

Carbanions. 22. Tautomerism between 2-*p*-Biphenyl-1,1,2-trimethylpropyl and 1,1,2,2-Tetramethyl-6-phenylspiro[2.5]octa-4,6-dienyl Anions. Alkali Metal Cation Effects¹

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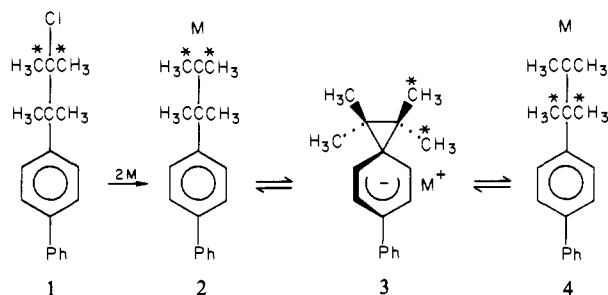
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Abstract: Reactions of Cs-K-Na alloy and lithium metal with 2-*p*-biphenyl-3-chloro-2,3-dimethylbutane, labeled with perdeuterio-*gem*-dimethyl groups in a ratio α/β (8/9) of 2.1/1, were investigated to study [1,2] sigmatropic migration of the *p*-biphenyl group. Reaction with Cs-K-Na in THF at -75°C gave upon carbonation a 2.8/1 ratio of spiro acid to open acid (11/10). While the perdeuterio-*gem*-dimethyl group was randomly distributed *cis* or *trans* to the carboxyl group in the spiro acid, the open acid had α/β perdeuterio-*gem*-dimethyl groups in a ratio of 1/1.6 (10a/10b). These ratios were invariant with time of reaction (26 s to 10 min) or the α/β ratio of perdeuterio-*gem*-dimethyl groups in the starting chloride. Reaction of the product from Cs-K-Na alloy with water or trimethylsilyl chloride gave detectably only open products, but these had an α/β ratio of perdeuterio-*gem*-dimethyl groups essentially like that in the open acid from carbonation. The results are interpreted on the basis of a facile equilibrium between open organo cesium compounds 2 and 4 via the spiro anion 3. The rather large secondary β -deuterium isotope effect of 1.6 is characteristic of the equilibrium between 2 and 4 and is attributable to anionic hyperconjugation. The reaction of the labeled chloride (8 + 9) with lithium in THF at -75°C gave upon carbonation only the open acids (10a + 10b) but in the same ratio as from reaction with Cs-K-Na alloy. The similarity of behavior of the present tertiary chloride with Cs-K-Na alloy and with lithium contrasts with that of the primary chloride, 1-chloro-2-*p*-biphenylethane, and suggests that the carbon-lithium bond in (2-*p*-biphenyl-1,1,2-trimethylpropyl)lithium in THF is stretched because of steric repulsions between the *gem*-dimethyl group α to the anionic center and the peripherally solvated lithium counterion.

In previous work² it was shown that 2-*p*-biphenyl-3-chloro-2,3-dimethylbutane (1) (Scheme I) reacts with Cs-K-Na alloy in THF at -75°C to give, according to the results of carbonation, both the open anion 2 ($M = \text{Cs}$) and the spiro anion 3 in about a 1/2 ratio. It was suggested that 2 and 3 are in mobile equilibrium since they have the same half-lives, 22 min in THF at -75°C . Also the same organometallic mixture upon reaction with dimethyl sulfate or chlorotrimethylsilane gives only the open products, 2-*p*-biphenyl-2,3,3-trimethylbutane (5), *p*-(C_6H_5) $\text{C}_6\text{H}_4\text{C}(\text{CH}_3)_2\text{C}(\text{CH}_3)_3$, or 2-*p*-triphenyl-2,3-dimethyl-3-trimethylsilylbutane (6), *p*-(C_6H_5) $\text{C}_6\text{H}_4\text{C}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{Si}(\text{CH}_3)_3$, and no appreciable spiro derivatives. These results may be understood in terms of a mobile equilibrium between 2 and 3 if carbon dioxide reacts indiscriminately with 2 and 3 but dimethyl sulfate and chlorotrimethylsilane react preferentially with 2. In contrast, lithium reacts with halide 1 to give only the open organolithium compound 2 ($M = \text{Li}$) as indicated by the results of carbonation.

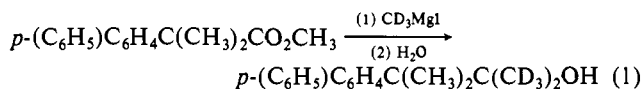
According to these interpretations, if the α -methyl groups of chloride 1 are labeled with deuterium at the carbons bearing asterisks, the initial organometallic compound should be labeled as in 2. Then if a mobile equilibrium exists between 2 and 3, a similar equilibrium must prevail between 3 and 4 such that with time the label redistributes between the α - and β -methyl groups. Alternatively stated, the label indicates whether or not the *p*-biphenyl group has undergone [1,2] sigmatropic rearrangement. The present work with the labeled chloride 1 was undertaken in order to study [1,2] migration of the *p*-biphenyl group, especially in the case of the organolithium compound where rearrangement is not implied by existence of detectable quantities of the spiro anion 3 according to the carbonation technique. Also the label in chloride 1 helps define the reaction path from 1 to 2.

