Supplementary Material Available: (I) Data and rationale for assignment of structure to (trimethylsilyl)isopropenyltoluenes **11** and **12** (includes ^{1}H and ^{13}C NMR, IR, and mass spectral data); (II) data and rationale for ring carbon ^{13}C NMR assignments for **7** and analysis of isotope labeling experiments (17 pages). Ordering information is given on any current masthead page.

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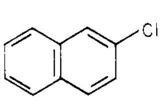
Generation of a 1,3-Dehydronaphthalene. Evidence for the Diyl Structure

Summary: The dichlorocarbene adduct of 2-bromoindene reacts with a solution of potassium *tert*-butoxide in tetrahydrofuran to yield derivatives of naphthalene which are consistent with the intermediacy of 1,3-dehydronaphthalene in the diradical form.

Sir: Although recent studies have shown that 1,4-dehydrobenzene may be generated and trapped in both the diradical[1] (1,4-benzenediyl) and bridged (butalene) forms,[2] only the bicyclic structure of 1,3-dehydrobenzene[3] (bicyclo[3.1.0]hexatriene) has been trapped. We now wish to report our evidence that 1,3-dehydronaphthalene can be generated and trapped as the diradical.

The starting material for the work, compound **1**, was prepared from indene, via 2-bromoindene, in ~10% yield (Scheme I).[4] Treatment of **1** with a solution of *t*-BuOK in THF at 0 °C for 1 h yielded products **2–11**.[6] When THF-d_8 is the solvent the same mixture of products is obtained, although in slightly different yields. Examination of the product mixture obtained from the deuterated solvent by GC–mass spectroscopy revealed that the chloronaphthalene is approximately 79% d_2, 13% d_1, and 8% d_0. The ^{13}C NMR spectrum helps to establish the location of the deuterium atoms, as in **2a**.[9]



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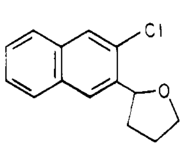

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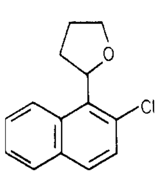

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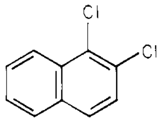

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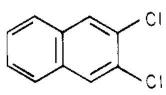

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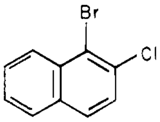

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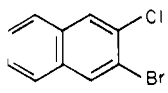

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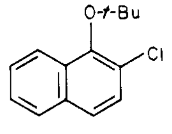

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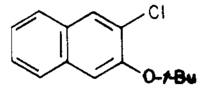

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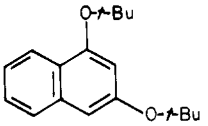

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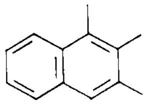

2a

Although it was not possible to establish the position

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(1) Jones, R. R.; Bergman, R. G. *J. Am. Chem. Soc.*, **1972**, *94*, 660.

(2) Breslow, R.; Napierski, J.; Clarke, T. C. *J. Am. Chem. Soc.*, **1975**, *97*, 6275.

(3) Washburn, W. N. *J. Am. Chem. Soc.*, **1975**, *97*, 1615. Washburn, W. N.; Zahler, R. *J. Am. Chem. Soc.*, **1976**, *98*, 7827, 7828. *Ibid.* **1977**, *99*, 2012. Washburn, W. N.; Zahler, R.; Chen, I. *Ibid.* **1978**, *100*, 5863. For earlier reference see: Berry, R. S.; Clardy, J.; Schafer, M. E. *Tetrahedron Lett.*, **1965**, 1011. McGriff, R. B. *Diss. Abstr. B* **1967**, *28*, 844. Bertorello, H. E.; Rossi, R. A.; de Rossi, R. H. *J. Org. Chem.* **1970**, *35*, 3332.

(4) A procedure similar to that reported by Joshi, Singh, and Pande[5] was used in the synthesis of **1**. The ^{1}H NMR spectrum of **1** proved to be surprisingly simple. What appears to be two singlets at δ 3.20 (1 H) and 3.71 (2 H) on expansion proved to be finely divided multiplets. The aromatic region is a four-proton complex multiplet around δ 7.02. In the decoupled ^{13}C NMR spectrum four quaternary carbons, two at 46.2 and 68.3 ppm and two aromatic at 138.1 and 142.6, could be detected easily. Of the remaining six signals two were at 45.9 and 50.0 ppm and the four aromatic ones at 123.6, 125.1, 126.7, and 128.0 ppm. The two signals at 45.9 and 50.0 ppm split into a triplet (J = ~2.2 ppm) and a doublet (J = ~2.2 ppm), respectively.

(5) Joshi, G. C.; Singh, N.; Pande, L. M. *Tetrahedron Lett.*, **1972**, 1461.

