

chain. Hydrozirconation may thus prove to be an attractive alternate to published synthetic procedures employing hydroboration or hydroalumination, especially when facile rearrangement of the functionalization unit in the alkyl intermediate is desired.

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## References and Notes

- B. Kautzner, P. C. Wailes, and H. Weigold, *Chem. Commun.*, 1105 (1969).
- Vitride, 0.5 mol, is added slowly to a solution of 1.0 mol of  $\text{Cp}_2\text{ZrCl}_2$  in THF. The white precipitate of 1 is filtered, washed with THF, benzene, and ether and then vacuum dried. It reacts with moisture and is slightly light sensitive.
- A reaction of 1 with three olefins was reported, but the alkylzirconium products were not properly characterized, and the product of reaction of 1 with 2-methyl-2-pentene was incorrectly assigned: (P. C. Wailes, H. Weigold, and A. P. Bell, *J. Organometal. Chem.*, **43**, C32 (1972).
- We have not observed metal migration past a 3° (or 4°) carbon at room temperature.
- For example, see C. P. Casey and C. R. Cyr, *J. Amer. Chem. Soc.*, **93**, 1280 (1971), and references cited therein.
- H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, **89**, 561 (1967), and references cited therein.
- L. I. Zakharkin and O. Y. Okhlobystin, *Bull. Acad. Sci. USSR*, 1236 (1958).
- Solvents were distilled from sodium benzophenone ketyl under argon. For benzene, this was made possible by admixing 5% tetraglyme. All reactions were performed under an argon atmosphere.
- Products, which were pale yellow oils, were characterized by nmr ( $\delta_{\text{CP}} = 5.9$ ;  $\delta_{\text{Zr}-\text{CH}_2} = 0.9-1.2$ ; an impurity, arising in the preparation of 1 has  $\delta_{\text{CP}} = 6.1$ ) and by comparison of bromination products with known materials. Yields of alkyl in excess of 90% have been obtained.
- Relative rates for olefin reaction with 1 at room temperature are: 1-octene > *cis*-4-octene > *trans*-4-octene > methylenecyclohexane > cyclopentene > cyclohexene >> 2-methyl-2-butene. Hydrozirconation of hindered olefins can be facilitated by reaction at 40°. The order of reactivity of various olefins with 1 may reflect relative ease of fitting bulky olefins into a somewhat sterically crowded bent "sandwich" structure. Indeed, 1-methylcyclohexene and tetramethylethylene fail to react with 1 even when heated to 40° overnight. Cyclooctene also fails to react with 1 under these conditions.

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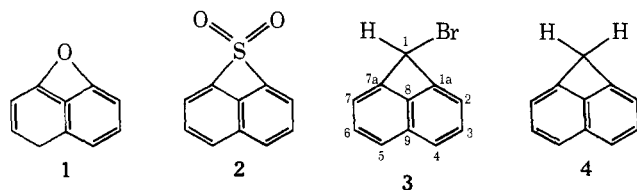
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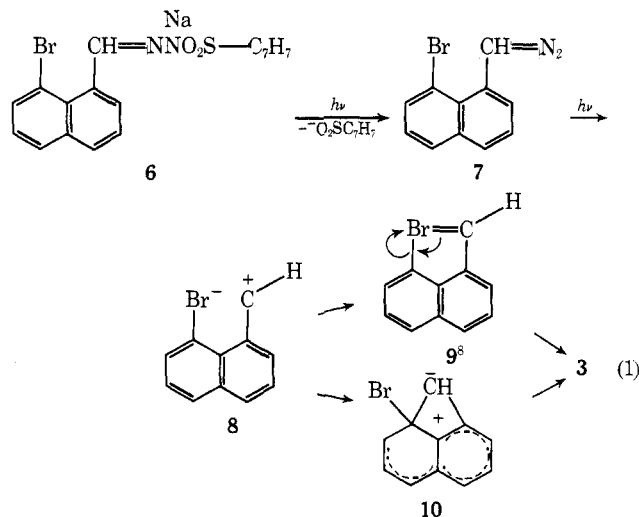
## 1*H*-Cyclobuta[de]naphthalene (1,8-Methanonaphthalene)

Sir:

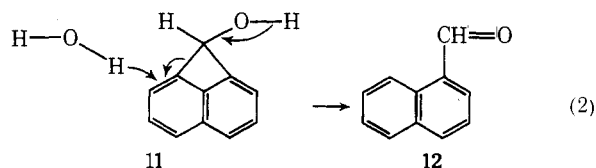
The interatomic distance between the hydrogen atoms at the C<sub>1</sub> and C<sub>8</sub> positions in naphthalene is 2.40 Å.<sup>1</sup> There are as yet few examples in which the peri positions of naphthalene or its analogs have been bridged by one atom. Naphth[1,8-*bc*]oxete (**1**, 1,8-monoxynaphthalene) is reported to be a product of dehydration of 1,8-naphthalenediol;<sup>2a</sup> however, its synthesis cannot be repeated.<sup>2b</sup> Naphtho[1,8-*bc*]thiete 1,1-dioxide (**2**, 1,8-sulfonaphthalene) has been prepared and gives products of 1,8-dehydronaphthalene upon thermolysis.<sup>3</sup> We now report synthesis of 1-bromo-1*H*-cyclobuta[de]naphthalene (**3**) and 1*H*-cyclobuta[de]naphthalene (**4**, 1,8-methanonaphthalene), the first examples of naphthalene bridged in its 1,8-positions by single carbon atom moieties.<sup>4</sup>



