The solid-state structure of 6 shows that it is monomeric with a distorted-tetrahedral geometry about indium.

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Supplementary Material Available: Tables of positional parameters of H atoms, anisotropic thermal parameters, and bond distances and angles (8 pages); listings of structure factor amplitudes (41 pages). Ordering information is given on any current masthead page.

Carbanions. 25. Phenyl Migration during Reactions of Triphenylmethane, 1,1,1-Triphenylethane, Tetraphenylmethane, and 3,3-Diphenyl-1-butene with Cesium–Potassium–Sodium Alloy[1]

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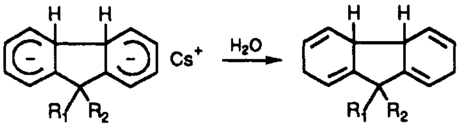
Both 3,3-diphenyl-1-butene and triphenylmethane react with excess Cs–K–Na alloy in THF at −75 °C to give a red dianion of unique structure involving [1,2]-phenyl migration into an adjacent benzene ring, according to structural characterization of the products of protonation and deuteration. The dianion from the butene is assigned the structure dicesium 6-(*cis*-1′-methyl-2′-propen-1′-id-1′-yl)-6-phenylcyclohexa-2,4-dien-1-ide (**6**) and that from triphenylmethane dicesium 6-(phenylmethanidyl)-6-phenylcyclohexa-2,4-dien-1-ide (**4f**). Tetraphenylmethane evidently undergoes a similar reaction with Cs–K–Na alloy, but the product of [1,2]-phenyl migration largely undergoes fragmentation prior to or following protonation. In contrast 1,1,1-triphenylethane reacts with Cs–K–Na alloy at −75 °C to give an ortho-cyclized dianion, dicesium 9-methyl-9-phenyl-*cis*-4a,4b-dihydrofluoren-2,5-diide (**2a**), which on protonation affords 9-methyl-9-phenyl-*cis*-2,4a,4b,7-tetrahydrofluorene (**3a**). The geometry of **3a** was established by X-ray crystallography. At higher temperatures, additional products are formed from 1,1,1-triphenylmethane and Cs–K–Na alloy via both [1,2]-phenyl migration and phenyl cleavage.

Introduction

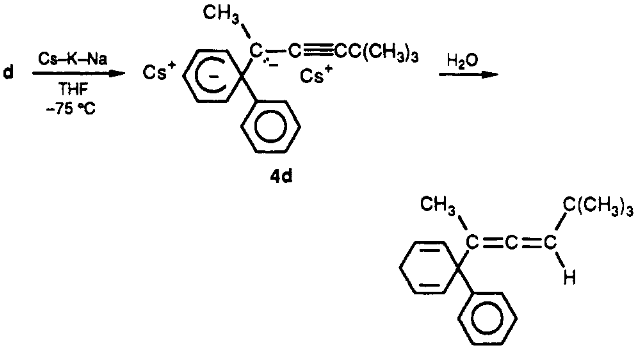
In previous work 1,1,1-triphenylethane, 1,1,1-triphenylpentane, and 2,2-diphenylpropane were reported[2] to react with Cs–K–Na alloy in tetrahydrofuran (THF) at −60 to −70 °C to give dianions (apparently **2a–c**) that upon protonation gave tetrahydrofluorene derivatives (**3a–c**).

1a: R_1 = Ph, R_2 = CH_3
b: R_1 = Ph, R_2 = n-C_4H_9
c: R_1 = CH_3, R_2 = CH_3
d: R_1 = CH_3, R_2 = $C{\equiv}CC(CH_3)_3$
e: R_1 = CH_3, R_2 = $CH{=}CH_2$
g: R_1 = Ph, R_2 = Ph
h: R_1 = H, R_2 = Ph



2a–c **3a–c**

In contrast, 5,5-dimethyl-2,2-diphenyl-3-hexyne (**1d**) was found[3] to react under similar conditions to give the product **5** of a [1,2]-phenyl migration, evidently via the rearranged dianion **4d**.



4d

5

Since the rearrangement of a phenyl group to the ipso position on a benzene ring under reducing conditions is, to our knowledge, without precedent and since the powerful reducing agent eutectic Cs–K–Na alloy has been little studied in organic chemistry, the present work was un-

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[1] Presented in part at the International Symposium on Chemistry of Carbanions, University of Durham, Durham, U.K., July 1984.

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

[3] Grovenstein, E., Jr.; Chiu, K.-W.; Patil, B. B. *J. Am. Chem. Soc.* **1980**, *102*, 5848–5859. For some related [1,2]-anionic rearrangements, especially the "Zimmerman–Grovenstein" rearrangement, see: Eisch, J. J.; Kovacs, C. A.; Chobe, P. *J. Org. Chem.* **1989**, *54*, 1275–1284 and references therein.

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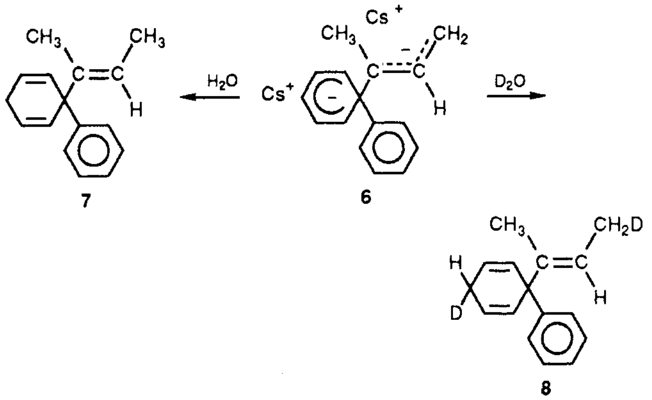
dertaken to find additional examples of such phenyl migration and to explain why some reactions of the alloy give products of type **3a–c** and others of type **5**. Toward this end, reactions of 3,3-diphenyl-1-butene (**1e**), triphenylmethane (**1f**), and tetraphenylmethane (**1g**) with eutectic Cs–K–Na alloy have been studied for the first time and the reaction products from 1,1,1-triphenylethane (**1a**) have been further defined.

Results

3,3-Diphenyl-1-butene (1e). Reaction of this hydrocarbon ($C_{16}H_{16}$) with eutectic Cs–K–Na alloy in THF at −75 °C gave a red carbanion that upon protonation gave a hydrocarbon (7) of C,H analysis and molecular weight corresponding to a dihydro derivative ($C_{16}H_{18}$) of the starting hydrocarbon. The ^{1}H and ^{13}C NMR spectra (see Experimental Section) indicated that **7** has only one phenyl group, a 2,5-cyclohexadienylidene group, and *cis*-1-methylpropenyl group; hence, **7** has the structure shown. Reaction of the red carbanion with heavy water gave a dideuterio derivative ($C_{16}H_{16}D_2$) whose ^{1}H and ^{13}C NMR spectra agree with structure **8**. The intermediate red carbanion evidently has the structure shown by **6**.



