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Carbanions. XI. Reactions of 4-Chloro-1,1,1-triphenylbutane, 5-Chloro-1,1,1-triphenylpentane, and 1,1,1-Triphenylethane with Alkali Metals. 1,4 and 1,5 Migration of Phenyl[1,2]

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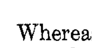
Whereas 1,2 migrations of phenyl are known in carbanions, corresponding 1,4 and 1,5 migrations have not been reported. In the present work such rearrangements were looked for in the reactions of 4-chloro- and 5-chloro-1,1,1-triphenylalkanes with alkali metals. Reaction of 4-chloro-1,1,1-triphenylbutane with lithium in tetrahydrofuran (THF) at −50 to −60° gives 4,4,4-triphenylbutyllithium; when the latter is warmed to 25° 1,1,1-triphenylbutane, but no detectable products of rearrangement, is obtained. With potassium metal in THF at reflux temperature, this chloride gives chiefly 1,1-diphenyl-1,2,3,4-tetrahydronaphthalene; with Cs–K alloy at −49°, the initial product is 1,1,1-triphenylbutane along with some 9% of 1,1,4-triphenylbutyl anion (product of 1,4-phenyl migration). Reaction of 5-chloro-1,1,1-triphenylpentane with potassium or with Cs–K and Cs–K–Na alloys in THF gives primarily 1,1,1-triphenylpentane as initial product along with (for cesium alloys) some 6% of a product of 1,5 migration of phenyl. 2-Chloro-1,1,1-triphenylethane with Cs–K–Na alloy in THF at −65° gives chiefly 1,1,2-triphenylethyl anion (product of 1,2-phenyl migration). Reaction of 1,1,1-triphenylethane with Cs–K–Na alloy in THF at −70° gives a novel red dianion which upon protonation gives 9-methyl-9-phenyl-2,4a,4b,7-tetrahydrofluorene in high yield as a single stereoisomer. Similar reactions occur with 1,1,1-triphenylbutane and 1,1,1-triphenylpentane. These reactions and some of the interesting variations with choice of alkali metal are discussed in terms of likely mechanisms. The synthetic utility of cesium alloys is emphasized.

Previous work has shown that 2,2,2-triphenylethyllithium[4] in tetrahydrofuran solution undergoes rearrangement to 1,1,2-triphenylethyllithium by an intramolecular process,[5a] apparently *via* a cyclic transition state or reaction intermediate[5b] such as **1**. In view of the observed ready 1,2 migration of phenyl in this and other carbanions,[6] it would be expected that corresponding 1,4 and 1,5 migrations of phenyl might also occur, thus *via* **2** and **3**, respectively. The present work was undertaken to test these possibilities.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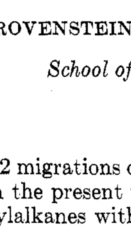
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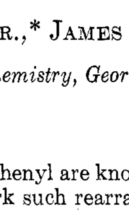
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Results and Discussion

Reactions of 4-Chloro-1,1,1-triphenylbutane with Alkali Metals.—Lithium metal reacts with 4-chloro-1,1,1-triphenylbutane in tetrahydrofuran at −50 to −60° to give 4,4,4-triphenylbutyllithium, as deduced from carbonation which gave 5,5,5-triphenylpentanoic acid. Attempts to effect thermal rearrangement of this organolithium compound to 1,1,4-triphenylbutyllithium in tetrahydrofuran solution at 0° or at 25° were unsuccessful, although a temperature of 0° had proven adequate for rearrangement of 2,2,2-triphenylethyllithium.[4] The reaction at 25° gave upon carbonation a product which contained predominantly neutral products and only 4% by weight of acidic material in which 46% of 5,5,5-triphenylpentanoic acid, but no 2,2,5-triphenylpentanoic acid, was found. The volatile neutral material contained predominantly 1,1,1-triphenylbutane and a little starting chloride. Thus, 4,4,4-triphenylbutyllithium in tetrahydrofuran extracts a proton from the solvent to give 1,1,1-triphenylbutane much faster than it rearranges to 1,1,4-triphenylbutyllithium.

Since previous work[4] had indicated that 2,2,2-triphenylethylpotassium undergoes 1,2 migration of phenyl much more readily than the corresponding lithium compound, reaction of 4-chloro-1,1,1-triphenylbutane with molten potassium in refluxing tetrahydro-

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[1] Abstracted in part from the M.S. Thesis of Y.-M. Cheng, Georgia Institute of Technology, 1967.

[2] Presented in part at Metrochem 69, Regional Meeting of the American Chemical Society, New York, N. Y., May 2, 1969.

[3] National Science Foundation Summer Faculty Research Participant.

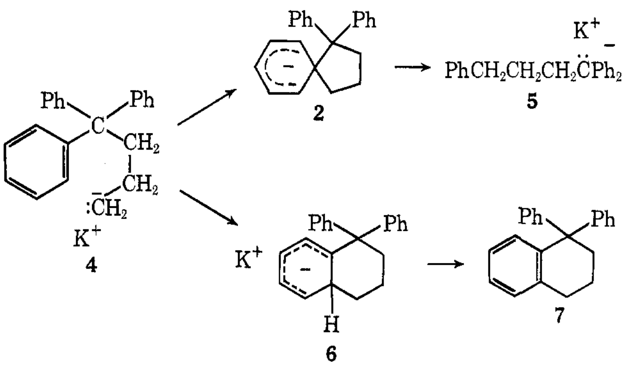
[4] E. Grovenstein, Jr., and L. P. Williams, Jr., *J. Amer. Chem. Soc.*, **83**, 412 (1961).

[5] (a) E. Grovenstein, Jr., and G. Wentworth, *ibid.*, **89**, 1852 (1967); (b) *ibid.*, **89**, 2348 (1967).

[6] See also H. E. Zimmerman and A. Zweig, *ibid.*, **83**, 1196 (1961).

furan was studied. The reaction was terminated by carbonation after 20 min and gave some 90% yield of neutral products and 10% of carboxylic acids. Analysis of the neutral product by gas–liquid partition chromatography (glpc) indicated that the volatile portion contained 84% of 1,1-diphenyl-1,2,3,4-tetrahydronaphthalene and 14% of 1,1,1-triphenylbutane. The structure of 1,1-diphenyl-1,2,3,4-tetrahydronaphthalene was confirmed on the purified product by melting point and spectral comparisons with an authentic sample.[7] The acidic fraction according to glpc analysis (of the methyl esters) contained small quantities of diphenylacetic acid, 2,2-diphenylpentanoic acid, triphenylacetic acid, and 2,2,5-triphenylpentanoic acid, and many unidentified acids. The present work indicates that 4,4,4-triphenylbutylpotassium (**4**) in refluxing tetrahydrofuran cyclizes to the spiro anion **2**, which ultimately yields 1,1,4-triphenylbutyl anion **5** in a yield of less than 1%; the predominant cyclization of **4** gives hydronaphthalene anion **6**, which loses hydride ion to give 1,1-diphenyl-1,2,3,4-tetrahydronaphthalene (**7**) (Scheme I). The reaction of 4-chloro-1,1,1-triphenylbutane with potassium to yield the tetrahydronaphthalene **7** is somewhat analogous to the reaction[8] of 3-methyl-3-phenyl-1-chlorobutane with potassium in refluxing cyclohexane to give a low yield of 1,1-dimethylindan (along with much 2,5-dimethyl-2,5-diphenylhexane).

Scheme I



Since the extent of cyclization of carbanion **4** to **2** *vs.* **6** is likely to depend upon the temperature and the alkali metal, other conditions of reaction were studied. Reaction of 4-chloro-1,1,1-triphenylbutane with liquid sodium–potassium alloy in tetrahydrofuran near 0° gave some 70% yield of carboxylic acids; the volatile portion of these acids according to analysis by glpc contained some 22% of 2,2-diphenylpentanoic acid, 3.7% of triphenylacetic acid, 5.5% of 2,2,5-triphenylpentanoic acid, and three major unidentified acids. The neutral fraction contained **7**,[9] unreacted chloride, and cleavage products.

Since the reaction with sodium–potassium alloy at the lower temperature afforded increased yields of acids relative to neutral materials over that obtained with potassium metal, efforts were next extended to study the reaction of 4-chloro-1,1,1-triphenylbutane with alkali metals at still lower temperatures. In view of the fact that reactions with finely divided potassium in THF at −78° had previously proven unsuccessful[4] because of agglomeration of the potassium metal, reactions with cesium and cesium alloys seemed to offer promise. Cesium has a melting point of 28.5°; its minimum-melting solid solution[10] with potassium (49 atom % K, 51 atom % Cs) has mp −45°; its ternary eutectic[11] with sodium and potassium (11.8 atom % Na, 47.4 atom % K, 40.8 atom % Cs) has mp −79°. In a preliminary experiment 4-chloro-1,1,1-triphenylbutane was allowed to react with the theoretical quantity of cesium metal at 33 to 40° in THF for 15 min before carbonation. There was obtained some 23% yield of acids along with neutral products; the volatile acids contained 2,2,5-triphenylpentanoic acid (6%), cleavage products (43%), and unidentified acids. The volatile neutral products contained 45% of 1,1,1-triphenylbutane, 7.8% of **7**,[9] and 35% of a novel product which was ultimately shown (see later discussion) to be 9-phenyl-9-*n*-propylfluorene (**9a**). The high yield of 1,1,1-triphenylbutane as opposed to tetrahydronaphthalene **7** is of interest in comparison to the reaction with potassium.

Reaction of 4-chloro-1,1,1-triphenylbutane with excess cesium–potassium alloy at −40° gave upon carbonation some 90% yield of acids. Since the acids proved to be a complex mixture, the reaction was repeated with decomposition by methanol rather than carbon dioxide. The volatile neutral products consisted of 32% of 1,1,1-triphenylbutane, 30% of **9a**, 20% of 9-phenyl-9-*n*-propyl-2,4a,4b,7-tetrahydrofluorene (**8a**), and 8% of 1,1,4-triphenylbutane. A duplicate run in which the solution was briefly warmed to −30° before protonation gave about the same yield of 1,1,4-triphenylbutane (11%), but a higher yield (55%) of **9a**. Reaction of 4-chloro-1,1,1-triphenylbutane at −45° with the theoretical amount of Cs–K alloy for conversion of all the halide to organoalkali compound gave upon carbonation a 36:64 ratio of acids to neutral material. The volatile neutral product consisted of 93% of 1,1,1-triphenylbutane and 4% of the fluorene **9a**. This run in conjunction with the other runs with cesium suggests that 1,1,1-triphenylbutane is a major early product of the reaction of 4-chloro-1,1,1-triphenylbutane and that reaction of this hydrocarbon with excess Cs–K alloy leads to the hydrofluorene and fluorene derivatives.

The identification of 9-phenyl-9-*n*-propylfluorene and of 1,1,4-triphenylbutane from these reactions was established by isolation of the products from methanolysis and comparison with authentic samples. The authentic sample of the fluorene was prepared by alkylation[12] of the potassium salt of 9-phenylfluorene[13] with *n*-propyl bromide; the sample of 1,1,4-triphenyl-

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[7] E. A. Braude, L. M. Jackman, R. P. Linstead, and G. Lowe, *J. Chem. Soc.*, 3128 (1960).

[8] H. Pines and L. Schaap, *J. Amer. Chem. Soc.*, **80**, 4378 (1958). See also G. Levin, J. Jagur-Grodzinski, and M. Szwarc, *ibid.*, **92**, 2268 (1970).

[9] Because 1,1-diphenyl-1,2,3,4-tetrahydronaphthalene and 1,1,4-triphenylbutane had the same retention time under the glpc conditions studied, this identification must remain somewhat tentative in this and other cases in which the product was not characterized as a pure substances; however, since 1,1,4-triphenylbutyl anion (like analogous anions which we have studied) is expected to be stable in tetrahydrofuran under the conditions used, we believe that the product is at least predominantly 1,1-diphenyl-1,2,3,4-tetrahydronaphthalene because it appeared with the neutral products from carbonation.

