warmed to −20 °C and allowed to react for 22 h. The usual isolation and Chromatotron separation (1:1 hexane–Et_2O) gave 56 mg (35%, R_f = 0.46) of product as a colorless oil: ^1H NMR ($CDCl_3$) δ 2.21 (s, 3, CH_3), 3.34 (d, J = 7.0 Hz, 2, CH_2), 6.32 (dt, J = 15.9, 7.0 Hz, 1, CH_2CH=), 6.47 (d, J = 15.9 Hz, 1, =CH), 7.2–7.4 (m, 5); IR (neat) 3060, 3030, 2970, 2930, 1716 (C=O), 1677, 1600, 1555, 1497, 1450, 1358, 1157, 962 cm^{-1}. Also formed was 1,6-diphenyl-3-acetyl-1,5-hexadiene: 42 mg (40%, R_f 0.56); ^1H NMR ($CDCl_3$) δ 2.22 (s, 3, $COCH_3$), 2.50 (m, 1, $CHCH_2$), 2.70 (m, 1, $CHCH_2$), 3.41 (m, 1, $CHCH_2$), 6.15 (m, 2, =CH), 6.50 (m, 2, =CH), 7.1–7.4 (m, 10); IR (neat) 3080, 3058, 3022, 2995, 2910, 1712 (C=O), 1598, 1493, 1448, 1351, 1152, 1065, 1022, 960, 736, 684 cm^{-1}.

***n*-Butyl *trans*-Cinnamyl Ketone.**[10] The carbonylate was formed over 0.75 h at −40 °C [650 mg of **1** (1.6 mmol), 700 μL of 2.3 M *n*-BuLi (1.6 mmol), 10 mL of THF], then cinnamyl bromide (197 mg, 1.0 mmol) was added, and the solution was warmed to −20 °C and allowed to react for 21 h. The usual isolation and Chromatotron separation (7:1 hexane–Et_2O) gave 70 mg (35%, R_f 0.31) of product as a colorless oil: ^1H NMR ($CDCl_3$) δ 0.91 (t, J = 7.3 Hz, 3, CH_2CH_3), 1.31 (m, 2, CH_2CH_3), 1.58 (m, 2, $CH_2CH_2CH_3$), 2.49 (t, J = 7.4 Hz, 2, $COCH_2CH_2$), 3.31 (d, J = 6.9 Hz, 2, =$CHCH_2$), 6.32 (dt, J = 16.0, 6.9 Hz, 1, =$CHCH_2$), 6.46 (d, J = 15.9 Hz, 1, CH=$CHCH_2$), 7.2–7.4 (m, 5); IR (neat) 3080, 3055, 3020, 2950, 2920, 2862, 1710 (C=O), 1595, 1492, 1461, 1445, 1400, 1374, 1252, 1118, 1062, 1020, 956, 730, 680 cm^{-1}.

3-Acetylcyclohexene. The carbonylate was formed over 0.5 h at −40 °C [650 mg of **1** (1.6 mmol), 1.14 mL of 1.4 M CH_3Li (1.6 mmol), 10 mL of THF], then 3-bromocyclohexene (116 μL, 1.0 mmol) was added, and the solution was warmed to −20 °C and allowed to react for 24 h. The usual isolation and Chromatotron purification (1:1 Et_2O–hexane) gave two major fractions. The second fraction was 25 mg (20%, R_f 0.50) of product as a colorless oil: ^1H NMR ($CDCl_3$) δ 2.18 (s, 3, CH_3), 1.2–2.4 (m, 6), 3.1 (m, 1, CH), 5.85 (m, 2, CH=CH); IR (neat) 3020, 2930, 2860, 2830, 1710 (C=O), 1642, 1445, 1430, 1354, 1275, 1226, 1164, 1045 cm^{-1}. Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.94. Found: C, 77.18; H, 9.71. The first fraction was 48 mg (59%, R_f 0.80) of 3-(3-cyclohexen-1-yl)cyclohexene (**6e**).[23] ^1H NMR ($CDCl_3$) δ 1.0–2.3 (m, 14), 5.56 (m, 4); IR (neat) 3018, 2925, 2855, 2835, 1650, 1445, 1432, 1338, 1309, 1140, 1129, 1052, 975, 901, 870, 862, 726 cm^{-1}.

Acylation with BF_3·Et_2O and/or Allylic Chlorides. The reactions were performed as with allylic bromides with the exception that if a Lewis acid was used, it was added 10–30 min after alkyllithium addition and the reaction mixture allowed to stir at −40 °C for 10–30 additional min. Then the appropriate allylic halide was introduced. A representative example follows.