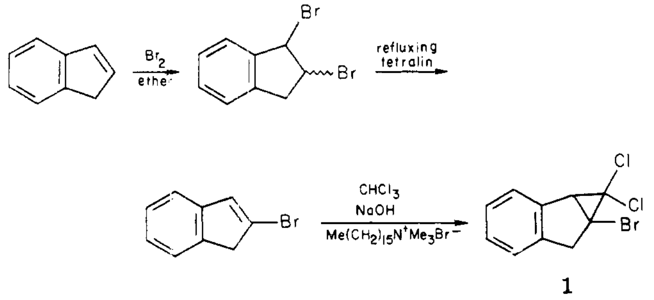
(6) The GC percentages (80% material balance) of compounds **2–11** are: **2**, 7%; **3**, 3.4%; **4**, 2.6%; **5** + **6**, 16%; **7** + **8**, 17%; **9**, 27%; **10**, 13%; **11**, 14%. Purification of the various products was achieved by TLC (silica gel, several solvents). Structures were assigned on the basis of the following data: Chloronaphthalene (**2**) was identified by comparison with a commercial sample (Aldrich Chemical Co. Inc.). A mixture of **3** and **4** exhibits NMR signals in $CDCl_3$ at δ 1.00–2.80 (m, 8 H), 3.70–4.12 (m, 2 H), 4.14–4.50 (m, 2 H), 5.20–5.40 (t, 1 H, J = 6 Hz), 5.60–5.80 (m, 1 H), 6.70–8.00 (m, 11 H), 8.25–8.50 (m, 1 H); IR (neat) 3060 (w), 2980 (s), 2870 (m), 1620 (w), 1590 (m), 1505 (m), 1460 (m), 1365 (m), 1325 (m), 1185 (m), 1165 (m), 1130 (m), 1070 (s), 1070 (s), 1050 (s), 805 (m), and 745 (s) cm^{-1}. Elemental composition was determined by high-resolution mass spectroscopy. These compounds were shown to be a 56:44 mixture by GC using a 250-ft SF-96 capillary column. Samples of **5** and **7** were prepared as described in the literature.[7,8] **6** and **8** were prepared by heating **1** in dimethyl sulfoxide at 40 °C. **6** has NMR signals in $CDCl_3$ at δ 7.34–7.50 (d of d, 2 H, J = 6 and 3 Hz), 7.56–7.70 (d of d, J = 6 and 3 Hz), and 7.86 (s, 24), whereas **8** has signals at δ 7.30–7.65 (AB quartet, 4 H, J = 9 Hz), 7.80 (s, 1 H), and 7.98 (s, 1 H). A sample of **9** was prepared from the corresponding chloronaphthol: NMR ($CDCl_3$) δ 1.47 (s, 9 H), 7.30–7.90 (m, 5 H), and 8.0–8.30 (m, 1 H). **10** has NMR signals at δ 1.47 (s, 9 H), 7.25–7.40 (m, 2 H), and 7.45 (s, 1 H). 1,3-Di-*tert*-butoxynaphthalene (**11**) exhibits the following spectral data: NMR ($CDCl_3$) δ 1.40 (s, 9 H), 1.48 (s, 9 H), 6.80–6.86 (d, 1 H, J = 3 Hz), 7.10–7.17 (d, 1 H, J = 3 Hz), 7.25–7.50 (m, 2 H), 7.55–7.75 (m, 1 H), and 8.05–8.23 (m, 1 H); IR (neat) 3060 (w), 2970 (s), 2940 (sh), 1622 (m), 1595 (m), 1575 (m), 1500 (m), 1390 (s), 1362 (s), 1280 (w), 1260 (w), 1230 (w), 1180 (s), 1160 (s), 1130 (s), 1080 (m), 995 (m), 905 (w), 880 (w), 840 (w), and 750 (m). Cleavage of this compound with 40% HBr in HOAc provided 1,3-naphthalenediol.

(7) Clemo, G. R.; Cockburn, J. G.; Spence, R. *J. Chem. Soc.*, **1931**, 1265.

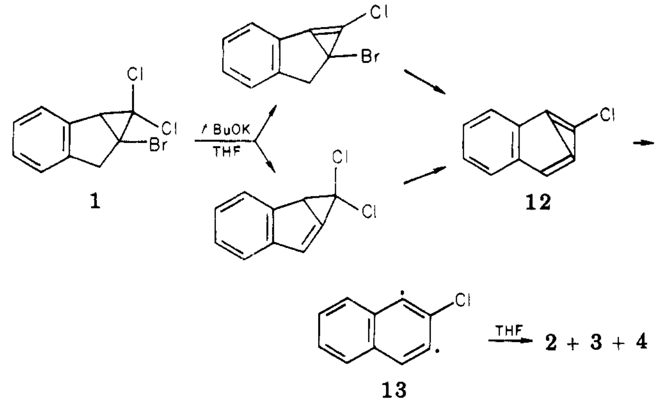
(8) Wilson, N. K.; Zehr, R. D. *J. Org. Chem.*, **1978**, *43*, 1768.