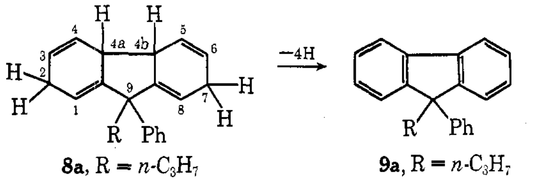
[10] C. Goria, *Gazz. Chim. Ital.*, **65**, 1226 (1935).

[11] F. Tepper, J. King, and J. Greer, "The Alkali Metals, An International Symposium Held at Nottingham on 19–22nd July, 1966," The Chemical Society, London, 1967, p 25.

[12] *Cf.* W. S. Murphy and C. R. Hauser, *J. Org. Chem.*, **31**, 85 (1966).

[13] A. Kliegel, *Chem. Ber.*, **38**, 284 (1905).

butane was similarly prepared by alkylation of diphenylmethylpotassium with 3-phenyl-1-bromopropane. The identity of the hydrofluorene **8a** rests upon



8a, R = n-C_3H_7
b, R = n-C_4H_9
c, R = CH_3

9a, R = n-C_3H_7
b, R = n-C_4H_9
c, R = CH_3

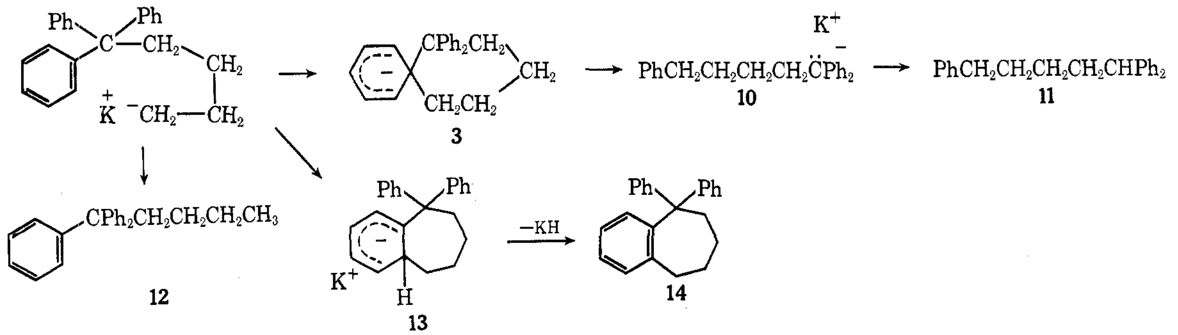
its conversion to **9a** upon dehydrogenation by sulfur in refluxing dimethylformamide, by bromine in hot *m*-dibromobenzene or simply by distillation. We believe that this compound is 9-phenyl-9-*n*-propyl-2,4a,4b,7-tetrahydrofluorene (**8a**) on the basis of our more detailed studies upon the reaction of 1,1,1-triphenylethane with Cs–K–Na alloy (see later discussion).

Reactions of 5-Chloro-1,1,1-triphenylpentane with Alkali Metals.—In view of the fact that 4-chloro-1,1,1-triphenylbutane reacted with molten potassium in THF to give a good yield of 1,1-diphenyltetrahydronaphthalene (**7**) *via* the six-membered cyclic intermediate **6** (Scheme I), it was hoped that a similar reaction of 5-chloro-1,1,1-triphenylpentane would occur (Scheme II) *via* the six-membered cyclic spiro anion **3** to give ultimately the product **11** of 1,5 migration of phenyl; the alternative ortho cyclization (to **13**) would involve formation of a seven-membered ring and hence was judged unlikely. Reaction of 5-chloro-1,1,1-triphenylpentane with potassium in refluxing THF followed by carbonation in fact gave only some 12% yield of carboxylic acids of which more than 90% were cleavage products; the predominant neutral products consisted of 60% of 1,1,1-triphenylpentane (**12**) along with mostly cleavage products. It appears that the yield of **11** and **14**, if any, did not exceed a few per cent.

The reaction of 5-chloro-1,1,1-triphenylpentane with cesium alloys was also studied. The reaction with excess Cs–K alloy at −35° and with Cs–K–Na alloy at −68° in tetrahydrofuran followed by carbonation gave, in each case, a high yield of a complex mixture of carboxylic acids. These results, along with the deep red color of the solutions, establish that a high yield of carbanions is produced under these conditions. To establish the structure of the anions, the products of decomposition by methanol were determined. The reaction with Cs–K alloy gave (according to glpc analysis) 30% of **12**, 7% of **11**, 54% of a mixture of 9-*n*-butyl-9-phenyl-2,4a,4b,7-tetrahydrofluorene (**8b**) and of 9-*n*-butyl-9-phenylfluorene (**9b**), and 9% of cleavage products.

In four runs upon 5-chloro-1,1,1-triphenylpentane with excess Cs–K–Na alloy at −68°, the products of decomposition with methanol or water were found to be 6 ± 3% of **11**, traces (3 ± 3%) of **12**, and the remainder (according to glpc analysis) a mixture of **8b** and **9b**. Since glpc analysis gave inconsistent ratios of tetrahydrofluorene to fluorene, the crude product was analyzed by nmr; this analysis showed that *all* of the fluorene derivative was present as 9-*n*-butyl-9-2,4a,-4b,7-tetrahydrofluorene, since, after correction for the known quantity of the triphenylpentanes, the ratio of aromatic to vinylic to allylic hydrogen was essentially the theoretical, 5:6:6, as expected for structure **8b**. The tetrahydrofluorene **8b** evidently dehydrogenated partially to the fluorene **9b** under our glpc conditions. This dehydrogenation also occurs on storage, especially on exposure as a thin film to light and air; most conveniently the dehydrogenation is effected by distillation *in vacuo* from a palladium–carbon catalyst at 115°. The ease of dehydrogenation agrees well with structure **8b**, since much more severe conditions are required to dehydrogenate perhydrofluorenes to fluorenes.[14] The identity of **9b** from these dehydrogenations was confirmed by isolation and comparison with an authentic sample prepared by the reaction of the potassium salt of 9-phenylfluorene with *n*-butyl bromide. While 1,1,5-triphenylpentane was not isolated in the present work, its presence was confirmed by its identity in retention time with an authentic sample on two columns upon glpc analysis.

SCHEME II



In a further run 5-chloro-1,1,1-triphenylpentane was allowed to react at −68° with only some 2 equiv of Cs–K–Na alloy. The product from decomposition with water contained 68% of **12**, 22% of the usual fluorenes (**8b** and **9b**), and small amounts of **11** and unreacted chloride. The identity of the 1,1,1-triphenylpentane (**12**) was confirmed by isolation. This experiment suggests that **12** is the major product of initial reaction of 5-chloro-1,1,1-triphenylpentane with cesium alloy; further reaction of **12** with excess alloy evidently gives rise to the precursor of the tetrahydrofluorene derivative.

To test this postulate, **12** was allowed to react with a large excess of Cs–K–Na alloy at −60° under the usual conditions. The reaction mixture upon decomposition with methanol gave an almost quantitative yield of the

[14] F. Korte and O. Behner, *Justus Liebigs Ann. Chem.*, **621**, 51 (1959).

tetrahydrofluorene **8b**, identical in all respects with the major product from reaction of 5-chloro-1,1,1-triphenylpentane with the alloy.

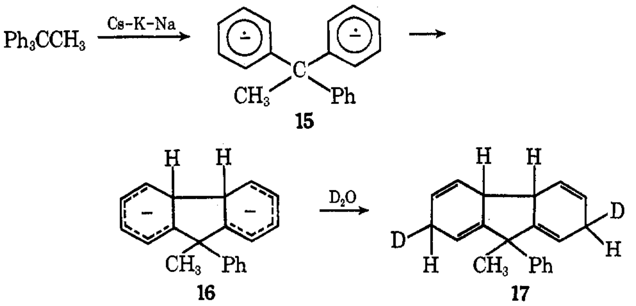
Reaction of 1,1,1-Triphenylethane with Cs–K–Na Alloy.—While the carbon skeletons of the substances previously referred to as "tetrahydrofluorenes" seem established on the basis of their ready dehydrogenation to fluorenes **9a** and **9b**, more evidence for the structures of the tetrahydrofluorenes seemed desirable. Toward this end the reaction of 1,1,1-triphenylethane with Cs–K–Na alloy was studied in some detail, since this reaction should, in terms of the previous discussion, give a simple tetrahydrofluorene **8c** which might be crystalline. In fact reaction at −70° in THF with a large excess of Cs–K–Na alloy gave the usual deep brown-red solution, which upon jetting into ice water gave an almost quantitative yield of a product, mp 96.5–97.5°, of molecular weight and analysis corresponding to the formula $C_{20}H_{20}$ as expected for 9-methyl-9-phenyl-2,4a,4b,7-tetrahydrofluorene (**8c**).

Further evidence for this structure is provided by the nmr spectrum, which shows aromatic, vinylic, allylic, and methyl hydrogens in a ratio of 5:6:6:3 as required by structure **8c**. Additional evidence is provided by the ultraviolet absorption spectrum (in ethanol) which exhibits $\lambda_{\max}$ 258 nm (ϵ 230) with typical benzenoid fine structure in the region of 247–268 nm and low absorbance even down to 220 nm (ϵ 643); this data shows that a benzene nucleus is present but that conjugated chromophores such as of diene or styrene type are missing. The combined nmr and uv data imply that one phenyl group is still present but that both of the other two phenyl groups of the reactant have been converted into 1,4-dihydroaromatic systems. In light of the fact that dehydrogenation under mild conditions gives 9-methyl-9-phenylfluorene (**9c**), structure **8c** is the only structure possible which is concordant with all of the data. It is obvious that structure **8c** can exist in several stereoisomeric forms. These may be classified according to whether the hydrogen atoms at 4a and 4b are cis or trans to one another; accordingly there should exist two cis isomers (both meso) and one trans-*dl* pair. It is interesting to note that evidently only one isomer is formed, in high yield, under the present reaction conditions. Indirect evidence[15] strongly suggests that this is one of the two possible cis isomers.

Decomposition of the red anion from reaction of 1,1,1-triphenylethane with Cs–K–Na alloy with D_2O gave **8c** in which 1.5 of the usual six allylic protons had been replaced by deuterium; this result implies that two protons are transferred to the anion during decomposition with protic solvents. The nmr spectrum at 100 MHz of the deuterated product showed two protons at τ 7.09 and 2.5 protons at τ 7.36, while the ordinary protium compound had two protons at τ 7.09 and four protons at τ 7.29. We assign the protons at τ 7.09 to the hydrogen atoms at 4a and 4b, while the four protons in the broad peak at τ 7.29 are assigned to the protons on C-2 and C-7. On this basis the upfield shift of 0.06 ppm in the location of the maximum for the protons on C-2 and C-7 in the deuterium compound might be attributed to a geminal deuterium isotope effect (increased shielding by D over H). This effect on proton resonances is typically 0.019 ppm toward higher magnetic field, as observed in CH_3D, but may be as high as 0.034 ppm, as in CD_3COCH_2D.[16] An alternative or additional reason for the large upfield shift may be that protonation of the red carbanion is stereospecific and that, for example, protonation occurs exclusively cis to the hydrogens at 4a and 4b; if in addition the entering protons at C-2 and C-7 absorb at somewhat lower field than the original protons, then the average center of gravity of the peak would shift upfield when D_2O was used to effect hydrolysis. Additional work is needed to confirm the postulate of stereospecific protonation and to establish conclusively the stereochemistry of the tetrahydrofluorene.

