45 mg, 95%) as purified by VPC: NMR ($CDCl_3$, δ) 0.95 (d, 6 H, $CH_3$), 2.07 (m, 1 H), 2.92 (d, 2 H, $CH_2$), 7.17–8.1 (m, 7 H, aromatic); exact mass, *m/e*(calcd) 184.1251, *m/e*(obsd) 184.1254. Anal. Calcd for $C_{14}H_{18}$: C, 91.25; H, 8.75. Found: C, 91.12; H, 9.17.

**Diimide Reduction of 2b.** Acetic acid (71.1 g) in methanol (50 mL) was added in 30 min to dipotassium azodicarboxylate (9.7 g, 49 mmol) suspended in a solution of **2b** (490 mg, 3.2 mmol) in anhydrous methanol (75 mL). After 1 h analysis of the product revealed that only 68% reduction had occurred. Resubjection of the product to the above conditions, workup, and spectral analysis of the reaction mixture revealed that >90% of **2b** had been reduced. The crude product on treatment with *m*-chloroperbenzoic acid in chloroform at 0 °C, workup, concentration, and chromatography on silica gel allowed separation of 1-methyl-1*H*-cyclobuta[*de*]naphthalene (**1g**; 300 mg, 61%):[26] bp 55 °C (0.24 mm); NMR ($CDCl_3$, δ) 1.67 (d, 3 H, *J* = 7 Hz, $CH_3$), 6.88 (d of d, 2 H, aromatic), 7.1–7.5 (m, 4 H, aromatic); $^{13}C$ NMR ($CDCl_3$, δ) 147.4 (2 C, $C_{1a,7a}$), 144.5 (1 C, $C_8$), 130.4 (2 C, $C_{3,6}$), 125.9 (1 C, $C_9$), 121.3 (2 C, $C_{4,5}$), 115.7 (2 C, $C_{2,7}$), 58.2 (1 C, $C_1$), 18.6 (1 C, $CH_3$); exact mass, *m/e*(calcd) 154.0782, *m/e*(obsd) 154.0784; UV max (95% EtOH) 322 (ε 91), 316 (261), 311 (382), 302 (578), 282 (4503), 277 (4358), 272 (4697), 226 nm (67 796). An analytical sample was obtained by preparative VPC (12.5% QF-1 on Chromosorb). Anal. Calcd for $C_{12}H_{10}$: C, 93.46; H, 6.54. Found: C, 93.28; H, 6.67.

**Addition of Hydrogen Bromide to 2c.** Hydrogen bromide (2 mL) was passed through copper turnings into **2c** (166 mg, 1 mmol) in methylene chloride (5 mL) at −78 °C. After having been kept at −78 °C for 2 h and room temperature for 6 h, the mixture was vacuum evaporated to yield 1-bromo-1-ethyl-1*H*-cyclobuta[*de*]naphthalene (**15c**, 220 mg, 89%) as the only identifiable product: NMR ($CDCl_3$, δ) 1.23 (t, 3 H, *J* = 6 Hz, $CH_3$), 2.50 (q, 2 H, *J* = 6 Hz, $CH_2$), 7.10 (d of d, 2 H, *J* = 2 and 6 Hz, ortho), 7.35–7.65 (m, 4 H, meta and para); exact mass for $C_{13}H_{11}Br$, *m/e*(calcd) 246.00446, *m/e*(obsd) 246.00494.[27]

**Addition of Hydrogen Bromide to 2a.** Hydrogen bromide was added to **2a** (180 mg, 1 mmol) using the same procedure as for **2c**. The product contained 1-bromo-1-isopropyl-1*H*-cyclobuta[*de*]naphthalene (**15a**) and 1-(1-bromoisopropyl)-1*H*-cyclobuta[*de*]naphthalene (**17a**) as an inseparable mixture (230 mg, 88%) in a ratio of 9:1: (1) **15a**: NMR ($CDCl_3$, δ) 1.27 (d, 6 H, *J* = 6 Hz, $CH_3$), 2.3 (sextet, 1 H, *J* = 6 Hz, $CH(CH_3)_2$), 7.0–7.7 (m, 6 H, aromatic).[27] (2) **17a**: NMR ($CDCl_3$, δ) 1.83 (s, 6 H, $CH_3$), 5.69 (s, 1 H, bridge H), 7.0–7.7 (m, 6 H, aromatic); exact mass for $C_{14}H_{13}Br$, *m/e*(calcd) 260.0201, *m/e*(obsd) 260.0206.