4,5-Dimethylene-2,7-octanedione. The carbonylate was made over 20 min at −40 °C [814 mg of **1** (2.0 mmol), 1.25 mL of 1.6 M CH_3Li (2.0 mmol), 10 mL of THF], then 1 equiv of BF_3·Et_2O (240 μL, 2.0 mmol) was added, and the mixture was stirred an additional 10 min. Then 2,3-bis(chloromethyl)-1,3-butadiene (91 mg, 0.6 mmol) was added and the reaction warmed to −20 °C and allowed to react for 7 h. The usual isolation and Chromatotron purification (3:1 Et_2O–hexane) gave 51 mg (51%, R_f 0.29) of product as a white crystalline solid: mp 55–57 °C; ^1H NMR ($CDCl_3$) δ 2.17 (s, 6, $COCH_3$), 3.38 (s, 4, CH_2), 5.16 (s, 2, =CHH), 5.24 (s, 3, =CHH); IR (KBr) 3094, 3000, 2959, 2906, 1820, 1709 (C=O), 1600, 1422, 1399, 1365, 1322, 1172, 1143, 1015, 904 cm^{-1}. Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.33; H, 8.26.

Reaction of β-Bromostyrene with 3. The carbonylate was made over 0.5 h at −40 °C [900 mg of **1** (2.21 mmol), 1.7 mL of 1.3 M CH_3Li (2.2 mmol), 20 mL of THF], then β-bromostyrene (91 μL, 0.7 mmol) was added, and the reaction was warmed to −20 °C for 48 h. The usual isolation and Chromatotron purification (1:1 hexane–Et_2O) gave 48 mg (36%, R_f 0.38) of 3-phenyl-2,5-hexanedione (**3a**) as product, identical in all respects with material made by an alternate procedure.[10]

Acknowledgment. Support for this research by National Science Foundation Grant CHE8200522 is gratefully acknowledged.

Registry No. **1**, 7632-00-0; **3a**, 25234-74-6; **3b**, 25234-75-7; **3c**, 98859-25-7; **3d**, 866-71-7; **3e**, 25234-81-5; **3f**, 4437-50-7; **3g**, 92803-31-1; **3h**, 98859-26-8; *cis*-**3j**, 98859-27-9; *trans*-**3j**, 98859-28-0; **3k**, 98859-29-1; **4a**, 98859-30-4; **4b**, 98859-31-5; **4c**, 98859-32-6; **4d**, 98859-33-7; **4e**, 98859-34-8; **4e'**, 98859-35-9; **4f**, 98859-36-0; **4g**, 98859-37-1; **6a**, 35162-77-7; **6e**, 41585-33-5; $Co(NO)(CO)_3$, 14096-82-3; $Co_2(CO)_8$, 15226-74-1; CH_3Li, 917-54-4; *n*-BuLi, 109-72-8; PhLi, 591-51-5; benzalacetone, 122-57-6; chalcone, 94-41-7; mesityl oxide, 141-79-7; *trans*-3-penten-2-one, 3102-33-8; phorone, 504-20-1; 1-acetylcyclohexene, 932-66-1; (+)-(*R*)-pulegone, 89-82-7; benzoquinone, 106-51-4; 2,3-dimethylbenzoquinone, 526-86-3; 2,5-dimethylbenzoquinone, 137-18-8; toluquinone, 553-97-9; 2,6-dimethylbenzoquinone, 527-61-7; duroquinone, 527-17-3; 4-acetyl-2,3,4,5,6-pentamethyl-2,5-cyclohexadienone, 98874-77-2; naphthoquinone, 130-15-4; *trans*-geranyl bromide, 6138-90-5; methyl *trans*-geranyl ketone, 61692-34-0; *n*-butyl *trans*-geranyl ketone, 98859-38-2; methyl *trans*-cinnamyl ketone, 42762-56-1; *trans*-cinnamyl bromide, 26146-77-0; *n*-butyl *trans*-cinnamyl ketone, 98859-39-3; *trans*-cinnamyl chloride, 21087-29-6; *trans*-geranyl chloride, 5389-87-7; 3-acetylcyclohexene, 29372-98-3; 3-bromocyclohexene, 1521-51-3; 3-chlorocyclohexene, 2441-97-6; 3-(3-cyclohexen-1-yl)cyclohexene, 41585-33-5; 4,5-dimethylene-2,7-octanedione, 98859-40-6; 2,3-bis(chloromethyl-1,3-butadiene), 19869-24-0; β-bromostyrene, 103-64-0; 1,6-diphenyl-3-acetyl-1,5-hexadiene, 98859-41-7.