The origin of 9-methyl-9-phenyl-2,4a,4b,7-tetrahydrofluorene under the present reaction conditions is of interest. In the earlier work in which 9-*n*-propyl and 9-*n*-butyl derivatives **8a** and **8b** of the tetrahydrofluorene were formed, it was shown that the precursor of the tetrahydrofluorene was a carbanion which upon carbonation gave a high yield of a complex mixture of carboxylic acids or on protonation gave the tetrahydrofluorene. In work with 1,1,1-triphenylethane it was found that the red solution formed by stirring with excess Cs–K–Na alloy in THF at −70° upon rapid titration with a solution of *tert*-butyl alcohol in THF required 1.96 ± 0.02 molar equiv of *tert*-butyl alcohol to discharge the red color of the solution. This experiment implies that during reaction with the alloy *two* electrons are transferred to the 1,1,1-triphenylethane to form a dianion. The decomposition with D_2O, previously discussed, provides corroborative evidence, though this was less quantitative presumably because of deuterium exchange or spurious sources of acidic protons. The obvious dianion which should lead to 9-methyl-9-phenyl-2,4a,4b,7-tetrahydrofluorene-2,7-d_2 (**17**) on decomposition with D_2O is **16** (Scheme III).

SCHEME III



15

16

17

A plausible path to **16** is *via* two-electron transfer to 1,1,1-triphenylethane to give the diradical dianion **15**, which upon cyclization at ortho positions gives **16**. This scheme is obviously incomplete, since the role of the alkali metal cation (presumably cesium ion) is not specified. That anion **16** is red is not surprising in view

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[15] Reaction of 2,2-diphenylpropane with Cs–K–Na alloy under similar conditions gives 9,9-dimethyl-2,4a,4b,7-tetrahydrofluorene, which shows nmr absorption at two slightly different locations for the two methyl groups; hence this product must have the hydrogens at 4a and 4b cis to one another since in the trans isomer the two methyl groups are in equivalent positions (unpublished work with Mr. Thomas H. Longfield).

[16] H. Batiz-Hernandez and R. A. Bernheim in "Progress in N.M.R Spectroscopy," Vol. 3, J. W. Emsley, J. Freeney, and L. H. Sutcliffe, Ed., Pergamon Press, Oxford, 1967, p 63.

of the color and spectra which have been reported[17] for some related organolithium compounds.

Scheme III is novel in that a simple phenyl radical anion is shown undergoing intramolecular cyclization with another phenyl radical anion to give a stable dianion. At first hand it is surprising that appreciable phenyl radical anion should form at all, since, in a solvent consisting of 2:1 by volume of THF and 1,2-dimethoxyethane with Na–K alloy as reducing agent, spin concentration measurements on samples 0.01 M in initial benzene concentration have shown that benzene radical anion concentrations at equilibrium ranged from 1 to 9×10^{-6} M over the temperature range of −20 to −83°.[18] It is possible that Cs–K–Na alloy may give a higher concentration of radical anion than Na–K. Indeed benzene has been reported[19] to form a black precipitate of unknown structure[20] when treated with cesium. Also, even though the concentration of **15** may be very low, its subsequent cyclization to **16** may drive the reaction forward. Dimerization of radical anions of pyridine, quinoline, and similar heteroaromatics is well known;[21] however, radical anions derived from aromatic hydrocarbons, such as naphthalene, anthracene, etc., are said not to dimerize because dimerization would bring about a substantial loss of resonance stability.[22] Intramolecular reactions such as **15** → **16** should, however, be more favorable than analogous intermolecular processes.

Szwarc[21] and coworkers have emphasized that radical anions of quinoline and similar substances dimerize much faster when paired with sodium cations in THF than when present as unpaired anions in hexamethylphosphoramide; association of cation and anion helps to reduce, or perhaps even avoid, repulsion between like negative charges in the dimer. We suggest that under our conditions both the formation of **15** and its dimerization to **16** are promoted by strong association between cesium (or potassium) cations and the respective anions. We note that the ionic radius of cesium (1.69 Å) is near that of a benzene ring (1.39 Å from center to the carbon atoms or 2.47 Å to the hydrogen atoms). Moreover, the cesium salt of fluorene in THF at −70° has been shown to exist essentially entirely as contact ion pairs whereas the sodium and lithium salts were completely solvent separated.[23] The reluctance of cesium cations to become solvated means that cesium ions are readily available for interaction with anions such as **15** and **16**. We suggest that the stereospecific cyclization of **15** is promoted by the presence of a cesium ion "sandwiched" between the negatively charged phenyl rings. On this basis we would predict that the hydrogen atoms at 4a and 4b in **17** should be oriented cis to one another, as appears to be the case.

Reactions analogous to those of Scheme III are known in cases where the hypothetical cyclic dianion (analogous to **16**) or dimeric dianion is removed from the presumably dynamic but unfavorable equilibrium by loss of hydride ion, by protonation, or by protonation and further reduction. Thus benzil dianil undergoes cyclodehydrogenation with lithium in THF to produce the dianion of 9,10-dianilinophenanthrene and lithium hydride,[24] benzil is converted into phenanthrenequinone trianion radical (and KH?) by potassium in refluxing THF,[25] 1,1′-binaphthyl with lithium in THF gives perylene,[26] and tetraphenylallene with lithium gives a dibenzocycloheptatriene derivative.[27] Lithium anthracene at high concentration in diethyl ether deposits a precipitate which when hydrolyzed gives 9,9′,10,10′-tetrahydro-9,9′-dianthryl in addition to a 1:1 mixture of anthracene and 9,10-dihydroanthracene.[28] Electrolysis of phenanthrene in dimethylformamide gives 9,9′,10,10′-tetrahydro-9,9′-biphenanthrene.[29] The reaction of naphthalene with sodium in the presence of amines yields numerous products, including products of reductive dimerization.[30]

Reaction of 2-Chloro-1,1,1-triphenylethane with Cs–K–Na Alloy.—In view of the fact that 4-chloro-1,1,1-triphenylbutane and 5-chloro-1,1,1-triphenylpentane react with cesium alloys in THF at low temperature to give primarily the corresponding hydrocarbons without rearrangement of carbon skeleton when excess of alloy is avoided, it was of interest to know if 2-chloro-1,1,1-triphenylethane behaves likewise. Reaction of the latter chloride with about the theoretical amount of Cs–K–Na alloy at −65° in THF, followed by carbonation, gave some 35% yield of 2,2,3-triphenylpropanoic acid and 4.6% of 1,1,1-triphenylethane, with unreacted chloride constituting most of the remainder. Thus 2-chloro-1,1,1-triphenylethane, unlike its two higher homologs, with cesium alloy gives mostly the rearranged carbanion just as had been found previously with sodium[31] in dioxane and with potassium[4] in THF or 1,2-dimethoxyethane. The failure to obtain predominant phenyl migration in reactions of 4-chloro-1,1,1-triphenylbutane and 5-chloro-1,1,1-triphenylbutane with alkali metals under conditions where 2-chloro-1,1,1-triphenylethane gives predominantly products of phenyl migration must be ascribed to some unfavorable structural characteristics of the higher homologs.

Summary and Conclusions

Rearrangements involving 1,4 and 1,5 migration of phenyl have been observed in the present reactions of 4-chloro-1,1,1-triphenylbutane and of 5-chloro-1,1,1-triphenylpentane with cesium alloys; however, such rearrangements did not constitute more than about

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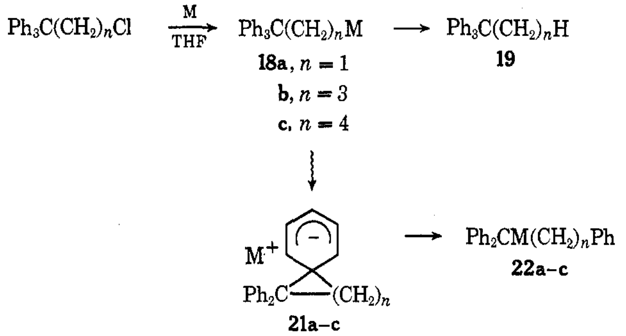
10% of the total reaction under any of the conditions studied. A more important reaction was reduction to the corresponding hydrocarbon, 1,1,1-triphenylbutane and 1,1,1-triphenylpentane, respectively. Both the rearrangement and reduction are interpreted (see Scheme IV) as proceeding by way of the same initial unrearranged organometallic compound **18**, although only for **18a** and **18b** where M = Li has direct evidence been obtained (results of carbonation). It is at first sight surprising that **18b** and **18c** do not undergo cyclization in better yield than **18a**, since ω-aminoalkyl bromides[32] undergo cyclization considerably more readily to five-membered rings and somewhat more readily to six-membered rings than to three-membered rings.[33] In **18a**, however, the triphenylmethyl group is considerably closer to the anionic charge than in **18b** and **18c**; since this group is expected[34] to help stabilize the carbanion and should stabilize more effectively the closer to the anionic center, the order of expected stability is **18a** > **18b** ≥ **18c**. The more stable the carbanion the more slowly it should be protonated by THF to give **19** and so the more time it should possess for cyclization to **21**. Implicit in this argument is the assumption that the reaction leading to **19** is retarded more by the triphenylmethyl group than that to **21**. Another factor favoring the more ready rearrangement of **18a** than of **18b** or **18c** is that in conversion of **18a** to **21a** there is probably some relief of steric compression among the phenyl groups.[35] On the other hand, in going from **18c** to **21c**, a phenyl group and a portion of the cyclohexadienyl group are placed at axial positions on the cyclohexane ring formed on cyclization. Complications such as these are missing in cyclization of simple ω-aminoalkyl bromides which, therefore, do not serve as good models for the present system.

SCHEME IV



Liquid alloys of cesium[10,11] with potassium and sodium have apparently not been used previously in reaction with alkyl halides and hydrocarbons. These alloys permit reactions of alkali metals to be run rapidly and conveniently at low temperature; we believe, therefore, that they may find considerable application. In the present work, use of Cs–K–Na alloy has permitted the discovery that 1,2 and 1,5 migration of phenyl are rapid even at −65° in the 2,2,2-triphenylethyl and 5,5,5-triphenylpentyl anions. What may prove to be a more important discovery, and to us was unexpected, is that 1,1,1-triphenylalkanes and 1,1-diphenylalkanes[15] undergo reductive cyclization by Cs–K–Na alloy at low temperature to novel dianions of unique stereochemistry. The synthetic utility of low-temperature reductions effected by cesium alloys appears to be great and to offer exciting opportunities for future investigation.

Experimental Section[36]

Materials.—9-*n*-Butyl-9-phenylfluorene, mp 99.0–99.5° (reported[37] mp 98–99°), was prepared by reaction of the potassium salt of 9-phenylfluorene with *n*-butyl bromide in diethyl ether. Cesium metal (99.9+%) was obtained from MSA Research Corp. in sealed glass ampules. Cesium–potassium–sodium alloy was of composition (g-atom %) 47.4% K, 40.8% Cs, and 11.8% Na, corresponding to the minimum melting alloy;[11] this alloy was conveniently prepared by warming suitable proportions of the alkali metals under a nitrogen atmosphere and was stored in a tightly sealed glass-stoppered ampule under pentane. 1,1-Diphenylbutane was prepared by reaction of diphenylmethylpotassium in liquid ammonia with 1-bromopropane. 2,2-Diphenylpentanoic acid, mp 153–154° (reported[38] mp 155.5°), was made by *saponification of methyl 2,2-diphenylpentanoate*, which was prepared by reaction[39] of the potassium salt of methyl diphenylacetate with *n*-propyl bromide in liquid ammonia–ether solution. 1,1-Diphenyl-1,2,3,4-tetrahydronaphthalene, mp 125–126°, was obtained (25% yield) by treatment of 1,1,4-triphenylbutanol-1 with cold 92% sulfuric acid.[7] 9-Methyl-9-phenylfluorene, mp 85–87° (reported[40] mp 86–86.5°), was prepared[12,41] by metalation of 9-phenylfluorene with KNH_2 in liquid ammonia followed by reaction with an ethereal solution of methyl iodide. Methyl triphenylacetate, mp 188–189° dec (reported[42] mp 184–185°), was prepared by reaction of triphenylacetic acid with diazomethane. 9-Phenylfluorene, mp 148–150°, was prepared from triphenylcarbinol by the procedure of Kliegl.[13] 1,1,1-Triphenylbutane, mp 78–80° (reported[43] mp 79°), was prepared by reaction of *n*-propylmagnesium bromide with triphenylchloromethane in diethyl ether. 1,1,4-Triphenylbutanol-1, mp 74–75° (reported[44] mp 74–75°), was prepared by addition of 3-phenylpropyllithium to benzophenone in THF (65% yield) and by addition of 3-phenylpropylmagnesium chloride to benzophenone in diethyl ether (76% yield). 1,1,1-Triphenylethane was prepared by the procedure of Gomberg and Cone.[41,45] 1,1,1-Triphenylpentane, mp 59.5–61.0° (reported[37,46] mp 60–61°), was prepared by hydrolysis of the Grignard reagent prepared from 5-chloro-1,1,1-triphenylpentane.

