J. Am. Chem. Soc. **1983**, *105*, 6290-6299

Carbanions. 23. Cleavages of 1,2-Diphenylethane and Derivatives by Cs–K–Na Alloy. Competitive Rates of Bond Scission[1]

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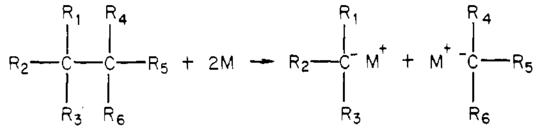
Abstract: The following hydrocarbons are cleaved at a C–C bond to allylic and/or benzylic cesium compounds within 2 h by Cs–K–Na alloy in THF at −75 °C: *meso*-2,3-diphenylbutane, 2,3-dimethyl-2,3-diphenylbutane, 1,2,2-triphenylpropane, 4-phenyl-1-butene, bibenzyl, and eight *o*-, *m*-, or *p*-methyl derivatives of bibenzyl. Under the same conditions 2-methyl- and 3-methyl-4-phenyl-1-butene were partially cleaved, 4,4′-dimethylbibenzyl was only slightly cleaved, and 9,10-dihydrophenanthrene was not detectably cleaved, while 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene underwent alternative C–H bond cleavage. Under the present reaction conditions 4,4′-dimethylbibenzyl and 9,10-dihydrophenanthrene were converted largely to dianions. It is suggested that all of the compounds undergoing cleavage are converted to dianions prior to cleavage. From competitive experiments the rates of reductive cleavage of most of these hydrocarbons relative to bibenzyl have been measured at −75 °C. The relative rates of cleavage of *m*- and *p*-methyl derivatives of bibenzyl may be correlated with the relative equilibrium acidities of toluene, *m*-xylene, and *p*-xylene in a modified Hammett relationship. Cleavages of benzylic C–C bonds are believed to occur by way of a preferred transition-state geometry, **7**, which permits the σ^* orbital of the bond undergoing cleavage to interact with the HOMO's of both aromatic rings. Compounds that cannot attain this transition-state geometry are cleaved slowly if at all. The variable effect upon reaction rate of methyl groups near the bond undergoing cleavage are discussed in terms of ground-state and transition-state strain, solvation, and polarizability of methyl groups. According to labeling experiments, (*o*-methylbenzyl)cesium undergoes ready intramolecular [1,4] sigmatropic migration of hydrogen from the methyl group to the methylene group when warmed from −75 °C to near room temperature.

The cleavage of carbon–carbon bonds by alkali metals (eq 1)



$$R_2-\overset{R_1}{\underset{R_3}{C}}-\overset{R_4}{\underset{R_6}{C}}-R_5 + 2M \rightarrow R_2-\overset{R_1}{\underset{R_3}{C^-}}M^+ + M^+\,{}^-\overset{R_4}{\underset{R_6}{C}}-R_5 \qquad (1)$$

is a topic that had its origin in early work of Schlenk[2] on the reaction of triarylmethyl radicals or "dissociable ethanes" with sodium amalgam. This work[2] led to the discovery that pentaphenylethane is cleaved by potassium sand in diethyl ether to (triphenylmethyl)potassium and (diphenylmethyl)potassium.[3] Later Ziegler and Thielmann[4] found that liquid sodium–potassium alloy in diethyl ether cleaves 1,1,2,2-tetraphenylethane to 2 mol of (diphenylmethyl)potassium and 1,1,1,2-tetraphenylethane to (triphenylmethyl)potassium and benzylpotassium (the latter was not, in fact, observed, likely because of reaction with the solvent).

In a systematic study of the cleavage of carbon–carbon bonds by Conant[5] and Bachmann,[3,6] the order of reducing power of alkali metals was found to increase along the series: 1% Na–Hg < 40% Na–Hg < Na–K. Thus pentaphenylethane is cleaved[2] in good yield by Na–K, only slightly by 40% Na–Hg, and not at all by 1% Na–Hg. Since 1% Na–Hg is known to react readily with triphenylmethyl radical to give (triphenylmethyl)sodium, the failure to cleave pentaphenylethane was taken as evidence that the cleavage that occurs with the more concentrated amalgam (or Na–K) is a direct reductive cleavage of the carbon–carbon bond, not a reaction involving prior dissociation into radicals.

1,2-Diphenylethane,[5b] *meso*-2,3-diphenylbutane, and other *vic*-diphenylalkanes[5c] are reported not to be cleaved by Na–K in diethyl ether. Conant and Garvey[5b] point out that the question of cleavage or noncleavage by alkali metals is "undoubtedly a question of relative rates of reaction", and exact data on rates of heterogeneous reactions is difficult to obtain for many reasons. Nevertheless the general order of ease of cleavage of carbon–carbon bonds by alkali metals is believed to be that given above, i.e., the ease increases with increasing numbers of phenyl groups for substituents R_1 through R_6 in eq 1 or with increasing stabilization of the products of cleavage. Confirmation comes from studies under homogeneous conditions. Thus the 2:1 lithium–biphenyl adduct, which is soluble in tetrahydrofuran (THF), cleaves both 1,1,2,2- and 1,1,1,2-tetraphenylethanes in 2 h at 25 °C to give good yields of (diphenylmethyl)lithium and (triphenylmethyl)lithium, respectively; however, this reagent cleaves 1,1,1-triphenylethane to give only 2% of (triphenylmethyl)lithium in 6 h at 66 °C.[7]

In more recent work, 1,2-diphenylethane was reported[8] to react with potassium in 1,2-dimethoxyethane (DME) at temperatures below −70 °C to give the radical anion of 1,2-diphenylethane as affirmed by an ESR spectrum; the radical anion was said to be "stable for hours at low temperatures". Subsequently this radical anion, prepared in DME or THF at −78 °C, was found[9] to decompose readily, even at −60 °C, to give an orange diamagnetic product of λ_{max} 360 nm that was thought to be benzylpotassium, since its absorption maximum was near the value of 355 nm reported[10] earlier for benzylsodium, and toluene was identified (in unspecified yield) upon quenching with methanol. The anion radicals of 1,2-di-1-naphthylethane and 1,2-di(9-anthryl)ethane similarly underwent cleavage of the C–C bond of the diarylethane to form arylmethide ions upon warming to room temperature; further reduction of these arylmethide ions occurs on contact with the alkali metal. The ease of reductive cleavage of 1,2-diarylethanes is expected to increase on going from anthracene to

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[1] A brief account of a portion of this work was given at the IUPAC Symposium on Ions and Ion Pairs and Their Role in Chemical Reactions, May 31, 1978, Syracuse, NY. See also: Quest, D. E., Ph.D. Thesis Georgia Institute of Technology, 1977; 22nd Annual Report of Research under Sponsorship of the Petroleum Research Fund, administered by the American Chemical Society, year ending Aug 31, 1977, p 233.

[2] Schlenk, W.; Marcus, E. *Chem. Ber.* **1914**, *47*, 1664–1678.

[3] Bachmann, W. E. *J. Am. Chem. Soc.* **1933**, *55*, 3005–3010.

[4] Ziegler, K.; Thielmann, F. *Chem. Ber.* **1923**, *56*, 1740–1745.

[5] (a) Conant, J. B.; Garvey, B. S., Jr. *J. Am. Chem. Soc.* **1927**, *49*, 2080–2088. (b) Conant, J. B.; Garvey, B. S., Jr. *Ibid.* **1927**, *49*, 2599–2603. (c) Conant, J. B.; Blatt, A. H. *Ibid.* **1928**, *50*, 551–558.

[6] Bachmann, W. E.; Wiselogle, F. Y. *J. Org. Chem.* **1936**, *1*, 354–382.

[7] Eisch, J. J. *J. Org. Chem.* **1963**, *28*, 707–710.

[8] Gerson, F.; Martin, W. B., Jr. *J. Am. Chem. Soc.* **1969**, *91*, 1883–1891.

[9] Pearson, J. M.; Williams, D. J.; Levy, M. *J. Am. Chem. Soc.* **1971**, *93*, 5478–5482.

[10] Asami, R.; Levy, M.; Szwarc, M. *J. Chem. Soc.* **1962**, 361–363.

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naphthalene to benzene according to Hückel molecular orbital calculations of the gain in π-resonance energy upon bond scission.[9]

The initial goal of the present work was to see if reactions of alkali metals with vicinal diphenylalkanes could be accomplished in a synthetically useful manner by use of Cs–K–Na alloy in place of the Na–K alloy of earlier workers. Indeed Gilman and Young[11] had reported that K–Rb alloy reacts with 1,2-diphenylethane in petroleum ether to give after carbonation 2,3-diphenylsuccinic acid. Earlier work had also shown that, unlike Na–K, Cs–K–Na alloy reacts[12] with benzene and toluene in THF to give good yields of radical anions or products derived therefrom. After preliminary account of a portion of our work had been given,[1] Collins and co-workers[13] reported that Na–K alloy in the solvent system glyme–triglyme at 0 °C reacts, for example, with 1,2-diphenylethane to give after 3 h of stirring followed by hydrolysis 55% yield of toluene, 7% of 1,2-diphenylbutane, and 35% recovery of starting materials; decomposition of the reaction mixture with methyl iodide gave toluene, ethylbenzene, and 1,2-diphenylpropane in a ratio of 37:42:21, respectively. These results imply that 1,2-diphenylethane undergoes carbon–carbon bond cleavage as well as carbon–hydrogen cleavage (or metalation) under the conditions employed.

A second goal, which developed as our work proceeded, was to understand the effect of structure upon reactivity through elucidation of the mechanism of reductive cleavage. The only previous study before initiation of our work was that of Lagendijk and Szwarc[14] who found for the reductive cleavage of 1,2-di-α-naphthylethane (NN) in THF to α-naphthylmethyl anions (N^-) a kinetic rate law that was second order in radical anion ($NN^{-}\cdot$) and inversely proportional to nonreduced NN. The kinetics was explained on the basis of the following mechanism:

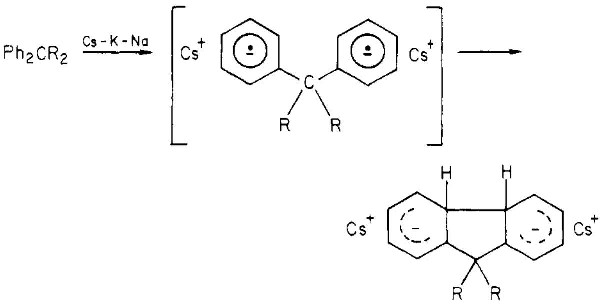
$$2NN^{-}\cdot{,}M^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NN^{2-}{,}2M^+ + NN \quad K_1 = k_1/k_{-1}$$

$$NN^{2-}{,}2M^+ \xrightarrow[k_2]{} 2N^-{,}M^+$$

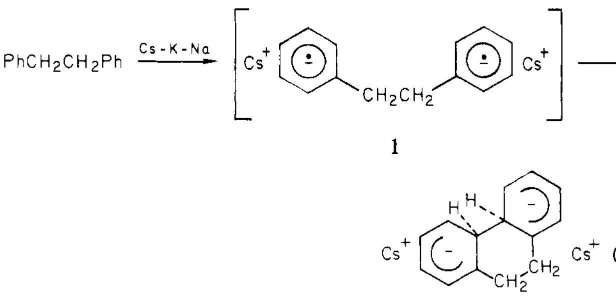
where the first reaction was taken to be fast and at equilibrium.[15] A subsequent study of the reductive cleavage of an aryl group from 9,9-diarylfluorenes by potassium in 1,2-dimethoxyethane gave cleavage by an identical rate law and was interpreted according to the same mechanism.[16] More commonly, but without detailed kinetic proof, reductive cleavages of carbon–carbon bonds have been assumed to occur by way of cleavage of radical monoanions,[17] but cleavage by injection of three or even four electrons[18] has been proposed.