**Addition of Hydrogen Bromide to 2b.** Gaseous hydrogen bromide (0.5 mmol) was condensed into **2b** (73 mg, 0.48 mmol) in methylene chloride (5 mL) at −196 °C (liquid nitrogen) in a high vacuum line. After being stored at −78 °C for 1 h and at −26 °C overnight, the mixture was concentrated and chromatographed on silica gel. The product, a colorless oil (110 mg), contained two major components (97% by NMR): initial **2b** (19%) and 1-bromo-1-methyl-1*H*-cyclobuta[*de*]naphthalene (**15b**, 78%). Treatment of the mixture with *m*-chloroperbenzoic acid in chloroform at 0 °C and chromatography on silica gel (pentane as eluent) produced **15b** (86 mg, 75%) which was purified by sublimation at 60–65 °C (0.13 mm): mp 90–92 °C; NMR ($CDCl_3$, δ) 2.47 (s, 3 H, $CH_3$), 7.08 (d of d, 2 H, ortho), 7.27–7.58 (m, 4 H, aromatic); $^{13}C$ NMR ($CDCl_3$, δ) 149.6 (2 C, $C_{1a,7a}$), 142.4 (1 C, $C_8$), 131.1 (2 C, $C_{3,6}$), 126.7 (1 C, $C_9$), 122.7 (2 C, $C_{4,5}$), 113.9 (2 C, $C_{2,7}$), 70.5 (1 C, $C_1$), 31.0 ($CH_3$); exact mass, *m/e*(calcd) 231.9888, *m/e*(obsd) 231.9892.[26] Anal. Calcd for $C_{12}H_9Br$: C, 61.83; H, 3.89. Found: C, 62.13; H, 3.69.

**Addition of Hydrogen Bromide to 2d.** 1-Benzyl-1-bromo-1*H*-cyclobuta[*de*]naphthalene (**15d**; 280 mg, 91%) was obtained upon reaction of hydrogen bromide with **2d** by the procedure for **2c**: NMR ($CDCl_3$, δ) 3.83 (s, 2 H, $CH_2$), 7.0–7.75 (m, 11 H, aromatic); exact mass for $C_{18}H_{13}Br$, *m/e*(calcd) 308.0201, *m/e*(obsd) 308.0209.[27]

**Addition of Hydrogen Bromide to 2e.** Excess hydrogen bromide (4 mL of liquid HBr) was condensed in a solution of **2e** (300 mg, 1 mmol) in methylene chloride (7 mL) at −78 °C. The resulting blue solution was stirred at −78 °C for 4 h and then at ~25 °C for ~8 h. During the latter period the blue solution turned orange. Removal of the solvent yielded 1,2-diphenylacenaphthylene (**21**; 285 mg, 95%) as red-orange needles:[27] mp 161–163 °C (from hexane) (lit.[13] 162–164 °C); *m/e* 304.

**3′-Methylspiro[1*H*-cyclobuta[*de*]naphthalene-1,2′-oxirane] (22).** A chloroform solution (2 mL) of **2c** (166 mg, 1 mmol) was added slowly to *m*-chloroperbenzoic acid (300 mg, 1.5 mmol) in chloroform (10 mL) at 0 °C, and the mixture was refrigerated 24 h. After the *m*-chlorobenzoic acid precipitate was filtered, the organic layer was extracted with aqueous sodium bicarbonate, 10% sodium thiosulfate, and saturated sodium chloride, dried ($MgSO_4$), and concentrated. Distillation of the residue (154 mg, 85%) yielded **22**,[26] a colorless liquid: bp 81–83 °C (0.35 mm); NMR ($CDCl_3$, δ) 1.62 (d, 3 H, *J* = 5 Hz, $CH_3$), 3.82 (q, 1 H), 7.0–7.19 (m, 2 H, aromatic), 7.34–7.78 (m, 4 H, aromatic); exact mass, *m/e*(calcd) 182.0731, *m/e*(obsd) 182.0734. Anal. Calcd for $C_{13}H_{10}O$: C, 85.69; H, 5.53. Found: C, 85.35; H, 5.16.

**1-Acetyl-1*H*-cyclobuta[*de*]naphthalene (1i).** Boron trifluoride etherate (1 mL) in ethyl ether (20 mL) was added dropwise to **22** (550 mg, 3 mmol) in ethyl ether (100 mL) at −78 °C. The mixture was stirred vigorously at −30 °C for 2 h at which time saturated aqueous sodium bicarbonate was added. Workup of the ether layer led to **1i** (510 mg, 93%),[26] identical with an authentic sample.