Irradiation (450-W mercury lamp through Pyrex, N<sub>2</sub>) of the sodium salt (**6**) of 8-bromo-1-naphthaldehyde *p*-tosylhydrazone (mp 193–195°)<sup>5</sup> or (8-bromo-1-naphthyl)diazomethane (**7**)<sup>6</sup> in ethyl ether yields **3** (45%) along with *trans*-bis(8-bromo-1-naphthyl)ethylene (**5**, 15%, mp 203–204°).<sup>7</sup> Strained bromide **3** is possibly formed from (8-bromo-1-naphthyl)methylidene (**8**) as in eq 1. Bromide **3** is



white (mp 102–104° from ethanol after chromatography on silica gel)<sup>5</sup> and of the following properties:<sup>9a</sup> *m/e* 218, 220 ( $\text{M}^+$ , theory 218), 139 ( $\text{M}^+ - \text{Br}$ ); mol wt (osmometry) 215 ( $\text{CHCl}_3$ ); nmr ( $\text{CDCl}_3$ )  $\delta$  6.76 (s, 1 H, H at C<sub>1</sub>), 7.18 (d of d, 2 H, H at C<sub>2,7</sub>,  $J = 5$  and 2 Hz), 7.30–7.68 (m, 4 H, H at C<sub>3-6</sub>); <sup>13</sup>C nmr ( $\text{CDCl}_3$ )  $\delta$  51.9 (1 C, C<sub>1</sub>), 115.8 (2 C, C<sub>2,7</sub>), 122.9 (2 C, C<sub>4,5</sub>), 126.3 (1 C, C<sub>9</sub>), 131.4 (2 C, C<sub>3,6</sub>), 143.6 (2 C, C<sub>1a,7a</sub>), 145.1 (1 C, C<sub>8</sub>). The structure of **3** is confirmed by its rapid reaction with silver nitrate in aqueous dioxane at 40° to give 1-naphthaldehyde (**12**, 25%), 1-(1*H*-cyclobuta[de]naphthyl) nitrate (*m/e* 201, theory 201; ir (KBr) 1630, 1275, 865, 790  $\text{cm}^{-1}$ ), and silver bromide; **12** apparently arises by isomerization (eq 2) of 1-hydroxy-1*H*-cyclobuta[de]naphthalene (**11**). Alcohol **11** is an (expletive deleted) unstable compound.

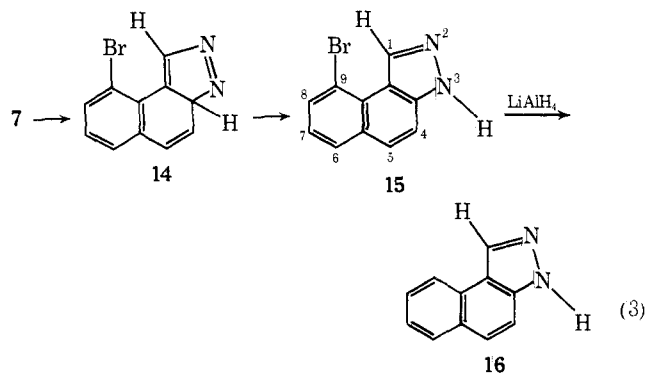


Reaction of **3** with magnesium in ethyl ether, hydrolysis with aqueous ammonium chloride, and gas chromatography at 135° yields **4** (60%), a colorless liquid:<sup>9b,10</sup> *m/e* 140.0628 ( $\text{M}^+$ , theory 140.0626); nmr ( $\text{CDCl}_3$ )  $\delta$  4.80 (s, 2 H, H at C<sub>1</sub>), 7.1 (d of d, 2 H, H at C<sub>2,7</sub>,  $J = 5$  and 2 Hz), 7.25–7.65 (m, 4 H, H at C<sub>3-6</sub>); <sup>13</sup>C nmr ( $\text{CDCl}_3$ )  $\delta$  47.31 (1 C, C<sub>1</sub>,  $J_{\text{C}^{13}-\text{H}} = 143.4$  Hz), 117.08 (2 C, C<sub>2,7</sub>), 121.29 (2 C, C<sub>4,5</sub>), 125.44 (1 C, C<sub>9</sub>), 130.57 (2 C, C<sub>3,6</sub>), 141.57 (2 C, C<sub>1a,7a</sub>), and 146.27 (1 C, C<sub>8</sub>). The 90-MHz pmr spectrum of **4** reveals that its apical protons do not display an AB pattern. Further the proton-coupled <sup>13</sup>C nmr spectrum of **4** shows the apical carbon to be a triplet rather than a doublet of doublets, indicating that its C<sub>1</sub> protons are magnetically equivalent. The strained hydrocarbon, **4**, is thus essentially planar or of a rapidly equilibrating puckered conformation. The uv spectra of **3** and **4** are compared in Table 1 with naphthalene (**13**). The slight shift to longer wavelengths and the significant decrease in the extinction coefficient of the E<sub>1</sub> bands of **3** and **4** are indicative of perturbed  $\pi$  electron systems.