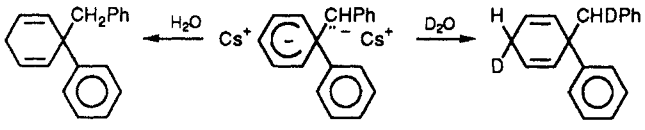
7 **6** **8**

Some confirmation of the structures of **7** and **8** is provided by electron-impact mass spectrometry, which gives as the most intense ions fragments with *m/e* 155 from **7** and *m/e* 156 from **8** corresponding to $C_{12}H_{11}^+$ and $C_{12}H_{10}D^+$, respectively. These are likely protonated (or deuterated) biphenyl ions from cleavage of the butenyl group from **7** (or **8**) under electron impact.

3,3-Diphenyl-1-butene (**1e**) thus reacts with Cs–K–Na alloy with [1,2]-sigmatropic migration of phenyl in a manner analogous to that found earlier for 5,5-dimethyl-2,2-diphenyl-3-hexyne (**1d**). This discovery led to a search for other examples of this rearrangement.

Triphenylmethane (1f). In previous work triphenylmethane was reported to react with potassium metal at 200 °C to give (triphenylmethyl)potassium.[4] Triphenylmethyl alkali-metal compounds are similarly formed with sodium in liquid ammonia,[5] with Na–K alloy in diethyl ether,[6] with lithium in THF both with[7] and without[8] the addition of biphenyl as metal carrier, and with potassium[9] in 1,2-dimethoxyethane (DME). In the last case at room temperature the byproducts diphenylmethane, biphenyl, and various reduction products were also reported; these byproducts were prevented by addition of butadiene to the reaction mixture.[9] The green radical anion of triphenylmethane is formed in DME, THF, and their mixtures with diethyl ether upon reaction with Na, K, and their alloys at −60 to −140 °C.[10] Above −80 °C the anion radical decomposes to a red carbanion, presumably triphenylmethyl anion, and, at higher concentrations, to the anion radical of biphenyl.[10]

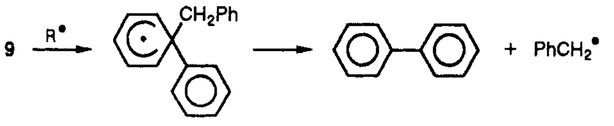
In the present work reaction of triphenylmethane with Cs–K–Na alloy in THF at −75 °C gave a red carbanion, evidently structure **4f**, which upon protonation gave a product that, under our optimum conditions, contained about an 80% yield of hydrocarbon **9**. The structure of this hydrocarbon was deduced from its C,H analysis, mass spectral molecular weight, and NMR spectra (^{1}H and ^{13}C) as given in the Experimental Section.



9 **4f** **10**

Deuteration of the red carbanion (**4f**) gives a dideuterio hydrocarbon that is assigned structure **10** on the basis of its spectral properties. Interestingly the two allylic hydrogens of the cyclohexadienyl moiety of **9** are, unlike in the case of **7**, no longer essentially NMR equivalent. One is centered at δ 2.22 and the other at δ 2.46 (vs a broad peak at δ 2.66 for **7**). If, as appears reasonable,[11] the peak at δ 2.22 is assigned to the methylene proton cis to the benzyl group, then the ^{1}H NMR spectrum of the deuterated hydrocarbon **10** corresponds to 87% of attack by deuterium oxide on the face of the cyclohexadienyl anion moiety of **4f** that is cis to the phenyl group (trans to benzyl). Evidently the benzylcesium (or benzyl) moiety rather effectively blocks deuteration on the side of the cyclohexadienyl anion cis to the benzylcesium (or benzyl) group.

In addition to **9**, some 2% of an unknown isomer of **9**, 1% of diphenylmethane, and variable amounts of toluene, biphenyl, and hydrobiphenyl are produced during reactions of triphenylmethane with Cs–K–Na alloy. Subsequent work revealed that hydrocarbon **9** decomposes on long storage at room temperature in the presence of air and light into biphenyl (and doubtlessly toluene) or rather rapidly into these products in presence of a small amount of dibenzoyl peroxide in benzene solution at reflux temperature. Evidently the hydrocarbon **9** is attacked by free radicals to give **11**, which decomposes into biphenyl and benzyl radical as shown. The benzyl radical then attacks **9** to give toluene and **11** in a chain process. The best yields of **9** were obtained when the protonation and isolation of **9** were conducted in the presence of hydroquinone and the



11

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[4] Hanriot, M.; Saint-Pierre, O. *Bull. Soc. Chim. Fr.* **1889**, *1*, 774–780 (3rd series).

[5] Krays, C. A.; White, G. F. *J. Am. Chem. Soc.* **1923**, *45*, 768–778. Kraus, C. A.; Kawamura, T. *Ibid.* **1923**, *45*, 2756–2763.

[6] Gilman, H.; Young, R. V. *J. Org. Chem.* **1936**, *1*, 315–331. See also: Theilacker, W.; Mollhoff, E. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 596–597.

[7] Eisch, J. J.; Kaska, W. C. *J. Org. Chem.* **1962**, *27*, 3745–3752.

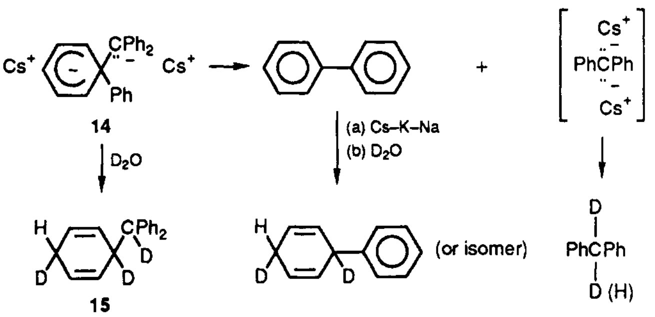
[8] Gilman, H.; Gaj, B. J. *J. Org. Chem.* **1963**, *28*, 1725–1727.

[9] House, H. O.; Kramer, V. *J. Org. Chem.* **1962**, *27*, 4146–4149.

[10] Nasirov, R. N.; Prokof'ev, A. I.; Solodovnikov, S. P.; Kabachnik, M. I. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*) **1973**, 1930–1933.

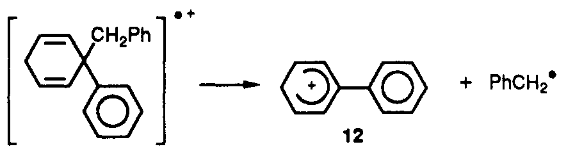
[11] Note that 1,4-dihydrobenzene has its allylic protons at δ 2.67 ($CDCl_3$), about the same location as cited for **7**; hence, the proton at δ 2.22 is taken to be shielded by the ring current of the cis benzyl group of **9** We are indebted to Dr. D. E. Quest for the NMR spectrum of 1,4-dihydrobenzene.

Scheme I

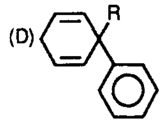


product was stored in the dark and in the cold.

On mass spectral analysis under electron impact **9** fragments chiefly into an ion with *m/e* 155, likely[12] the 3-phenyl-2,4-cyclohexadienyl cation (**12**). Similarly the



dideuterio hydrocarbon **10** gives as base peak an ion with *m/e* 156. As noted earlier, similar fragmentation of **7** and **8** was observed. This fragmentation appears to be diagnostic of compounds of the general structure **13**.