(23) Kropp, P. J.; Snyder, J. J.; Rawlings, P. C.; Fravel, H. G., Jr. *J. Org. Chem.* **1980**, *45*, 4471.

Notes

Reductive Debenzylation of 1-Benzylnaphthalene by a Na–K Alloy

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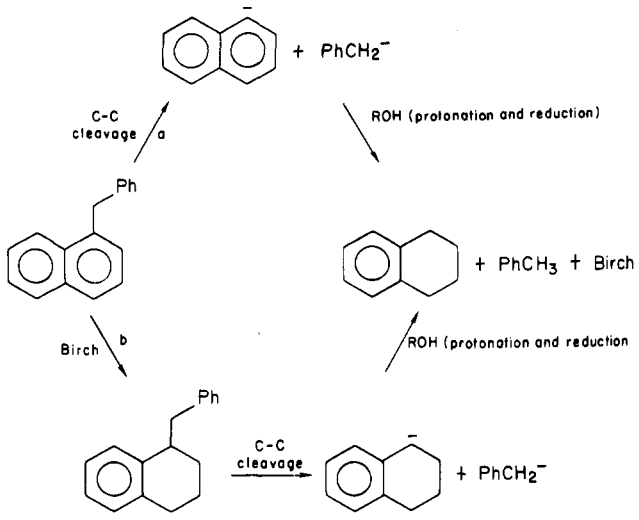
It has been reported that a Na–K alloy, when dissolved in a mixture of glyme–triglyme at 0 °C, is an excellent reagent for cleaving certain carbon–carbon bonds under mild conditions.[1,2] When applied to coal, this blue solution of "solvated electrons" is an excellent reducing medium for converting coal to a pyridine-soluble product.[3]

(1) (a) Collins, C. J.; Hombach, H.-P.; Maxwell, B.; Woody, M. C.; Benjamin, B. M. *J. Am. Chem. Soc.* **1980**, *102*, 851–853. (b) Collins, C. J.; Hombach, H.-P.; Maxwell, B. E.; Benjamin, B. M.; McKamey, D. *J. Am. Chem. Soc.* **1981**, *103*, 1213–1214. (c) Collins, C. J.; Hombach, H.-P.; Maxwell, B. E.; Benjamin, B. M. *Proc.-Int. Kohlenwiss. Tag.* **1981**, 121–126. (d) Collins, C. J.; Chambers, R. R., Jr., unpublished results.

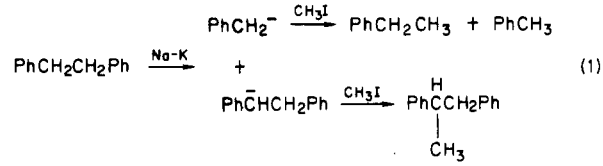
(2) For a related study using K in a glyme/octaglyme mixture, see: Schanne, L.; Haenel, M. W. *Tetrahedron Lett.* **1979**, *44*, 4245–4248.

0022-3263/85/1950-4960$01.50/0

Scheme I



Under appropriate conditions (Na–K, 50/50 (v/v) glyme–triglyme, 0 °C, 15 min), the sp^3–sp^3 carbon–carbon bond in 1,2-diphenylethane is readily cleaved to $PhCH_2^-$ (91% conversion) which, upon a methyl iodide quench, yields ethylbenzene and toluene (ratio, 2.7:1.0).[1a] A secondary product, 1,2-diphenylpropane (3% yield), is also formed indicating that competitive carbon–hydrogen cleavage (or metalation) occurs under these conditions.[1a] The observation of $PhCH_3$ as a major side product from the methyl quench suggests that $PhCH_2^-$ is unstable in glymes at this temperature, undergoing protonation by the solvent.[4]



(1)

Further studies[1d] demonstrated that the use of an ethanol quench gives those products expected from protonation of the respective anions accompanied by large amounts of material derived from Birch reduction of aromatic rings. For example, Na–K reduction of 1,2-diphenylethane gives 2,5-dihydrotoluene and $PhCH_3$ in a ratio of 0.96:1.0. However, the dihydrotoluene is absent if *tert*-butyl bromide is substituted for ethanol as the quencher. The alkyl bromide serves the dual roles of proton source[5] for the various anions and as oxidizing agent[6] toward excess alloy. Thus, the excess reducing equivalents which remain prior to the quench, and which are responsible for Birch reduction, are consumed by the *tert*-butyl bromide.