General Procedure for Alkali Metal Reactions.—Reactions with alkali metals were normally conducted in a 500-ml Morton flask equipped with a Morton high-speed stirrer,[47] a condenser,

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[32] G. Salomon, *Helv. Chim. Acta*, **16**, 1361 (1933); **17**, 851 (1934).

[33] For trimethylsilyl migration, however, it has been observed that 1,2 migration in silylhydrazide anions occurs more readily than 1,4 migration in etilylethylenediamine anions, while 1,4 migration in the more rigid silyl-*o*-phenylenediamine anions approaches that of silylhydrazide anions [R. West, M. Ishikawa, and S. Murai, *J. Amer. Chem. Soc.*, **90**, 727 (1968); H. F. Stewart, D. G. Koepsell, and R. West, *ibid.*, **92**, 846 (1970)].

[34] Some idea about the effectiveness of the triphenylmethyl group in stabilization of anions is provided by the relative rates (statistically corrected) of cleavage from quaternary nitrogen by sodium in liquid ammonia; for Ph_3CCH_2, $Ph_3CCH_2CH_2$, and CH_3 the relative rates are 10,000:92:1 [E. Grovenstein, Jr., and L. C. Rogers, *J. Amer. Chem. Soc.*, **86**, 854 (1964)].

[35] E. Grovenstein, Jr., and L. P. Williams, Jr., *J. Amer. Chem. Soc.*, **83**, 2537 (1961).

[36] Melting points are uncorrected. Proton magnetic resonance (nmr) spectra were obtained at 60 MHz on a Varian A-60D spectrometer and at 100 MHz on a JEOLCO 4H100 spectrometer and were taken relative to tetramethylsilane as an internal standard. Ultraviolet spectra were determined on a Cary Model 14 spectrometer and infrared spectra on a Perkin-Elmer Model 237 Infracord. Mass spectra were run on a Varian M-66 mass spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

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[41] We are indebted to Mr. Ronald H. Carter for this preparation.

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[43] M. Gomberg and L. H. Cone, *Chem. Ber.*, **39**, 2957 (1906).

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[46] J. Cason and F. J. Schmitz, *J. Org. Chem.*, **25**, 1293 (1960).

[47] A. A. Morton and L. S. Redmon, *Ind. Eng. Chem.*, **40**, 1190 (1948)

a thermometer well, and a dropping funnel. The flask was flame dried under a stream of dry nitrogen and all reactions were conducted under an atmosphere of nitrogen. For reactions of cesium and its alloys the entire apparatus was contained in a glove box under a nitrogen atmosphere in order to reduce fire hazards in working with these readily oxidizable metals. Tetrahydrofuran (THF) was stored over sodium wire and freshly distilled into the reaction flask from sodium aluminum hydride under a nitrogen atmosphere before use. In runs with liquid alkali metals, the THF was stirred with the molten metal (at 40–65°) for normally 1 hr before addition of alkyl halide; this procedure ensured both that the solvent was freed of impurities and that the alkali metal was finely divided.

4-Chloro-1,1,1-triphenylbutane.—This compound has previously been reported,[48] but without details, from reaction of triphenylmethylsodium with 1-bromo-3-chloropropane. Triphenylmethylsodium,[49] prepared from sodium amalgam (12.7 g of Na, 524 g of Hg) and triphenylchloromethane (69.7 g, 0.250 mol) in 340 ml of anhydrous ether, was siphoned under nitrogen from the mercury and added with stirring over a 10-min period to 440 ml of 1-bromo-3-chloropropane at 12 ± 3°. The red color of the triphenylmethylsodium was discharged almost immediately upon contact. The solution was filtered and the ether and excess bromochloropropane were removed finally *in vacuo* at a bath temperature of 64°. The remaining light yellow crystals (51 g, 64% yield based on triphenylchloromethane) had mp 125–170°. Recrystallization from acetone and subsequent vacuum sublimation (at a bath temperature up to 150°) gave 26.3 g of crystals, mp 129–131.5°. The analytical sample was recrystallized again from acetone to give colorless needles, mp 130.5–131.5° (reported[48] mp 130°).

Anal. Calcd for $C_{22}H_{21}Cl$: C, 82.35; H, 6.60; Cl, 11.05. Found: C, 81.92, 81.89; H, 6.59, 6.53; Cl, 11.29, 11.25.

During the purifications of the above chloride, 2.3 g of a substance of mp 164–167° and 3.6 g of a substance of mp 205–230° were obtained. In another preparation similar to the above but from 238 g of triphenylchloromethane, the product after one recrystallization from acetone amounted to 166 g (69% yield), mp 115–131°; a second recrystallization from acetone gave 120 g of 4-chloro-1,1,1-triphenylbutane, mp 129–131°.

This product was also similarly prepared by reaction of triphenylmethylsodium (from 69.7 g of triphenylchloromethane) with 400 ml of 1,3-dichloropropane. After filtration and removal of solvent and 1,3-dichloropropane *in vacuo*, oily crystals were obtained; these were washed with *n*-pentane to give 23 g (29% yield) of product, mp 122–125°. Further purification yielded a product identical (mixture melting point and ir spectral comparisons) with that from 1-chloro-3-bromopropane.

9-Phenyl-9-*n*-propylfluorene (9a).—To a solution of potassium amide, prepared from 2.86 g (0.0733 g-atom) of potassium in 200 ml of liquid ammonia, was added 1.67 g (6.89 mmol) of 9-phenylfluorene in 100 ml of diethyl ether. The brown-yellow solution was stirred at reflux for 1 hr and then 7.5 ml (0.082 mol) of *n*-propyl bromide was added. Since there was no obvious color change after 2 hr of stirring, 100 ml more of ether was added and the ammonia was allowed to evaporate. Additional *n*-propyl bromide (10 ml) was added and the solution was stirred for 2.5 hr before addition of excess ammonium chloride. The usual work-up gave 1.63 g (84% yield) of light yellow crystals which after washing with petroleum ether (bp 30–60°) amounted to 0.90 g of white solid, mp 112–115°. Two recrystallizations from ethanol gave crystals, mp 115.5–116.5°.

Anal. Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 92.78; H, 7.25.

5,5,5-Triphenylpentanenitrile.—Into a flask was placed 2.00 g (6.05 mmol) of 4-chloro-1,1,1-triphenylbutane, 0.47 g (9.6 mmol) of sodium cyanide, 0.92 g (6.1 mmol) of sodium iodide, and 180 ml of dimethyl sulfoxide.[50] The flask was stoppered and stirred with a magnetic stirrer at room temperature for 10 days. After filtration the reaction mixture was poured into 100 ml of water. The solid which formed was removed by filtration, washed with 100 ml of water, and dried to give 1.80 g (95% yield) of nitrile, mp 147–149°. Two recrystallizations from acetone gave white crystals, mp 149–150°.

Anal. Calcd for $C_{23}H_{21}N$: C, 88.70; H, 6.80; N, 4.50. Found: C, 88.15; H, 6.90; N, 4.71.

5,5,5-Triphenylpentanoic Acid.—A solution of 2.86 g (9.20 mmol) of 5,5,5-triphenylpentanenitrile and 1.58 g of potassium hydroxide in 95 ml of ethylene glycol was heated at reflux for 12 hr. After the usual work-up there was obtained 2.85 g (97% yield) of white solid, mp 222–225°. The product, after recrystallization from benzene, sublimation *in vacuo* (20 μ, bath at 190°), and recrystallization from ethanol, had mp 225–227.5° dec.

Anal. Calcd for $C_{23}H_{22}O_2$: C, 83.60; H, 6.71. Found: C, 83.53; H, 6.69.

A compound, mp 222–223°, believed to be 5,5,5-triphenylpentanoic acid has been reported previously from cleavage of a substance thought to be 1,1,1,6,6,6-hexaphenylhexan-2-one by methanolic potassium hydroxide.[51]

Methyl 5,5,5-Triphenylpentanoate.—This compound, mp 97.0–97.7° (from ethanol), was prepared by reaction of the corresponding acid with diazomethane.

Anal. Calcd for $C_{24}H_{24}O_2$: C, 83.69; H, 7.02. Found: C, 83.49; H, 7.04.

2,2,5-Triphenylpentanoic Acid.—To 18.1 g (60 mmol) of 1,1,4-triphenylbutanol-1 in 85 ml of anhydrous methanol was added 0.9 ml of concentrated sulfuric acid. A precipitate rapidly formed and after 1 hr at room temperature the contents of the flask had completely solidified. The solid was recrystallized from methanol to yield,[52] after drying in air on the filter, 11.1 g (59% of 1-methoxy-1,1,4-triphenylbutane, mp 81–82°. Since a sample of this ether was found to undergo decomposition (evidently loss of methanol to give olefin) on drying *in vacuo* at room temperature, it was used without further purification or analysis. This ether, 9.73 (30.8 mmol), in 35 ml of tetrahydrofuran (THF), was added dropwise over a period of 30 min to 2.9 g (74 mg-atoms) of potassium stirred vigorously in 250 ml of THF at reflux temperature, according to our general procedure for alkali metal reactions. After 1.5 hr of additional stirring, the mixture was forced onto solid carbon dioxide. The usual work-up gave 6.7 g (68% yield) of crude acid,[53] mp 162–168°. After recrystallization from cyclohexane and then chloroform this acid had mp 168–169.5° dec.

Anal. Calcd for $C_{23}H_{22}O_2$: C, 83.60; H, 6.71. Found: C, 83.59; H, 6.58.

1,1,4-Triphenylbutane.—Diphenylmethylpotassium was prepared in 250 ml of liquid ammonia solution from reaction of 5.45 g (32.4 mmol) of diphenylmethane (in 30 ml of ether) with potassium amide (from 1.52 g, 38.9 mg-atoms, of potassium) and the red organopotassium compound was treated dropwise at reflux temperature with a solution of 1-bromo-3-phenylpropane in 30 ml of ether until the red color was discharged. Solid ammonium chloride (2.3 g) was added and the ammonia was allowed to evaporate. The residue was treated with water and extracted with ether. The ether extract yielded 7.1 g of oil which by glpc analysis contained some 84% of 1,1,4-triphenylbutane and the remainder diphenylmethane. After several distillations *in vacuo*, a sample of pure 1,1,4-triphenylbutane was obtained: $n^{27.5}$D 1.5838; nmr (CCl_4) peaks at τ 2.89 and 2.93 (15 H, two peaks in *ca.* 2:1 ratio), 6.17 (1 H, triplet, J = 7.5 Hz), 7.43 (2 H, triplet, J = 7.2 Hz), 7.8–8.8 (4 H, multiplet). This compound is variously reported as a liquid,[54] n^{20}D 1.5993, and a solid,[55] mp 78–79°; attempts to obtain a crystalline product were unsuccessful in our hands.

Anal. Calcd for $C_{22}H_{22}$: C, 92.26; H, 7.74. Found: C, 92.27; H, 7.72.

Reaction of 4-Chloro-1,1,1-triphenylbutane with Lithium.—In the usual apparatus was placed 250 ml of THF, 0.63 g (0.090 g-atom) of finely cut lithium wire (from Lithium Corp. of America, 0.05% Na max), and 0.15 ml of methyl iodide. The reaction flask was cooled to −5 ± 5, some 5% of a solution of 4-chloro-1,1,1-triphenylbutane (4.0 g, 12 mmol) in 20 ml of THF was added, and vigorous stirring was continued for 2 hr. An additional 0.1 ml of methyl iodide and 5% of the chloride solution was then added and stirring was continued for 1.5 hr, by which time the color of the solution was orange. The solution was then cooled to −55 ± 5°, the remainder of the chloride was added

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(48) J. C. Charlton, I. Dostrovsky, and E. D. Hughes, *Nature (London)*, **167**, 986 (1951).