13

Tetraphenylmethane (1g). This hydrocarbon has been reported to react with Na–K in ether to give (after hydrolysis) diphenylmethane, tetrahydrodiphenylmethane, triphenylmethane, and a small amount of benzene;[14] however, solid tetraphenylmethane is reported to react with potassium to give the tetraphenylmethane radical anion, which is said to be stable both in the solid state and in solution in 1,4-dioxane and THF.[15]

In the present work, reaction of tetraphenylmethane with Cs–K–Na alloy in THF at about −75 °C for 1 h was found to give after protonation or deuteration some 0.5–1% of triphenylmethane and about 40% yield each of biphenyl and diphenylmethane (including dihydro derivatives of these). The formation of these cleavage products was not much affected by having hydroquinone present in the protonation medium and during workup. The ineffectiveness of hydroquinone in preventing cleavage to biphenyl and diphenylmethane suggests that much cleavage occurs prior to protonation plausibly as shown in Scheme I, or else hydroquinone is ineffective in preventing free radical cleavage of **15**. This facile cleavage is evidently promoted by the phenyl groups (stabilization of the diphenylmethyl dianion) and relief of steric compression in **14**.

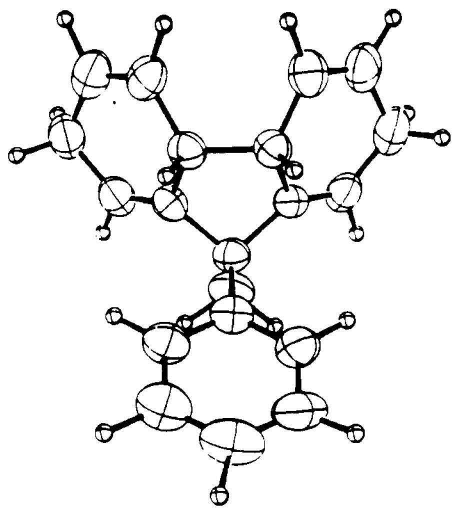
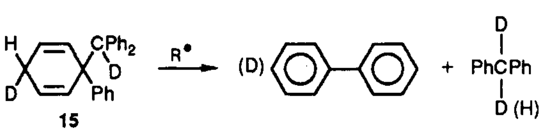


Figure 1. ORTEP drawing of the structure of compound **3a** as determined by X-ray crystallography.

That much biphenyl is formed prior to protonation is confirmed by the appearance of dideuteriodihydrobiphenyl in the products of deuteration. Also the yield of a dihydro derivative of tetraphenylmethane, likely structure **15**, decreased with time of stirring prior to deuteration, in agreement with **15** coming from the intermediate **14**, which was rather unstable even at −75 °C. The structure of **15** rests upon its mass spectrum, which shows extensive cleavage, under conditions of electron impact, into an ion with *m/e* 156, which is expected, as noted above, for a compound of general structure **13**. The other product expected from the cleavage of Scheme I is the dianion of diphenylmethane. The presence of this dianion is implied by the formation of nearly an equal mixture of dideuteriodiphenylmethane and monodeuteriodiphenylmethane. The formation of the latter product may be attributed to prior protonation of the dianion to a monoanion by either the solvent or other proton source such as biphenyl (which was about half monodeuterated). The available data do not preclude some of the products coming also from a facile free-radical fission of **15**:



1,1,1-Triphenylethane (1a). The predominant product of reaction of 1,1,1-triphenylethane with Cs–K–Na Alloy in THF at −75 °C, followed by protonation, is confirmed to be 9-methyl-9-phenyl-2,4a,4b,7-tetrahydrofluorene (**3a**) on the basis of X-ray diffraction upon the crystalline product. This work extends a prior study,[2] in which the structure of the product was deduced from spectral data, and reveals, for the first time, the unique stereochemistry of the product as shown in Figure 1. The hydrogens at positions 4a and 4b are to one another, as was true also in the similar product[2] (**3c**) from 2,2-diphenylpropane (**1c**). The 9-phenyl substituent of **3a** is cis to the hydrogens at positions 4a and 4b; this geometry likely minimizes steric strain in the molecule. The reaction of cesium alloy with 1,1,1-triphenylethane at −75 °C exemplifies the utility of cesium (and potassium) in the synthesis of stereochemically discrete products. In the present case the binding of cesium cations to the dianion (**2a**) is probably most favored in a dianion of stereochemistry like that of the hydrocarbon product shown in Figure 1.

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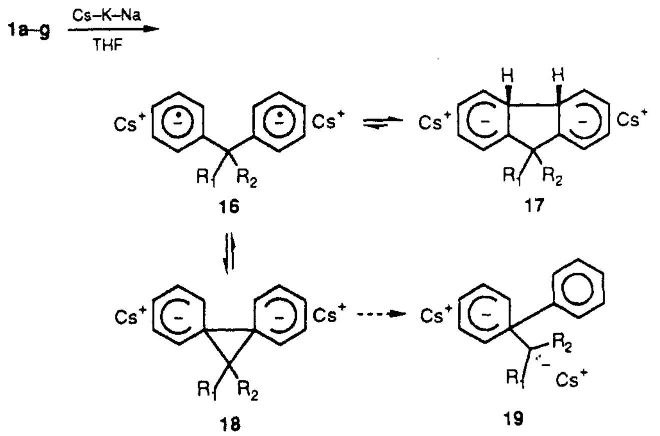
[12] In view of the ease of carbocation rearrangements and, in particular, of the formation of tropylium ions rather than benzyl cations[13] under some mass spectral conditions, the structure of these mass spectral ionic fragments remains in some doubt.

[13] Cf.: McLafferty, F. W. *Interpretation of Mass Spectra*, 2nd ed.; Benjamin: London, 1973; pp 109–110.

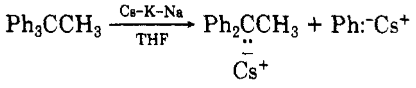
[14] Schorygin, P. P.; Matschinskaja, I. W. *Chem. Zentralbl.* **1940**, *111*, 703. Carbonation is said to give a complex mixture of products containing up to 5% of triphenylacetic acid and 13% of diphenylacetic acid (Theilacker, W.; Mollhoff, E. *Angew. Chem., Int. E. Engl.* **1962**, *1*, 596–597).

[15] Brandes, K. K.; Suhrmann, R.; Gerdes, R. J. *J. Org. Chem.* **1967**, *32*, 741–745.