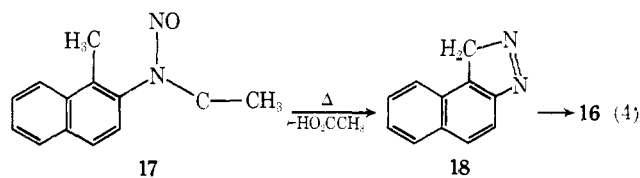
**Table I.** Ultraviolet Absorption of **3**, **4**, and **13**

Compound	$\lambda_{\max}^{\text{EtOH}}$ , nm ( $\epsilon$ )
<b>3</b>	320 (570), 307 (730), 284 (4650), and 225 (67,000)
<b>4</b>	312 (341), 302 (512), 282 (4400), 276 (4330), 272 (4640), 224 (69,500)
<b>13</b>	312 (255), 298 (324), 286 (3800), 276 (5,550), 221 (115,000)

The thermal behavior of **7** is different from that of photolysis. Thus **7** isomerizes at 120° in chlorobenzene to 9-bromo-3*H*-benz[*e*]indazole (**15**, >50%)<sup>11a</sup> possibly as in eq 3. The properties of **15**, a white solid, are the following: mp 231–232°; *m/e* 245.9798 ( $M^+$ , theory 245.9793); nmr ( $\text{CDCl}_3$ -DMSO- $d_6$ )  $\delta$  7.14–8.11 (m, 5 H, H at C<sub>4–8</sub>), 9.19 (s, 1 H, H at C<sub>1</sub>), 13.4 (broad s, exch, 1 H, H at N<sub>3</sub>). Lithium aluminum hydride reduces **15** in ethyl ether to 3*H*-benz[*e*]indazole (**16**, 80%),<sup>11a</sup> a white solid: mp 234–235°



(from chloroform); *m/e* 168.0690 ( $M^+$ , theory 168.0687); nmr ( $\text{CDCl}_3$ -DMSO- $d_6$ )  $\delta$  7.34–8.33 (m, 6 H, aromatic H), 8.45 (s, 1 H, C<sub>1</sub>), 13.12 (broad s, 1 H, exch, N<sub>3</sub>). Indazole **16** is identical with that (**16**) derived from thermolysis of *N*-(1-methyl-2-naphthyl)-*N*-nitrosoacetamide (**17**)<sup>11b</sup> assigned initially as **18**<sup>11b</sup> and now reassigned.



The chemistry of **4** and **6**, their derivatives, and their analogs is being investigated with all deliberate speed.

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#### References and Notes

- (1) D. W. J. Cruickshank, *Acta Crystallogr.*, **10**, 504 (1957).
- (2) (a) E. Ayers, British Patent 394,511 (June 29, 1933); *Chem. Abstr.*, **28**, 181 (1934); (b) A. J. Gordon, *J. Org. Chem.*, **35**, 4261 (1970).
- (3) R. W. Hoffmann and W. Sieber, *Justus Liebigs Ann. Chem.*, **703**, 96 (1967).
- (4) Synthesis of 1*H*-cyclobuta[*de*]naphthalenes by Wolff ring contractions of 2-diazoacenaphthenone has been unsuccessful: W. Reid and H. Lowasser, *Justus Liebigs Ann. Chem.*, **683**, 118 (1965); D. C. DeJongh and R. Y. Van Fossen, *Tetrahedron*, **28**, 3603 (1972).
- (5) All new compounds so indicated give satisfactory analyses.
- (6) Prepared by thermal decomposition of **6** in methanol by the procedure of W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952).
- (7) *M/e* (obsd) 435.946 (435.9463); ir (KBr) 910, 820, 810, 760, 710, 680  $\text{cm}^{-1}$ ; nmr ( $\text{CDCl}_3$ )  $\delta$  6.0–8.0 (m, aromatic H).
- (8) Attempts to isolate **9** have been unsuccessful.
- (9) (a) Ir (KBr) 785, 775, 680, 475  $\text{cm}^{-1}$ . (b) Ir (neat) 3030, 2960, 1470, 1340, 1000, 765  $\text{cm}^{-1}$ . (c) Ir (KBr) 3250–2800 (m), 1620, 1595, 1450, 1375, 1185, 1075, 1030 (m), 950, 860, 815, 750 (s)  $\text{cm}^{-1}$ .
- (10) Bromide **3** is also reduced by sodium bis(2-methoxyethoxy)aluminum hydride (Red-al) in ether to **4** (>80%).
- (11) (a) The assignments of structure as **15** and **16** rather than as their tautomers with hydrogen on N<sub>2</sub> are made on the expectation that they are more stable; (b) R. Huisgen and H. Nakaten, *Justus Liebigs Ann. Chem.*, **586**, 84 (1954).

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