(49) W. B. Renfrow, Jr., and C. R. Hauser in "Organic Syntheses," Collect. Vol. II, A. H. Blatt, Ed., Wiley, New York, N. Y., 1943, p 607.

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(54) A. D. Petrov and V. M. Vdovin, *Zh. Obshch. Khim.*, **27**, 45 (1957).

(55) F. Bergmann, S. Israelashvili, and D. Gottlieb, *J. Chem. Soc.*, 2522 (1952).

dropwise, and stirring was continued for 3 hr before the solution was forced onto solid crushed carbon dioxide. The next day some of the unreacted lithium metal was removed, 200 ml of water was added (to decompose the remaining lithium), and the THF was removed *in vacuo* on a steam bath. The aqueous residue was acidified with 10% sulfuric acid and extracted well with ether. The ethereal phase was extracted with dilute sodium hydroxide. The ether phase yielded 3.0 g of neutral material. The alkaline solution was acidified with 10% sulfuric acid and extracted with ether. The ether extract, after drying over anhydrous MgSO$_4$, yielded 1.2 g of crude acid,[56] mp 180–230°. One recrystallization from benzene gave 0.86 g of acid, mp 222–225° dec. Two more recrystallizations from benzene gave material, mp 223–224° dec, which gave no mixture melting point depression with authentic 5,5,5-triphenylpentanoic acid (prepared *via* the nitrile).

In another run after the usual initiation at −5°, 7.53 g (23.5 mmol) of 4-chloro-1,1,1-triphenylbutane was allowed to react with 0.51 g of lithium in 250 ml of THF with vigorous stirring at −60 ± 5° for 3.5 hr. The reaction mixture was then stirred at 0 ± 3° for 2 hr before carbonation. The usual work-up yielded 1.28 g of acid, mp 207–220°. One recrystallization from benzene gave 0.50 g of acid, mp 217–223°; a mixture melting point of this acid with the 5,5,5-triphenylpentanoic acid obtained in the previous run was not depressed.

In a final run after the usual initiation at −5°,4-chloro-1,1,1-triphenylbutane (10.0 g, 31.1 mmol) was allowed to react with 0.64 g (92 mg-atoms) of lithium in 250 ml of THF at −60° for 4 hr. The reaction mixture was then stirred at 25 ± 2° for 2 hr before carbonation. The usual work-up gave 9.1 g of neutral material and 0.37 g of acidic material. The acids were methylated with diazomethane before analysis by gas–liquid partition chromatography[57] (glpc). There was obtained (as methyl esters) 46% of 5,5,5-triphenylpentanoic acid, 17% of a likely isomeric acid at 0.81 times the retention time of 5,5,5-triphenylpentanoic acid, and seven acids of lower molecular weight (products of pyrolysis or fragmentation); none of the methyl ester of 2,2,5-triphenylpentanoic acid could be detected. Analysis (glpc) of the neutral material gave 87% of 1,1,1-triphenylbutane, 3% of a substance of 34% longer retention time (likely[9] 1,1-diphenyltetrahydronaphthalene), and 10% of 4-chloro-1,1,1-triphenylbutane. A sample (2.0 g) of the neutral material was distilled in a sublimation apparatus at 0.01 mm and 103° to give 1.2 g of white solid, mp 55–74°. Two recrystallizations from ethanol gave 0.47 g of compound, mp 77–79°, which was identified as 1,1,1-triphenylbutane by comparisons of melting point, mixture melting point, and ir spectra with those of an authentic sample.[43]

Reaction of 4-Chloro-1,1,1-triphenylbutane with Potassium.—In the usual apparatus was placed 250 ml of THF and 3.44 g (0.088 g-atom) of freshly cut potassium. The mixture was heated at reflux with vigorous stirring for 50 min and then a solution of 10.08 g (31.4 mmol) of 4-chloro-1,1,1-triphenylbutane in 70 ml of THF was added over a period of 10 min. On addition of the first portion of halide the solution turned a deep red; the final color was like that of bromine. After cooling to room temperature in 10 min, the mixture was forced onto a large excess of solid carbon dioxide. A 300-ml portion of absolute ethanol was added to destroy any unreacted potassium. The next day, solvents were largely removed *in vacuo*, water was added to the residual viscous liquid, and the mixture was extracted with three 200-ml portions of ether. The ether extract, after drying over anhydrous MgSO$_4$, yielded 9.5 g of crude, semisolid neutral material. The aqueous layer, after acidification with 10% hydrochloric acid and extraction by ether, yielded 1.08 g of oily acids. Analysis of the neutral fraction by glpc[57] showed the presence of 84% of 1,1-diphenyl-1,2,3,4-tetrahydronaphthalene (**7**), 14% of 1,1,1-triphenylbutane, and 0.8 and 0.4% of two cleavage products (apparently 1,1-diphenylbutane and triphenylmethane, respectively). Analysis (glpc) of the methyl esters of the acids at 284° gave the following products, listed as area per cent (relative retention time, identity of acid): 0.8 (0.38, diphenylacetic acid); 4.5 (0.52, 2,2-diphenylpentanoic acid), 47 (0.58), 5 (0.67), 2.7 (1.00, triphenylacetic acid), 1 (1.62), 5.7 (1.79, 2,2,5-triphenylpentanoic acid), 28 (2.10), and 5 (2.96). A sample of 7.3 g of the neutral material was sublimed at 0.3 mm at a bath temperature of 102° to give 3.7 g of white solid, mp 80–115°. Recrystallization of 1.89 g of this product from ethanol gave 1.11 g (indicative of 32% yield based on chloride) of product, mp 125–126°; this compound is identified as **7** based on melting point, mixture melting point, and ir spectral comparisons with an authentic sample.[7] The nmr spectrum provided confirmatory evidence: nmr (CDCl$_3$) τ 2.8–3.5 (14 H, complex multiplet), 7.3 (4 H, overlapping triplets), and 8.3 (2 H, complex multiplet). A repetition of this run but with a total reaction time of 1.7 hr at reflux temperature gave 7 g of a very complex mixture of acids.

Reaction of 4-Chloro-1,1,1-triphenylbutane with Sodium–Potassium Alloy.—To sodium–potassium alloy, prepared from 10.3 g (0.26 g-atom) of potassium and 3.1 g (0.13 g-atom) of sodium in 250 ml of THF, was added 10.0 g (31.1 mmol) of 4-chloro-1,1,1-triphenylbutane in 70 ml of THF over a period of 40 min while the solution was stirred vigorously with cooling by an ice bath (0°). The red mixture was stirred for an additional 1 hr at ice-bath temperature before carbonation. The usual work-up gave 3.0 g of neutral material and the remainder acids (*ca.* 7 g). Analysis[57] of the neutral material by glpc showed the presence of 15% of 4-chloro-1,1,1-triphenylbutane, 32% of **7**,[9] a trace of 1,1,1-triphenylbutane, and the remainder some five cleavage products of which only triphenylmethane (3%) was identified. Analysis of the methyl esters of the acids by glpc at 284° gave the following products, listed as area per cent (relative retention time, identity): 22 (0.52, 2,2-diphenylpentanoic acid), 38 (0.58), 16 (0.67), 3.7 (1.00, triphenylacetic acid), 5.5 (1.79, 2,2,5-triphenylpentanoic acid), 12 (2.10).

Reaction of 4-Chloro-1,1,1-triphenylbutane with Cesium.—In the usual apparatus was placed 4.09 g (0.0308 g-atom) of cesium metal and 250 ml of THF. Upon stirring the solution developed a pale blue color. After stirring for 35 min at 40 ± 5°, 5.01 g (15.6 mmol) of 4-chloro-1,1,1-triphenylbutane was dusted into the reaction mixture over a period of 4 min at 33°. A dark red color rapidly developed in the solution. Stirring was continued for 11 min more at 40° before carbonation. The usual work-up gave 1.22 g of acids and 4.0 g of crude neutral product. Analysis[57] of the methyl esters of the acids by glpc at 284° gave the following products, listed as area per cent (relative retention time, identity): 1.6 (0.38, diphenylacetic acid), 6.5 (0.52, 2,2-diphenylpentanoic acid), 3 (0.67), 4.8 (1.00, triphenylacetic acid), 26 (1.54), 6.1 (1.79, 2,2,5-triphenylpentanoic acid), 35 (2.1), 16 (2.8). Analysis of the neutral material by glpc at 274° gave (listed as before): 6.7 (0.21), 5.1 (0.40), 45 (1.00, 1,1,1-triphenylbutane), 35 (1.05, **9a**), and 7.8 (1.33, **7**[9]).

Reaction of 4-Chloro-1,1,1-triphenylbutane with Cesium–Potassium Alloy.—In a run with 1.16 g (0.0297 g-atom) of potassium and 3.93 g (0.0296 g-atom) of cesium in 250 ml of THF, 4.45 g (13.9 mmol) of 4-chloro-1,1,1-triphenylbutane in 50 ml of THF was added dropwise at −25° over a period of 30 min and stirring was continued for 34 min before carbonation. There was isolated 4.1 g of a complex mixture of acids, mp 70–160°. The acids were converted to their methyl esters with diazomethane; some 48% of these esters were volatile in a preparative glpc separation. The volatile esters *via* glpc analysis consisted of 10.8% of methyl triphenylacetate, 14% of methyl 2,2,5-triphenylpentanoate, and the remainder of seven unidentified esters. Methyl triphenylacetate was isolated as crystals, mp 187–189°, and was shown to be identical (melting point, mixture melting point, nmr spectrum) with an authentic sample. Methyl 2,2,5-triphenylpentanoate, however, was not isolated as a pure substance. A repetition of this run at a temperature of −40 ± 5° with 5.9 g of 4-chloro-1,1,1-triphenylbutane (5.9 g of Cs, 1.5 g of K) gave 5.5 g of acids; glpc analysis[57] of the methyl esters at 275° gave the following products, listed as area per cent (relative retention time, identity): 3 (0.40, 2,2-diphenylpentanoic acid?), 13.8 (1.00, triphenylacetic acid), 1.2 (1.70), 27.6 (2.14, 2,2,5-triphenylpentanoic acid), 32 (2.60), 5.5 (2.90), 1.8 (3.2), 1.1 (3.6), 1.1 (4.0), 3.9 (4.6), 1.1 (5.2), and 6.8 (6.1).

In another run 12.56 g (39.2 mmol) of 4-chloro-1,1,1-triphenylbutane in 50 ml of THF was added dropwise over a period of 20 min to 5.54 g (0.0416 g-atom) of cesium and 1.45 g (0.0371 g-atom) of potassium stirred vigorously in 250 ml of THF at −45 ± 5°. Stirring was continued for 30 min more before carbonation.

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[56] This yield may be low because the reaction flask was not flame-dried.

[57] The analyses were ordinarily run at about 280° on an F & M Scientific Co. Model 810 chromatograph equipped with flame ionization detectors with 6 ft × 0.25 in. columns packed with 10% silicone gum rubber (SE-30) on 60–80 mesh Chromosorb G (acid washed and silanized with dimethyldichlorosilane). The analyses are reported as area per cent of total volatile constituents; therefore, while these analyses should indicate the correct relative amounts of isomers, including compounds differing only in the number of hydrogen atoms, the analyses are ordinarily only of semiquantitative significance.

The usual work-up gave 4.4 g of acids and 7.8 g of neutral product. Analysis[57] of the neutral product by glpc showed that the volatile portion consisted of 93% of 1,1,1-triphenylbutane, 3.8% of **9a**, and 3.0% of **7**.[9] A quantitative glpc analysis showed that the neutral product contained 3.7 g (33% absolute yield based on starting chloride) of 1,1,1-triphenylbutane. The acid fraction consisted of the usual complex mixture; methyl 2,2,5-triphenylpentanoate constituted 8.5 area % of the volatile esters, although the absolute yield was only 1.4% (based on starting chloride). Only about half of both the methyl esters and neutral products were glpc volatile in this run.