**Conversion of 22 to 27 by Boron Trifluoride.** A mixture of boron trifluoride etherate (5 mL), **22** (91 mg, 0.5 mmol), and ethyl ether (20 mL), upon stirring 3 h at room temperature, neutralization with aqueous sodium bicarbonate and workup, yielded 2-methylacenaphthenone (**27**; 85 mg, 93%), identical with an authentic sample.

**Spiro[1*H*-cyclobuta[*de*]naphthalene-1,1′-cyclopropane] (28).** Methylene iodide (540 mg, 2 mmol) was added to powdered zinc (200 mg) which had been heated (~1 h) with cupric acetate (50 mg) in acetic acid (15 mL), washed with acetic acid and then ethyl ether (250 mL), and suspended in dry ethyl ether (50 mL). The mixture was refluxed for 2 h under nitrogen while **2b** (200 mg, 1.3 mmol) was added and then for 12 h. Filtration, removal of volatiles, and vacuum distillation of the residue gave **28** (180 mg, 82%),[27] a clear oil: bp 135–140 °C (0.1 mm); NMR ($CDCl_3$, δ) 1.53 (s, 4 H, $CH_2$), 6.88 (d of d, 2 H, *J* = 2 and 4 Hz, ortho), 7.4–7.65 (m, 4 H, meta and para); exact mass, *m/e*(calcd) 166.0782, *m/e*(obsd) 166.0786. Anal. Calcd for $C_{13}H_{10}$: C, 93.94; H, 6.06. Found: C, 93.58; H, 6.22.

**Reaction of 2b with Tetraphenylcyclopentadienone.** A solution of **2b** (152 mg, 1 mmol) and tetraphenylcyclopentadienone (385 mg, 1 mmol) in xylene (15 mL) was refluxed 16 h. After removal of solvent, chromatography of the residue on silica gel (hexane-benzene as eluent) gave three fractions: (1) **2b** (30 mg, 20%): identical with the original sample. (2) 1′,4′,5′,6′-Tetraphenylspiro[1*H*-cyclobuta[*de*]naphthalene-1,2′-[5]-norbornen-7′-one] (**29**; 370 mg, 69%):[27] mp 122–126 °C; NMR ($CDCl_3$, δ) 6.65–8.0 (m, 28 H, aromatic and methylene H); exact mass minus C=O peak for $C_{40}H_{28}$, *m/e*(calcd) 508.2191, *m/e*(obsd) 508.2201. (3) Tetraphenylcyclopentadienone (90 mg, 23%): identical with an authentic sample. Anal. Calcd for $C_{41}H_{28}O$: C, 91.76; H, 5.26. Found: C, 92.06; H, 5.62.

**Homolytic Addition of Hydrogen Bromide to 2c.** Hydrogen bromide which had been passed through copper turnings was bubbled into a carbon tetrachloride (50 mL) solution of **2c** (330 mg, 2 mmol) and azobis(isobutyronitrile) (20 mg). The temperature of the mixture rose from 24 °C to 29 °C. Addition of hydrogen bromide was continued for 20 min after the solution temperature returned to 24 °C. Upon removal of the solvent at reduced pressure, a pale yellow oil remained assigned as 1-(1-bromoethyl)-1*H*-cyclobuta[*de*]naphthalene (**31**; 450 mg, 91%) on the basis of its IR,[27] NMR, and MS properties: NMR ($CDCl_3$, δ) 1.78 (d, 3 H, *J* = 6 and 8.5 Hz, CHBr), 5.40 (d, 1 H, *J* = 8.5 Hz, bridge H), 7.09 (d of d, 2 H, *J* = 2 and 5 Hz, ortho), 7.3–7.6 (m, 4 H, meta

and para); exact mass for $C_{13}H_{11}Br$, *m/e*(calcd) 246.0045, *m/e*(obsd) 246.0051. The spectral properties of **31** are distinctly different from **15c** (see previous experimental).

**Elimination of 31 to 2c by Bases.**[27] 1,5-Diazabicyclo[5.4.0]undec-5-ene (90 mg, 0.6 mmol) in tetrahydrofuran (10 mL) was added to **31** (125 mg, 0.5 mmol) in tetrahydrofuran 10 mL) at −78 °C. The mixture was warmed to room temperature and then stirred 6 h. Upon solvent removal, solution of the residue in pentane and concentration, **2c** (75 mg, 90%) was obtained identical with an authentic sample.