Results and Discussion

Preparative Cleavages with Cs–K–Na Alloy in THF. In view of the greater solubility of cesium in THF at low rather than high temperatures (as revealed by the deepening of the blue color of the solution as the temperature is lowered) and because organoalkali compounds are more stable at low temperatures, reactions with hydrocarbons were studied at −75 °C. Initially it was thought that at this low temperature intermediate radical anions would undergo intramolecular coupling as observed for 2,2-diphenylpropane and 1,1,1-triphenylethane[19] (eq 2). Hence 1,2-diphenylethane might have been expected[20] to undergo the reaction of eq 3. Instead 1,2-diphenylethane underwent essentially quantitative cleavage into benzylcesium within 80 min (see eq 1, R_1 and R_4 are Ph, other R's H). Since *gem*-dimethyl groups sometimes aid cyclization reactions (Thorpe–Ingold effect[21]), this reaction was repeated with 2,3-dimethyl-2,3-diphenylbutane; but again quantitative cleavage was observed (eq 1, R_1 and R_4 are Ph, other R's CH_3).



(2)



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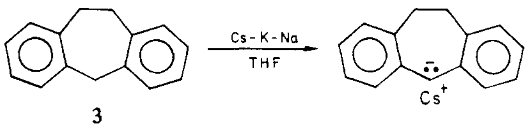
(3)

These preliminary experiments lead to a study of the effect of structure, especially methyl substituent effects, upon the course of the reaction. The results are summarized in Chart I. Of the 15 compounds in the chart containing a 1,2-diarylethane moiety, all but three undergo essentially quantitative cleavage with Cs–K–Na alloy in THF at −75 °C in 155 min or less. The compounds resistant to cleavage were 1,2-di-*p*-tolylethane, 9,10-dihydrophenanthrene and 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene (**3**). The latter compound underwent an alternative more rapid cleavage of a carbon–hydrogen bond (eq 4) while the former undergoes carbon–carbon cleavage but at a greatly reduced rate. Only 9,10-dihydrophenanthrene was resistant to either type of cleavage at −75 °C.



3

(4)

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[11] Gilman, H.; Young, R. V. *J. Org. Chem.* **1936**, *1*, 330.

[12] Grovenstein, E., Jr.; Longfield, T. H.; Quest, D. E. *J. Am. Chem. Soc.* **1977**, *99*, 2800–2802.

[13] Collins, C. J.; Hombach, H.-P.; Maxwell, B.; Woody, M. C.; Benjamin, B. M. *J. Am. Chem. Soc.* **1980**, *102*, 851–853. Collins, C. J.; Hombach, H.-P.; Maxwell, B. E.; Benjamin, B. M.; McKamey, D. *Ibid.* **1981**, *103*, 1213–1214.

[14] Lagendijk, A.; Szwarc, M. *J. Am. Chem. Soc.* **1971**, *93*, 5359–5363.

[15] In fact Lagendijk and Szwarc[14] drew this conclusion for M^+ equal Li^+, Na^+, and K^+ but *not* for Cs^+. For the latter cation they concluded that k_2 and k_{-1}(NN) were of similar magnitude and hence applied a steady-state treatment to their four kinetic runs at different concentrations of NN to give a value of $2k_2K_1$ of $\sim 70 \times 10^{-3}$ s^{-1} and $k_1 \sim 10$ M^{-1} s^{-1}. The latter value seems small compared to the probable value of 10^6 M^{-1} s^{-1} for disproportionation of sodium tetraphenylethylene and related alkali-metal compounds [Szwarc, M.; Jagur-Grodzinski, J. In "Ions and Ion Pairs in Organic Reactions"; Szwarc, M., Ed.; Wiley: New York, 1974; Vol. 2, pp 99–106]. If the two kinetic runs with cesium ion at lowest concentrations of NN are assumed to be in some error (by a factor of 2 or less), the remaining two runs, by a treatment identical with that used for the Li^+, Na^+, and K^+ compounds give values of $2k_2K_1$ of 60×10^{-3} s^{-1} in accord with expectations for the trend with variation of M^+.

[16] Walsh, T. D.; Megremis, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 3897–3898.

[17] For example, see: Kleinschroth, J.; Hopf, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 472. Boche, G.; Wintermayr, H. *Ibid.* **1981**, *20*, 874–876. Staley, S. W.; Fox, M. A.; Hirzel, T. K. *J. Am. Chem. Soc.* **1976**, *98*, 3910–3916. Bauld, N. L.; Cessac, J. *Ibid.* **1975**, *97*, 2284–2285. Bauld, N. L.; Chang, C.-S.; Farr, F. R. *Ibid.* **1972**, *94*, 7164–7165. Walborsky, H. M.; Arnoff, M. S.; Schulman, M. F. *J. Org. Chem.* **1971**, *36*, 1036–1040. Rieke, R.; Ogliaruso, M.; McClung, R.; Winstein, S. *J. Am. Chem. Soc.* **1966**, *88*, 4729–4730.

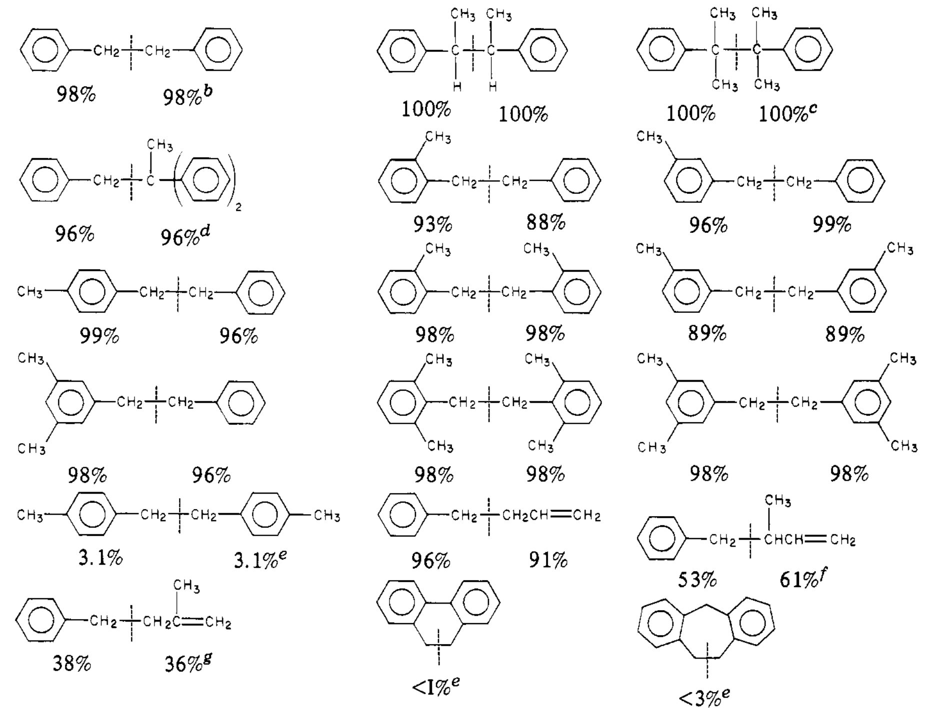
[18] Hammerich, O.; Saveant, J.-M. *J. Chem. Soc., Chem. Commun.* **1979**, 938–940.

[19] Grovenstein, E., Jr.; Beres, J. A.; Cheng, Y.-M.; Pegolotti, J. A. *J. Org. Chem.* **1972**, *37*, 1281–1292.

[20] The countercation in products from reaction of Cs–K–Na alloy with hydrocarbons is taken to be cesium in conformity with published results[12] for analogous reactions.

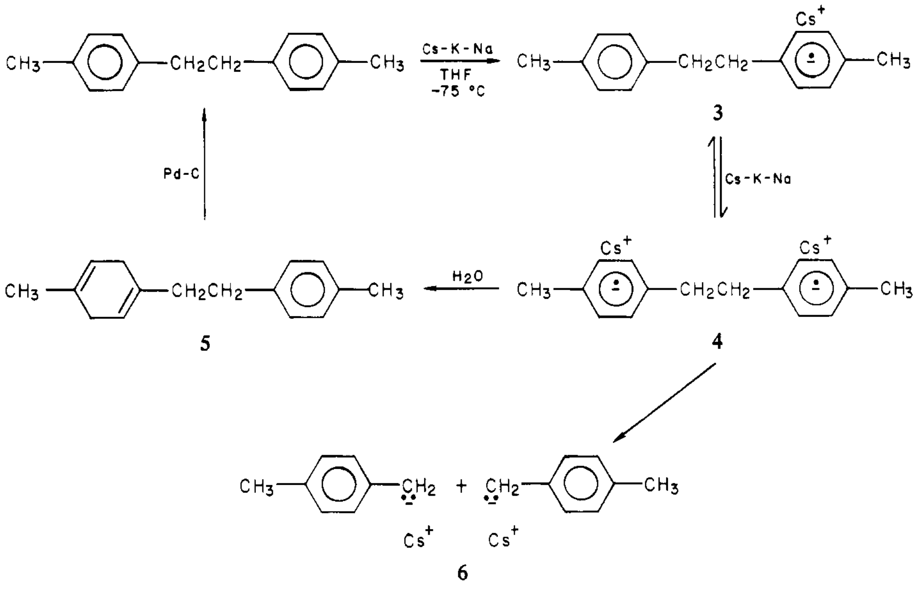
[21] Hammond, G. S. In "Steric Effects in Organic Chemistry"; Newman, M. S., Ed.; Wiley: New York, 1956; pp 460–469. Capon, B.; McManus, S. P. "Neighboring Group Participation"; Plenum Press: New York and London, 1976; Vol. 1, pp 58–75. Maercker, A.; Gunthlein, P.; Wittmayr, H. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 774–775.