In another run, 6.12 g (19.1 mmol) of 4-chloro-1,1,1-triphenylbutane in 40 ml of THF was added over a period of 18 min to 5.72 g (0.0431 g-atom) of cesium and 1.47 g (0.0376 g-atom) of potassium (as Cs–K alloy) stirred in 250 ml of THF at −42 ± 2°. Stirring was continued at the same temperature for 40 min before addition of 50 ml of methanol to the red solution. The usual work-up gave 5.6 g of crude product; analysis[57] by glpc at 250° showed the presence of the following substances, listed as area per cent (retention time in minutes, identity): 4.2 (1.9–9.2, six unknown products), 32 (10.5, 1,1,1-triphenylbutane), 30 (10.9, **9a**), 20 (11.5, **8a**) and 8 (11.8, 1,1,4-triphenylbutane). A 0.257-g portion of the crude product was heated with 0.029 g of sulfur in 15 ml of *N*,*N*-dimethylformamide at reflux for 5.5 hr. After washing with water, the organic fraction was evaporated to give 0.195 g of brown tar. Analysis of this tar by glpc showed that **8a** had disappeared while **9a** had increased in amount relative to the other components. In another dehydrogenation procedure,[58] to 0.209 g of the crude product in 10 ml of *m*-dibromobenzene at 215° was added dropwise over 5 min 0.16 ml of 2.5% (by volume) bromine in *m*-dibromobenzene and the mixture was heated at 215° for 2.5 hr. Analysis by glpc showed again that the tetrahydrofluorene had disappeared and more **9a** had appeared. A similar dehydrogenation was run on another 0.103 g of the crude product. The two bromination products were combined; solvent was removed *in vacuo*; and the residue was combined with 0.186 g of the product from the sulfur treatment. The mixture was distilled in a sublimation apparatus at 100° and 50 μ to give 0.206 g of semisolid product. Recrystallization of 0.152 g of this product from ethanol gave 0.036 g of crystals, mp 113–114°; another recrystallization from ethanol gave a pure product, mp 115.3–116.0° (9-phenyl-9-*n*-propylfluorene, **9a**).

In a final run 6.65 g (20.7 mmol) of 4-chloro-1,1,1-triphenylbutane in 30 ml of THF was added over a 25-min period to Cs–K alloy prepared from 6.39 g (0.0480 g-atom) of cesium and 1.61 g (0.0411 g-atom) of potassium in 250 ml of THF at −45° in the usual manner, except that *ca.* 10% of the halide was prematurely added to the flask at room temperature before refluxing the solvent with alkali metal. The reaction mixture was then stirred at −45 ± 3° for 30 min, allowed to warm to −30°, and then forced into 110 ml of methanol at −55°. The mixture was neutralized with 5% hydrochloric acid. The usual work-up gave 4.95 g of a colorless oil (another 1.54 g of product was recovered from the reaction flask). Analysis[57] of this oil by glpc at 250° gave the following results, listed as area per cent (retention time in minutes, identity): 8.9 (1.9–7.4, four unknown compounds), 9.5 (10.5, 1,1,1-triphenylbutane), 55 (10.9, **9a**), 15 (11.5, **8a**), 11 (11.8, 1,1,4-triphenylbutane). Since other work indicated that the tetrahydrofluorene derivative was generally converted to the fluorene on distillation *in vacuo*, a portion (3.44 g) of the colorless oil was distilled at 100° and 10 μ to give 2.69 g of semisolid product. One recrystallization of 1.90 g of this material from ethanol gave 0.84 g of crystals, mp 108–114°, and mother liquor A. Sublimation of 0.174 g of these crystals at 100° and 10 μ and recrystallization from ethanol gave 0.132 g of white crystals, mp 113–115°; after another recrystallization from ethanol the melting point was 115.0–115.8°.

Anal. Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.09; mol wt, 284. Found: C, 93.37; H, 6.76; mol wt (mass spectrum[59]), 284.

The compound of mp 115–116° gave nmr absorption (CCl_4) at τ 2.2–3.0 (13 H, complex multiplet), 7.63 (2 H, triplet, J = 7 Hz), 9.28 (5 H, complex multiplet); $\lambda_{\max}^{\mathrm{EtOH}}$ 266 nm (ϵ 14,300), 294 (5310), 306 (8900). This compound was found to be identical with the synthetic sample of 9-phenyl-9-*n*-propylfluorene (prepared from 9-phenylfluorene) on the basis of melting point, mixture melting point, ir, and uv spectral comparisons.

The mother liquor A above was evaporated on a steam bath and the residue was distilled at 20 μ. A 0.285-g portion of the distillate was subjected to liquid phase chromatography on 80 g of silica gel (E. Merck A.-G., Darmstadt, Germany, No. 7734) in a 2.0 × 60 cm column. Elution with petroleum ether gave fractions 3 and 4 (0.15 g), which consisted of a 2 : 1 mixture of **9a** and 1,1,1-triphenylbutane, and fractions 8 and 9 (0.050 g), which contained some 90% of 1,1,4-triphenylbutane. The identity of fraction 8 was confirmed, after distillation *in vacuo*, by ir and nmr spectral comparisons with the synthetic sample of 1,1,4-triphenylbutane (prepared from diphenylmethane).

5-Chloro-1,1,1-triphenylpentane.—This compound was prepared[60] by a procedure analogous to that used for 4-chloro-1,1,1-triphenylbutane except that triphenylmethylsodium (from 278.8 g of triphenylchloromethane) in 1250 ml of diethyl ether was added slowly over a period of 2 hr under nitrogen to 500 ml of 1,4-dichlorobutane stirred in a 3-l. Morton flask cooled to −40°. After the usual work-up, the oily product was crystallized from petroleum ether to give 161 g (48% yield) of crude crystals, mp 65–73°. Several recrystallizations from acetone gave 84.5 g of white crystals, mp 75–78°; after further recrystallization the most highly purified sample had mp 79.0–79.6°.

Anal. Calcd for $C_{23}H_{23}Cl$: C, 82.49; H, 6.92; Cl, 10.60. Found: C, 82.55; H, 7.12; Cl, 10.14.

6,6,6-Triphenylhexanenitrile.—Into a flask was placed 3.34 g (10.0 mmol) of 5-chloro-1,1,1-triphenylpentane, 0.90 g (18 mmol) of sodium cyanide, 1.75 g (12 mmol) of sodium iodide, and 250 ml of dimethyl sulfoxide. The flask was stoppered and stirred at room temperature for 12 days. The work-up was like that for 5,5,5-triphenylpentanenitrile. There was obtained 2.95 g (91% yield) of nitrile, mp 84.5–86°. After two recrystallizations from acetone and sublimation *in vacuo*, the product had mp 85.5–86.5°.

Anal. Calcd for $C_{24}H_{23}N$: C, 88.57; H, 7.12; N, 4.30. Found: C, 88.48; H, 7.20; N, 4.34.

6,6,6-Triphenylhexanoic Acid.—A solution of 1.55 g (4.8 mmol) of 6,6,6-triphenylhexanenitrile and 0.91 g of potassium hydroxide in 40 ml of ethylene glycol was heated at reflux for 9 hr. The usual work-up gave 1.50 g (91% yield) of white crystals, mp 140–142°. Two recrystallizations from benzene yielded product, mp 141.5–142.0°. The analytical sample was sublimed twice *in vacuo* (final mp, 141.8–142.7°).

Anal. Calcd for $C_{24}H_{24}O_2$: C, 83.68; H, 7.02. Found: C, 83.60; H, 7.03.

1,1,5-Triphenylpentanol-1.—To the Grignard reagent prepared from 40.2 g (0.238 mol of 4-phenyl-1-chlorobutane and 6.8 g (0.28 g-atom) of magnesium in 130 ml of diethyl ether was added 30.9 g (0.170 mol) of benzophenone in 125 ml of ether. The solution was stirred at reflux for 3 hr and then decomposed with 150 ml of saturated ammonium chloride solution. The solution was extracted with ether; the ether extract was washed with 5% $NaHCO_3$ and dried over anhydrous $MgSO_4$. After removal of ether, the residue was washed with hexane to give 25 g of crude crystals, mp 54–64°. Recrystallization of 14.3 g of this product from ethanol gave 5.7 g, mp 78–86°. Recrystallization further from ligroin (bp 90–120°), with discarding of the first crystals which separated and contained benzpinacol, and then recrystallization from carbon tetrachloride followed by petroleum ether gave 2.2 g of alcohol, mp 84.5–86.0°.

Anal. Calcd for $C_{23}H_{24}O$: C, 87.28; H, 7.65. Found: C, 87.06; H, 7.64.

1,1,5-Triphenylpentane (**11**).—To 2.0 g (6.3 mmol) of 1,1,5-triphenylpentanol-1 in 15 ml of anhydrous methanol was added four drops of concentrated sulfuric acid; after some 15 min the entire mass solidified and was stored overnight at 0°. The precipitate was washed with cold methanol and after drying in a desiccator over KOH amounted to 1.24 g of product: mp 61–63°; nmr (CCl_4) peaks at τ 2.80 and 2.93 (15 H, two peaks in *ca.* 2 : 1 ratio), 7.03 (3 H, singlet, CH_3O), 7.3–9.2 (8 H). Since this ether appears to be unstable on storage, it was used the next day. In the general apparatus for alkali metal reactions was placed 200 ml of THF and 0.52 g (0.013 g-atom) of potassium and the mixture was stirred at reflux for 1 hr. A solution of 1.18 g (3.6 mmol) of the methyl ether in 10 ml of THF was added over a period of 10 min. The solution developed an orange color which

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(58) *Cf.* O. W. Webster and W. H. Sharkey, *J. Org. Chem.*, **27**, 3354 (1962).

(59) We are indebted to the Department of Biochemistry and Nutrition, University of Pittsburgh, Pittsburgh, Pa., for the mass spectral analysis.

(60) We are greatly indebted to Mr. Carver Anthony Hunt for this preparation.

deepened to orange-red. Stirring at reflux was continued for 35 min longer and then methanol (10 ml) was added. Most of the solvent was then removed on a rotating evaporator, water was added, and the mixture was extracted with ether. After removal of ether, the residue was distilled *in vacuo* and purified by chromatography on 100 g of silica gel (E. Merck A.-G., Darmstadt, Germany, No. 7734) with elution by petroleum ether. There was separated 0.60 g of an oil which solidified on storage at 0°: mp 37.0–38.0; nmr (CCl$_4$) peaks at τ 2.89 and 2.93 (15 H, two peaks in *ca.* 2:1 ratio), 6.20 (1 H, triplet), 7.49 (2 H), 7.7–9.0 (complex multiplet). The analytical sample was redistilled *in vacuo.*

Anal. Calcd for C$_{23}$H$_{24}$: C, 91.95; H, 8.05. Found: C, 91.83; H, 8.08.

Reaction of 5-Chloro-1,1,1-triphenylpentane with Potassium.—In the usual apparatus was placed 230 ml of THF and 2.10 g (0.0536 g-atom) of potassium; the mixture was heated at reflux with vigorous stirring for 30 min. A solution of 5.98 g (17.8 mmol) of 5-chloro-1,1,1-triphenylpentane in 40 ml of THF was then added dropwise over a period of 20 min. The solution was allowed to cool to room temperature over a period of 20 min with continued stirring before carbonation of the deep red colored solution. The usual work-up gave 0.64 g of acids and 4.69 g of neutral material. Analysis[57] of the methyl esters of the acids by glpc at 295° showed the presence of the following substances, listed as area per cent (retention time relative to methyl 6,6,6-triphenylhexanoate): 1 (0.29), 6 (0.32), 67 (0.35), 8 (0.48), 2 (0.67), 3 (0.77), and 3 (1.1). Analysis of the neutral material by glpc at 250° gave the products, listed as area per cent (relative retention time): 1.1 (0.29), 18 (0.39), 7.5 (0.63), 11 (0.73), 60 (1.00, 1,1,1-triphenylpentane, **12**), 1.7 (1.4). A portion (2.24 g) of the neutral material was chromatographed on 180 g of neutral aluminum oxide (Merck, reagent grade) with elution by petroleum ether–benzene; there was separated 0.41 g of product, mp 59–60°, and another 0.26 g, mp 56–60°. This product was identified as **12** on the basis of melting point and mixture melting point comparisons with the hydrocarbon prepared by hydrolysis of the Grignard reagent from 5-chloro-1,1,1-triphenylpentane.