Similarly, reactions of **31** (0.5 mmol) with (1) potassium triethylcarbinoxide [0.5 mmol, prepared from potassium (20 mg), triethylcarbinol (58 mg), and tetrahydrofuran (10 mL)] and (2) lithium 2,2,6,6-tetramethylpiperidide [0.5 mmol, prepared from *tert*-butyllithium (0.5 mmol in pentane), 2,2,6,6-tetramethylpiperidine (70 mg), and tetrahydrofuran (10 mL)] yielded **2c** (~90%), identical with the previous sample.

**1-Acetyl-1*H*-cyclobuta[*de*]naphthalene (*p*-Tolylsulfonyl)hydrazone (32).** A mixture of **1i** (560 mg, 3 mmol), *p*-tosylhydrazine (560 mg, 3 mmol), and ethanol (6 mL) was refluxed 2 h and cooled. Filtration of the white precipitate (760 mg, 69%) and recrystallization from ethanol gave **32**:[27] mp 172–174 °C; NMR ($CDCl_3$, δ) 1.76 (s, 3 H, C(=O)-$CH_3$), 2.45 (s, 3 H, tosyl $CH_3$), 5.93 (s, H, bridge H), 7.0–7.95 (m, 10 H, aromatic); exact mass for $C_{20}H_{18}N_2SO_2$, *m/e*(calcd) 350.1089, *m/e*(obsd) 350.1094. Anal. Calcd for $C_{20}H_{18}N_2SO_2$: C, 68.56; H, 5.18. Found: C, 68.31; H, 5.26.

**Conversion of 32 by *tert*-Butyllithium to 2c.**[27] A solution of **32** (350 mg, 1 mmol), *tert*-butyllithium (2.1 equiv in pentane), and tetrahydrofuran (25 mL) was stirred under nitrogen at −78 °C and then 24 h at room temperature. Hydrolysis of the mixture, vacuum evaporation of the solvents, and chromatography of the residue on silica gel (hexane as eluent) resulted in **2c** (35 mg, 21%), identical with authentic material.

**Attempted Base-Catalyzed Isomerization of 2c.** *tert*-Butyllithium (0.55 mmol) in hexane was added under nitrogen to **2c** (83 mg, 0.5 mmol) in tetrahydrofuran (15 mL) at −78 °C. When the mixture was stirred 20 min, deuterium oxide (2 mL) was added via syringe and the solution allowed to warm to room temperature. Ethyl ether extraction, drying the ethereal layer with magnesium sulfate, and solvent evaporation left a pale yellow oil (75 mg, 90%), 1-(ethylidene-2-*d*)-1*H*-cyclobuta[*de*]naphthalene (**2g**):[27] NMR ($CDCl_3$, δ) 2.0 (d, 2 H, *J* = 6.5 Hz, $CH_2D$), 5.8 (t, 1 H, *J* = 6.5 Hz, olefinic), 6.9–7.6 (m, 6 H, aromatic); a large mass spectral peak for $C_{13}H_{10}D$, *m/e*(calcd) 167, *m/e*(obsd) 167.

Using the above procedure except that the mixture was quenched with water yielded **2c** (~90%) identical with an authentic sample.

**Thermolysis of 1g.** Decomposition of **1g** (63.1 mg) at 0.1 mmHg through a Vycor column packed with quartz helices and heated to 456 °C yielded 1-vinylnaphthalene (**5n**; 50 mg, 80%);[28] NMR ($CDCl_3$, δ) 5.28–5.92 (m, 3 H, olefinic), 7.17–8.17 (m, 7 H, aromatic); IR spectrum identical with an authentic sample.

**1,1-Bi-1*H*-cyclobuta[*de*]naphthalene (36).** Zinc (200 mg) activated with silver,[30] **1a** (440 mg, 2 mmol), and water (20 mL) were refluxed vigorously in the dark for 10 h. Extraction with ethyl ether and chromatography on silica gel (hexane as eluent) yielded the following: (1) **1b** (31 mg, 11%): identical with an authentic sample. (2) **36** (360 mg, 65%): mp 135–137 °C; NMR ($CDCl_3$, δ) 5.80 (s, 2 H, bridge H), 6.90 (d of d, *J* = 2 and 5.5 Hz, 4 H, ortho), 7.28–7.55 (m, 8 H, meta and para); $^{13}C$ NMR ($CDCl_3$, δ) 64.906 (1 C, $C_1$), 116.378 (2 C, $C_{2,7}$), 121.692 (2 C, $C_{4,5}$), 125.712 (1 C, $C_9$), 130.325 (1 C, $C_{3,6}$), 144.407 (1 C, $C_8$), 145.486 (2 C, $C_{1a,7a}$); exact mass for $C_{22}H_{14}$, *m/e*(calcd) 278.1095; *m/e*(obsd) 278.1104. Anal. Calcd for $C_{22}H_{14}$: C, 94.93; H, 5.07. Found: C, 94.51; H, 5.47.