Chart I. Yields in Cleavage of Carbon–Carbon Bonds of Hydrocarbon by Cs-K-Na in THF at −75 °C[a]



[a] Yields are those of carboxylic acids from carbonation after 2-h reaction time unless otherwise specified. [b] Consisted of 93.4% yield of phenylacetic acid and 4.4% yield of toluene after 80-min reaction time with 6.1 mol of Cs/mole of bibenzyl. [c] Consisted of 98.9% yield of 2-methyl-2-phenylpropanoic acid and 0.7% yield of cumene after 155-min reaction time with 7.4 mol of Cs/mole of 2,3-dimethyl-2,3-diphenylbutane. [d] Consisted of 84.8% of phenylacetic acid, 87.3% of 2,2-diphenylpropanoic acid, 11.5% of toluene, and 8.2% of 1,1-diphenylethane after 75-min reaction time with 11.6 mol of Cs/mole of 1,2,2-triphenylpropane. [e] See text and Experimental Section for additional products. [f] Also 33% recovery of unreacted 4-phenyl-3-methyl-1-butene; some unidentified components were also present. [g] Also 14% recovery of unreacted 4-phenyl-2-methyl-1-butene; four unidentified components of longer retention time than methyl phenylacetate were detected. This reaction was conducted for 6 h at −75 °C prior to carbonation.

Scheme I



The failure of 9,10-dihydrophenanthrene and of 1,2-di-*p*-tolylethane to undergo appreciable cleavage is *not* due to failure to react with Cs–K–Na alloy; these compounds gave largely dianion accompanied by some mono radical anion under the reaction conditions according to the products of protonation. It was thought possible that the dianion from 1,2-di-*p*-tolylethane might have undergone intramolecular cyclization as suggested above for 1,2-diphenylethane (see eq 3); however, the chief product of protonation had spectral properties in agreement with the structure of 1-(2,5-dihydro-4-methylphenyl)-2-*p*-tolylethane (**5**, Scheme I) and reverted to 4,4′-dimethylbibenzyl upon dehydrogenation over Pd–C rather than give 3,6-dimethylphenanthrene. Any lingering uncertainty about the structure of the dihydro derivative was removed by an X-ray crystal study (see Experimental Section), which fully confirmed structure **5**. The chief reaction product of 1,2-di-*p*-tolylethane with Cs–K–Na alloy at −75 °C is therefore **4** accompanied by some of the mono radical anion **3**. The hydrocarbon 1,2-di-*p*-tolylethane is believed to differ from most other 1,2-diarylethanes of Chart I chiefly in the slowness of cleavage to (4-methylbenzyl)cesium. Evidently anion radicals and dianions of 9,10-dihydrophenanthrene cleave even more slowly if at all at −75 °C.

Chart I shows that 4-phenyl-1-butene undergoes cleavage by Cs–K–Na alloy to give good yields of benzylcesium and allylcesium. Thus one phenyl group of 1,2-diphenylethane may be replaced by a vinyl group in cleavages with cesium alloy under our standard conditions without appreciable diminution of yield. Introduction of one methyl group at either the 2- or 3-position of 4-phenyl-1-butene now appreciably lowers the yield in a manner reminiscent of 1,2-di-*p*-tolylethane.

Relative Rates of Cleavages of Hydrocarbons with Cs–K–Na Alloy in THF. In the qualitative discussion of preparative cleavages by Cs–K–Na alloy, it was suggested that the failure to obtain good yields of products in certain cases was a matter of slow reaction rates. For this reason it seemed desirable to quantify some of the reaction rates in order to understand better the effect of structure upon yields. Further it was hoped that such a study would lead to a better understanding of the mechanism of reductive cleavage.

Since cleavage of 1,2-diphenylethane by Cs–K–Na alloy in THF appears to be fast at –75 °C and evidently occurs almost as readily as cesium is extracted from the alloy by stirring in THF under our heterogeneous conditions, it was deemed most practical to obtain *relative rates* of cleavage by a competitive technique. To this end mixtures of two hydrocarbons were dissolved in THF and stirred with the alloy for a period of time and with quantities of hydrocarbon adjusted such that much of each hydrocarbon remained unreacted at the termination of reaction by carbonation. From the quantities of carboxylic acids produced, the extent of cleavage of each hydrocarbon could be determined.

If the two hydrocarbons that are to be cleaved competitively are designated as R_1R_2 and R_3R_4 and if cleavage occurs in their respective dianions $(R_1R_2)^{2-},2Cs^+$ and $(R_3R_4)^{2-},2Cs^+$ as expected by the mechanism of Lagendijk and Szwarc at rate constants $k'_{1,2}$ and $k'_{3,4}$, respectively, then the relative rate of cleavage is

$$\frac{d[(R_1R_2)^{2-},2Cs^+]}{d[(R_3R_4)^{2-},2Cs^+]} = \frac{k'_{1,2}[(R_1R_2)^{2-},2Cs^+]}{k'_{3,4}[(R_3R_4)^{2-},2Cs^+]} \quad (5)$$

The dianions may be considered to be formed from the corresponding hydrocarbons by the equilibria:

$$R_1R_2 + 2Cs \rightleftharpoons (R_1R_2)^{2-},2Cs^+ \quad (6)$$

$$R_3R_4 + 2Cs \rightleftharpoons (R_3R_4)^{2-},2Cs^+ \quad (7)$$

whose equilibrium constants are designated as $K_{1,2}$ and $K_{3,4}$, respectively. Subtraction of eq 7 from eq 6 gives the following:

$$R_1R_2 + (R_3R_4)^{2-},2Cs^+ \rightleftharpoons (R_1R_2)^{2-},2Cs^+ + R_3R_4 \quad (8)$$

whose equilibrium constant is $K_{1,2}/K_{3,4}$. Because of the heterogenous nature of the present reaction and the speed of the cleavages, equilibrium between cesium metal in the alloy and the hydrocarbons R_1R_2 and R_3R_4 as given by eq 6 and 7 may not be attained. The equilibrium of eq 8, however, involves species that (at their expected low concentrations) are assumed to be in solution and are expected[22] to be in ready equilibrium. Substitution of eq 8 into eq 5 gives eq 9. Equation 9 is readily integrated and

$$\frac{d[(R_1R_2)^{2-},2Cs^+]}{d[(R_3R_4)^{2-},2Cs^+]} = \frac{k'_{1,2}K_{1,2}[R_1R_2]}{k'_{3,4}K_{3,4}[R_3R_4]} \equiv \frac{k_{1,2}[R_1R_2]}{k_{3,4}[R_3R_4]} \quad (9)$$

permits calculation of values of $k_{1,2}/k_{3,4}$ from experimental data upon competitive cleavages. The results are given in Table I.

These data permit calculation of rates of cleavage of hydrocarbons ($k_{1,2}$) relative to bibenzyl ($k_{0,0}$); the values of $k_{1,2}/k_{0,0}$ are listed in Table II according to diminishing relative reactivity. In general consistent results were obtained provided that the hydrocarbon is one of those in Chart I that is cleaved in essentially quantitative yield. The hydrocarbon 4,4′-dimethylbibenzyl gave variable values of $k_{1,2}/k_{0,0}$ dependent upon the hydrocarbon used in the intercomparison of relative rates. In order to attempt to obtain accurate relative rates for 4,4′-dimethylbibenzyl, the hydrocarbons used in the intercomparisons were the four of lowest relative reactivity preceding 4,4′-dimethylbibenzyl in Table II.

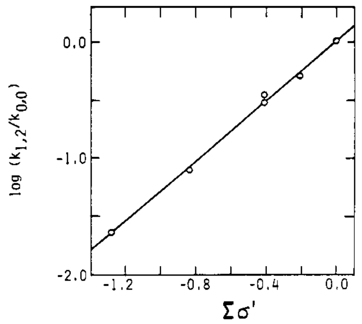


Figure 1. Plot of log $(k_{1,2}/k_{0,0})$ values for *m*- and *p*-methyl derivatives of bibenzyl vs. $\sum\sigma'$ values from equilibrium acidities of toluene, *m*-xylene, and *p*-xylene (eq 10).

It is believed that in these intercomparisons of unreactive hydrocarbons appreciable amounts of radical anions and dianions built up and likely precipitated. The equilibrium of eq 8 may not be readily attained in cases involving insoluble precipitates. Moreover an assumption in solution of eq 9 was that the quantity of any intermediates was small and negligible relative to the amount of reactant hydrocarbons and products of cleavage. Likely these assumptions were not met in the reactions of 4,4′-dimethylbibenzyl and indeed the recovery of uncleaved 4,4′-dimethylbibenzyl was found to be low in the comparative run with 4-phenyl-1-butene. Nevertheless it appears that the range of experimental values listed for 4,4′-dimethylbibenzyl in Table II bracket the true value.

The assumption that cesium is the countercation in these reductive cleavages finds support in Table I. In runs 17 and 38 the relative reactivities found with pure cesium (as finely divided sand) agree within experimental error with the values obtained with Cs–K–Na alloy.

Table I also records the effect of 18-crown-6 upon $k_{1,2}/k_{3,4}$ (see runs 6, 19, 26–28). In all cases the crown ether reduces the selectivity in reductive cleavages; this is more pronounced the greater the selectivity. In presence of 18-crown-6, the relative rate of cleavage of 4,4′-dimethylbibenzyl vs. bibenzyl increases until it becomes intermediate between that of the tetramethylbibenzyls in the absence of crown ether.

How may the relative rates of cleavage of these hydrocarbons be explained? The data for 3- and 4-methyl derivatives of bibenzyl may be correlated with the relative equilibrium acidities (per hydrogen) of toluene, *m*-xylene, and *p*-xylene as determined by Gau and Marques[23] in the solvent decalin at 25 °C with sodium complexed with tetramethyl-1,2-diaminocyclohexane as the countercation (eq 10). From these equilibrium acidities, values

$$R_1H + R_2^-Na^+\text{–diamine} \rightleftharpoons R_1^-Na^+\text{–diamine} + R_2H \quad (10)$$

of σ'_m (–0.21) and σ'_p (–1.28) were calculated from log $(K_{m\text{-xylene}}/K_{\text{toluene}})$ and log $(K_{p\text{-xylene}}/K_{\text{toluene}})$, respectively ($\rho' \equiv 1.000$). A plot of log $(k_{1,2}/k_{0,0})$ values of Table II vs. $\sum\sigma'$ values[24] is linear[25] as shown in Figure 1 and accords[27] with eq 11. This

$$\log (k_{1,2}/k_{0,0}) = 1.29\sum\sigma' \quad (11)$$

modified Hammett relationship[27,28] for meta and para derivatives

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[22] See the discussion in footnote 15 and the reference cited therein.