This reductive C–C cleavage reaction parallels the observations of Lagendijk and Swarc[7] where 1,2-dinaphthylethane was found to undergo bond fission upon exposure to Na (in THF, THP, DME, etc.) and the more recent report of Grovenstein et al.[8] which describes the reductive cleavages of 1,2-diphenylethanes by a Cs–K–Na alloy (THF, −75 °C). These previous studies all point toward a common mechanism for sp^3–sp^3 C–C bond fission in which a dianion is the reactive intermediate producing the cleavage products. Both absolute rate measurements for the 1,2-dinaphthylethane cleavage[7] and relative rate studies using methyl-substituted 1,2-diphenylethanes[8,9] are consistent with rate-determining cleavage of a dianion.

$$2(ArCH_2CH_2Ar)^{-\cdot} \rightleftarrows (ArCH_2CH_2Ar)^{2-} + (ArCH_2CH_2Ar)$$

$$(ArCH_2CH_2Ar)^{2-} \xrightarrow{\text{slow}} 2ArCH_2^- \qquad (2)$$

There are indications that the reductive cleavages of sp^3–sp^2 C–C bonds may be more complex and may follow distinctly different pathways depending upon the substrate and the reducing conditions. For example, the aryl cleavage of 9,9-diarylfluorenes[10] by K in 1,2-dimethoxyethane proceeds according to a rate law consistent with a mechanism similar to (2). Diphenylmethane, on the other hand, ruptures at the aliphatic–aromatic C–C bond using a Na–K alloy in glymes, by a process possibly involving an ipso-aromatic attack of $(PhCH_2Ph)^{-\cdot}$ on $PhCH_2Ph$ followed by loss of a benzyl anion.[1b] This apparent variation in reaction pathway may be a general property of diarylmethane cleavages. Presumably, this diversity of mechanism reflects the greater energy required to break the sp^3–sp^2 C–C bond of $ArCH_2Ar$ compared to the sp^3–sp^3 C–C bond of $ArCH_2CH_2Ar$.[11] The result is that each $ArCH_2Ar$ substrate will undergo bond cleavage by the lowest energy pathway available for that particular compound.

Here, we describe the reductive debenzylation of 1-benzylnaphthalene by a Na–K alloy (0 °C) in a mixture of glymes. All of the experimental evidence is consistent with an alternative mechanism for sp^3–sp^2 C–C bond cleavage involving initial Birch reduction to give a 1,2-diarylalkane unit which then fragments by fission of an sp^3–sp^3 C–C bond.

When 1-benzylnaphthalene is subjected to Na–K reduction followed by an ethanol quench, the cleavage products (19% conversion) are $PhCH_3$ plus dihydrotoluene and tetralin plus dihydrotetraline in a ratio of 1.1:1.0, respectively, for the two product sums. In addition, there are numerous Birch products derived from the parent 1-benzylnaphthalene. The presence of 1-benzyltetralin (14% yield) among these was confirmed by independent synthesis and comparison of GC retention times and mass spectral properties. Analogous reduction of [*methylene*-^{14}C]-1-benzylnaphthalene produces Ph-$^{14}CH_3$ as the sole carbon-14 labeled cleavage product.[13] The absence of other labeled fragmentation products precludes the al-

(3) Niemann, K.; Richter, U.-B. *Fuel* **1979**, *58*, 838–840. Neimann, K.; Hombach, H.-P., *Fuel* **1979**, *58*, 853–856. Niemann, K.; Richter, U.-B., *Fuel* **1982**, *61*, 423–429. Hagaman, E. W.; Woody, M. C. *Fuel* **1982**, *61*, 53–57.

(4) With extended reaction times (3 h, ref 1a) the yield of toluene approaches that of ethylbenzene. Also, see: ref 6b, pp 266–268.

(5) House, H. O. "Modern Synthetic Reactions", 2nd ed.; W. A. Benjamin, Inc.: Reading, MA, 1972; pp 530–531.

(6) For discussions and examples of alkyl halides as electron acceptors, see: (a) Garst, J. F., *Acc. Chem. Res.* **1971**, *4*, 400–406. (b) Holy, N. L. *Chem. Rev.* **1974**, *74*, 243–277. (c) Bank, S.; Bank, J. F., *ACS Symp. Ser.* **1978**, *69*, pp 343–358. (d) Grovenstein, E., Jr. In "Advances in Organometallic Chemistry"; Stone, F. G. A., West, R., Eds.; Academic Press: New York, 1977; pp 167–210.