**1-(1-Naphthylidene)-1*H*-cyclobuta[*de*]naphthalene (38).** Reaction of 1-naphthaldehyde (2 mL) at 20–25 °C with **3c** [prepared from **1u** (1.44 g, 3 mmol) and *tert*-butyllithium (4.0 mmol in pentane) in tetrahydrofuran (30 mL)] for 3 h, product isolation, and chromatography on silica gel (hexane as eluent) yielded **38** (460 mg, 83%),[27] a white solid: mp (from hexane) 107–109 °C; NMR ($CDCl_3$, δ) 6.9–8.15 (m, aromatic and olefinic H); exact mass, *m/e*(calcd) 278.1095, *m/e*(obsd) 278.1101. Anal. Calcd for $C_{22}H_{14}$: C, 94.93; H, 5.07. Found: C, 94.62; H, 5.09.

Addition of bromine (340 mg, 2.1 mmol) in carbon tetrachloride (40 mL) to **38** (280 mg, 1.0 mmol) in carbon tetrachloride (10 mL) at 0 °C (2 h) and vacuum concentration yielded 1-bromo-1-[bromo(1-naphthyl)methyl]-1*H*-cyclobuta[*de*]naphthalene (410 mg, 94%): white crystals; mp (from hexane) 154–156 °C; NMR ($CDCl_3$, δ) 6.69 (s, 1 H, benzylic H), 6.85–8.2 (m, 13 H, aromatic H); exact mass, *m/e*(calcd) 435.9463, *m/e*(obsd) 435.9472.[27] Anal. Calcd for $C_{22}H_{14}Br_2$: C, 59.85; H, 3.22. Found: C, 60.10; H, 3.29.

**Thermal Rearrangement of 36.** Volatilization of **36** through a Vycor tube (30 cm) at 430 °C (0.1 mmHg), condensation of the effluent, and crystallization of the product from hexane gave **38** identical with the previous sample.

**Thermal Rearrangements of 2b–d.**[28] Volatilization of **2b** (70 mg) at 550 °C (0.1 mmHg) through a Vycor tube packed with quartz chips and condensation of the effluent gave a three-component product (60 mg, 86%). Separation and isolation via preparative VPC (20% QF-1 on Chromosorb W, 120 °C) yielded (91% of the mixture): (1) **2b** (6%) and (2) 1-ethynylnaphthalene (**40a**, 85%; NMR ($CDCl_3$, δ) 3.41 (s, 1 H, C≡C—H), 7.19–7.92 (m, 6 H, aromatic); IR and NMR, identical with those of an authentic sample).

Similarly, decomposition of (1) **2c** at 550 °C (0.1 mmHg) results in 1-(1-propynyl)naphthalene (**40b**, 44%) and 56% recovery of **2c** and (2) **2d** at 650 °C (0.1 mmHg) yields 1-(1-phenylethynyl)naphthalene (**40c**, 66%) along with **2d**. Assignments of **40b** and **40c** were made from their IR and NMR properties.

**Ozonolysis of 2a.** Ozone was passed into **2a** (900 mg, 5 mmol) in ethyl acetate (75 mL) at −78 °C. The cold mixture was treated with dimethyl sulfide (5 mL) and stirred at room temperature for 5 h. Aspiration of the solvent and chromatography of the residue on silica gel (2:1 hexane/benzene as eluent) yielded: (1) **2a** (125 mg, 29%) and (2) 1*H*-cyclobuta[*de*]naphthalen-1-one (**3a**, 250 mg, 71%);[26] sublimed at 40–44 °C (0.15 mm); mp 51.5–53.5 °C; NMR ($CDCl_3$, δ) 7.34 (d of d, 2 H, *J* = 6 and 2 Hz), 7.5–7.90 (m, 4 H); $^{13}C$ NMR ($CDCl_3$, δ) 178.2 (1 C, $C_1$), 162.1 (1 C, $C_8$), 156.0 (2 C, $C_{1a,7a}$), 131.4 (2 C, $C_{3,6}$), 127.3 (1 C, $C_9$), 124.9 (2 C, $C_{4,5}$), 116.8 (2 C, $C_{2,7}$); exact mass, *m/e*(calcd) 154.0418, *m/e*(obsd) 154.0421. Anal. Calcd for $C_{11}H_6O$: C, 85.70; H, 3.92. Found: C, 85.62; H, 3.94.