Scheme II



In a run with 1,1,1-triphenylethane and Cs–K–Na alloy in which the initial product from the reaction at −75 °C was warmed to −45 °C for 1 h before protonation, the predominant product was still **3a** but contained 2% of an unknown hydrocarbon isomeric with **3a**, 1% of biphenyl, and 2% of 1,1-diphenylethane. The yields of biphenyl and 1,1-diphenylethane rose to 8 and 9% of the isolated product when the warming at −45 °C was increased to 3 h. The unknown hydrocarbon could have the general structure **13** (R = 1-phenylethyl), since its mass spectrum shows a very strong peak at *m/e* 155. Biphenyl likely comes from cleavage of an anionic precursor of **13**. 1,1-Diphenylethane, which was formed in a yield of 56% when the temperature was raised to 0 °C, points to the existence of yet another cleavage pathway:



$$Ph_3CCH_3 \xrightarrow[THF]{Cs\text{-}K\text{-}Na} Ph_2\underset{Cs^+}{\underset{\cdot\cdot}{C}}CH_3 + Ph{:}^-Cs^+$$

A similar cleavage of 9,9-diarylfluorenes by potassium in 1,2-dimethoxyethane to give (9-arylfluorenyl)potassium and arylpotassium has been reported.[16]

Discussion

gem-Diphenylalkanes (**1a–g**) react with alkali-metal mirrors in ethereal solvents at low temperatures to give radical anions, some of which have been characterized by ESR studies.[10–15] In the present work, however, when an excess of finely divided liquid Cs–K–Na alloy is utilized with high-speed stirring, at −70 to −75 °C, the initial deep blue THF solution ("solvated electrons") rapidly develops a deep red to brown color upon addition of the diphenylalkane. In the case of 1,1,1-triphenylethane (**1a**), rapid titration[2] of the reaction mixture with *tert*-butyl alcohol required 2 molar equiv of *tert*-butyl alcohol per mole of hydrocarbon to discharge the red color. Decomposition of the red reaction mixture with deuterium oxide gave a dihydro product (**3a**) containing two deuterium atoms per mole of hydrocarbon. These experiments imply that the hydrocarbon has added two electrons per molecule. Other experiments[17] have shown that cesium is the predominant alkali metal which is extracted from the liquid cesium alloy under the present reaction conditions. This work is in accord with the formation of either the diradical dianion **16** or the dianion **17** (see Scheme II) for the reaction of *gem*-diphenylalkanes (**1a–g**) with excess Cs–K–Na alloy.

While it would seem desirable to characterize these dianions by spectroscopic techniques, the insolubility and high reactivity of these organocesium compounds give great experimental difficulties. The deep red "solution" of **1a** upon cessation of stirring and standing in the cold deposits a red precipitate of the product from a blue THF solution.[18] Such organocesium products are contaminated with excess cesium alloy; manipulation of these products, even in a glovebox, can result in an *explosion*, evidently because of the presence of a small amount of oxygen.[18,19] Characterization of the organocesium products in the present work has accordingly been limited to study of the structures of the hydrocarbons produced by hydrolysis with H_2O or D_2O.

Prior work[17] with benzene has shown, by correlation of broad-line ESR spectra with hydrolytic studies, that while a radical anion (cesium benzenide) is first formed as an insoluble black precipitate, upon vigorous stirring this radical anion disappears with formation of a dimer of the radical anion and disappearance of the ESR absorption. Toluene behaves similarly. By analogy with the chemical behavior of benzene and toluene, and since entropy changes should favor an intramolecular cyclization over a dimerization, we suggest that the dianions from *gem*-diphenylalkanes exist largely in the cyclic form **17** rather than the diradical form **16**. That **17** is predominantly the cis-fused isomer is confirmed in the present work by X-ray crystallography of the hydrolysis product **3a**.

An alternative for the dianion is the spirocyclic structure **18**. Because this structure has a three-membered ring as opposed to the five-membered ring of **17**, it is expected to be considerably less stable then **17**. A few anions having a *spiro*-cyclopropane ring, somewhat similar to **18**, have in fact been characterized and found to be in mobile equilibrium with open acyclic isomeric structures.[20] It is suggested that a dynamic equilibrium exists between the three dianions (**16**, **17**, **18**) as revealed in part by the irreversible decomposition into **19**, or products derived from **19**, when the substituents R_1 and R_2 are favorable as with compounds **1d–g**, which have at least one phenyl, vinyl, or acetylenic group to stabilize what would otherwise be a localized negative charge in **19**. Compounds **1a** and **1b**, however, where one substituent group is phenyl and the other alkyl, give only **17** at low temperature. This has been attributed[3] to steric crowding by the alkyl group, which prevents the phenyl substituent from attaining a suitable conformation for delocalizing negative charge in the transition state leading to **19**. The present work shows that when the temperature is raised some transformation into **19** occurs but the yield from **1a** is low because of competing phenyl cleavage. When both substituents are phenyl (**1g**), comparable unfavorable steric effects might have been anticipated, yet products that are expected to be formed from **19** occur in good yield. Evidently when R_1 and R_2 are both phenyl groups, greater latitude exists in the steric orientation of the phenyls such that conformations can be found which minimally increase steric compression and yet adequately delocalize negative charge.

Only a simple mechanism of rearrangement has been considered in this discussion. Whether the observed rearrangement is intermolecular rather than intramolecular and whether or not the migrating phenyl retains its point

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

(17) Grovenstein, E., Jr.; Longfield, T. H.; Quest, D. E. *J. Am. Chem. Soc.* **1977**, *99*, 2800–2802.

(18) Unpublished experiments with T. H. Longfield and D. E. Quest.

(19) Cf.: hackspill, L. *Proc. Int. Congr. Appl. Chem., 8th* **1912**, *2*, 113.

(20) Grovenstein, E., Jr.; Lu, P. C. *J. Org. Chem.* **1982**, *47*, 2928–2938; *J. Am. Chem. Soc.* **1982**, *104*, 6681–6684 and references therein.

of attachment at the same phenyl carbon atom are questions that can be answered only by additional experiments.

Experimental Section

^{1}H NMR spectra were determined at 60 MHz with a Varian Model T-60A NMR spectrometer or at 300 MHz with a Bruker Model WM-300 NMR spectrometer. ^{13}C NMR spectra were determined at 75 MHz with the Bruker Model WM-300 spectrometer; the multiplicity of the ^{13}C spectra was determined by off-resonance decoupling or by distortionless enhancement of population transfer. The spectra are reported in parts per million (δ) downfield from tetramethylsilane as an internal standard. Mass spectra were run on a Hitachi (Perkin-Elmer) RMU-7L or a Varian MAT 112S (with SS 200 data system) mass spectrometer equipped with a gas chromatograph; electron-impact spectra are given unless otherwise indicated.

Gas chromatographic (GC) analyses were done on a Perkin-Elmer Model 881 chromatograph equipped with a hydrogen-flame ionization detector. Quantitative GC analysis were made with an internal standard and calibrations based upon authentic samples. Qualitative GC analyses are reported as "area percent" of total volatile constituents. The GC columns were a 12 ft long, $^1/_8$ in. diameter column packed with 15% FFAP (free fatty acid phase Carbowax 20M reacted with nitroterephthalic acid) on 100/120 mesh Chromosorb W, acid washed and reacted with dimethyldichlorosilane, and an 8 ft long, $^1/_8$ in. diameter column packed with 10% GE SE 30 on 100/120 mesh Gas-Chrom Q.

All reactions involving Na-K and Cs-K-Na alloys were run in the usual Morton[21] apparatus enclosed in a glovebox under an atmosphere of nitrogen to reduce fire hazards.[2] Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, GA.