[23] Gau, G.; Marques, S. *J. Am. Chem. Soc.* **1976**, *98*, 1538–1541.

[24] Jaffe H. H. *Chem. Rev.* **1953**, *53*, 191–261.

[25] A similar correlation may also be based upon the rate[26] of proton exchange per acidic hydrogen of *m*- and *p*-xylene catalyzed by KO-*t*-Bu in dimethyl sulfoxide at 30 °C; the σ' value of *p*-xylene derived here needs to be decreased from –1.48 to –1.60 for *p*-methylbibenzyl to fall on the line with the *m*-methyl compounds.

[26] Hofmann, J. E.; Muller, R. J.; Schriesheim, A. *J. Am. Chem. Soc.* **1963**, *85*, 3002–3006.

[27] The correlation coefficient (r) of the usual least-squares plot was 0.998 and the standard deviation (s) was 0.039. These data indicate an excellent fit to the modified Hammett equation.[24]

[28] Attempts to correlate the $k_{1,2}/k_{0,0}$ data with ordinary Hammett substituent constants[24] (σ_{meta}, –0.069; σ_{para}, –0.170) satisfactorily correlate the meta compounds with ρ = 3.9 but 4-methylbibenzyl requires a σ_{para} of –0.40 to fall on the same line.

[29] Hammett, L. P. "Physical Organic Chemistry", 2nd ed.; McGraw-Hill: New York, 1970; pp 357, 369–373, 393–394.

Table I. Relative Rates of Cleavage of Hydrocarbons in Tetrahydrofuran^{a} at −75 °C by Cs–K–Na Eutectic Alloy

run	Cs, mmol	R_1R_2, mmol	R_3R_4, mmol	$k_{1,2}/k_{3,4}$^{b}
1	20.8	2-methylbibenzyl, 9.36	bibenzyl, 10.33	1.90
2	17.7	2-methylbibenzyl, 8.72	bibenzyl, 9.84	1.86
3	10.7	3-methylbibenzyl, 20.6	bibenzyl, 5.30	0.509
4	8.77	3-methylbibenzyl, 19.0	bibenzyl, 4.35	0.515
5	16.8	4-methylbibenzyl, 20.1	bibenzyl, 8.31	0.021
6	13.6	4-methylbibenzyl, 13.0	bibenzyl, 6.78	0.049^{c}
7	16.9	4-methylbibenzyl, 8.53	2,2′,6,6′-tetramethylbibenzyl, 8.36	1.02
8	12.6	4-methylbibenzyl, 6.33	2,2′,6,6′-tetramethylbibenzyl, 6.38	1.05
9	25.1	2,2′-dimethylbibenzyl, 12.5	bibenzyl, 12.5	2.06
10	16.5	2,2′-dimethylbibenzyl, 8.21	bibenzyl, 13.9	2.06
11		2,2′-dimethylbibenzyl, 1.76	2,2′-dimethylbibenzyl-α,α,α′,α′-d_4, 1.05	1.0^{d}
12	8.81	2,2′-dimethylbibenzyl-α,α,α′,α′-d_4, 3.29	bibenzyl, 4.43	2.50
13	10.4	2,2′-dimethylbibenzyl, 8.41	2,6-dimethylbibenzyl, 5.17	0.477
14	25.3	2,2′-dimethylbibenzyl, 12.60	2,6-dimethylbibenzyl, 12.16	0.453
15	6.23	3,3′-dimethylbibenzyl, 5.71	bibenzyl, 3.11	0.344
16	8.95	3,3′-dimethylbibenzyl, 18.61	bibenzyl, 3.98	0.341
17	5.99^{e}	3,3′-dimethylbibenzyl, 5.71	bibenzyl, 2.98	0.342
18^{f}	13.9	3,3′-dimethylbibenzyl, 7.93	bibenzyl, 2.82	0.339
	13.9	3,3′-dimethylbibenzyl, 7.93	3,5-dimethylbibenzyl, 6.97	1.07
19	14.8	3,3′-dimethylbibenzyl, 14.2	bibenzyl, 7.39	0.61^{g}
20	3.57	3,3′-dimethylbibenzyl, 1.79	*meso*-2,3-diphenylbutane, 6.37	1.12
21	6.72	3,3′-dimethylbibenzyl, 3.35	*meso*-2,3-diphenylbutane, 7.01	1.12
22	5.71	3,5-dimethylbibenzyl, 6.98	bibenzyl, 2.82	0.27
23	9.53	4,4′-dimethylbibenzyl, 14.2	2,2′,6,6′-tetramethylbibenzyl, 4.66	(0.166)^{h}
24	7.56	4,4′-dimethylbibenzyl, 26.4	2,2′,6,6′-tetramethylbibenzyl, 3.77	(0.166)^{h}
25	2.18	4,4′-dimethylbibenzyl, 3.25	3,3′,5,5′-tetramethylbibenzyl, 1.05	(0.042)^{h}
26	11.49	4,4′-dimethylbibenzyl, 12.36	bibenzyl, 5.73	0.051^{g}
27	13.75	4,4′-dimethylbibenzyl, 12.78	bibenzyl, 5.75	0.035^{g}
28	11.76	4,4′-dimethylbibenzyl, 12.41	bibenzyl, 5.87	0.049^{g}
29	4.91	4,4′-dimethylbibenzyl, 2.45	4-phenyl-1-butene, 2.58	(0.035)^{h}
30	5.32	4,4′-dimethylbibenzyl, 10.79	4-methylbibenzyl, 2.55	(0.027)^{h}
31	6.15	2,2′,6,6′-tetramethylbibenzyl, 3.51	bibenzyl, 3.05	0.021
32	7.61	2,2′,6,6′-tetramethylbibenzyl, 3.87	3,3′-dimethylbibenzyl, 3.80	0.080
33	10.14	2,2′,6,6′-tetramethylbibenzyl, 4.27	3,3′-dimethylbiphenyl, 4.92	0.069
34	5.77	3,3′,5,5′-tetramethylbibenzyl, 18.74	bibenzyl, 2.84	0.077
35	9.92	3,3′,5,5′-tetramethylbibenzyl, 4.70	bibenzyl, 4.71	0.077
36	18.32	2,3-dimethyl-2,3-diphenylbutane, 9.32	bibenzyl, 9.14	17.9
37	23.02	2,3-dimethyl-2,3-diphenylbutane, 11.53	bibenzyl, 31.23	25
38	11.27^{e}	2,3-dimethyl-2,3-diphenylbutane, 11.02	bibenzyl, 5.61	17.6
39	17.3	4-phenyl-1-butene, 55.3	2,2′,6,6′-tetramethylbibenzyl, 8.53	0.049
40	16.5	4-phenyl-1-butene, 33.1	3,3′-dimethylbibenzyl, 8.25	0.0041

[a] In 250 mL of THF. [b] The average deviation of repetitive values from the mean value for 35 determinations of $k_{1,2}/k_{3,4}$ is ±6%. [c] In presence of 27.0 mmol of 18-crown-6. [d] Analysis by ^{1}H NMR; the precision is only 1.0 ± 0.3. [e] Pure cesium metal used in this run. [f] Competitive cleavage of a mixture of the three hydrocarbons. [g] Runs 19, 26, 27, and 28 were made in presence of 28.3, 24.8, 27.5, and 11.8 mmol of 18-crown-6, respectively. [h] Apparent value; this value is believed to be unreliable for reason discussed in text.

Table II. Rates of Cleavage of Hydrocarbons Relative to Bibenzyl in THF at −75 °C

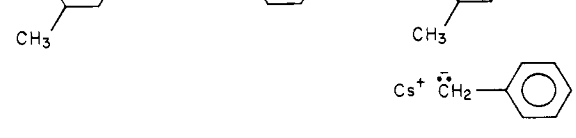
hydrocarbon	$k_{1,2}/k_{0,0}$^{a}	n^{b}
2,3-dimethyl-2,3-diphenylbutane	20 ± 3	3
2,6-dimethylbibenzyl	4.43 ± 0.11	2
2,2′-dimethylbibenzyl-α,α,α′,α′-d_4	2.28 ± 0.24	2
2,2′-dimethylbibenzyl	2.06 ± 0.05	4
2-methylbibenzyl	1.88 ± 0.02	2
bibenzyl	1.000	
3-methylbibenzyl	0.512 ± 0.003	2
3,3′-dimethylbibenzyl	0.341 ± 0.002	9
meso-2,3-diphenylbutane	0.304	2
3,5-dimethylbibenzyl	0.295 ± 0.023	3
3,3′,5,5′-tetramethylbibenzyl	0.079 ± 0.001	2
2,2′,6,6′-tetramethylbibenzyl	0.0229 ± 0.0021	4
4-methylbibenzyl	0.0228 ± 0.0015	3
4-phenyl-1-butene	0.00127 ± 0.00014	2
4,4′-dimethylbibenzyl	(0.004–0.00004)^{c}	5

[a] The rate of cleavage of the specified hydrocarbon ($k_{1,2}$) divided by the rate of cleavage of bibenzyl ($k_{0,0}$). The ± entry refers to the average deviation in repetitive runs. [b] Number of runs. [c] See discussion in text.

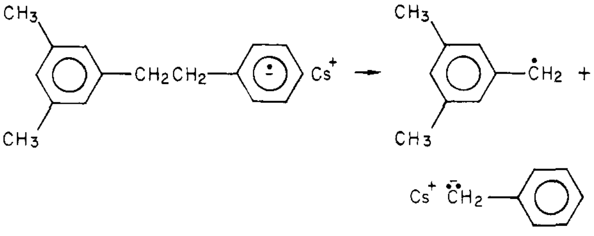
of bibenzyl suggests that the electron distribution in the transition state for reductive cleavage of bibenzyls is similar to that in *two* benzylic anions or that the transition state is late with scission of the σ bond linking the benzylic moieties well advanced.

A late transition state resembling two benzylic anions would have its charge further separated than in the reactant bibenzyl dianion, which likely binds tightly two cesium cations. Further separation of charge in the transition state implies looser ion pairing that is accommodated by increased solvation. The multidentate ligand 18-crown-6 can supply this solvation better than THF and in doing so can help overcome the inhibition of rate supplied by alkyl groups; this appears to be the origin of the reduction in selectivity (Table I) brought about by 18-crown-6.