(7) Lagendijk, A.; Swarc, M. *J. Am. Chem. Soc.* **1971**, *93*, 5359–5363.

(8) Grovenstein, E., Jr.; Bhatti, A. M.; Quest, D. E.; Sengupta, D.; VanDerveer, D. *J. Am. Chem. Soc.* **1983**, *105*, 6290–6299.

(9) We find in our system that the conversion to cleavage products (*tert*-butyl bromide quench) decreases in the order bibenzyl (83%) > 4-methylbibenzyl (39%) > 4,4′-dimethylbibenzyl (0%). This is reminiscent of the relative cleavage rates found by Grovenstein et al. (ref 8) for the same substrates (Cs–K–Na alloy, −75 °C) where the rates decrease in the order bibenzyl (1.00) > 4-methylbibenzyl (0.0228) > 4,4′-dimethylbibenzyl (0.004–0.00004).

(10) Walsh, T. D.; Megremis, T. L., *J. Am. Chem. Soc.* **1981**, *103*, 3897–3898.

(11) Cleavage of $ArCH_2CH_2Ar$ will produce two resonance stabilized anions, a feature which is not possible with $ArCH_2Ar$.

(12) Negishi, E.; King, A. O.; Okukado, N. *J. Org. Chem.* **1977**, *42*, 1821–1823.

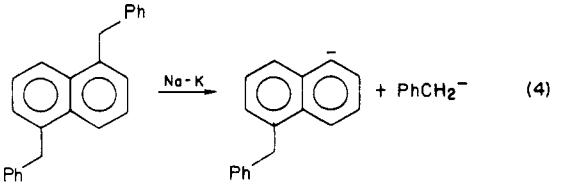
(13) Analysis was performed on a Packard 430 GC (Dexsil 300, Chromosorb WHP) equipped with a carbon-14 monitor.

ternative mode of reaction depicted in eq 3.

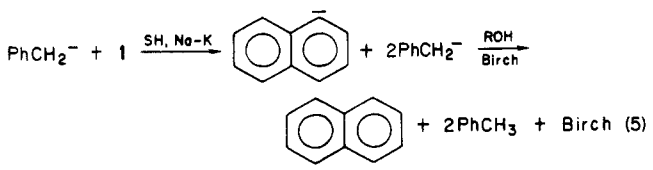
$$\text{1-naphthyl-}^{14}\text{CH}_2\text{Ph} \xrightarrow{\text{Na-K}} \text{1-naphthyl-}^{14}\text{CH}_3 + \text{PhH} \quad (3)$$

There are two reasonable pathways which can account for these observations (Scheme I). In path a, direct sp^3–sp^2 C–C cleavage produces a naphthalene and benzyl fragment which for simplicity are shown as their respective anions. Subsequent protonation and Birch reduction of the naphthalene anion to tetralin plus dihydrotetralin and protonation accompanied by reduction of $PhCH_2^-$ to $PhCH_3$ plus dihydrotoluene would account for the observed products. The alternative route, path b, proceeds by initial Birch reduction to 1-benzyltetralin followed by a facile sp^3–sp^3 C–C clevage of the corresponding dianion to tetralin anion and $PhCH_2^-$. Subsequent protonation and reduction during the ethanol quench would result in the tetralin and toluene products. In a separate experiment, it was confirmed that the reaction of 1-benzyltetralin under similar conditions does yield $PhCH_3$ plus dihydrotoluene and tetralin plus dihydrotetralin products (ethanol quench, 71% conversion) in the expected 1:1 ratio. In path b, we have chosen to show the initial Birch product as benzyltetralin. Alternatively, the initial hydroaromatic species could be envisioned as 1-benzyl-1,4-dihydronaphthalene or 1-benzyl-1,2-dihydronaphthalene. However, in each case, the subsequent bond fission would involve an sp^3–sp^3 C–C bond cleavage. Further reduction of these dihydronaphthalene products to tetralin would likewise account for the observed products. In order for path b to be operative, it is necessary that there be available, prior to the alcohol quench, a proton source which can supply the required hydrogens for Birch reduction. The identity of the proton donor(s) was not established in this work. Presumably, either the solvent (vide supra) or the substrate itself, which has acidic hydrogens at the benzylic carbon, could satisfy this requirement.[6b] Both pathways are consistent with the observed product distribution; the major difference between them is the timing of events. In a, sp^3–sp^2 C–C cleavage occurs initially followed by Birch reduction whereas in b, Birch reduction is a prerequisite to bond cleavage.