Scheme I

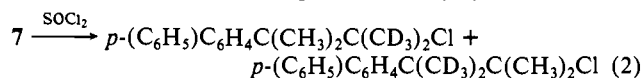


Results and Discussion

3-*p*-Biphenyl-3-methyl-2-(methyl-*d*₃)-2-butanol-1,1,1-*d*₃ (7) was readily synthesized by reaction of methyl 2-*p*-biphenyl-2-methylpropanoate with (methyl-*d*₃)magnesium iodide (eq 1).



Attempts to convert 7 into the corresponding chloride, 2-*p*-biphenyl-3-chloro-2-methyl-3-(methyl-*d*₃)butane-4,4,4-*d*₃ (8), by reaction with thionyl chloride were complicated by the simultaneous formation of 2-*p*-biphenyl-3-chloro-2-(methyl-*d*₃)-3-methylbutane-1,1,1-*d*₃ (9) (eq 2), doubtlessly by incursion of the



ionization mechanism with neighboring group participation³ and ultimate migration of the *p*-biphenyl group. Under most satisfactory conditions found, the ratio of 8 to 9 was 2.1 according to NMR and mass spectral analysis.

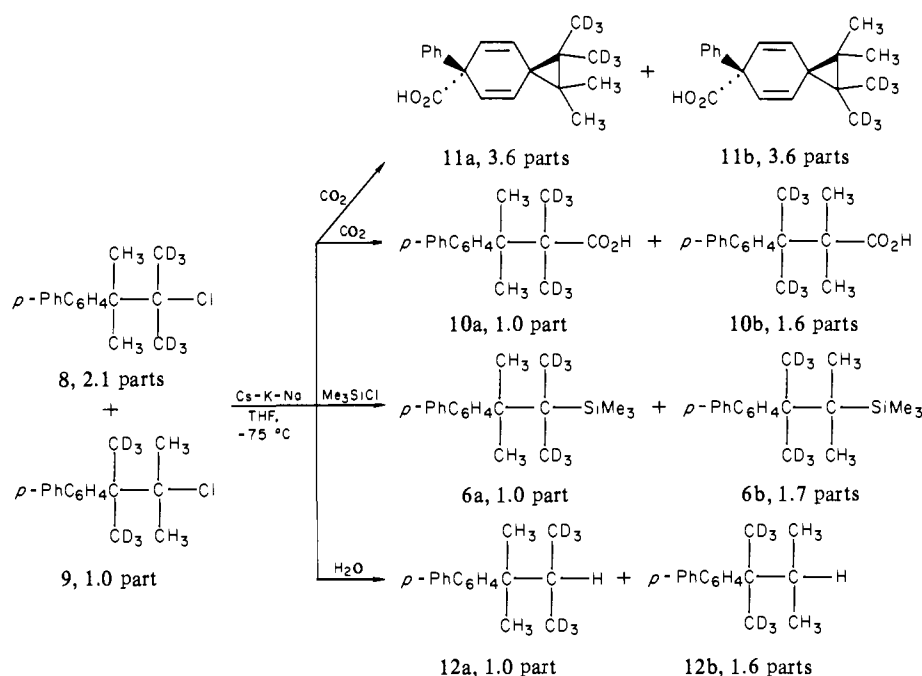
The reactions of the chloride (8 + 9) with Cs-K-Na alloy in THF at -75°C are summarized in Scheme II, which gives the distribution of the deuterium label in the reactant and products

(1) Based upon the Ph.D. Thesis of P.-C. Lu, Georgia Institute of Technology, Sept 1977, which should be consulted for more complete experimental details.

(2) (a) Bertrand, J. A.; Grovenstein, E., Jr.; Lu, P.-C.; Van Derveer, D. *J. Am. Chem. Soc.* 1976, 98, 7835-7836. (b) Grovenstein, E., Jr.; Lu, P.-C. *J. Org. Chem.* 1982, 47, 2928-2939.

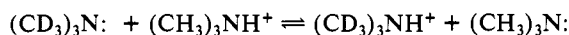
(3) Cram, D. J. *J. Am. Chem. Soc.* 1953, 75, 332-338.