3,3-Diphenyl-1-butene (1e). A. In the most successful synthesis modeled after that of Weinstock and Lewis,[22] 1,1-diphenylethane [^{1}H NMR (60 MHz, CCl_4) δ 1.59 (3 H, d, J = 7 Hz), 4.08 (1 H, q, J = 7 Hz), and 7.11 (10 H, bd s)] was converted to 3,3-diphenyl-1-butanol in an 83% yield of twice-distilled product by advantageous use of KNH_2 in place of $NaNH_2$ (which gave only 62% yield[22]). The butanol [^{1}H NMR (CCl_4) at δ 1.61 (3 H, s), 1.88 (1 H, bd s), 2.30 (2 H, t, J = 7 Hz), 3.35 (2 H, t, J = 7 Hz), 7.11 (10 H, bd s)] was converted to methyl 3,3-diphenyl-1-butyl xanthate in a 59% yield of the product with mp 61–63 °C [^{1}H NMR (CCl_4) δ 1.68 (3 H, s), 2.43 (3 H, s), 2.56 (2 H, t, J = 7 Hz), 4.40 (2 H, t, J = 7 Hz), 7.08 (10 H, bd s)]. Pyrolysis of the xanthate at a bath temperature of 240–270 °C gave, after two distillations in vacuo, a 55% yield of pure 3,3-diphenyl-1-butene [^{1}H NMR (CCl_4) δ 1.71 (3 H, s), 4.79 (1 H, d of d, J = 1.5 and 10 Hz), 5.03 (1 H, d of d, J = 1.5 and 7 Hz), 6.28 (1 H, d of d, J = 10 and 17 Hz), 7.07 (10 H, bd s)] along with a 21% yield of a forerun of about 95% pure 3,3-diphenyl-1-butene containing an unknown impurity with a prominent ^{1}H NMR peak at δ 2.63 (s).

B. An alternative synthesis was modeled after the highly regiospecific alkylation of the 1,1-diphenyl-2-butynyl anion.[3] The starting 1,1-diphenyl-2-propen-1-ol was prepared in >95% yield (^{1}H NMR) by reaction of excess vinylmagnesium bromide with benzophenone in THF and was converted to the corresponding methyl ether by reaction with a small excess of *n*-butyllithium in THF at −60 °C and then with a 3-fold excess of methyl iodide in THF at room temperature for 5 days. Recrystallization of the product from pentane gave a 48% yield of white crystals with mp 26–28 °C. The purest sample of the methyl ether had mp 27.5–28.2 °C: ^{1}H NMR (60 MHz, $CDCl_3$) δ 3.15 (3 H, s), 5.22 (1 H, d of d, J = 17 and 1.6 Hz), 5.41 (1 H, d of d, J = 11 and 1.6 Hz), 6.50 (1 H, d of d, J = 17 and 11 Hz), 7.31 (10 H, bd s). Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.60; H, 7.20.

Cleavage of the methyl ether of 1,1-diphenyl-2-propen-1-ol (21.18 g, 0.094 mol) with 14.2 g of eutectic Na-K alloy (0.29 mol of K) in diethyl ether was performed in the usual manner.[3] Mercury (20 mL) was added dropwise to deactivate the remaining alkali metal, and then the red carbanion was methylated with methyl iodide (0.11 mol). The usual workup gave 20 g of hydrocarbon whose composition by ^{1}H NMR and GC analysis (column packed with SE 30 on Chromosorb G, 180 °C) was 30% 3,3-diphenyl-1-butene and 70% 1,1-diphenyl-1-butene and hence was similar to the mixture previously reported[22] from methylation in liquid ammonia.

Reaction of 3,3-Diphenyl-1-butene (1e) with Cs-K-Na Alloy. A. Followed by Protonation. Tetrahydrofuran (THF, 225 mL) was distilled from $LiAlH_4$ into the usual Morton high-speed stirring apparatus under an atmosphere of nitrogen. Eutectic Cs-K-Na[23] alloy (6.4 g, containing 35 mmol of Cs) was added and the mixture stirred for 3 min at 25 °C and then for 15 min at −75 °C to give a fine suspension of the alloy in a blue solution. A solution of 1e (2.51 g, 12.0 mmol) in 5 mL of THF was added rapidly, and the solution was then stirred for 1 h at −75 °C before addition of 10 mL of mercury in fine droplets over a period of 15 min. Some 80% of the red solution was forced as a fine stream into 350 mL of ice water. The solution was saturated with NaCl. The THF phase was separated and the brine solution extracted three times with ether. The combined ethyl ether and THF solutions, after being dried over anhydrous $MgSO_4$, yielded 2.08 g of product that by GC analysis (SE 30 column at 180 °C) contained 95 area % of 3-phenyl-3-(1-methyl-1-propenyl)cyclohexa-1,4-diene (7) of retention time 6.6 min and 0.5% and 4% of two unknowns of retention time 5.0 and 25.6 min, respectively. A bulb to bulb distillation of the product at 0.1-mm pressure and a jacket temperature of 140–200 °C gave a clear colorless liquid: ^{1}H NMR (300 MHz) δ 1.48 [3 H, quintet, $J \simeq$ 1.0 Hz, $-C(\mathit{CH}_3){=}CHCH_3$], 1.66 [3 H, d of q, J = 0.93 and 6.7 Hz, $-C(CH_3){=}CH\mathit{CH}_3$], 2.66 [2 H, bd s, $C\mathit{H}_2(CH{=}CH-)_2$], 5.54 [1 H, q of q, J = 1.2 and 6.7 Hz, $-C(CH_3){=}C\mathit{H}(CH_3)$], 5.84 (4 H, m, $CH_2(C\mathit{H}{=}C\mathit{H}-)_2$], 7.1–7.3 [5 H, bd m, phenyl H]. The group $-C(CH_3){=}CHCH_3$ is assigned a likely cis relationship[24] of methyl groups on the basis that the allylic coupling constant (J = 1.2 Hz) of vinylic hydrogen to methyl hydrogen has the value expected[25] for J_{transoid} rather than J_{cisoid} (1.7 and 1.9 Hz) found in 3-methyl-1-butene and 1-butene, respectively. The ^{1}H NMR assignments are corroborated[26] by other spectral evidence (see also product of deuteration): ^{13}C NMR ($CDCl_3$) δ 13.69 (q, $CH_3CH{=}C<$), 13.87 (q, $-C(\mathit{CH}_3){=}CH-$), 26.06 (t, CH_2 of cyclohexa-1,4-diene ring), 51.1 (s, quaternary C of cyclohexa-1,4-diene ring), 121.4, 122.8, 125.7, 127.2, 128.2, and 131.5 (all doublets, aromatic and vinylic CH), 140.3 and 147.0 (both singlets, quaternary vinylic and aromatic C); mass spectrum *m/e* (relative intensity) 210 (21, M$^+$), 195 (17), 181 (22), 180 (6), 168 (11), 167 (10), 166 (5), 165 (9), 155 (100), 154 (36), 153 (18), 152 (13), 142 (6), 141 (6), 129 (10), 128 (14), 119 (8), 117 (16), 116 (6), 115 (22), 106 (8), 105 (20), 104 (6), 102 (5), 91 (43). Anal. Calcd for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 90.98; H, 8.84.