**1-(Thiophenoxy)-1*H*-cyclobuta[*de*]naphthalene (1w).** A mixture of **1a** (2.19 g, 10 mmol), sodium methoxide (540 mg, 10 mmol), thiophenol (1.1 g, 10 mmol), and ethanol (160 mL) was refluxed 48 h, cooled, and concentrated. The residue was dissolved in ethyl ether, and the ethereal layer was washed with 1 N hydrochloric acid, dried ($MgSO_4$), and vacuum concentrated. Chromatography on silica gel (hexane eluent) gave **1a** (200 mg, 10%) and **1w** (2.06 g, 83%):[28] mp (from hexane at −78 °C) 59–61 °C; NMR ($CDCl_3$, δ) 6.30 (s, 1 H, bridge), 6.87–7.45 (m, 11 H, aromatic); $^{13}C$ NMR ($CDCl_3$, δ) 62.96 (1 C, $C_1$), 116.5 (2 C, $C_{2,7}$), 122.3 (2 C, $C_{4,5}$), 125.9 (1 C, $C_9$), 127.0 (1 C, $C_4$ on phenyl ring), 128.7 (2 C, aromatic), 130.7 (2 C, aromatic), 135.0 (1 C, $C_1$ on phenyl ring), 143.7 (2 C, $C_{1a,7a}$), 145.0 (1 C, $C_8$); exact mass, *m/e*(calcd) 248.0658, *m/e*(obsd) 248.0662. Anal. Calcd for $C_{17}H_{12}S$: C, 82.22; H, 4.87. Found: C, 82.20; H, 4.94.

**1-Chloro-1-(thiophenoxy)-1*H*-cyclobuta[*de*]naphthalene (41) and Its Hydrolysis to 3a.** Removal of the solvent and recrystallization of the residue (from hexane at −78 °C) from reaction of *N*-chlorosuccinimide (800 mg, 6 mmol) and **1w** (1.24 g, 5 mmol) in refluxing carbon tetrachloride (25 mL) for 12 h yielded **41** (1.56 g, 93%): mp 74–75 °C; NMR ($CDCl_3$, δ) 6.93 (d of d, 2 H, aromatic), 7.14–7.67 (m, 9 H, aromatic); $^{13}C$ NMR ($CDCl_3$, δ) 80.8 (1 C, $C_1$), 115.8 (2 C, $C_{2,7}$), 122.6 (2 C, $C_{4,5}$), 126.3 (1 C, $C_9$), 128.9 (2 C, aromatic), 130.4 (2 C, aromatic), 133.0 (1 C, $C_1$ on phenyl ring), 134.9 (2 C, aromatic), 142.7 (1 C, $C_8$), 147.2 (2 C, $C_{1a,7a}$); mass spectrum, *m/e* 282 ($M^+$).

Hydrolysis of **1w** (1–3 mmol) for 24–48 h at 20–25 °C with the indicated reagents (2 equiv) and preparative thin-layer chromatography (2:1 hexane/benzene as eluent) gave the following results: (1) aqueous sodium carbonate (24 h), **3a** (~5%), and **1w** (38%); (2) aqueous sodium carbonate (48 h): **3a** (12%) and **1w** (41%); (3) aqueous mercuric chloride/cadmium carbonate: **3a** (5%), **1w** (53%), and diphenyl disulfide, and (4) chloramine-T in aqueous methanol, **3a** (~8%) and 5 (14%).

**Ring Opening of 3a by Methanol, Potassium Hydroxide, Aniline, and 2,4-(Dinitrophenyl)hydrazine, Respectively.**[26] (a) A solution of **3a** (90 mg, 0.584 mmol) in methanol (5 mL) was stirred overnight at room temperature, concentrated, and chromatographed on silica gel (hexane/benzene as eluent) to give methyl 1-naphthoate (**5j**; 75 mg, 69%): mp 58–60 °C, identical with an authentic sample.

(b) After 3.5 h no ketone remained upon storing **3a** (30 mg, 0.19 mmol) in anhydrous hexamethylphosphoric triamide (~2 mL) containing a small amount of potassium hydroxide. When the mixture was poured in 1 N hydrochloric acid and the solid was purified 1-naphthoic acid (30 mg, 88%) was obtained as a white solid: mp 160–162 °C, identical with an authentic sample.