Scheme II



as determined by ^1H NMR and mass spectral analyses. The products of carbonation of the deuterium-labeled compound gave a ratio of spiro acid **11** to open acid **10** of 2.8 ± 0.2 , which is slightly greater than that (2.2 ± 0.3) found² for the protium compound. The ratios of carboxylic acids were the same regardless of whether the carbonation was after 26 s or after 10 min. Moreover, a reaction in which the ratio of starting chlorides **8** to **9** was 1.2 rather than 2.1 gave an identical ratio of acids **10b** to **10a**. Finally, the ratios of the products of silylation (**6b/6a**) and of protonation (**12b/12a**) were essentially the same as the ratios of the corresponding open acids (**10b/10a**), but these differed from the ratios of spiro acids (**11b/11a**).

These ratios of products correspond to isotope effects. The ratio of **11b** to **11a** of 1.00 means that there is no measurable isotopic discrimination in carbonation of the spiro organocesium compound **3** (Scheme I). Carbon dioxide attacks this anion as readily syn to the *gem*-dimethyl group as syn to the *gem*-perdeuteriodimethyl group, doubtlessly because of the great distance from the reaction center to the isotopic label. In contrast, a considerable secondary β -deuterium isotope effect is exhibited by the reactions of the open organocesium compound. We suggest that this isotope effect reflects a 1.6-fold higher equilibrium concentration of the open organocesium compound **4** than of **2**. That this secondary β -deuterium isotope effect is large has good precedent in reactions such as



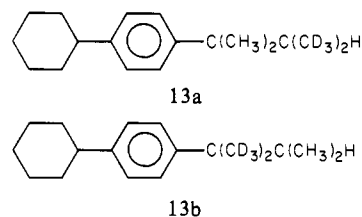
for which ΔG° is -0.33 ± 0.06 kcal/mol in the gaseous phase, as measured by ion cyclotron resonance spectroscopy⁴ (or -0.255 kcal/mol in aqueous solution⁵). If ΔG° for $\mathbf{2} \rightleftharpoons \mathbf{4}$ is taken as two-thirds of the gas-phase result (because there are two-thirds as many CD_3 groups present), then the ratio of **4** to **2** at equilibrium at -75°C is calculated to be 1.7 ± 0.2 , essentially as found.

Carbonation is thought to give products that reflect the equilibrium concentration of organocesium compounds **2**, **3**, and **4**. Protonation is likely similar to carbonation; however, the spiro hydrocarbon from protonation of **3** has not been isolated, possibly because of its instability under usual reaction conditions.^{2b} In contrast, silylation (and methylation) is believed to occur with preferential reaction of the open organocesium compounds **2** and

4 with isomerization of the spiro anion **3** to **2** and **4** prior to reaction. Hence the isotope effect in silylation may reflect the relative stability of the transition states for silylation. That this relative stability is similar to that of the anions **2** and **4** is understandable if the transition state for silylation comes early along the reaction coordinate and thus has a charge distribution similar to that in **2** and **4**. Similar reasoning holds if the isotope effect for silylation reflects the relative rate of formation of **2** and **4** from the spiro anion in a late transition state.

The present work appears to be the first work upon secondary β -deuterium isotope effects in carbanions and lends support to the theory of anionic hyperconjugation.^{4,6} According to this theory the nonbonding electron pair of the anion interacts with CH linkages of adjacent methyl groups. Since this interaction involves partial delocalization of the nonbonding electron pair into antibonding orbitals (π^* of CH_3 groups), the interaction weakens CH linkages with reduction in CH stretching force constants and resultant thermodynamic preference for formation of the anion with deuterium in β -methyl groups (**4**) rather than in α -methyl groups (**2**).

When the deuterium-labeled chloride (2.1 parts of **8** to 1.0 part of **9**) was allowed to react with Cs-K-Na alloy in THF containing *tert*-butyl alcohol, the resulting hydrocarbon contained 1.2 parts of **12a** and 1.0 part of **12b** (see Scheme II). When the reaction was repeated in presence of a larger quantity of methanol, the ratio of **12a** to **12b** was 1.4; in addition **13a** and **13b** were formed in a ratio of 1.5. These results are taken to mean that the reaction



with Cs-K-Na alloy proceeds as shown in Scheme I; i.e., reaction with alloy gives first the unrearranged open organocesium compound **2** and that this is largely protonated prior to rearrangement

(4) (a) DeFrees, D. J.; Taagepera, M.; Levi, B. A.; Pollack, S. K.; Summerhays, K. D.; Taft, R. W.; Wolfsberg, M.; Hehre, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 5532-5536. (b) Wolf, J. F.; Delvin, J. L.; DeFrees, D. J.; Taft, R. W.; Hehre, W. F. *Ibid.* **1976**, *98*, 5097-5101.

(5) Northcote, D.; Robertson, R. E. *J. Phys. Chem.* **1969**, *73*, 1559-1563.