B. Followed by Deuteration. The above reaction was repeated under the same conditions with 2.24 g of 1e and 5.9 g of Cs-K-Na eutectic except that, after the THF solution was stirred at −75 °C with mercury, the reaction mixture was forced into 100 mL of THF containing 10 mL of deuterium oxide (98.9 atom % D) at 0 °C. The usual workup gave 2.23 g of a product (8) whose ^{1}H NMR spectrum (60 MHz, $CDCl_3$) was essentially identical with that of the previous protonated sample save that the area of the two methyl peaks at δ 1.48 and 1.66 now summed to only 5.1 H. The δ 1.66 peak was now reduced in intensity and broadened until it overlapped the peak at δ 1.48; also, the peak at δ 2.66 now contained only 1.0 H and was broadened. The peaks at δ 1.66 and 2.66 for the protonated sample were shifted upfield about 0.02 ppm in the deuterated sample.

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(21) Morton, A. A.; Redman, L. M. *Ind. Eng. Chem.* **1948**, *40*, 1190.

(22) Weinstock, J.; Lewis, S. N. *J. Am. Chem. Soc.* **1957**, *79*, 6243–6247.

(23) Tepper, F.; King, J.; Greer, J. In *The Alkali Metals, an International Symposium Held at* Nottingham *on 19-22nd July, 1966*; The Chemical Society: London, 1967; pp 24–26.

(24) For other examples of the preferential formation of cis-allylic anions see: Schlosser, M.; Hartmann, J. *J. Am. Chem. Soc.* **1976**, *98*, 4674–4676.

(25) Jackman, L. M.; Sternhell, S. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd ed.; Pergamon Press: Oxford, England, 1969; pp 316, 323.

(26) See especially the ^{13}C chemical shifts of the two methyl groups, which are much closer to the value reported[27] for the C-1 methyl group of *cis*-2-octene (δ 13.0) than to that for *trans*-2-octene (δ 19.0).

(27) Stothers, J. B. *Carbon-13 NMR Spectroscopy*; Academic Press: New York, 1972; pp 80–83

The ^{13}C NMR spectrum (CDCl$_3$) of the deuterated sample (8) was nearly identical with that of the protonated sample except that, in the *proton-decoupled* spectra, the singlet methyl resonance at δ 13.69 now appeared as a triplet at δ 13.43 (J = 19.5 Hz) and the singlet methylene resonance at δ 26.06 appeared as a triplet at δ 25.71 (J = 19.5 Hz). Such triplets are expected if one deuterium atom each is on the methyl and the methylene groups. The centers of the two triplets are shifted upfield from the corresponding singlets of the protonated samples by 0.26 and 0.35 ppm, as is expected[28] for isotropic substitution by deuterium directly onto carbon atoms whose NMR absorption is being monitored. Interestingly only two other carbon signals, δ 121.4 and 122.8, of the deeuterated sample are shifted upfield, 0.026 and 0.029 ppm, respectively, relative to the protonated sample; the eight other carbon signals are shifted downfield by 0.040 ± 0.018 ppm in the deuterated sample. Hence, the carbon signals at δ 121.4 and 122.8 are shifted upfield in the deuterated sample 0.066 and 0.069 ± 0.018 ppm from what might have been expected. These small upfield shifts are of the right magnitude expected for deuterium substitution onto a carbon atom adjacent to the carbon atoms being monitored.[28] On this basis the signal at δ 121.4 evidently is that for $>C{=}CHCH_2D$, while that at δ 122.8 is for $CHD(CH{=}CH{-})_2$ since the former is about half the intensity of the latter; the signal at δ 131.5 is essentially of the same intensity as the latter and therefore likely belongs to $CH_2(CH{=}CH{-})_2$. These assignments are in general agreement with the value of δ 123.9 found for the olefinic carbons of 1,4-hexadiene[11] and the observation that aromatic and aliphatic substituents at the 3-position of cyclohexene decrease the shielding of the closer olefinic carbon.[29] Also, the signal at δ 125.7 is of about half the intensity of the two signals at δ 127.2 and 128.2 and evidently belongs to the para carbon stom of a phenyl group, while the more intense signals belong to ortho and meta carbons.

The GC mass spectrum of the preponderant component 8 of the deuterated sample (GC analysis revealed three very minor impurities in the crude sample) gave ions at m/e (relative intensity) 214 (0.6), 213 (8.6) 212 (47.5), 211 (5.4), 197 (16), 196 (19), 183 (12), 182 (28), 181 (14), 180 (8), 170 (12), 169 (6), 168 (14), 167 (11), 166 (14), 165 (7), 156 (100), 155 (65), 154 (31), 153 (18), 152 (8), 142 (7), ... 92 (17), 91 (9). From the relative intensities of the ions at m/e 214–209 from the protonated and deuterated samples, we estimate that the deuterated product contained 92% $C_{16}H_{16}D_2$ and 8% $C_{16}H_{17}D$.

Reaction of Triphenylmethane (1f) with Cs–K–Na Alloy. A. Followed by Protonation. These reactions were run with the same general procedure as for 3,3-diphenyl-1-butene. To finely divided, vigorously stirred eutectic Cs–K–Na alloy (6.55 g, 36.5 mmol of Cs) in 300 mL of anhydrous THF at −75 °C was added dropwise 2.39 g (9.78 mmol) of triphenylmethane dissolved in 20 mL of THF. The addition required 15 min, during which time the reaction mixture became reddish brown. Stirring was continued at −75 °C for 30 min more before addition of 10 mL of mercury in fine droplets over a 10-min period. After 10 min more of stirring, the dark red reaction mixture was forced into a solution of 7 mL of water in 100 mL of THF at −75 °C. The flask residue was similarly decomposed. The combined product mixtures were treated with 200 mL of water saturated with NaCl, extracted three times with diethyl ether, and dried over anhydrous MgSO$_4$. Quantitative GC analysis of the extract for toluene on the FFAP column at 80 °C and for the other components on the SE 30 column at 190 °C and the FFAP column at 220 °C gave (mole percent yields based on triphenylmethane) 23% toluene, 18% biphenyl, 2% unknown, 57% 9, and 2% unreacted triphenylmethane. Rotary evaporation of the ethereal solvents gave 2.36 g of oily residue. Of this 2.00 g was chromatographed on 150 g of silica gel (0.2–0.5 mm, E. Merck AG, Darmstadt, West Germany) on a column 3.4 cm in diameter with elution by hexane to give first 0.40 g of biphenyl followed by 1.16 g of nearly pure 9. Distillation of the latter fraction twice at 170 °C (0.3 mmHg) gave a viscous oil: ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.22 (1 H, m of d, J = 23 Hz), 2.46 (1 H, m of d, J = 23 Hz), 3.13 (2 H, s), 5.73 (2 H, t of d, J = 10.6 and 2.6 Hz), 5.76 (2 H, t of d, J = 10.6 and 1.8 Hz), 7.6–7.0 (10 H, m); ^{13}C NMR (75 MHz, CDCl$_3$, assignment by distortionless enhancement through polarization transfer (DEPT)) δ 25.77 (t, CH$_2$), 45.12 (s, quat C), 47.12 (t, CH$_2$), 123.83 (d, CH), 125.75 (d, CH), 125.91 (d, CH), 126.67 (d, CH), 127.20 (d, CH), 128.24 (d, CH), 130.74 (d, CH), 132.00 (d, CH), 138.21 (s, quat C), 147.87 (s, quat C); MS m/e (relative intensity) 155 (100), 154 (19), 153 (11), 91 (9), 77 (16); MS m/e (chemical ionization) 247 (M + 1, 9) 155 (100), 91 (70). Anal. Calcd for $C_{19}H_{18}$: C, 92.64; H, 7.36. Found: C, 92.49; H, 7.47.