(c) Heating **3a** (77 mg, 0.5 mmol) and aniline (46 mg, 0.5 mmol) in benzene (10 mL) at ~65 °C for 4 h and removal of the solvent yielded 1-naphthanilide (**5l**, 100 mg, 81%) as a white solid, mp 160–163 °C (lit.[31] 163 °C).

(30) Nasek, J. *Collect. Czech. Chem. Commun.* **1964**, *29*, 597.

(31) Hydrolysis of **5m** yields 1-naphthoic acid and (2,4-dinitrophenyl)-hydrazine.

(d) Addition of **3a** to (2,4-dinitrophenyl)hydrazine in ethanol at room temperature led to 1-naphthoyl (2,4-dinitrophenyl)hydrazide (**5m**): mp 275–278 °C dec; amide carbonyl absorption at 1640 $cm^{-1}$; mass spectrum, *m/e* 352 ($M^+$).[31] In a separate experiment reaction of **3a** (77 mg, 0.5 mm) occurred violently with (2,4-dinitrophenyl)hydrazine (99 mg, 0.5 mmol) in concentrated sulfuric acid to give, after the mixture was poured on ice, 1-naphthoic acid (50 mg, 58%), mp 159–161 °C, identical with an authentic sample.

**Reaction of 3a with Methylenetriphenylphosphorane.** *tert*-Butyllithium (1.5 equiv) in hexane was added to methyltriphenylphosphonium bromide (179 mg, 0.5 mmol) in tetrahydrofuran (10 mL) at 0 °C, and the mixture was warmed to ~25 °C and stirred until homogeneous. When the solutions were cooled to −78 °C, **3a** (77 mg, 0.5 mmol) in tetrahydrofuran (10 mL) was added by syringe and the mixture was stirred at −78 °C for 1 h and then slowly warmed to room temperature. TLC indicated that **2b** was not present. Aqueous sodium hydroxide was added, and the mixture was refluxed 24 h, cooled, and poured into water/ethyl ether. The ethereal layer, on drying ($MgSO_4$) and chromatography on silica gel (benzene as eluent), yielded 1-acetonaphthalene (**5o**; 15 mg, 18%), identical with an authentic sample. All attempts to prepare **2b** by reactions of **3a** with methylenetriphenylphosphorane were unsuccessful.

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**Registry No. 1a**, 54125-11-0; **1b**, 24973-91-9; **1b**·picrate, 85924-72-7; **1c**, 85864-98-8; **1d**, 85924-73-8; **1e**, 85864-99-9; **1f**, 85924-74-9; **1g**, 85924-75-0; **1h**, 85924-76-1; **1h** methyl ester, 85924-77-2; **1i**, 85924-78-3; **1j**, 85924-79-4; **1k**, 85924-80-7; **1l**, 85924-81-8; **1m**, 85924-82-9; **1o**, 85924-83-0; **1p**, 85924-84-1; **1p**·picrate, 85924-85-2; **1r**, 85924-86-3; **1s**, 85924-87-4; **1t**, 85924-88-5; **1u**, 85924-89-6; **1w**, 85924-90-9; **2a**, 85924-91-0; **2b**, 85924-92-1; **2c**, 85924-93-2; **2d**, 85924-94-3; **2e**, 85924-95-4; **2g**, 85924-96-5; **3a**, 85924-97-6; **3c**, 85924-98-7; **5a**, 90-12-0; **5b**, 18410-58-7; **5c**, 66-77-3; **5d**, 33250-32-7; **5e**, 64002-53-5; **5f**, 13098-88-9; **5g**, 4780-79-4; **5i**, 16727-91-6; **5j**, 2459-24-7; **5l**, 6833-19-8; **5m**, 39164-30-2; **5n**, 826-74-4; **5o**, 941-98-0; **11**, 86-53-3; **15a**, 85924-99-8; **15b**, 85925-00-4; **15c**, 85925-01-5; **15d**, 85939-43-1; **17a**, 85939-44-2; **21**, 13638-84-1; **22**, 85925-02-6; **27**, 18093-83-9; **28**, 85925-03-7; **29**, 85925-04-8; **31**, 85925-05-9; **32**, 85925-06-0; **36**, 85925-07-1; **38**, 85925-08-2; **40a**, 15727-65-8; **40b**, 32137-38-5; **40c**, 4044-57-9; **41**, 85925-09-3; chlorotrimethylsilane, 75-77-4; ethylene oxide, 75-21-8; diphenylacetonitrile, 86-29-3; 9-cyanofluorene, 1529-40-4; acetaldehyde, 75-07-0; benzaldehyde, 100-52-7; benzophenone, 119-61-9; tetraphenylcyclopentadienone, 479-33-4; *p*-tosylhydrazine, 1576-35-8; 1-bromo-1-[bromo(1-naphthyl)methyl]-1*H*-cyclobuta[*de*]naphthalene, 85925-10-6; thiophenol, 108-98-5; 1-naphthoic acid, 86-55-5; (2,4-dinitrophenyl)hydrazine, 119-26-6; 3′-phenylspiro[1*H*-cyclobuta[*de*]-naphthalene-1,2′-oxirane], 85925-11-7; 2,2-diphenylacenaphthenone, 85925-12-8.