From another viewpoint, one *m*-methyl group reduces the relative rate of cleavage of bibenzyl approximately by a factor of 0.53, two *m*-methyl groups by 0.53^2 or 0.28-fold for both 3,3′-dimethylbibenzyl and 3,5-dimethylbibenzyl, and four *m*-methyl groups by 0.53^4 or 0.079-fold for 3,3′,5,5′-tetramethylbibenzyl. This linear free energy relationship suggests that negative charge in the transition state for cleavage is evenly distributed on the two benzylic moieties of bibenzyl. This charge distribution is readily understood if cleavage occurs in a dianion (see eq 12) but would be hard to understand for cleavage in a monoanion (see eq 13) for then the negative charge would be



(12)



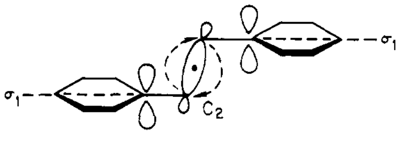
(13)

capable of escaping most of the destabilizing effect of the methyl groups by having the unsymmetrical distribution of charge shown in the reactants and products of eq 13. Hence our study of methyl substituent effects for reductive cleavage of bibenzyls agrees with the mechanism of Lagendijk and Szwarc[14] for cleavage of 1,2-di-α-naphthylethane. The rate-determining step, therefore, involves cleavage of a dianion.

Confirmatory evidence is provided by our study of 4,4-dimethylbibenzyl, which, as noted (Scheme I), is largely converted to the dianion **4**, which only slowly undergoes cleavage to 4-methylbenzyl anion (**6**). The anticipated relative rate of cleavage of 4,4′-dimethylbibenzyl, based upon the $k_{1,2}/k_{0,0}$ value of 0.0228 for 4-methylbibenzyl and the assumption of a linear free energy relationship, is 0.0228^2 or 0.00052. This value is bracketed by the experimental values given in Table II.

Interpretation of substituent effects for substituents closer to the reaction center than meta or para positions is normally difficult[27] but is likely beneficial in the present case. The relative equilibrium acidities[23] (per acidic hydrogen) of ethylbenzene and isopropylbenzene are 2.2×10^{-2} and 1.0×10^{-3}, respectively. If these values are converted into σ' values to calculate the effect of substituents upon the rate of reductive cleavage of *meso*-2,3-diphenylbutane and 2,3-dimethyl-2,3-diphenylbutane, respectively, according to eq 11, the calculated values of $k_{1,2}/k_{0,0}$ are 2×10^{-4} and 5×10^{-9} times those recorded for these compounds in Table II. The strain enthalpies of *meso*-2,3-diphenylbutene and 2,3-dimethyl-2,3-diphenylbutane have been estimated[30] at 3.6 and 18.4 kcal/mol, respectively; if all of this strain energy is lost during reductive cleavage, accelerations by factors of about 10^4 and 10^{20}, respectively, would be expected at −75 °C. Hence steric acceleration is likely a major factor in assuring ready reductive cleavage in contrast to what might have been expected on the basis of the acidities of the hydrocarbons from the anions of reductive cleavage. These considerations help to explain why our attempts to bring about *ortho*-cyclization of 1,2-diphenylethane dianions (eq 3) by introduction of α-methyl groups were unsuccessful. For ground-state steric compression to be greatly relieved in the transition state, the sigma bond linking the benzylic moieties of bibenzyl must be considerably stretched; this conclusion is in agreement with arguments above based on the Hammett correlation (eq 11).

The relative rates of cleavage of derivatives of bibenzyl are advantageously discussed in terms of the likely optimum conformation of the transition state for cleavage of the dianion. We propose that this conformation has the phenyl groups anti to one another and in essentially parallel planes as in **7**. Interestingly, X-ray diffraction of the crystalline dihydro derivative of 4,4′-dimethylbibenzyl reveals this same conformation (see Figure 2). The advantage of conformation **7** for the transition state is that, in terms of frontier orbital theory, it permits the HOMO's of the aromatic rings (only one p orbital of each ring is shown in **7** for simplicity) to interact with the σ^* orbital (LUMO) of the carbon–carbon bond linking the benzylic groups with resultant cleavage.[31] This σ–π interaction[32] breaks the degeneracy of the HOMO and permits the dianion to transform smoothly (with minimal activation energy) into two benzyl anions. Such transformation, however, requires effective overlap between the central carbon–carbon σ-bond and the two aromatic rings; optimally these are oriented as in **7**.



7

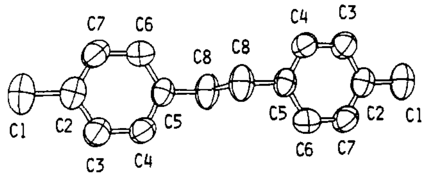


Figure 2. ORTEP drawing of 1-(2,5-dihydro-4-methylphenyl)-2-*p*-tolylethane. See Experimental Section for discussion of this X-ray crystal structure.

As evidence in favor of such overlap we cite our failure to detect cleavage of 9,10-dihydrophenanthrene at the C(9)–C(10) bond; in this nearly planar molecular the relevant σ-bond is nearly orthogonal to the π-system. It may be argued, however, that the dianion of 9,10-dihydrophenanthrene is more stable than that of bibenzyl because of conjugation of the aromatic rings. In terms of HMO theory, the cleavage of bibenzyl dianion is expected to be 0.53 β units more exothermal than that of the dianion of 9,10-dihydrophenanthrene.

Another model compound is 10,11-dihydro-5*H*-dibenzo[*a*,*d*]-cycloheptene (**3**), which was not detectably cleaved at the C(10)–C(11) bond. Molecular models show that while the C(10)–C(11) bond in **3** is nearly parallel to the π-system of one aromatic ring, it is nearly orthogonal to the other. Instead of C–C bond cleavage, C–H cleavage occurs. Models show that one C(5)–H bond in **3** is nearly parallel to both π-systems. We suggest that C–H cleavage occurs in the dianion of **3** with both aromatic rings contributing antibonding electrons to the σ^* orbital of the C–H bond undergoing cleavage in analogy with the above proposed mechanism of C–C bond cleavage. In agreement with this proposal, the anion radical of toluene at −75 °C in THF does not undergo appreciable C–H cleavage.[33]

The proposed transition-state geometry **7** appears to be accessible to *meso*-2,3-diphenylbutane and 2,3-dimethyl-2,3-diphenylbutane and to afford some relief of steric compression upon stretching the σ-bond linking the benzylic moieties in a late transition state. This transition state also provides a useful model for discussion of the effects of *o*-methyl groups upon the relative rates of cleavage of bibenzyls (see Table II). One *o*-methyl group approximately doubles the rate of cleavage of bibenzyl in surprising contrast to one *p*-methyl, which reduces the rate 44-fold. A second *o*-methyl group only slightly (1.1-fold) further increases the relative rate if it is on the other benzene ring (2,2′-dimethylbibenzyl) but about doubles again the rate if on the same benzene ring (2,6-dimethylbibenzyl). We suggest that these *o*-methyl substituents are displaying an approximate linear free energy relationship if correction is made for a statistical factor for 2,2′-dimethylbibenzyl. This correction arises from steric interactions (repulsion) in the conformer in which the two methyl groups lie on the same side of the plane of symmetry (σ_1) in **7** such that the probability of attaining the transition state is reduced by about a factor of 2, with net approximate cancellation of the expected doubling of rate from the second *o*-methyl group. If the second *o*-methyl group is introduced on the same phenyl group as the first, the expected doubling of rate occurs. For 2,2′,6,6′-tetramethylbibenzyl, however, the transition state **7** has appreciable steric repulsion between

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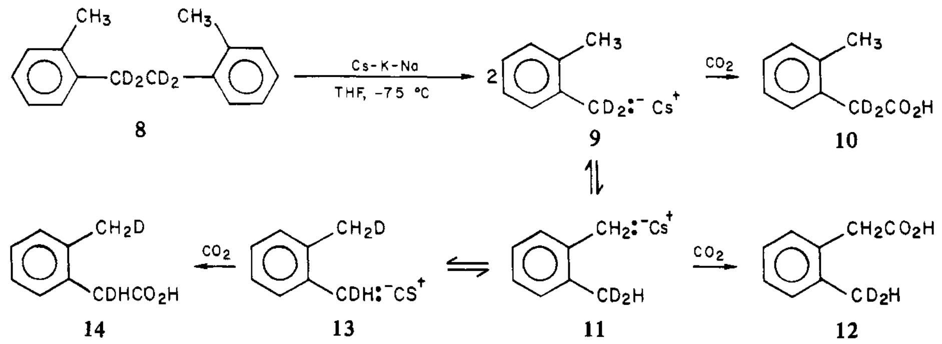
[30] Rüchardt, C.; Beckhaus, H.-D. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 429–440. We are greatly indebted to Professor Rüchardt for giving us estimates of these values prior to publication.

[31] Conformers that differ from 7 only by rotation about the central carbon–carbon bond linking the benzylic moieties also permit such σ–π interaction; however, rotation encounters torsional barriers and ultimately unfavorable steric interactions between the aromatic rings.

[32] A detailed orbital correlation diagram is given in Figure 3, supplementary material.

[33] Toluene gives 0.2% benzylcesium after 6-h reaction with Cs-K-Na alloy in THF at −75 °C (unpublished work of A.M.B.; see also ref 12).

Scheme II



o-methyl groups of opposing rings whereas the ground state can escape such repulsion by rotation of the phenyl groups to a strainless but unreactive conformation; hence this compound undergoes reductive cleavage 44 times more slowly than bibenzyl or at about the same relative rate as 4-methylbibenzyl.

Why does an *o*-methyl group accelerate while a *m*- or *p*-methyl group retards reductive cleavage? First it should be noted that this general effect is observed sometimes in other systems but to variable extents. Thus *o*-xylene undergoes hydrogen exchange on a methyl group faster than toluene with $KOC(CH_3)_3$ in dimethyl sulfoxide[26] but slower than toluene with lithium cyclohexylamide in cyclohexylamine.[34] The equilibrium acidity of *o*-xylene in decalin containing tetramethyl-1,2-diaminocyclohexane is intermediate between that of toluene and *m*-xylene but much higher than that of *p*-xylene.[23]

The usual explanation of methyl substituent effects is to regard methyl groups as "electron donating" and therefore to destabilize carbanions as found for anions of *m*- and *p*-xylene. On this basis *o*-xylene is judged to be exceptional. The special explanation offered for *o*-xylene was either that ionization relieves steric strain or that there is hydrogen bonding between the carbanion and hydrogen of the *o*-methyl group.[26]

To test the latter explanation we have cleaved 2,2′-dimethylbibenzyl-$\alpha,\alpha,\alpha',\alpha'$-$d_4$ (**8**, Scheme II) with Cs–K–Na alloy in THF. By analogy to one known case,[35] an intramolecular hydrogen bond linking C–H to a carbanion center ($C:^-$ H–C) might be expected to undergo rapid proton exchange between the two carbons, especially for a symmetrical system. Carbonation of our reaction mixture after 2 h of reaction at −75 °C, however, gave only *o*-tolylacetic-α,α-d_2 acid (**10**). Thus at low temperature isomerization of *o*-methylbenzyl-α,α-d_2 anion (**9**) to **11** and **13** is inappreciable. Carbonation of the organoalkali-metal reaction solution after it had been held at room temperature for 45 min gave, in contrast, *o*-tolylacetic acid with an almost random distribution of deuterium and protium between the methyl and methylene groups. Mass spectrometric analysis indicated that this rearrangement occurred primarily by an intramolecular process. Faster proton migration in **9** than in *p*-methylbenzyl-α,α-d_2-cesium confirms the intramolecular pathway for rearrangement of **9**.