Analysis of the analytical sample by GC on the FFAP column at 220 °C indicated that it contained (area precent) 93.7% of 9, 0.7% of Ph$_3$CH, 2.7% of a compound isomeric with 9, and 3.0% of biphenyl. Many attempts were made to obtain crystals of 9 for X-ray analysis by recrystallization from pentane or methanol; after almost 4 months, crystals were obtained, but these on X-ray diffraction proved to be biphenyl. A repeat GC analysis on the combined crystals and mother liquor indicated that the composition was now 2.4% of 9, 0.6% of Ph$_3$CH, and 97% biphenyl (all area percentages).

A repetition of the prior reaction was made but with decomposition by forcing the organo-alkali-metal solution into 100 mL of THF containing 0.10 g of hydroquinone, 7 mL of water, and 7 mL of methanol at −75 °C. The product solution was then extracted with three 100-mL portions of water saturated with NaCl, and the extracts were dried over anhydrous MgSO$_4$, treated with 0.10 g of hydroquinone, and then stored in the refrigerator (−10 °C). Quantitative GC analysis (on SE 30 and FFAP columns) gave more percent yields of products (based on starting triphenylmethane) of 6.4% of toluene, 2.9% of biphenyl, 0.5% of a dihydrobiphenyl, 1.0% of diphenylmethane, 1.5% of an isomer of 9, 80% of 9, and 0.6% of Ph$_3$CH. A 50-mL portion of the THF solution containing 0.18 g of the product mixture was concentrated on a rotary evaporator to remove THF; 50 mL of benzene was added and the solution extracted three times with aqueous KOH to remove hydroquinone and then concentrated on the rotatory evaporator to 1 mL. To the solution was added 5.8 mg of dibenzoyl peroxide, and the solution was held at reflux temperature. The initial molar ratio of biphenyl to 9 was 3.5/96.5; after 4 h at reflux the ratio was 24/76, and after 24 h the ratio was 38/62. Another 5.0-mg portion of dibenzoyl peroxide was added, and after another 24 h at reflux the ratio was 62/38.

B. Followed by Deuteration. The reaction was run exactly as in the protonation experiments except that after triphenylmethane (2.00 g) was stirred with eutectic Cs–K–Na alloy (5.0 g) in THF at −75 °C for 1 h and with mercury (8 mL) for $^1/_2$ h the reaction mixture was forced into 100 mL of anhydrous THF containing 0.097 g of hydroquinone and 10 mL of D$_2$O (98.9% D) cooled to 0 °C. Quantitative GC analysis (mole percent yields based on starting Ph$_3$CH) gave 18% of toluene, 13% of biphenyl, 0.5% of a dihydrobiphenyl, 2.3% of diphenylmethane, 1.6% of an isomer of 10, 70% of 10, and 1.8% of triphenylmethane. Liquid chromatographic separation as for the protonated reaction mixture gave a nearly pure sample of 10: ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.16 (0.89 H, ~bd s), 2.40 (0.13 H, ~bd s), 3.09 (1.00 H, s), 5.69 (2 H, J = 10 and 2.5 Hz), 5.74 (2 H, d of d, J = 10 and 1.3 Hz), 7.4–7.0 (10 H, m); ^{13}C NMR (75 MHz, multiplicity by off-resonance decoupling) δ 25.34 (d ot t, CHD), 45.00 (s, quat C), 46.67 (d of t, CHD), 123.67 (d, CH), 125.69 (d, CH), 125.83 (d, CH), 126.61 (d, CH), 127.13 (d, CH), 128.15 (d, CH), 130.65 (d, CH), 132.02 (d, CH), 138.05 (s, quat C), 147.74 (s, quat C); MS m/e (relative intensity) 156 (100), 155 (34), 154 (27), 153 (11), 92 (12), 91 (1.0), 78 (13), 77 (16).

Reaction of Tetraphenylmethane (1g) with Cs–K–Na Alloy. A. Followed by Protonation. In a preliminary experiment under the general conditions of the prior reactions of Cs–K–Na alloy, 0.199 g (0.62 mmol) of tetraphenylmethane in 250 mL of THF was stirred with 1 mL of Cs–K–Na eutectic alloy (7.9 mmol of Cs) at −70 °C for 1 h before forcing the reaction mixture into 220 mL of water at room temperature. The product mixture was saturated with sodium chloride, the THF phase separated, and the aqueous solution extracted with pentane. The combined THF and pentane phases were dried over anhydrous MgSO$_4$, concentrated, and subjected to GC analysis on an OV-17 column. The yields of products based on starting tetraphenylmethane were as follows: various dihydrobiphenyls (30%), bi-

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[28] Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; Wiley: New York, 1981; p 257.

[29] See ref 27, p 78.

phenyl (12%), diphenylmethane (28%), an unknown (likely C$_{13}$) compound (4%), triphenylmethane (1%), and tetraphenylmethane (6%, possibly containing some hydrotetraphenylmethanes or isomers thereof).

B. Followed by Deuteration. In a similar manner, 0.401 g (1.25 mmol) of tetraphenylmethane in 85 mL of THF was added over a period of 4 min to 6.30 g of finely divided, eutectic Cs-K-Na alloy (35 mmol of Cs), vigorously stirred in 220 mL of THF at -75 °C. The brownish black solution was stirred for 1 h at -75 °C. Mercury (8 mL) was added in fine droplets over a period of 15 min with stirring continued at -75 °C for 15 min more before forcing the mixture into 100 mL of THF containing 20 mL of D$_2$O (99 atom % D), 10 mL of CH$_3$OD (99 atom % D), and 0.091 g of hydroquinone cooled to -70 °C. The reaction mixture was decomposed with a similar THF solution, and the combined solutions were saturated with NaCl and worked up as in part A except that the THF-pentane extract, after it was dried over anhydrous MgSO$_4$ and after 0.096 g of hydroquinone was added, was stored in a refrigerator (-15 °C) prior to analysis. Analysis by GC on both 15% FFAP and 10% SE-30 columns gave 12% yield of a dihydrobiphenyl, 18% of biphenyl, 30% of diphenylmethane, 19% of various dihydrobiphenyls and dihydrodiphenylmethanes, 0.5% of triphenylmethane, 5% of a dihydrotetraphenylmethane derivative (**15**), 1% of an unknown tetrahydrotetraphenylmethane, and 6% of unreacted tetraphenylmethane (all mole % yields). A GC-MS analysis showed that the hydrogens introduced were primarily deuterium. If isotope effects are assumed to be negligible for the M + 1, M, and M - 1 ion intensities, the product biphenyl was about a 43:57 ratio of C$_{12}$H$_9$D to C$_{12}$H$_{10}$, the diphenylmethane was about a 45:55 ratio of C$_{13}$H$_{10}$D$_2$ to C$_{13}$H$_{11}$D, triphenylmethane was a 65:35 ratio of C$_{19}$H$_{15}$D to C$_{19}$H$_{16}$, and the structure **15** was >84% C$_{25}$H$_{20}$D$_2$. The MS of **15** was as follows: *m/e* (relative intensity) 324 (30), 269 (16), 246 (24), 245 (38), 244 (39), 243 (13), 240 (14), 230 (16), 229 (17), 219 (14), 218 (12), 217 (18), 216 (22), 204 (20), 203 (24), 169 (29), 168 (88), 167 (76), 166 (100), 165 (65), 157 (15), 156 (23), 155 (12), 154 (14), 153 (20), 152 (14). The MS of the dihydrobiphenyl was as follows: *m/e* (relative intensity) 159 (14), 158 (100), 157 (98). Hence, it is extensively C$_{12}$H$_{10}$D$_2$.