(6) (a) DeFrees, D. J.; Bartmess, J. E.; Kim, J. K.; McIver, R. T.; Hehre, W. F. *J. Am. Chem. Soc.* **1977**, *99*, 6451-6452. (b) Pross, A.; Radom, L. *Ibid.* **1978**, *100*, 6572-6575. (c) Since our work was completed, an NMR study upon β -deuterium isotope effects in benzylic cations and anions has been published. See: Forsyth, D. A.; Lucas, P.; Burk, R. M. *J. Am. Chem. Soc.* **1982**, *104*, 240-245.

to **4**, methanol being a better trap than *tert*-butyl alcohol for the anion **2**. The results also imply that the [1,2] migration of *p*-biphenyl occurred in an intermediate carbanion, not a free radical, since *tert*-butyl alcohol is an effective trap for carbanions but is less reactive than THF with radicals.⁷

Reaction of the deuterium-labeled chloride (2.1 parts of **8** to 1.0 part of **9**) with lithium in THF at -75°C for 1 h followed by carbonation gave the acids **10b** and **10a** in a ratio of 1.6/1.0, respectively, just as in the case of Cs–K–Na alloy (Scheme II). Thus the organolithium compounds **2** and **4** (Scheme I, M = Li) have evidently equilibrated even though no spiro anion **3** is detectable with lithium as counterion. This fast equilibration is a surprising result since 1-chloro-2-*p*-biphenylethane-1,1-*d*₂ reacts with lithium in THF at -70°C to give detectably only the unrearranged (2-*p*-biphenylethyl)lithium-1,1-*d*₂; moreover, this lithium reagent does not undergo appreciable rearrangement even at 0°C .⁸ The reaction of the chloride (2.1 parts of **8** to 1.0 part of **9**) with lithium was repeated at -75°C in THF containing *tert*-butyl alcohol. The resulting hydrocarbon had a ratio **12b/12a** of 1.0/1.5 (cf. Scheme II); therefore, *tert*-butyl alcohol was somewhat more effective in the reaction with lithium than with Cs–K–Na alloy in trapping an intermediate organoalkali compound (or carbanion) prior to rearrangement (Scheme I). We conclude that (2-*p*-biphenyl-1,1,2-trimethylpropyl)lithium (**2**, M = Li), unlike (2-*p*-biphenylethyl)lithium, undergoes facile [1,2] migration of the *p*-biphenyl group, doubtlessly via the spiro anion **3**.

The lithium compound **2** evidently rearranges nearly as readily as the corresponding cesium compound. Also the charge distribution, as far as can be judged by the magnitude of the secondary β -deuterium isotope effect, is similar to that in the cesium compound. Nevertheless the nature of the counterion is still important; only with cesium is there detectable spiro anion **3**, and the organolithium compound (**2**, M = Li) has a half-life about 8 times longer^{2b} than that of the organocesium compound (**2**, M = Cs) in THF at -75°C . Evidently the *gem*-dimethyl group adjacent to the carbanionic center of **2**, which is responsible for **2** being a tertiary rather than a primary carbanion, is in good part responsible for the high reactivity of the organolithium compound **2** in comparison with (2-*p*-biphenylethyl)lithium. Likely the second *gem*-dimethyl group plays a supportive role. We suggest that the methyl groups of **2** by their steric bulk tend to decrease cation–anion interactions such that the lithium compound is almost as reactive as the corresponding cesium compound, likely because lithium ion is almost as far from the anionic center as cesium. The solvent tetrahydrofuran plays an essential role here. It is reasonable to assume that it is the peripheral solvent^{9a} about lithium, along with the ligands on lithium from association^{9b} with other molecules of organolithium reagent or lithium salts, which creates the steric bulk of what is otherwise a small lithium ion. As the carbon–lithium bond is lengthened in organolithium compounds by steric interaction with the carbanion, likely solvation of lithium is increased. In this manner organolithium compounds can experience cation–anion interactions similar to those in organocesium compounds and have similar chemical reactivity.¹⁰

Experimental Section¹¹

Proton NMR spectra were recorded on a Varian A-60 or T-60A NMR spectrometer; ¹³C NMR spectra were recorded at 25 MHz and

¹H spectra at 100 MHz with a JEOL Fourier transform spectrometer, Model PFT-100, with multiplicity determined in off resonance decoupled spectra. Both spectra are reported in parts per million (δ) downfield from tetramethylsilane as an internal standard. Mass spectra were run upon either a Varian M-66 or an Hitachi (Perkin-Elmer) RMU-7L mass spectrometer.

Gas chromatographic (GC) analyses were ordinarily made on a Perkin-Elmer Model 881 chromatograph equipped with a hydrogen flame ionization detector and utilized a 6 ft \times 1/8 in. column packed with 3% silicone gum rubber (SE-30) on 100–200 mesh Chromosorb G (acid washed and treated with dimethyldichlorosilane). Quantitative GC analyses were made with an internal standard and calibrations based upon authentic samples² and are expressed in mole percent yield based upon the moles of starting organic reactant (alkyl chloride, unless otherwise specified).