1,5-Dibenzylnaphthalene was reduced (ethanol quench), and the product mixture was analyzed by GC/MS to probe which pathway is operative. If 1,5-dibenzylnaphthalene were to cleave according to path a, then the initial products would be $PhCH_2^-$ and 1-benzylnaphthalene anion 1 (reaction 4). Protonation of 1 (by solvent) followed by a

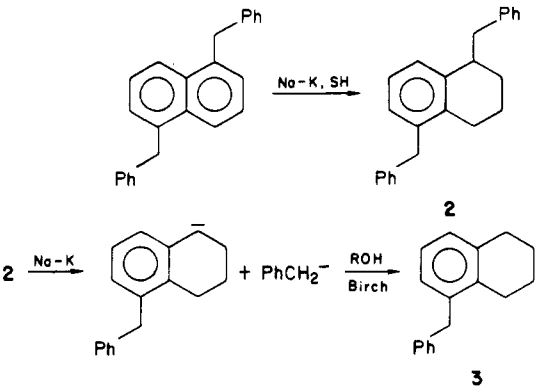


(4)



(5)

second bond cleavage reaction would ultimately produce, after a protic quench, a naphthalene fragment and 2 equiv of toluene (reaction 5). Conversely, with path b, dibenzyltetralin **2** would be formed initially (reaction 6). In **2** there is only one weak sp^3–sp^3 C–C bond for reductive cleavage. Thus, the expected product from an ethanol



(6)

$PhCH_3$ + Birch (7)

quench would be a 1:1 mixture of benzyltetralin **3** and $PhCH_3$. Experimentally, reduction of 1,5-dibenzylnaphthalene gives $PhCH_3$ plus dihydrotoluene and hydrogenated benzylnaphthalenes in a 1.0:1.1 ratio, respectively. This result along with the notable absence of hydrogenated naphthalenes as major products lend support to path b.

In conclusion, this study has identified an alternative mechanism by which $ArCH_2Ar'$ can undergo reductive C–C bond fission under dissolving metal conditions. This involves initial Birch reduction of the substrate to generate an sp^3–sp^3 C–C bond which then cleaves readily in the presence of a Na–K alloy.

Experimental Section

Materials. Bibenzyl (Aldrich) was purified by recrystallization from ethanol. 4,4′-Dimethylbibenzyl was synthesized by coupling 4-methylbenzyl bromide (1 mol) with magnesium turnings (0.5 mol) in ether. The product was recrystallized from 95% ethanol, mp 79–81 °C (lit.[8] mp 80–82 °C). 4-Methylbibenzyl was obtained by catalytic hydrogenation (10% Pd/C, 40 psi H_2, solvent ethanol) of 4-methylstilbene (gift from Ben M. Benjamin, ORNL). Chromatography (alumina activity I, eluent hexane) afforded the pure compound as a low-melting solid: ^{1}H NMR ($CDCl_3$) δ 7.0–7.4 (m, 9 H), 2.93 (s, 4 H), 2.33 (s, 3 H); MS, *m/e* (relative intensity) 197 (4.2), 196 (22.8), 106 (5.9), 105 (100.0), 103 (4.9), 91 (12.5), 79 (8.0), 78 (4.4), 77 (11.6), 65 (8.4).

1-Benzylnaphthalene. This was prepared according to the procedure outlined by Negishi et al.[12] for the synthesis of unsymmetrical diarylmethanes, using 1-bromonaphthalene (Aldrich), benzylzinc bromide, and tetrakis(triphenylphosphine)nickel(0). The final product had mp 54–57 °C; ^{1}H NMR ($CDCl_3$) δ 7.8 (m, 3 H), 7.2 (m, 9 H), 4.4 (s, 2 H); MS, *m/e* (relative intensity) 219 (15.0), 218 (100.0), 217 (59.6), 216 (10.6), 215 (31.5), 203 (30.3), 202 (35.2), 189 (10.2), 141 (17.7), 115 (19.9). Anal. Calcd for $C_{17}H_{14}$: C, 93.54; H, 6.46. Found: C, 93.41; H, 6.35.