We conclude that a strong intramolecular hydrogen bond does *not* exist in *o*-methylbenzyl anion; however, the rudiment of such bonding, a pole-induced dipole interaction, is likely present and may account for the acceleration of cleavage of bibenzyl by an *o*-methyl substituent. It is notable that in the gas phase the radical anions of toluene and of *o*-, *m*-, and *p*-xylene are more stable than that of benzene[36] while the opposite is true in ethereal solvents in the presence of alkali-metal countercations.[37] We accordingly regard the effect of *m*- and *p*-methyl groups in destabilizing benzylic anions as arising from steric inhibition of solvation (and possibly of cation–anion interactions). The rather variable effect of *o*-methyl groups on formation of benzylic anions depends on the nature of the transition state. In the case of **7**, the solvent tetrahydrofuran likely cannot interpenetrate the region between the phenyl groups; however one or two *o*-methyl groups replacing *o*-hydrogen can occupy this region without steric crowding. The *o*-methyl groups then stabilize the transition state **7** during cleavage, thanks to their polarizability and possibly also to "anionic hyperconjugation"[38a] and through-space overlap of orbitals,[38b] without appreciably diminishing solvation.

Conclusions

The scissions of hydrocarbons reported here proceed by way of dicesium adducts or dianions. The driving force for the reaction, in frontier-orbital terms, is provided by demotion of electrons from antibonding π-orbitals of the dicesium adduct to nonbonding benzylic or allylic orbitals of the product. This cleavage of carbon–carbon bonds is unusual in that it proceeds readily at low temperatures and is subject to large alkyl substituent effects. These effects have been interpreted variously as proceeding from relief of ground-state steric compression (steric acceleration), steric inhibition of solvation and of preferred transition-state geometry (both rate retarding), and polarizability of alkyl groups (weakly accelerating provided that steric inhibition of solvation is not overwhelming). These cleavages proceed in many cases in quantitative yield and provide a useful method of preparation of pure benzylic and allylic anions free of byproducts (such as alkali-metal halides or alkoxides) accompanying many alternative methods of preparation. Occasionally the reaction should prove useful in degradation of more complex molecules and in introduction of functionality into hydrocarbons. Finally in view of the proposed nature of the transition state and the effect of 18-crown-6 ether upon relative reactivities, it appears likely that compounds less reactive than the present hydrocarbons may be cleaved readily in better solvents for alkali metals than THF such as the methyl ethers of ethylene glycol, diethylene glycol, triethylene glycol, etc. The work of Collins and co-workers[13] with the weaker reducing agent Na–K alloy can be understood on this basis.

Experimental Section

The following 1,2-diphenylethane derivatives were obtained from commercial sources: dibenzyl (Eastman Kodak); 2,3-dimethyl-2,3-diphenylbutane (Chemical Samples Co.); 1,2-di-*p*-tolylethane, 9,10-dihydrophenanthrene, and 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene (all from Aldrich Chemical Co.). The other symmetrical 1,2-diphenylethane derivatives were prepared by addition of 2 mol of the corresponding benzylic chloride to 1 mol of magnesium in diethyl ether solution at reflux temperature (to give about 85% yield of purified product). The 2,3-diphenylbutane that was prepared[39] in low yield in similar manner from α-phenylethyl bromide had mp 123.5–124.5 °C after recrystallization from 95% ethanol and was, therefore, the meso isomer.[5c,40] When

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[34] Streitwieser, A., Jr.; Koch, H. *J. Am. Chem. Soc.* **1964**, *86*, 404–409.

[35] Mueller-Westerhoff, U. T.; Nazzal, A.; Prössdorf, W. *J. Am. Chem. Soc.* **1981**, *103*, 7678–7681.

[36] Jordan, K. D.; Michejda, J. A.; Burrow, P. D. *J. Am. Chem. Soc.* **1976**, *98*, 1295–1296.

[37] Lawler, R. G.; Tabit, C. T. *J. Am. Chem. Soc.* **1969**, *91*, 5671–5672.

[38] (a) DeFrees, D. J.; Bartmess, J. E.; Kim, J. K.; McIver, R. T., Jr.; Hehre, W. J. *J. Am. Chem. Soc.* **1977**, *99*, 6451–6452. Pross, A.; Random, L. *Ibid.* **1978**, *100*, 6572–6575. Pross, A.; DeFrees, D. J.; Levi, B. A.; Pollack, S. K.; Random, L.; Hehre, W. J. *J. Org. Chem.* **1981**, *46*, 1693–1699. (b) Schleyer, P. v. R.; Dill, J. D.; Pople, J. A.; Hehre, W. J. *Tetrahedron* **1977**, *33*, 2497–2501.

[39] We are indebted to R. Beauvais Randall, Jr., for this preparation.

[40] Greene, F. D. *J. Am. Chem. Soc.* **1955**, *77*, 4869–4873.

unavailable from commercial sources, the benzylic chlorides were prepared from the corresponding alcohol by reaction with thionyl chloride in pyridine. The benzylic alcohols were prepared, where necessary, from the corresponding benzoyl chlorides by reduction with $LiAlH_4$ (or $LiAlD_4$) in diethyl ether. Unsymmetrical 1,2-diphenylethane derivatives were prepared by Wolff-Kishner reduction[41] of the corresponding phenyl benzyl ketone; the necessary ketones were prepared by reaction of suitably substituted phenylacetyl chlorides with benzene and 1.5 molar equiv of $AlCl_3$. 4-Phenyl-1-butene, 2-methyl-4-phenyl-1-butene, and 3-methyl-4-phenyl-1-butene were from Chemical Samples Co. Cesium metal (99.9%) was from Callery Chemical Co., Division of Mine Safety Appliances Co.

Eutectic Cs-K-Na alloy[42] containing 47.4% K, 40.8% Cs, and 11.8% Na (all given as atom %) of mp −79 °C was prepared in a glovebox under a nitrogen atmosphere and, prior to use, was stored in sealed glass ampules under a nitrogen atmosphere.

General Method for Quantitative Cleavage of Hydrocarbons by Cs–K–Na Alloy. The reactions were run in a 500-mL five-necked Morton flask equipped with a stainless-steel high-speed stirrer,[43] a Friedrich condenser, a thermometer well, a pressure-equalizing dropping funnel, and a 4-mm bore Teflon-brand stopcock fitted with a rubber septum. The apparatus contained 1 atm of prepurified nitrogen supplied through a mercury bubbler. For safety the entire apparatus was placed in a glovebox that was kept filled with nitrogen during reactions with cesium alloy.

Before use, the apparatus was thoroughly flame dried under a flow of nitrogen. A flask containing tetrahydrofuran (THF) and $NaAlH_4$ (ca. 1 g) was attached to the condenser and THF (250 mL) was distilled into the reaction flask. The distillation flask was removed. Cesium alloy was then added and the alloy was stirred for 90 min at room temperature to produce a fine dispersion of the alkali metal. While stirring was continued, the dispersion was cooled to −75 ± 1 °C by means of a solid carbon dioxide–acetone bath. The hydrocarbon to be cleaved was dissolved in 5–10 mL of THF and was then added over a 5-min period from the dropping funnel. The reaction solution changed in color from an initial blue color of cesium dissolved in THF to green and frequently to orange and a final dark brown or red black. Vigorous stirring was continued for 120 min at −75 °C; thereafter the reaction mixture was forced under nitrogen pressure through a 12-gauge stainless-steel cannula (inserted into the reaction solution through the septum attached to the Teflon-brand stopcock) onto freshly crushed solid carbon dioxide. The residue remaining in the Morton flask was also carbonated with solid carbon dioxide. To each of the reaction mixtures after standing for 30 min was added 30 mL of methanol to decompose any remaining alkali metal.

The contents of the two carbonation flasks were combined with the aid of 100 mL of rinse water. The aqueous solution was concentrated on a rotary evaporator to remove most of the THF and methanol (the distillate was saved for hydrocarbon analysis), and the cold aqueous solution was extracted with two 50-mL portions of diethyl ether to remove remaining neutral materials. The ethereal extract was combined with the $THF–CH_3OH$ distillate. The aqueous solution was acidified with concentrated hydrochloric acid and then extracted with four 50-mL portions of diethyl ether. The ethereal extract after drying over anhydrous $MgSO_4$ was concentrated to one-tenth of its volume by distillation through a column packed 14 in. of length with glass helices.

The acids were converted to methyl esters by reaction with diazomethane and after addition of an internal standard (frequently methyl benzoate) were analyzed quantitatively by gas chromatography (GC) on a 10% Carbowax 20M column (either a 6 ft, $^1/_4$-in. diameter column packed with 60/80 mesh Chromosorb W or a 12 ft, $^1/_8$-in. diameter column packed with 100/120 mesh Chromosorb Q). The chromatograph was a Perkin-Elmer Model 881 equipped with hydrogen-flame ionization detectors. Calibration factors were determined with authentic samples. The products were identified qualitatively by comparisons of GC retention times with authentic samples, and their identities were confirmed after separation (where required by preparative GC) by NMR analysis and IR, mp, and/or mass spectral comparisons with authentic samples. Analysis by GC of the ethereal extract of neutral materials for unreacted hydrocarbon was similarly made on a 6 ft, $^1/_8$-in. diameter column packed with 10% SE-30 on 60/80 mesh Chromosorb G or on a 4 ft, $^1/_8$-in. diameter column packed with 3.6% OV-17 on 100/120 mesh Chromosorb W. Hydrocarbon cleavage products were sometimes determined on a 12 ft, $^1/_8$-in. diameter column packed with 15% FFAP on 100/120 Chromosorb W.

The results are reported in Chart I. The quantity of hydrocarbon cleaved in the runs of this table varied from 2.2 to 15 mmol and the ratio of moles of cesium per mole of hydrocarbon from 3.3 to 11.6 with yields of cleavage products being close to quantitative for all of the 1,2-diphenylethane derivatives except 1,2-di-*p*-tolylethane.