3-*p*-Biphenyl-3-methyl-2-(methyl-*d*₃)-2-butanone-1,1,1-*d*₃ (**7**). This alcohol was synthesized (75% yield) by reaction of methyl 2-*p*-biphenyl-2-methylpropanoate with the Grignard reagent made from iodomethane-*d*₃ (99+ atom % D, Aldrich Chemical Co.) by the procedure given for the unlabeled alcohol.^{2b} A little unreacted methyl ester was removed from the crude product by saponification with 4% alcoholic KOH for 12 h. After sublimation in vacuo and recrystallization from CCl₄, the product had mp 71–72 $^{\circ}\text{C}$: ¹H NMR (CDCl₃) δ 7.3–7.7 (9.0 H, m), 1.43 (7.0 H, s, ArC(CH₃)₂ and OH), 1.16 (0.0 H, C(CH₃)₂OH); MS, *m/e* (rel intensity) 260 (0, M⁺), 242 (11), 241 (17), 240 (2), 227 (4), 226 (13), 225 (3), 224 (5), 196 (100), 195 (39).

2-*p*-Biphenyl-3-chloro-2-methyl-3-(methyl-*d*₃)-butane-4,4,4-*d*₃ (**8**) and 2-*p*-Biphenyl-3-chloro-2-(methyl-*d*₃)-3-methylbutane-1,1,1-*d*₃ (**9**). Twenty experiments were performed in an attempt to optimize the yield of **8** relative to **9**. While reaction of **7** with SOCl₂ in tetrahydrofuran at 0°C gave a 4.0/1 ratio of **8** to **9**, the conversion of **7** into chloride was only 20%. The following procedure was the most satisfactory found. A solution of **7** (7.39 g, 0.0284 mol) in 175 mL of CCl₄ was added dropwise to 2.28 g (0.0288 mol) of pyridine in 500 mL of purified¹² thionyl chloride at 0°C . The solution after standing at room temperature for 5 days was poured slowly into ice water and the mixture stirred overnight. The reaction mixture was extracted with ether. The ethereal extract, after drying over anhydrous MgSO₄, yielded 6.8 g of crude chloride. The chloride after sublimation at 0.1 mm and bath at 90–120 $^{\circ}\text{C}$ and recrystallization from hexane amounted to 3.7 g (47% yield) of white crystals: mp 109–110 $^{\circ}\text{C}$; ¹H NMR (CDCl₃) δ 7.3–7.7 (9.0 H, m), 1.58 (4.05 H, s), 1.56 (1.95 H, s); ¹³C NMR (in aliphatic region) δ 77.2 (s), 45.8 (s), 29.3 (q, peak height 8.8), 25.1 (q, peak height 19.2); MS, *m/e* (rel intensity) 195 (100, C₁₅H₁₅⁺), 201 (48, C₁₅H₉D₆⁺). The ion at *m/e* 195 is derived by the α -cleavage reaction¹³ (benzylic cleavage) of the molecular ion of **8** while that at *m/e* 201 similarly comes from **9**; thus the ratio of **8/9** by MS is 100/48 or 2.08. The ¹H NMR singlet at δ 1.58 evidently belongs to the CH₃ group of **8** while the singlet at δ 1.56 belongs to the CH₃ group at **9**; the corresponding relative numbers of hydrogens give the ratio of **8/9** of 2.08. The ¹³C NMR quartet at δ 25.1 reasonably¹⁴ belongs to the CH₃ carbons of **8** while the quartet at δ 29.3 belongs similarly to **9**; the relative peak heights (in the proton-decoupled spectra) give a ratio of **8/9** of 2.18. The three analyses give an average ratio of **8/9** of 2.11 \pm 0.04.

In another preparation of the chloride, 1.82 g (6.99 mmol) of **7** dissolved in 25 mL of CS₂ was added dropwise to 50 mL of CS₂ containing 5.0 mL (70 mmol) of thionyl chloride at reflux. The reaction mixture was held at reflux for 8 h before removing the solvent and washing an ethereal solution of the residue with water. Since ¹H NMR analysis indicated that only one-third of the alcohol had been converted to chloride, the crude product (after removal of ether) was dissolved in 15 mL of CHCl₃; 5.0 mL of thionyl chloride was added and the solution heated at reflux for 2 h before decomposition with ice water. The usual workup and recrystallization from hexane gave 1.06 g (55%) of chloride whose ¹H NMR and mass spectral analysis indicated a ratio of **8/9** of 1.22 \pm 0.02.

2-(4-Cyclohexylphenyl)-2,3-dimethylbutane (**13**). This compound was prepared according to a general method¹⁵ of preparation of a 1-alkyl-4-cyclohexylbenzene from a 4-alkylbiphenyl by dropwise addition of a solution of 2-*p*-biphenyl-2,3-dimethylbutane **12** (0.663 g, 2.78 mmol) in 65 mL of THF containing 4.96 g (66.9 mmol) of *tert*-butyl alcohol

(7) (a) Pryor, W. A.; Henderson, R. W. *J. Am. Chem. Soc.* **1970**, *92*, 7234–7236. (b) Pryor, W. A.; Stanley, J. P. *Ibid.* **1971**, *93*, 1412–1418. (c) Pryor, W. A. *Chem. Eng. News* **1971**, *49*, 42 (June 7).