[*methylene*-^{14}C]-1-Benzylnaphthalene was obtained similarly from 15 mCi/mol of Ph-$^{14}CH_2ZnBr$.

1,5-Dibenzylnaphthalene. 1,5-Diaminonaphthalene (Aldrich, 6.00 g, 75.9 mmol) was combined with cooling with 150 mL of water and 10 mL of concentrated H_2SO_4. $NaNO_2$ (5.80 g, 167 mmol) in water (50 mL) was charged in small portions, and the resulting mixture was stirred for 45 min at 0 °C. This mixture was filtered, and the filtrate was added to $(CuBr)_2$ (15.0 g, 52.3 mmol) which had been dissolved in a mixture of 48% HBr (225 mL) and water (225 mL). After stirring at 0 °C (1 h), room temperature (1–2 h), and then 70 °C (30 min), nitrogen evolution had ceased. The reaction was extracted with C_6H_6, dried (Na_2SO_4), and concentrated in vacuo. A total of 5.9 g (27%) of 1,5-dibromonaphthalene[14] was obtained. This was converted to 1,5-dibenzylnaphthalene (mp 147–148 °C) by the same procedure used to make 1-benzylnaphthalene: ^{1}H NMR ($CDCl_3$) δ 8.0 (m, 2 H), 7.4 (m, 12 H), 4.5 (s, 4 H); MS, *m/e* (relative intensity) 309 (19.4), 308 (100.0), 230 (7.8), 229 (7.0), 228 (5.9), 218 (14.2), 217 (100.0),

(14) Hodgson, H. H.; Whitehurst, J. S. *J. Chem. Soc.* **1947**, 80–81.

215 (36.9), 202 (21.5), 91 (22.0). Anal. Calcd for $C_{24}H_{20}$: C, 93.46; H, 6.54. Found: C, 93.11; H, 6.48.

1-Benzyltetralin. α-Tetralone (12.3 g, 84.3 mmol) in ether (70 mL) was added to benzylmagnesium chloride prepared in 100 mL of ether from benzyl chloride (11.7 g, 92.1 mmol) and magnesium (3.00 g, 123 mmol). After 72 h of stirring, the reaction was poured into an ice/HOAC mixture. Extraction (ether), neutralization (Na_2CO_3), and drying (Na_2SO_4) gave the crude product, which was loaded onto an alumina column (neutral, activity I) and eluted sequentially with hexane, 20% (v/v) ether/hexane, and then ether. The combined eluents were concentrated in vacuo to give 12.9 g (64%) of 1-benzyl-1-tetralol. Dehydration of the alcohol (7.2 g, 30 mmol) to 1-benzyl-3,4-dihydronaphthalene was accomplished by stirring in HCO_2H (100 mL, 30 min). The addition of water followed by an extraction (ether) ultimately yielded 6.1 g (92%) of 1-benzyl-3,4-dihydronaphthalene. Catalytic hydrogenation (40 psi H_2, 10% Pd/C) of the olefin (5.0 g, 23 mmol) produced 4.8 g (95%) of 1-benzyltetralin: ^1H NMR ($CDCl_3$) δ 7.25 (m, 9 H), 2.9 (m, 5 H), 1.7 (m, 4 H); MS, *m/e* (relative intensity) 222 (2.1), 132 (11.0), 131 (100.0), 130 (23.4), 129 (9.9), 128 (8.9), 127 (3.4), 116 (8.5), 115 (12.8), 91 (28.4). Anal. Calcd for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.52; H, 8.74.

General Na-K Reduction Procedure. All reductions were carried out under Ar using Na-K (1:4, w/w) in a 50/50 (v/v) mixture of glyme/triglyme. The ethereal solvents were distilled from Na-K prior to use and stored under an Ar atmosphere. Typically, Na-K (6 mequiv) was added to a cooled (0 °C) mixture of glymes (20 mL). After the deep blue solution formed (1 min of vigorous stirring), the substrate (1 mmol) in 1 mL of solvent was added, and stirring was maintained for 15 min. The reaction was terminated by adding ethanol (10 mL), methyl iodide (6 mmol), or *tert*-butyl bromide (6 mmol). After 5 min, water (50 mL) and an internal GC standard (biphenyl or *o*-xylene) were added, and the concentrated reaction mixture was analyzed by GC (Hewlett-Packard 5880, OV-101 fused silica capillary column, FID detection) and GC/MS (Hewlett-Packard 5995, EI, 70 eV). Product identity was confirmed by comparison of GC and GC/MS properties with authentic standards and yields were calculated by using the appropriate response factors. In the case of Birch products, the response factors were taken to be the same as for the parent hydrocarbon.