In a repetitive experiment of shorter duration, a solution of 0.437 g (1.36 mmol) of tetraphenylmethane in 85 mL of THF was added over a period of 1 min to 4.3 g of finely divided eutectic Cs-K-Na alloy (24.0 mmol of Cs) vigorously stirred in 220 mL of THF at -75 °C. The red-black solution was then stirred for 10 min before being forced over a period of 5 min into a medium of the same composition and temperature as in the previous experiment. The usual workup and GC analysis gave (mol % yields) 9% of a dihydrobiphenyl, 17% of biphenyl, 22% of diphenylmethane, 11% of various dihydrobiphenyls, 1.7% of triphenylmethane, 14% of **15**, and 26% of tetraphenylmethane.

Reaction of 1,1,1-Triphenylethane (1a) with Cs-K-Na Alloy. A solution of 1,1,1-triphenylethane (2.60 g, 10.1 mmol) in 50 mL of THF was added over a period of 4 min to 6.64 g of finely divided eutectic Cs-K-Na alloy (36.7 mmol of Cs) vigorously stirred in 300 mL of THF at -75 °C. After 1 h of stirring, 6 mL of mercury was added in the form of tiny droplets over a period of 15 min. After an additional 15 min of stirring, about 85 mL of the dark red solution was forced into 100 mL of THF containing 20 mL of methanol and 10 mL of water at -75 °C (fraction A). The temperature of the remaining solution was allowed to rise to -45 °C, and stirring was continued at this temperature for 2.7 h before forcing the mixture into aqueous methanolic THF (same composition as previously used) containing 0.11 g of hydroquinone (fraction B). After the usual workup the products were subjected to quantitative GC analysis (on both the SE-30 and FFAP columns). Fraction A contained 0.014 g (0.05 mmol) of Ph$_3$CCH$_3$, 0.53 g (2.0 mmol) of 9-methyl-9-phenyl-2,4a,4b,7-tetrahydrofluorene (**3a**), and no appreciable amount of biphenyl or 1,1-diphenylethane. Fraction B contained 0.89 g (3.5 mmol) of Ph$_3$CCH$_3$, 0.49 g (1.9 mmol) of **3a**, 0.077 g (0.50 mmol) of biphenyl, 0.106 g (0.58 mmol) of 1,1-diphenylethane, and some ethylbenzene (not quantified since much of this volatile material was likely lost during product isolation). These products were confirmed by GC mass spectral analysis.

In a repetitive reaction 1.55 g (6.0 mmol) of 1,1,1-triphenylethane was allowed to react with 3.51 g of eutectic Cs-K-Na alloy (19.5 mmol of Cs) in THF for 1 h at -75 °C and then 1 h at -45 °C before adding 6 mL of finely divided mercury, stirring for 10 min, and protonating (in the presence of hydroquinone) as previously described. Quantitative GC analysis gave 0.023 g (0.09 mmol) of Ph$_3$CCH$_3$, 1.18 g (4.5 mmol) of **3a**, 0.03 g (0.12 mmol) of an unknown, 9.3 mg (0.06 mmol) of biphenyl, and 24 mg (0.13 mmol) of 1,1-diphenylethane (82% of starting material accounted for). The unknown by GC mass spectral analysis had *m/e* (relative intensity) 260 (17, M$^+$), 245 (17, M$^+$ - CH$_3$), 181 (31, M$^+$ - Ph - 2H), 167 (100, M$^+$ - Ph - CH$_3$ - H), 165 (35, M$^+$ - Ph - CH$_3$ - 3H), 155 (99, M$^+$ - PhCHCH$_3$). The ortho-cyclization product (**3a**) by comparison has *m/e* (relative intensity) 260 (27), 245 (24), 181 (23), 167 (100), 165 (33), 155 (26).

In an experiment in which 0.61 g (2.3 mmol) of Ph$_3$CCH$_3$ was allowed to react with 2.0 mL of eutectic Cs-K-Na alloy (15.9 mmol of Cs) in 250 mL of THF at -70 °C for 1 h and then at 0 °C for 2 h before forcing into ice water, the GC yield of 1,1-diphenylethane was 56% (GC MS confirmation of structure) along with unidentified products.

In a final reaction 2.93 g (11.3 mmol) of Ph$_3$CCH$_3$ was allowed to react with 7.05 g of eutectic Cs-K-Na alloy (34.0 mmol of Cs) in 300 mL of THF at -75 °C for 2 h before adding 6 mL of finely divided mercury, stirring 15 min more, and then forcing into 100 mL of THF containing 25 mL of CH$_3$OH and 10 mL of water at -75 °C. The solution was treated with 300 mL of saturated sodium chloride solution. The phases were separated. The aqueous layer was extracted with 100 mL of ether, and the ethereal extract was added to the THF solution. The combined ethereal solutions were extracted with three 100-mL portions of saturated NaCl solution and then dried over anhydrous MgSO$_4$. A GC analysis of the product indicated the presence of 5 area % of Ph$_3$CCH$_3$ and 95 area % of **3a**. After removal of ethereal solvent on a rotary evaporator, the crude product was recrystallized from ethyl alcohol to give 0.92 g of crystals with mp 95-96 °C and a second batch (0.32 g) with mp 91.5-93 °C. The first batch of crystals was allowed to recrystallize slowly from ethanol to give crystals suitable for X-ray analysis. The ^{1}H NMR spectrum of these crystals was identical with that reported earlier.[2]

For the crystal structure of **3a**, a crystal was mounted and data were collected by procedures described in the supplementary material. The crystal belonged to the monoclinic system, and the data collected were consistent only with space group $P2_1/c$ (no. 14).[30] From a total of 2621 reflections collected in a complete quadrant of data, 1700 were accepted as statistically above background. A full-matrix least-squares refinement[31] converved at $R = 0.066$ and $R_w = 0.070$ for a total of 201 variables. Parameters refined included coordinates and anisotropic temperature factors for all non-hydrogen atoms and isotropic temperature factors for hydrogens. Hydrogen coordinates were determined from a difference Fourier electron density map. Lists of final atomic coordinates and bond distances and angles are available in the supplementary material.

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Supplementary Material Available: Crystal structure determination for **3a** including a description of the data collection, an ORTEP structure, and tables of atomic coordinates, bond distances, and angles (6 pages); a table of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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(30) *International Tables for X-ray Crystallography*, 2nd ed.; Henry, N. F. M., Lonsdale, K., Eds.; Kynoch Press: Birmingham, England, 1965; Vol. 1.

(31) Programs utilized were Sheldrick's SHELX-76, Main's MULTAN78, and Jonnson's ORTEPII.