(9) The studies of monosubstituted naphthalenes by Kitching, Bulpitt, Doddrell, and Adcock[10] provided a reference for the effects observed on deuteration of naphthalenes.

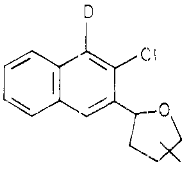
Scheme I



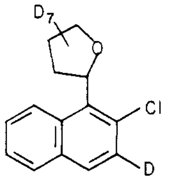
Scheme II



of the label in compounds 3 and 4, the incorporation of eight deuterium atoms (mass spectroscopy) suggests structures **3a** and **4a**. The remaining products, **5–11**, were not deuterated.



3a

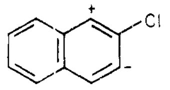


4a

The introduction of deuterium into the chloronaphthalene and the detection of **3** and **4** helps to establish the intermediacy of the diyl **13**. The formation of **2**, **3**, and **4** can then be rationalized by assuming one (or both) of the paths in Scheme II.

The origin of compounds **5–11** is puzzling. However, several control experiments show that all of the products are stable to the reaction conditions. Furthermore, no incorporation of deuterium is detected when the crude reaction mixture or the individual products are treated with t-BuOK in THF-d_8.

We tend to discount zwitterions **15** and **16** as viable



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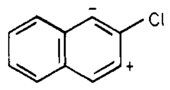

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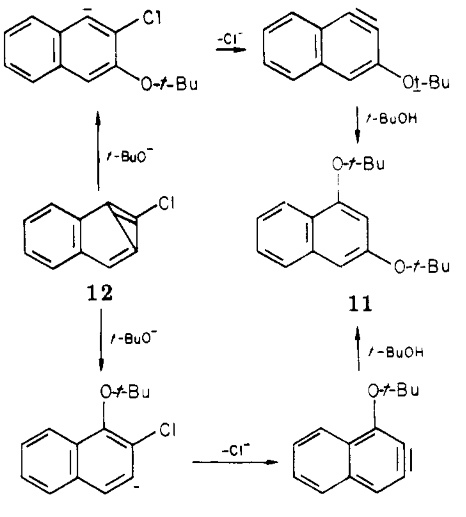
intermediates to **5–11** since they are probably much less stable (higher energy) than the diyl **13**. A possible route to **5–11** is the nonregiospecific addition of nucleophile (Cl^-, Br^-, t-BuO^-) to the bridging bond of **12**. This process would lead directly to products **5–10**, whereas **11** could arise via one (or both) of the naphthalynes illustrated in Scheme III.

Scheme III



Thus, some ambiguity still exists with regard to the origin of the products which result from incorporation of nucleophile. However, it seems clear that diradical **13** is implicated as an intermediate in the formation of **2–4**. The contrasting properties of the parent compound[3] and the naphthalene derivative observed here also await explanation.

Acknowledgment. We gratefully acknowledge The Robert A. Welch Foundation and Eli Lilly and Company for support of this work.

Registry No. **1**, 71436-63-0; **2**, 91-58-7; **3**, 71436-64-1; **4**, 71436-65-2; **5**, 2050-69-3; **6**, 2050-75-1; **7**, 71436-66-3; **8**, 71436-67-4; **9**, 71436-68-5; **10**, 71436-69-6; **11**, 71436-70-9; indene, 95-13-6; 2-bromoindene, 10485-09-3.

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(10) Kitching, W.; Bulpitt, M.; Doddrell, D.; Adcock, W. *Org. Magn. Reson.*, **1974**, *6*, 289.

Copper-Catalyzed α Addition of Perfluoroalkyl Iodides to Isocyanides

Summary: α Addition of perfluoroalkyl iodides to isocyanides (alkyl or/aryl) affords perfluoroalkylimidoyl iodides in good yield; the addition is catalyzed by copper powder.

Sir: Insertion of divalent carbon species into the carbon–iodine bond of a perfluoroalkyl iodide (R_FI; $R_F = CF_3(CF_2)_n$) is a very unusual reaction. This condensation failed with dichlorocarbene, diazo ketones, and diazo esters and was only achieved with diazomethane, giving a mixture of mono and bis homologation products.[1,2] Furthermore,

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(1) Hudlicky M.; König, J. *Collect. Czech. Chem. Commun.* **1963**, *28*, 2824–2826.

(2) Knunyants, I. L.; Pervova, E. Ya., *Bull. Acad. Sci. USSR (Engl. Transl.)* **1965**, 860–861.