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Registry No. $PhCH_3$, 108-88-3; $Ph^{14}CH_3$, 22151-42-4; 1-benzylnaphthalene, 611-45-0; dihydrotoluene, 4313-57-9; dihydrotetralin, 51854-29-6; [*methyl*-^{14}C]-1-benzylnaphthalene, 98577-50-5; tetralin, 119-64-2; 1-bromonapthalene, 90-11-9; benzylzinc bromide, 62673-31-8; tetrakis(triphenylphospine)nickel, 15133-82-1; 1,5-diaminonaphthalene, 2243-62-1; 1,5-dibromonaphthalene, 7351-74-8; 1,5-dibenzylnaphthalene, 54811-17-5; α-tetralone, 529-34-0; 1-benzyl-1-tetralol, 98577-49-2; 1-benzyl-3,4-dihydronaphthalene, 85035-87-6; 1-benzyltetralin, 38899-49-9.

A Theoretical Study of the Decomposition of Alkyldiazenyl Radicals

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The mechanism of the thermal decomposition of azoalkanes continues to be the subject of much attention. The question of whether the reaction generally proceeds as a concerted two-bond cleavage (reaction 1a) or a stepwise mechanism (reaction 1b) has received heightened attention.

$$R{-}N{=}N{-}R' \rightarrow [R{-}N{=}N{-}R']^{\ddagger} \rightarrow R\cdot + N_2 + R'\cdot \quad (1a)$$

$$R{-}N{=}N{-}R' \rightarrow R{-}N{=}N\cdot + R'\cdot \rightarrow R\cdot + N_2 + R'\cdot \quad (1b)$$

In a recent MNDO study of the reaction path for the thermal decompositions of azoethane and 1,1-diethyldiazene,[1] we suggested that the mechanisms involve stepwise cleavage to an intermediate ethyl/ethyldiazenyl radical pair that can either recombine or further decompose to two ethyl radicals and a nitrogen molecule (reactions 2 and 3). We further suggested that reaction 2 could be competitive with reaction 3 under proper reaction conditions. Although the proposed mechanism is capable of explaining most of the existing experimental results, the suggestion that both the decomposition of the ethyldiazenyl radical (reaction 3) and the recombination of the ethyl and ethyldiazenyl radicals (the reverse of reaction 2) have measurable activation energies was surprising to many chemists.

$$CH_3CH_2{-}N{=}N\cdot + CH_3CH_2\cdot \rightarrow CH_3CH_2{-}N{=}N{-}CH_2CH_3 \quad (2)$$

$$CH_3CH_2{-}N{=}N\cdot + CH_3CH_2\cdot \rightarrow 2CH_3CH_2\cdot + N_2 \quad (3)$$

Since our study, two experimental reports that support the mechanism of reactions 2 and 3 have appeared. Using arguments based upon volumes of activation, Neuman has concluded that recombination of the adamantyl/adamantyldiazenyl radical pair formed upon thermolysis of *cis*-azoadamantane must occur.[2] Most recently, Engel has shown that recombination of azoalkanes containing the 1,1-dimethylallyl moiety as one of the alkyl groups can rearrange to form what Engel calls "turnaround azoalkanes" (reaction 4) in some but not all cases.[3] Clearly, the formation of these "turnaround alkanes" will be manifest only when recombination of the alkyl/alkyldiazenyl radical pair competes favorably with either the decomposition of the diazenyl radical or the diffusion of the radicals out of the initial cage.

$$R{-}N{=}N{-}C(CH_3)_2CH{=}CH_2 \rightarrow R{-}N{=}N\cdot + \cdot C(CH_3)_2CH{=}CH_2 \rightarrow R{-}N{=}N{-}CH_2C{=}C(CH_3)_2 \quad (4)$$

We believed it to be of interest to conduct further theoretical studies on the decomposition of diazenyl radicals in order to better understand the factors leading to the calculated activation energies, especially in the context of Engel's recent report.[3] A discussion of the causes of possible activation energies for radical recombination reactions has been reported elsewhere.[4]

Methods

The reaction paths for the decomposition of various alkyldiazenyl radicals were calculated by using the half-electron method in the MNDO approximation of molecular orbital theory.[5] This method has been successful in our previous study of the decomposition of diazenes[1] as well as recent studies of radical recombinations[4] and the thermal rearrangements of several derivatives of semi-

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