# Anti and Syn Eliminations from 2,3-Dihalo-2,3-dihydrobenzofurans. The Role of the Substrate Structure and the Base–Solvent System on the Reaction Mechanism

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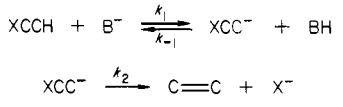
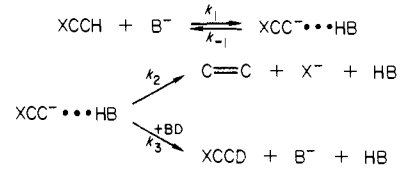
**Abstract:** The anti and syn β-eliminations from a series of 31 2,3-dihalo-2,3-dihydrobenzofurans (to give 3-halobenzofuran) have been kinetically investigated in *t*-BuOK–*t*-BuOH, in the presence and in the absence of 18-crown-6 ether (18C6), and in EtOK–EtOH. Reaction mechanisms have been assigned on the basis of leaving group, kinetic deuterium isotope, ring substituent (5-chlorine), and β-halogen effects. These data have provided information concerning structure and solvent effect on the mechanism of β-elimination reactions that lead to the following conclusions: (a) an $E1cB_1$ mechanism is likely to be operating, regardless of stereochemistry, with chlorine as a β-activating atom and fluorine as the leaving group and (b) an E2 reaction is likely to be operating for the opposite structural situation, i.e., with β-fluorine activation and chlorine as the leaving group. The mechanism is likely to change from E2 to $E1cB_1$ as the reaction stereochemistry changes from anti to syn and as we move from EtOK–EtOH to *t*-BuOK–*t*-BuOH and from here to *t*-BuOK–*t*-BuOH–18C6.

The determination of the factors that determine the crossover from a stepwise to a concerted mechanism (and vice versa) for a given reaction are receiving continuous attention.[1] The HX β-elimination is certainly one of the reactions that has been more intensively investigated in the last decade, from this point of view.[2-12]

Scheme I



Scheme II



A concerted mechanism (E2 reaction) has been long considered most probable for β-eliminations,[13] but more recently this view

(1) Jencks, W. P. *Chem. Soc. Rev.* **1982**, *11*, 345–375.
(2) Gandler, J. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1982**, *104*, 1937–1951. Keeffe, J.; Jencks, W. P. *Ibid.* **1981**, *103*, 2457–2459.
(3) Baciocchi, E.; Ruzziconi, R.; Sebastiani, G. V. *J. Org. Chem.* **1982**, *47*, 3237–3241.
(4) More O'Ferrall, R. A. *J. Chem. Soc., Perkin Trans. 2*, in press.
(5) Koch, H. F.; Tumas, W.; Knoll, R. *J. Am. Chem. Soc.* **1981**, *103*, 5423–5429.
(6) Koch, H. F.; Dahlberg, D. B. *J. Am. Chem. Soc.* **1980**, *102*, 6102–6107.
(7) Thibblin, A. *Chem. Scr.* **1980**, *15*, 121–127.
(8) (a) Thibblin, A.; Ahlberg, P. *J. Am. Chem. Soc.* **1977**, *99*, 7926–7930. (b) *Ibid.* **1979**, *101*, 7311–7318.
(9) Marshall, D. R.; Thomas, P. J.; Stirling, C. J. M. *J. Chem. Soc., Perkin Trans. 2*, **1977**, 1914–1919.
(10) Saunders, W. H., Jr. *Acc. Chem. Res.* **1976**, *9*, 19–25.
(11) Fiandanese, V.; Marchese, G.; Naso, F. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1538–1542.

0002-7863/83/1505-6114$01.50/0 