Reaction of 5-Chloro-1,1,1-triphenylpentane with Cs–K Alloy.—In the usual apparatus were placed 4.20 g (0.0316 g-atom) of cesium and 1.14 g (0.0292 g-atom) of potassium in 250 ml of THF. The solution was stirred at reflux temperature for 30 min and then cooled to −35 ± 2°. To the deep blue solution was added 5-chloro-1,1,1-triphenylpentane (4.53 g, 13.1 mmol) in 30 ml of THF over a period of 30 min; the solution developed a deep red-brown color like that of bromine and was stirred at −35° for an additional 30 min. Some 60% of the solution was then forced onto solid carbon dioxide and to the remainder in the flask was added 10 ml of methanol over a period of several minutes. After the usual work-up the carbonated portion yielded 2.2 g of acids and 0.16 g of neutral material. According to glpc analysis[57] of the methyl esters, the acids consisted of some 14 components, seven of which, constituting 90 area per cent of the total, were of a molecular weight near that of the starting chloride, while the remainder were cleavage products. The neutral material from the carbonation consisted of some 83% of **12** containing a small quantity, evidently, of **9b**. The product from the decomposition with methanol amounted to 1.7 g. According to glpc at 245° this consisted primarily of four components, listed as area per cent (retention time in minutes, identity): 30 (9.2, **12**), 19 (9.8, **9b**), 35 (11.4, **8b**), 6.7 (13.2, **11**), along with some 9% of cleavage products of which that of longest retention time (4.6 min) was evidently triphenylmethane (*ca.* 1%). The nmr spectrum of this mixture of hydrocarbons (in CCl$_4$) had characteristic absorption (complex multiplets) at τ 2.87 (aromatic H), 4.28 (vinyl H), and 7.28 (allylic H) in a ratio of 2.2:1.0:1.0; the high ratio of vinyl to aromatic hydrogen suggests that the fluorene **9b**, found on glpc analysis, was present in the original reaction mixture as the corresponding tetrahydrofluorene **8b**. We have found that, whereas crude **8b** can sometimes be distilled at 0.1 mm at a bath temperature of 110° without dehydrogenation, yet on standing for 5 days at room temperature in an open evaporating dish some half of the tetrahydrofluorene was dehydrogenated (oxidized?) to **9b**; after 4 more days this dehydrogenation was nearly complete. A portion of the product from decomposition with methanol was subjected to chromatographic separation on silica gel (elution with pentane–benzene); a fraction, which according to glpc was a 50:50 mixture of **12** and **9b**, absorbed at $\lambda_{\max}^{\mathrm{EtOH}}$ 266, 294, and 306 nm, just as found, but at essentially half the intensity, for **9a**.

A repetition of this run, but after addition of 5-chloro-1,1,1-triphenylpentane with stirring for 1 hr at 0° (rather than 30 min at −35°), gave upon carbonation a 39:61 (by weight) of neutral products to acids. Some 90% of both the acids and neutral products were products in which one or more of the C–C bonds of the original 1,1,1-triphenylpentane derivative had been cleaved.

Reaction of 5-Chloro-1,1,1-triphenylpentane with Cs–K–Na Alloy.—In the usual apparatus was placed 4.83 g (0.0363 g-atom) of cesium, 1.59 g (0.041 g-atom) of potassium, and 0.20 g (0.0087 g-atom) of sodium in 250 ml of THF. The mixture was stirred vigorously at reflux for 1 hr, then cooled to −68 ± 2°, and held at this temperature while 4.48 g (14.4 mmol) of 5-chloro-1,1,1-triphenylpentane in 30 ml of THF was added over a 30-min period. Stirring was continued for an additional 30 min; then 10% of the brown-red solution was forced onto solid carbon dioxide; and to the remainde rin the Morton flask was added rapidly, through a dropping funnel, 250 ml of methanol. The usual work-up of the carbonated portion gave, after esterification with diazomethane, 0.50 g of methyl esters and 0.08 g of neutral material. Analysis[57] of these by glpc at 255° gave products listed as area per cent (retention time in minutes, identity): for the esters, 6 (3.6 and 3.9), 43 (6.4), 17 (7.4), 17 (11.3), and 17 (14.2); for the neutral material, >90 (6.3, **12**), trace (6.9, **9b**). The neutral product from decomposition with methanol amounted to 3.71 g; analysis by glpc at 255° gave (similarly listed): ~3 (6.3, **12**), 17 (6.9, **9b**), 75 (7.8, **8b**), and 5 (9.0, **11**). An nmr analysis (CCl$_4$) upon the crude product from methanol decomposition gave characteristic peaks at τ 2.84 (aromatic H), 4.25 (vinyl H), and 7.25 (allylic H) in a ratio of 1.10:1.00:0.94. The glpc analysis, however, leads to a ratio of aromatic to vinyl hydrogens of 1.59; evidently all of the fluorene **9b** is contained in the original product as the tetrahydrofluorene **8b**, but the latter dehydrogenates in part under glpc conditions. If this assumption is correct, the predicted ratio of aromatic to vinyl hydrogen is 1.05 (essentially that found). Storage of the CCl$_4$ solution used for nmr analysis for 53 days at 5°, followed by repeated nmr analysis, gave the original peaks now in a ratio of 1.80:1.00:1.07 for aromatic, vinyl, and allylic hydrogen, respectively. The neutral product (3.7 g) was chromatographed on 300 g of neutral alumina (Merck) with elution by petroleum ether–benzene; there was obtained some 1.5 g of a mixture of the fluorene and the tetrahydrofluorene. A midcut of this (0.41 g) was intimately mixed with 0.10 g of 10% Pd on carbon catalyst, put into a sublimation apparatus, and heated at 90–110° at 0.01 mm for 8 hr. There was sublimed 0.28 g of product, mp 88–90°; recrystallization from ethanol gave 0.12 g, which after vacuum sublimation had mp 97.5–98.0°. This compound was found to be identical with an authentic sample of 9-*n*-butyl-9-phenylfluorene according to mixture melting point and ir spectral comparisons; the uv spectrum was identical with that of **9a**.

In four runs similar to that described above (in one of these the reaction mixture was jetted into 1200 ml of ice water rather than decomposed with methanol) the average yield (glpc) of **11** was 6 ± 3%, that of **12** was 3 ± 3%, and the remainder was, according to nmr analysis, primarily **8b**, although glpc analysis again showed variable quantities of **9b**. The yield of hydrocarbons was quantitative in these runs. Distillation at a bath temperature of 100° and a pressure of 0.1 mm showed that at least 84% of the hydrocarbon was volatile; this distillation sometimes, but not always, converted tetrahydrofluorene partially to fluorene according to nmr analysis. For complete conversion of tetrahydrofluorene to fluorene, the best procedure found was to heat (115°) with and ultimately distil *in vacuo* from 5% Pd/C catalyst (see above); this procedure converted some 80% of the volatile hydrocarbon mixture to **9b** according to nmr analysis (based on the characteristic peaks of the fluorene at τ 2.31 and 2.38 and the common peak for all aromatics near 2.9). The identity of the 1,1,5-triphenylpentane in these runs rests on its identity in retention time with an authentic sample in glpc analysis on two columns (silicone gum rubber on Chromosorb G and Apiezon L on Chromosorb P).

In a further run 5-chloro-1,1,1-triphenylpentane (3.00 g, 9.0 mmol) was allowed to react, exactly according to the previous procedure, with 1.5 g (0.019 ± 0.002 g-atom) of Cs–K–Na alloy. The reaction was terminated by forcing the reaction mixture into a large excess of ice water. After extraction with ether, the ethereal extract was dried over anhydrous MgSO$_4$ and then P$_2$O$_5$. Analysis by glpc indicated the presence of **12** (68%), **9b** (22%), **11** (3%), and 5-chloro-1,1,1-triphenylpentane (6%). After distillation *in vacuo*, analysis by nmr indicated the presence of 6% **8b** and 13% **9b** in the distillate. Chromatography of 0.97 g of the distillate on 150 g of neutral alumina (Merck) with elution by petroleum ether–benzene gave, after repeated chromatography of mixtures obtained from the first chromatograph, 0.41 g of **12** (mp 58–60°), whose identity was established by mixture melting point, ir, and nmr spectral comparisons with an authentic sample, and 0.10 g of **9b** (95% pure by glpc), whose identity was confirmed by ir spectral comparison with an authentic sample.

Reaction of 1,1,1-Triphenylpentane with Cs–K–Na Alloy.—To 1.47 g (0.0194 g-atom) of CS–K–Na alloy in 250 ml of THF at −60 ± 3° was added over a 3-min period 0.281 g (0.935 mmol) of 1,1,1-triphenylpentane in 5 ml of THF; vigorous stirring was continued for 57 min more before decomposition by rapid addition of a large excess of methanol. The usual work-up gave 0.32 g of crude product, which according to glpc analysis[57] contained >90% of a mixture of **9b** and **8b** (repetitive analyses gave variable ratios of these) and traces of **12** and a cleavage product (retention time relative to **9b** 0.30 at 260°). The nmr spectrum (CCl_4) had complex multiplets at τ 2.84, 4.25, and 7.25 in a ratio of 0.91:1.0:1.1; the ratio of aromatic to vinyl hydrogen here is in agreement with a composition of 97% of **8b** and 3% of **12**. The product was mixed with 0.16 g of 5% Pd on carbon and subjected to slow distillation in a sublimation apparatus at 0.05 mm and a bath temperature of 115° for 4 hr. The nmr spectrum of the distillate showed disappearance of all vinylic and allylic hydrogens and appearance of characteristic complex multiplets at τ 2.31 and 2.38 and at 2.86 and 2.91 in a ratio of 13:94, as expected for a mixture containing 89% of **9b** and 11% of **12**.

Reaction of 1,1,1-Triphenylethane with Cs–K–Na Alloy. A. Preparation of 9-Methyl-9-phenyl-2,4a,4b,7-tetrahydrofluorene (8c).—The alloy (2.00 ml, 38.8 mg-atoms) was vigorously stirred in the usual apparatus with 240 ml of THF at reflux for 1 hr. The solution was cooled to −70° (deep blue solution, doubtlessly containing some dissolved alkali metal) and a solution of 1,1,1-triphenylethane (0.61 g, 2.37 mmol) in 10 ml of THF was added dropwise with vigorous stirring over a period of 3 min. The solution readily acquired a red color and after 1 hr of stirring at −70° the deep brown-red solution was jetted into a 650-ml slush of ice and water. The mixture was concentrated to 200 ml on a rotating evaporator, chilled in an ice bath, and filtered to yield 240 mg of crystals, mp 94–96°. Analysis of these crystals by glpc[61] on a 6 ft × $^1/_8$ in. column packed with 5% SE-30 on 100/120 mesh Aeropak-30 at 180° indicated that they consisted of about 97% of a compound identified as **8c** and 3% of a compound tentatively identified as 9-methyl-9(2,5-dihydrophenyl)-2,4a,4b,-7-tetrahydrofluorene. In another experiment extraction of the concentrated aqueous reaction mixture with ether gave a product which consisted of >90% of **8c** according to analsysis by glpc. Recrystallization from ethyl alcohol gave 165 mg of white crystals, mp 96.5–97.5°.

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.09, 91.93; H, 7.94, 7.87.