(8) Grovenstein, E., Jr.; Cheng, Y.-M. *J. Am. Chem. Soc.* **1972**, *94*, 4971–4977.

(9) Cf.: Schlosser, M. "Struktur und Reaktivität polarer Organometalle"; Springer-Verlag: Berlin, 1973; (a) pp 16–19; (b) pp 8–16.

(10) Somewhat similar conclusions concerning lengthening and weakening of lithium–carbon bonds upon alkylation of carbanionic centers have been drawn from ¹³C NMR studies of derivatives of allyllithium. See: Schlosser, M.; Stähle, M. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 487–489.

(11) Melting points are uncorrected. The compound numbers **6**, **10**, **11**, and **12** refer to the same products, without designation of the numbers of location of deuterium atoms, whose isotopic structures are further designated as **a** or **b** in Scheme II.

(12) Cottle, D. L. *J. Am. Chem. Soc.* **1946**, *68*, 1380–1381.

(13) McLafferty, F. W. "Interpretation of Mass Spectra", 2nd ed.; W. A. Benjamin: Reading, MA, 1973; pp 46–49.

(14) As deduced from carbon-13 shieldings in 1-chloroalkanes and alkylbenzenes. Cf. Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972; pp 98–133.

(15) (a) Grovenstein, E., Jr.; Rhee, J.-U. *J. Am. Chem. Soc.* **1975**, *97*, 769–779. (b) Grovenstein, E., Jr.; Akabori, S. *Ibid.* **1975**, *97*, 4620–4626.

to a suspension of 2.22 g (56.7 mol) of molten, finely divided potassium vigorously stirred in 100 mL of THF at reflux. The solution was heated at reflux with continued stirring for 10 h until all of the potassium had dissolved. The usual workup gave 0.68 of crude product, which was distilled at 0.07 mm at a bath temperature of 100 °C to give a colorless oil: ¹H NMR δ (CDCl₃) 7.0–7.4 (4 H, m), 1.3–2.2 (12 H, m), 1.24 (6 H, s), 0.75 (6 H, d, *J* = 6.4 Hz); UV (95% EtOH) λ_{max} (ε) 251 (307), 256 (312), 262 (293), 272 (213); MS, *m/e* (rel intensity) 244 (2, M⁺), 242 (3), 220 (11), 207 (10), 205 (54), 201 (100, M⁺ - C₂H₅). Anal. Calcd for C₁₈H₂₈: C, 88.45; H, 11.55. Found: C, 88.41; H, 11.58.

Reactions of 2-*p*-Biphenyl-3-chloro-2,3-dimethylbutane-*d*₆ (8 and 9) with Alkali Metals. The general procedure for reactions with alkali metals is that which has been given previously.^{2,8} Unless otherwise specified, the 2-*p*-biphenyl-3-chloro-2,3-dimethylbutane-*d*₆ has a ratio of 8/9 of 2.11 ± 0.04.