10,11-Dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene with Cs–K–Na Alloy. To Cs–K–Na alloy (27.2 mmol of Cs) finely dispersed in 300 mL of THF at −75 °C was added a THF solution of 0.994 g (5.12 mmol) of 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene over a 25-min period. The reaction mixture was then stirred at −75 °C for 120 min before carbonation and standard workup. Quantitative GC analysis gave 94.3% yield of 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene-5-carboxylic acid and 3.1% recovery of unreacted starting hydrocarbon. After recrystallization from 95% ethanol the acid had mp 216–217 °C (lit.[44] mp 215–217 °C); esterification with diazomethane gave a methyl ester of mp 92.0–93.5 °C (lit.[44] mp 93.5–95 °C) whose NMR spectrum agreed with that reported.[44] Finally a search by GC analysis for a dimethyl ester of a dicarboxylic acid derived from cleavage of the C(9)–C(10) bond of the present hydrocarbon was negative.

9,10-Dihydrophenanthrene with Cs–K–Na Alloy. Reaction of Cs–K–Na alloy (39.5 mmol of Cs) with 1.625 g (9.02 mmol) of 9,10-dihydrophenanthrene in 300 mL of THF at −75 °C under standard conditions gave a dark brown product, which after 2 h of reaction was forced into ice water. Analysis of the product by GC on a 10% Carbowax 20M column (8 ft × $^1/_8$ in.) at 180 °C gave product listed as % yield (retention time in min, mass spectrum *m*/*e*): 3.5 (12.5, 184), 4.8 (14.2, 184), 6.2 (18.2, 184), 15.4 (20.9, 182), 14.1 (22.9, 182), 20.3 (28.3, 182), and 32.2 (31.5, 180, starting hydrocarbon). This analysis assumes that the calibration factors for dihydro and tetrahydro derivatives are the same as that of the starting hydrocarbon and is in agreement with a 60:40 ratio of dicesium to monocesium adduct of 9,10-dihydrophenanthrene. The retention time (5.0 min) of a known sample of 2,2′-dimethylbiphenyl (K & K Labs) was different from that of any of the above reduction products. A 0.100 g of sample of the crude product was heated with 1.0 g of 5% Pd on carbon in toluene solution at reflux overnight under a slow stream of nitrogen. The product had a ^1H NMR (CCl_4) peak at δ 2.79 as expected for the methylene groups of 9,10-dihydrophenanthrene but lacked a peak at δ 2.05 as found in 2,2′-dimethylbiphenyl. Also GC analysis confirmed the presence of 9,10-dihydrophenanthrene and the absence of 2,2′-dimethylbiphenyl under GC conditions wherein as little as 1% of 2,2′-dimethylbiphenyl in 9,10-dihydrophenanthrene could have been detected.

Cleavage of 3,3′-Dimethylbibenzyl with Cesium Metal. Cesium sand was prepared by stirring vigorously 2.37 g (17.9 mmol) of cesium metal in 250 mL of THF at a temperature a few degrees above the melting point of cesium (28.5 °C) in the usual high-speed stirring apparatus until a fine (powder-like) dispersion was produced and then cooling rapidly to −75 °C. Reaction with 3,3′-dimethylbiphenyl (0.929 g, 4.42 mmol) for 2 h at −75 °C gave a deep brown product. Carbonation followed by the usual workup gave a carboxylic acid that after recrystallization from ethyl alcohol and sublimation in vacuo amounted to 0.72 g (4.8 mmol or 54% yield) of material of mp 62–63 °C as expected for *m*-tolylacetic acid (lit.[45] mp 60.5–61.5 °C). The ^1H NMR was identical with that of an authentic sample.

Reaction of 1,2-Di-*p*-tolylethane with Cs–K–Na Alloy. In the first reaction Cs–K–Na alloy (49.1 mmol Cs, 53.5 mmol K, 16.6 mmol Na) was finely dispersed in 250 mL of THF at −75 °C. To this blue solution 0.832 g (3.95 mmol) of 1,2-di-*p*-tolylethane in 5 mL of THF was added rapidly; after 2.5 h of stirring at −75 °C the solution had acquired a green color. The reaction mixture was then stirred for 2.5 more h during which time the mixture was allowed to warm slowly to 12 °C before carbonation. The reaction mixture changed in color from green to red at −10 °C. After the usual workup 1.08 g of crude acid was isolated. The usual GC analysis gave 6.2% yield of *p*-tolylacetic acid and 0.1% recovery of *p*-xylene; no *p*-phenylenediacetic acid could be detected in the acidic fraction. Analysis of the methyl esters on the Carbowax 20-M column at 189 °C (rather than 130 °C as for methyl (*p*-methylphenyl)acetate gave three unknown peaks listed as area % (retention time in min): 9 (8.8), 16 (9.8), 75 (11.0). The ^1H NMR spectrum of the crude acid (CS_2) had adsorbance at δ 1.76 (0.8 H, s, CH_3), 2.00 (0.9 H, s, CH_3), 2.20 (0.9 H, s, CH_3), 2.27 (0.9 H, s, CH_3), 2.53 (1.4 H, m), 3.47 (0.8 H, s), 5.60 (0.6 H, m, vinylic H), 6.8–7.5 (2.7 H, m, aromatic H), and 9.90 (1.0 H, s, CO_2H); since the ratio of CH_3 to CO_2H groups is 1.2:1, the acid fraction is primarily composed of dicarboxylic acids. The vinylic hydrogens suggest that two carboxyl groups are in good part on a di-

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Table III. Crystal Data for 1-(2,5-Dihydro-4-methylphenyl)-2-*p*-tolylethane (5)

formula	$C_{16}H_{20}$
crystl. system	monoclinic
a, Å	8.252 (4)
b, Å	6.038 (2)
c, Å	13.71 (1)
β, deg	103.23 (5)
V, Å³	664.8 (7)
space group	$P2_1/c$
Z	2
ρ(calcd), g/cm³	1.06
Data Collection Parameters	
diffractometer	Syntex P2₁
radiatn	Mo Kα (λ = 0.71069 Å)
monochromator	graphite
scan technique	θ–2θ
2θ max, deg	50
total unique reflcns	1181
reflcns with $F > 3\sigma(F)$	829

hydroaromatic ring. The mass spectrum of the methyl ester of the crude acid confirms these conclusions; *m/e* (relative intensity) 328 (2, $C_{20}H_{24}O_4$), 327 (1), 326 (4), 296 (8), 295 (6), 294 (11), 269 (15), 268 (7), 237 (49), 221 (9), ..., 105 (100). Repetition of this reaction under the standard conditions of Chart I gave 3.1% yield of *p*-tolylacetic acid and higher molecular weight products of which the chief product, after separation by preparative GC, had a mass spectrum essentially like that reported for the crude methyl ester above.

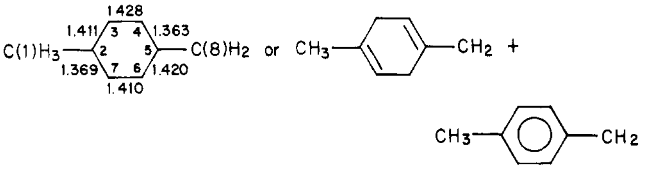
In another reaction 3.43 g of Cs–K–Na eutectic (18.3 mmol of Cs) in 250 mL of THF was allowed to react with 0.960 g (4.57 mmol) of 4,4′-dimethylbibenzyl at −75 °C for 2 h. About one-third of the reaction mixture was forced into cooled D_2O and the remainder into ice water. The THF was removed on a rotatory evaporator, and the organic product was recovered by extraction of the aqueous phase with ether. The protonated product amounted to 0.62 g; a 300-mg portion of this was chromatographed on a column (1-in. diameter) packed with 60 g of silica gel (0.2–0.5 mm, E. Merck A.G., Darmstadt). Elution with 40:60 benzene/pentane yielded 225 mg of product, which gave crystals from benzene–pentane: mp 56–58 °C; ^{1}H NMR (CCl_4) δ 1.64 (3 H, bd s, CH_3), 2.0–3.0 (11 H, m), 5.37 (2 H, bd s, vinylic H), 7.00 (4 H, s, aromatic H); ^{13}C NMR ($CDCl_3$) δ 20.9 (q), 22.9 (q), 30.1 (t), 31.5 (t), 33.6 (t), 38.9 (t), 118.1 (d), 127.6 (d), 128.3 (d), 130.0 (s), 134.0 (s), 134.4 (s), 138.7 (s); mass spectrum, *m/e* (relative intensity) 212 (25, M$^+$), 210 (13), 119 (13), 107 (95), 105 (100), 91 (38). Anal. Calcd for $C_{16}H_{20}$: C, 90.51; H, 9.49. Found: C, 90.42; C, 9.47. These data agree with the structure of 1-(2,5-dihydro-4-methylphenyl)-2-*p*-tolylethane (**5**). Continued elution yielded 37 mg of recovered 4,4′-dimethylbibenzyl. The product from decomposition with D_2O amounted to 0.30 g of crude product; ^{1}H NMR (CCl_4) δ 1.64 (3.0 H, bd s), 1.9–3.6 (8.7 H, m), 5.35 (1.6 H, bd s), 6.98 (4.2 H, s).

Dehydrogenation of 254 mg of the crude product from the above protonation (of the Cs–K–Na alloy reaction mixture) over 1.2 g of 5% Pd on carbon catalyst in toluene at reflux overnight under a slow stream of nitrogen gave after filtration, sublimation in vacuo, and recrystallization from 95% ethanol 210 mg of crystals: mp 81–82 °C; ^{1}H NMR (CCl_4) δ 2.27 (6 H, s), 2.80 (4 H, s), 6.93 (8 H, s); all as expected for 4,4′-dimethylbibenzyl. Likewise dehydrogenation of 200 mg of the product from decomposition with D_2O gave 170 mg of hydrocarbon: mp 80–82 °C; ^{1}H NMR (CCl_4) δ 2.28 (6.0 H, s), 2.80 (4.0 H, s), 6.92 (6.2 H, s).

Analysis by means of gas chromatography (on an OV-17 column at 160 °C) and mass spectrometry of the crude hydrocarbon from protonation of a similar reaction of Cs–K–Na alloy with 4,4′-dimethylbibenzyl at −75 °C gave products listed as area % yield (retention time in min, *m/e* of M$^+$): 0.6 (5.4, 214), 2.4 (6.1, 214), 0.3 (7.6, 214), 16 (9.2, 210), 68 (10.4, 212), and 13 (21, unknown). Here the compound of *m/e* 210 corresponds to unreacted 4,4′-dimethylbibenzyl, 212 to the dihydro derivative isolated above, and 214 to three tetrahydro derivatives.

X-ray Crystal and Molecular Structure of the Dihydro Derivative of 1,2-Di-*p*-tolylethane (5). A benzene–pentane solution of the dihydro derivative upon storage in a refrigerator for about 1 month slowly deposited rather large crystals. The crystal data and data collection parameters are summarized in Table III. The structure was solved by using the automatic centrosymmetric direct methods routine of SHELX-76. A full-matrix least-squares refinement converged at $R = 0.073$ and $R_W = 0.088$ for 106 variables.