A. With Cs–K–Na Alloy Followed by Carbonation. To 11.1 g of finely dispersed eutectic Cs–K–Na alloy¹⁶ (0.0596 mol of Cs) in 250 mL of THF at –75 °C was added with vigorous stirring 1.78 g (6.39 mmol) of chloride (8 + 9) in 20 mL of THF over a period of 13 s. The initially blue solution changed to yellow and then red immediately. After 15 s of additional stirring, about half of the now green solution was forced onto excess solid carbon dioxide (“carbonated”) over a period of 9 s. The remaining solution was held at –75 °C (dry ice–acetone bath) for 570 s and likewise carbonated. The usual workup gave, in the first fraction, 0.49 g of acid and 0.23 g of neutral material and, in the second fraction, 0.86 g of acid and 0.32 g of neutral material. Each of the acidic products was chromatographed on a column (3.6 cm in diameter) packed with 230 g of silica gel (0.05–0.20 mm, E. Merck A.G., Darmstadt) with elution by solvent ranging from 30 parts (by volume) of ether and 70 parts of hexane to pure ethyl ether. From the first carbonated fraction the purified 3-*p*-biphenyl-2,2,3-trimethylbutanoic acid (10) had the following spectral properties: ¹H NMR (acetone-*d*₆) δ 7.3–7.7 (9.0 H, m), 1.53 (2.3 H, s), 1.14 (3.7 H, s); MS, *m/e* (rel intensity) 2.88 (1, M⁺), 201 (100, C₁₅H₉D₆⁺), 195 (64, C₁₅H₁₁⁺). The purified 1,1,2,2-tetramethyl-6-phenylspiro[2.5]octa-4,7-diene-6-carboxylic acid (11) had ¹H NMR (CDCl₃) δ 7.34 (5 H, br s), 6.01 (4 H, AB quartet, Δν = 20 Hz, *J* = 11 Hz), 1.19 (3.0 H, s), 1.14 (3.0 H, s). The second carbonated fraction gave 10 and 11 with (±0.1 H) NMR spectra identical with those found for the first fraction. Also the neutral materials from the two carbonations, after distillation in vacuo, contained 2-*p*-biphenyl-2,3-dimethylbutane (12) of identical ¹H NMR (CDCl₃): δ 7.2–7.7 (9 H, m), 1.92 (1 H, ca. septet, *J* = 7 Hz), 1.25 (2.75 H, s), 0.78 (3.25 H, d, *J* = 7 Hz); MS, *m/e* (rel intensity) 201 (100), 195 (82). From quantitative GC analyses (of methyl esters and hydrocarbons) for the first fraction the yields of volatile products were 7.0% 10, 18% 11, and 22% 12, and for the second fraction 4.9% 10, 14% 11, and 21% 12. These data give half-lives of 3 and 2 of 26 and 19 min, respectively, or an average value of 22 ± 4 min for the anions at –75 °C. In a repetitive run with 1.28 g (4.60 mmol) of chloride (8 + 9) with 5.31 g of eutectic Cs–K–Na alloy (0.0287 mol of Cs) gave after carbonation of an aliquot in 25 s 5.9% 10, 15.3% 11, and 22% 12; the remaining solution was warmed to –50 °C in 4 min and held at –50 °C for 6 min to give, upon carbonation, 4.1% 10, 10.4% 11, and 22% 12. These data give half-lives of 3 and 2 of 19.3 and 20.5 min, respectively (average of 20 ± 1 min), at temperatures of –75 to –50 °C.

In a final run, to 5.88 g of finely dispersed eutectic Cs–K–Na alloy (0.0314 mol of Cs) in 250 mL of THF at –75 °C was added 0.917 g (3.29 mmol) of chloride (1.22 ± 0.02 ratio of 8/9) in 20 mL of THF over a period of 8 s. The solution was stirred for another 41 s before it turned green and was forced onto solid carbon dioxide during a period of 30 s. The usual workup gave 0.63 g of acid and 0.31 g of neutral material which by quantitative GC analysis contained 9.0% 10, 27.5% 11, and 32% 12. The products were separated by preparative GC and analyzed by ¹H NMR (CDCl₃) for CH₃ groups: 10, δ 1.53 (2.3 H, s) and 1.14 (3.7 H, s); 12, δ 1.25 (2.6 H, s) and 0.78 (3.4 H, d).

B. With Cs–K–Na Alloy in the Presence of *tert*-Butyl Alcohol. To 6.52 g of finely dispersed eutectic Cs–K–Na alloy (0.0353 mol of Cs) in 250 mL of THF at –75 °C was added with vigorous stirring 0.379 g (1.36 mmol) of chloride (8 + 9) and 0.370 g (4.99 mmol) of *tert*-butyl alcohol in 15 mL of THF over a period of 12 s. After stirring for another 18 s, the solution was forced onto excess solid carbon dioxide. Quantitative GC analysis indicated that the product contained 18% yield of 12 and 70% of unreacted chloride. The crude product was separated by liquid

chromatography on a column (2.6 cm in diameter) packed with 100 g of silica gel with elution by hexane to give 34 mg of pure 12 of ¹H NMR (CDCl₃) δ 1.25 (3.3 H, s) and 0.78 (2.7 H, d) for the CH₃ groups.

C. With Cs–K–Na Alloy in the Presence of Methanol. The previous reaction was repeated by reacting 6.44 g of eutectic Cs–K–Na alloy (0.0348 mol of Cs) with 0.630 g (2.26 mmol) of chloride (8 + 9) but in the presence of 1.00 mL (0.0247 mol) of methanol in 250 mL of THF at –75 °C for 35 s. Quantitative GC analysis gave 14% of unreacted chloride, 43% of 2-(4-cyclohexylphenyl)-2,3-dimethylbutane-*d*₆ (13) (identified by comparisons of GC retention time, NMR and mass spectra with authentic nondeuterated compound), and 12% of 12. The crude product was separated by medium-pressure chromatography through a column (100 cm × 2.5 cm) filled with silica gel (0.2–0.5 mm, E. Merck A.G., Darmstadt) with hexane as eluent. The first pure component collected (50 mg) was 13 which had ¹H NMR δ 1.24 (3.56 H, s) and 0.75 (2.42 H, d) for the CH₃ groups; MS, *m/e* (rel intensity) 207 (33, C₁₅H₁₅D₆⁺) and 201 (49.5, C₁₅H₂₁⁺). The second component 12 (36 mg) had ¹H NMR δ 1.25 (3.5 H, s) and 0.78 (2.5 H, d) for the CH₃ groups.