As soon as the space group and density were determined, it was apparent that the two six-membered rings of the molecule could be related by a crystallographic inversion center leading to a significant disorder. Data collection and structure solution proceeded under the assumption that the inversion center would lead to a solution in which the phenyl ring and the reduced ring would be superimposed so that the location of the 12 carbon atoms of the two rings would be averaged. This indeed proved to be the case (see Figure 2). Inspection of the carbon–carbon distances allowed determination of which carbons in one ring had been reduced as shown below. Four of the carbon–carbon distances are significantly greater than 1.395 Å (the normal phenyl carbon–carbon distance); two are shorter. In addition, observed electron density in the region of C(3) and C(6) shows three probable hydrogen positions; this result is consistent with superimposed vinyl and methylene geometries. Only one vinyl hydrogen each can be located on C(4) and C(7). These data are therefore in agreement with the assigned structure of 1-(2,5-dihydro-4-methylphenyl)-2-*p*-tolylethane. The ORTEP perspective view of this molecule (Figure 2) clearly shows that the intramolecular distance between carbons C(4) and C(5) of the two six-membered rings is too great for this molecule to be a hydrophenanthrene derivative.



Reaction of 2,2′-Dimethylbibenzyl-α,α,α′,α′-d_4 with Cs–K–Na Alloy; Proton Migration in *o*-Methylbenzyl Anion. A sample of 2,2′-dimethylbibenzyl-α,α,α′,α′-d_4 [^{1}H NMR ($CDCl_3$) δ 7.10 (8 H, bd s), 2.80 (<0.1 H), 2.25 (6 H, s)] was allowed to react with excess of Cs–K–Na alloy in THF at −75 °C according to the general method given previously. After 2-h reaction time, a portion of the reaction mixture was carbonated. The usual workup gave *o*-tolylacetic acid, which after recrystallization and sublimation in vacuo gave: ^{1}H NMR (CCl_4) δ 7.09 (4.0 H, bd s), 3.6 (<0.1 H), 2.32 (3.0 H, s); mass spectrum, *m/e* (relative intensity) 150 (0.6), 151 (2.8), 152 (100, M$^+$ = $C_9H_8D_2O_2$), 153 (9.6), 154 (1.1), 155 (0.0). Hence this sample is essentially pure *o*-tolylacetic-α,α-d_2 acid (98.5 atom % *d* or 97.4% d_2, 2.2% d_1, 0.4% d_0 from mass spectrometric comparisons with protium compound).

The same reaction mixture was then warmed to room temperature and held at 25–28 °C for 45 min before carbonation of a second portion. The isolated *o*-tolylacetic acid from this carbonation had ^{1}H NMR (CCl_4) δ 7.10 (4.0 H, bd s), 3.60 (0.62 H, s), 3.56 (0.41 H, s), 2.29 (1.91 H, s); mass spectrum, *m/e* (relative intensity) 150 (1.5), 151 (7.5), 152 (100), 153 (13.9), 154 (1.4), 155 (0.2). The NMR absorption at δ 3.60 likely corresponds chiefly to the methylene group of 2-(methyl-d_2)phenylacetic acid and that at 3.56 to the methylene group of 2-(methyl-d_1)phenylacetic-α-d_1 acid since an α-deuterium atom has been found to shield a proton 0.015–0.057 ppm in analogous cases.[46] The NMR spectrum shows that the protons and deuterons in the methylene and methyl groups have approached random distribution[47] (1.20 H for CH_2 and 1.80 H for CH_3). Such a distribution might be achieved by intramolecular or intermolecular processes. The mass spectrum after correction for ^{13}C and intercomparison for M − 1 with the pure protium compound gives a composition of about 1.1% d_0, 6.3% d_1, 90.0% d_2, 2.6% d_3, and 0.0% d_4 or d_5. The product retains 96.4% of its deuterium content measured at −75 °C, and hence little deuterium has been lost to the solvent or otherwise; however, an intermolecular redistribution of deuterium between *o*-methylbenzyl anions has begun but is far from the random statistical distribution[47] (7.8% d_0, 25.9% d_1, 34.6% d_2, 23.0% d_3, 7.7% d_4, 1.0% d_5). The nearly random distribution of protons and deuterons in the methylene and methyl groups, therefore, was accomplished primarily by an intramolecular process.

Another portion of the same reaction mixture was held at room temperature for 12 h before carbonation. The usual workup gave *o*-tolylacetic acid: ^{1}H NMR (CCl_4) δ 7.07 (4.0 H, bd s), 3.57 (1.3 H, bd s), 2.29 (1.7 H, bd s); mass spectrum, *m/e* (relative intensity) 150 (22.4), 151 (57), 152 (100), 153 (42), 154 (8.4), 155 (1.5). This mass spectrum, after correction as above, gives a composition of approximately 11% d_0, 27% d_1, 46% d_2, 15% d_3, 1.5% d_4, and 0.2% d_5. The product retains 87% of its deuterium content measured at −73 °C; therefore some deuterium has evidently been lost by exchange with solvent or other substance. The composition is now closer to that calculated above for a random statistical

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(46) Bovey, F. A. "Nuclear Magnetic Resonance Spectroscopy"; Academic Press: New York, 1969; p 86.

(47) We are greatly indebted to Professors Henry M. Neumann and Robert A. Pierotti for aid with these calculations that assume no isotope effect and a pure d_2 compound.

distribution by an intermolecular process.

In other runs (*o*-methylbenzyl)cesium was generated by cleavage of 2,2′-dimethylbibenzyl-$\alpha,\alpha,\alpha',\alpha'$-$d_4$ at −75 °C in THF as above and then was warmed rapidly to −6 ± 3 °C. Samples were then carbonated at about 15–20-min intervals over a period of some 2 h. Analysis of the product acids by ^{1}H NMR permitted the rate of appearance of protons in the methylene group (and the equivalent rate of disappearance of protons in the methyl group) to be measured. A plot of $-\ln (x_e - x)$ vs. t, where x_e and x correspond to the number of protons in the methylene group of *o*-tolylacetic acid at equilibrium and time t respectively, gave a reasonably good linear relationship as expected for a reversible first-order reaction[48] whose slope corresponds to the sum of the forward and reverse rate constants, $k_+ + k_-$. In the present case these rate constants are each likely weighted averages for two reversible microscopic processes (see Scheme II). The value taken for x_e was 1.40 since this gave the best linear relationship; however, the initial slope is not very dependent upon the precise value of x_e. The average value of $(k_+ + k_-)$ for three runs was $(1.9 \pm 0.1) \times 10^{-4}$ s^{-1} (after 20 min 0.35 proton was in the methylene group after starting with 0.11 proton at zero time).

For comparison with *o*-methylbenzyl anion, *p*-methylbenzyl anion was similarly prepared by cleavage of *p*-$CH_3C_6H_4CD_2OCH_3$ (2.2 mmol) with excess Cs–K–Na alloy (8.7 mmol of Cs) in 250 mL of THF at −75 °C for 2 h (carbonation gave 96% yield of *p*-tolylacetic acid in an experiment with the nondeuterated ether) followed by warming rapidly to −6 ± 3 °C. Carbonation and ^{1}H NMR analysis just as for the *o*-methylbenzyl anion gave pseudo-first-order rate constants, $k_+ + k_-$, of 3.8×10^{-6} s^{-1} for scrambling of protons between the methylene group and the methyl group (after 8 h 0.24 proton was in the methylene group after starting with 0.10 proton at zero time).

General Method for Competitive Cleavages of Hydrocarbons with Cs–K–Na Alloy. The general technique for the competitive cleavages was like that described earlier for quantitative cleavages except that in the competitive studies an excess of hydrocarbons over cesium was employed such that measurable amounts of *both* hydrocarbons were present after reaction with Cs–K–Na alloy at the time of carbonation. Also stirring was stopped before rapid injection of the solution of hydrocarbons (in 10 mL of THF) via a syringe; stirring was then commenced slowly for 1 min (to insure uniform distribution of hydrocarbons in the flask prior to appreciable reaction) and then at the usual rapid rate (ca. 6000 rpm) for 90 min at −75 °C before carbonation. After the usual workup, the carboxylic acids produced were analyzed by quantitative gas chromatography in the manner previously described. The relative reactivity $k_{1,2}/k_{3,4}$ for cleavage of hydrocarbon R_1R_2 vs. hydrocarbon R_3R_4 was calculated from the equation:

$$\ln \left[\frac{(R_1R_2)_0}{(R_1R_2)} \right] = \frac{k_{1,2}}{k_{3,4}} \ln \left[\frac{(R_3R_4)_0}{(R_3R_4)} \right]$$

where the terms in parentheses refer to concentrations with the subscript zero referring to initial concentrations at time of mixing and the absence of subscript to concentrations at the time of carbonation as deduced from the yields of carboxylic acids. The results are summarized in Table I.

Acknowledgment. Financial support of this work by the National Science Foundation (Grants CHE-76-0270 and CHE-8009810) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Registry No. 5, 71776-86-8; Cs, 7440-46-2; Cs-K-Na alloy, 37219-16-2; *o*-methylbenzylcesium, 86846-71-1; 4,4′-dimethylbibenzyl, 538-39-6; 9,10-dihydrophenanthrene, 776-35-2; 10,11-dihydro-5*H*-dibenzo-[*a*,*d*]cycloheptene, 833-48-7; bibenzyl, 103-29-7; *meso*-2,3-diphenylbutane, 3755-79-1; 2,3-dimethyl-2,3-diphenylbutane, 889-67-4; 1,2,2-triphenylpropane, 16876-18-9; 2-methylbibenzyl, 34403-05-9; 3-methylbibenzyl, 34403-06-0; 4-methylbibenzyl, 14310-20-4; 2,2′-dimethylbibenzyl, 952-80-7; 3,3′-dimethylbibenzyl, 4662-96-8; 3,5-dimethylbibenzyl, 86846-72-2; 2,2′,6,6′-tetramethylbibenzyl, 25115-79-1; 3,3′,5,5′-tetramethylbibenzyl, 63376-64-7; 4-phenyl-1-butene, 768-56-9; 4-phenyl-2-methyl-1-butene, 6683-51-8; 4-phenyl-3-methyl-1-butene, 1647-06-9.

Supplementary Material Available: Table IV, fractional coordinates and temperature factors for 1-(2,5-dihydro-4-methylphenyl)-2-*p*-tolylethane (**5**); Table V, observed and calculated X-ray structure factors for **5**; Figure 3, orbital correlation diagram for dianion of bibenzyl transforming into two benzyl anions (7 pages). Ordering information is given on any current masthead page.

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(48) See ref 29, p 69.