D. With Cs–K–Na Alloy Followed by Addition of Water. The green solution from reaction of 7.52 g of eutectic Cs–K–Na alloy (0.0411 mol of Cs) with 0.640 g (2.29 mmol) of chloride (8 + 9) in THF for 36 s at –75 °C, as in part A, was forced onto a slurry of ice and water over a period of 40 s. The usual workup gave 0.61 g of crude product which by quantitative GC analysis consisted of 41% of 12 and 7% of 13 and likely other products of reduction. Liquid chromatography as in part C gave 0.17 g of 12 of ¹H NMR (CDCl₃) δ 1.25 (2.3 H, s) and 0.78 (3.7 H, d) for the CH₃ groups.

E. With Cs–K–Na Alloy Followed by Addition of Chlorotrimethylsilane. To 5.80 g of finely dispersed Cs–K–Na alloy (0.0316 mol of Cs) in 250 mL of THF at –75 °C was added with vigorous stirring 0.762 g (2.73 mmol) of chloride (8 + 9) in 16 mL of THF over a period of 15 s with stirring for 17 s more until the solution turned green. A solution of 18 mL (0.14 mol) of chlorotrimethylsilane diluted with 18 mL of THF was then added over a period of 22 s. The black reaction mixture after carbonation and the usual workup yielded 1.16 g of crude neutral product. Quantitative GC analysis at 206 °C gave volatile products listed as percent yield (rel retention time, identity): 23 (1.0, 12), 19 (3.5, 6), and several percentage each of three unknowns at rel retention time of 2.5, 2.9, and 3.1. The chief products were separated by preparative GC and analyzed by ¹H NMR (CDCl₃) for CH₃ groups: 12, δ 1.25 (2.25 H, s) and 0.78 (3.75 H, d); 6, δ 1.47 (2.20 H, s) and 0.92 (3.80 H, s).

F. With Lithium Followed by Carbonation. To 0.812 g (0.117 mol) of finely cut lithium wire in 200 mL of THF at –15 °C was added 0.6 mL of iodomethane and 10 drops of a solution of 0.607 g (2.18 mmol) of chloride (8 + 9) in 20 mL of THF. After rapid stirring for 40 min, a pink color developed and the solution was cooled to –75 °C. The rest of the chloride solution was added dropwise and vigorous stirring was continued for 60 min longer until the solution turned dark brown. The solution after carbonation and the usual workup yielded 0.20 g of crude acid and 0.46 g of neutral material. These by quantitative GC analysis contained 20% 10, 43% 12, and 8% unreacted chloride. Analysis of the products by ¹H NMR (CDCl₃) for CH₃ groups: 12, δ 1.25 (2.55 H, s) and 0.78 (3.45 H, d); 10 (mp 207.0–208.5 °C after recrystallization from hexane) δ 1.53 (2.3 H, s) and 1.15 (3.7 H, s).

G. With Lithium in the Presence of *tert*-Butyl Alcohol. Lithium (1.78 g, 0.256 mol) in 250 mL of THF was activated with 0.2 mL of CH₃I at –15 °C, and then 0.766 g (0.0275 mol) of chloride (8 + 9) in 20 mL of THF containing 2.01 g (27.1 mmol) of *tert*-butyl alcohol was added dropwise to the reaction mixture with vigorous stirring at –75 °C. After stirring for another 2 h, the solution was forced onto solid carbon dioxide. The usual workup gave 0.82 g of crude neutral product, which by quantitative GC analysis contained 41% yield of 12 and 38% of unreacted chloride. Analysis of the product by ¹H NMR (CDCl₃) for the CH₃ groups of 12 gave δ 1.25 (3.6 H, s) and 0.78 (2.4 H, d).

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Registry No. 2-Cs, 83364-34-5; 2-Li, 83364-33-4; 3-Cs, 83378-71-6; 4-Cs, 83364-36-7; 4-Li, 83364-35-6; 6a, 83364-25-4; 6b, 83364-26-5; 7, 83364-31-2; 8, 83364-19-6; 9, 83364-20-9; 10a, 83364-23-2; 10b, 83364-24-3; 11a, 83364-21-0; 11b, 83364-22-1; 12, 81770-30-1; 12a, 83364-27-6; 12b, 83364-28-7; 13, 83364-32-3; 13a, 83364-29-8; 13b, 83364-30-1; D, 7782-39-0; Li, 7439-93-2; CO₂, 124-38-9; H₂O, 7732-18-5; Cs–K–Na alloy, 37219-16-2; Me₂SiCl₂, 75-77-4; methanol, 67-56-1; *tert*-butyl alcohol, 75-65-0; methyl 2-(*p*-biphenyl)-2-methylpropanoate, 81770-34-5; iodomethane-*d*₃, 865-50-9.

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