This compound exhibited the following properties: nmr (CS_2) at 60 MHz τ 2.85 (5.0 H, multiplet, C_6H_5–), 4.25 and 4.37 (6.1 H, complex multiplet, vinylic H), 7.25 (6.2 H, broad multiplet, allylic H), 8.67 (3.0 H, singlet, CH_3–); at 100 MHz vinylic H τ 4.26 and 4.37 (6.0 H), allylic H 7.09 (2.0 H) and 7.29 (4.2 H); $\lambda_{\max}^{\text{EtOH}}$ 247 nm (ϵ 130), 253 (180), 258 (230), 264 (180), 268 (140); ir (KBr pellet) 3010 (m), 2955 (w), 2940 (w), 2900 (w), 2860 (m), 2825 (m), 2795 (m), 1630 (w), 1595 (w), 1485 (m), 1440 (m), 1360 cm^{-1} (m); mass spectrum, molecular ion M^+ 260, fragments *m/e* 245 ($M - CH_3$), 182 ($M - C_6H_5 - H$), 181 ($M - C_6H_5 - 2\,H$), 167 ($M - C_6H_5 - CH_3 - H$), 165 ($M - C_6H_5 - CH_3 - 3\,H$).

B. Preparation of 9-Methyl-9-phenyl-2,4a,4b,7-tetrahydrofluorene-*2,7-d*$_2$.—1,1,1-Triphenylethane (600 mg, 2.32 mmol) was again allowed to react with 2.0 ml of Cs–K–Na alloy according to the previous procedure. This time the red solution was titrated at −70° with a 1.2 *M* solution of D_2O (98.7 atom % D) in THF until the color changed from red to blue-green (9.9 mmol of D_2O was consumed; evidently there was much direct reaction of alloy with D_2O). The reaction mixture was jetted into 650 ml of ice water and then concentrated to 200 ml on a rotating evaporator. The mixture was extracted with three 70-ml portions of ether and the ether extract was dried over anhydrous $MgSO_4$. The ethereal solution upon evaporation yielded a light yellow, crystalline residue which upon recrystallization from ethyl alcohol gave 430 mg (71% yield) of crystals, mp 96–97.5°. This compound gave nmr absorption in CS_2 at 60 MHz at τ 2.85 (5.0 H), 4.25 (6.2 H), 7.12 and 7.30 (4.5 H), 8.67 (3.0 H); at 100 MHz the vinylic protons were at τ 4.26 and 4.37 (6.0 H) and the allylic protons at 7.09 (1.9 H) and 7.35 (2.5 H).

C. Dehydrogenation of 9-Methyl-9-phenyl-2,4a,4b,7-tetrahydrofluorene.—A carbon disulfide solution of a 100-mg portion of the above 9-methyl-9-phenyl-2,4a,4b,7-tetrahydrofluorene-*2,7-d*$_2$ was intimately mixed with 100 mg of 5% palladium on carbon catalyst (from Englehard Industries), the solvent was removed *in vacuo*, and the mixture was heated for 2.5 hr at 100–120° under a nitrogen atmosphere. The product was then distilled from the catalyst at 0.1 mm with a bath temperature of 100°. This oily product, according to analysis by glpc, consisted of about 95% **9c** and 5% 1,1,1-triphenylethane. The oil was recrystallized from ethyl alcohol to give crystals of mp 79–81° which when mixed with an authentic sample of **9c** (mp 85–87°) melted at 80–83.5°. The infrared spectrum of this product was essentially identical with that of authentic **9c**.

Repetition of this dehydrogenation procedure with a protium sample of **8c** (mp 96.5–97.5°) but with a time of only 2 hr gave by glpc analysis a product which consisted of 68% **9c**, 6% 1,1,1-triphenylethane, and the remainder starting material. The presence of **9c** in one such dehydrogenation mixture was further confirmed by the uv spectrum of the mixture, which showed characteristic maxima at 265, 293, and 304 mμ as found for authentic **9c**.

As a test of the present dehydrogenation procedure a sample of 1,1,1-triphenylethane (0.30 g) in carbon disulfide was mixed with 0.30 g of the 5% palladium on carbon catalyst, the solvent was removed *in vacuo*, and the mixture was held at 100–110° under a nitrogen atmosphere for 3 hr. The product was separated by sublimation at 0.1 mm and was shown by glpc analysis to consist of only 1,1,1-triphenylethane. This hydrocarbon is, therefore, not dehydrogenated to **9c** under the present mild conditions.

D. Titration with *tert*-Butyl Alcohol.—1,1,1-Triphenylethane (600 mg, 2.32 mmol) was allowed to react with 2.0 ml of Cs–K–Na alloy in 200 ml of tetrahydrofuran at −70° for 1 hr according to the procedure given previously. The deep red solution, while being stirred at −70°, was then rapidly titrated with a 0.906 *M* solution of *tert*-butyl alcohol in tetrahydrofuran to an end point changing from red to blue-green. This required 4.98 ml (4.52 mmol) of *tert*-butyl alcohol (1.95 mol of alcohol per mol of 1,1,1-triphenylethane). In a repetition of this experiment 1.98 mol of *tert*-butyl alcohol was required per mol of 1,1,1-triphenylethane. The reaction mixture was immediately jetted into ice water. Analysis of the product by glpc showed the presence of about 91% **8c** and 9% of a material of slightly longer retention time believed to be 9-methyl-9(2,5-dihydrophenyl)-2,4a,4b,7-tetrahydrofluorene. Recrystallization from ethyl alcohol gave a product, mp 95–97°, whose composition (*via* glpc analysis) was, however, the same as before recrystallization.

Repetition of the experiment with 0.300 g (1.16 mmol) of 1,1,1-triphenylethane and 1.00 ml (19.4 mg-atoms) of Cs–K–Na alloy but with a slow addition of 1.77 g (24 mmol) or *tert*-butyl alcohol in 10 ml of tetrahydrofuran over a period of 45 min to the initial deep red solution, followed by jetting into ice water, gave a product which by glpc analysis consisted of about 67% of **8c** and 33% of 9-methyl-9(2,5-dihydrophenyl)-2,4a,4b,7-tetrahydrofluorene. The nmr spectrum in CS_2 showed aromatic (τ 2.8), vinylic (4.15 and 4.25–4.60), and allylic (7.2–7.4) hydrogen peaks in a ratio of 1.0:1.9:2.0. A 2:1 mixture of the above tetrahydrofluorene and hexahydrofluorene should give a theoretical ratio of 1.0:2.1:2.2 for these protons. Dehydrogenation of this product with 5% palladium on carbon at 100–110° for 3 hr gave a mixture which consisted of 45% of 1,1,1-triphenylethane and 55% of 9-methyl-9-phenylfluorene (glpc analysis). Evidently the hexahydrofluorene gives largely 1,1,1-triphenylethane under the present conditions of dehydrogenation.

Reaction of 2-Chloro-1,1,1-triphenylethane with Cs–K–Na Alloy.—In the usual apparatus was placed 2.0 ml (0.036 g-atom) of Cs–K–Na alloy and 200 ml of THF. The mixture was stirred at reflux for 1 hr and then cooled to −65°. A solution of 4.39 g (15.0 mmol) of 2-chloro-1,1,1-triphenylethane[31] in 25 ml of THF was added dropwise over a period of 30 min and stirring was continued for 7 min more at −65° before carbonation of the deep brown solution. Quantitative glpc analysis of the product gave 35% yield of 2,2,3-triphenylpropanoic acid, 2% yield of a mixture of some 10 volatile (as methyl esters) acids, some 4% of nonvolatile acids, 4.6% of 1,1,1-triphenylethane, 42% of un-

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(61) At the flow rate used under these conditions the following retention times in minutes were observed: 1,1,1-triphenylethane, 7.2; 9-methyl-9-phenylfluorene, 8.5; 9-methyl-9-phenyl-2,4a,4b,7-tetrahydrofluorene, 9.6; and the compound tentatively identified as 9-methyl-9(2,5-dihydrophenyl)-2,4a,4b,7-tetrahydrofluorene, 10.8.

reacted 2-chloro-1,1,1-triphenylethane, and nonvolatile neutral products. During the course of work-up of the reaction products a crystalline material, mp 151.0–152.5° (from acetone), was isolated.

Anal. Calcd for 1:1 compound of $C_{20}H_{17}Cl$ and $C_{21}H_{18}O_2$: C, 82.74; H, 5.93; Cl, 5.96, average mol wt, 297.5 Found: C, 82.59; H, 6.14; Cl, 5.32; mol wt (acetone), 289.

The above analysis is in essential agreement with a 1:1 compound of 2-chloro-1,1,1-triphenylethane[31] (mp 101.0–101.8°) and 2,2,3-triphenylpropanoic acid[31] (mp 132.0–133.0°). This postulated composition was qualitatively confirmed[62] by glpc, nmr, uv, and mass spectral analyses.

Registry No.—**8c**, 33884-94-5; **9a**, 33884-95-6; **11**, 33884-96-7; 4-chloro-1,1,1-triphenylbutane, 33884-97-8; 5-chloro-1,1,1-triphenylpentane, 33884-98-9; 1,1,1-triphenylethane, 5271-39-6; lithium, 7439-93-2; potassium, 7440-09-7; cesium, 7440-46-2; sodium, 7440-23-5; 1,1,1-triphenylpentane, 13630-39-2; 2-chloro-1,1,1-triphenylethane, 33885-01-7; 5,5,5-triphenylpentanenitrile, 33885-02-8; 5,5,5-triphenylpentanoic acid, 33885-03-9; methyl 5,5,5-triphenylpentanoate, 33885-04-0; 2,2,5-triphenylpentanoic acid, 33885-05-1; 1,1,4-triphenylbutane, 33885-06-2; 6,6,6-triphenylhexanenitrile, 33885-07-3; 6,6,6-triphenylhexanoic acid, 33885-08-4; 1,1,5-triphenylpentanol-1, 33885-09-5; 9-methyl-9-phenyl-2,4a,4b,7-tetrahydrofluorene-2,7-d_2, 33885-10-8; 1:1 compound of 2-chloro-1,1,1-triphenylethane and 2,2,3-triphenylpropanoic acid, 33885-11-9.

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[62] We are indebted to Mr. Thomas H. Longfield for this identification.

The Influence of Chelation on the Grignard Reactions of Some β-Hydroxy Ketones[1]

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β-Hydroxy ketones, having one of the oxygen-containing functions situated on a five- or six-membered carbon ring and the other on a side chain, undergo highly stereoselective Grignard reactions except when chelation is sterically inhibited. Thus, 2-α-hydroxyalkyl- (or 2-hydroxyaryl-) cyclopentanones and cyclohexanones yield pure diols. *cis*-2-Acylcyclopentanols also undergo stereospecific additions whereas similar reactions of *trans*-acylcyclopentanols resulted in poor yields and low stereoselectivity. By contrast, *trans*-2-acylcyclohexanols reacted stereospecifically and in high yields with Grignard reagents. The results are correlated with the readiness of reactants to form chelates.

The preferential formation of a major diastereomer in Grignard reactions of open-chain α-hydroxy ketones, in which the carbonyl group is adjacent to a chiral center, has been explained by the intermediacy of a chelate.[2] Similar reactions of β-hydroxy ketones were found to be less stereoselective and the results were explained by an "open-chain" instead of a "cyclic" transition state.[3]

Grignard reactions of β-hydroxy ketones in which one of the oxygen-containing functions is situated on a five- or six-membered carbon ring constitute the present study. The purpose of this investigation was to correlate the results of reactions (expressed in stereoselectivity and yields) with the stereochemical readiness of the organic substrates to form chelates with the metallic ion.

Results

Stereoisomeric *cis*- and *trans*-2-hydroxycyclopentanecarboxylic ethyl esters were used for the synthesis of several β-hydroxy ketones in the cyclopentane series. The chromatographic separation into cis (**1a**) and trans (**1b**) esters was achieved and therefore the previously used[4] procedure *via* separation of their 3,5-dinitrobenzoates was unnecessary. The difference between the chemical shifts of the methylene quartet of the ester function in the nmr spectrum proved to be a better criterion for the determination of isomeric purity than the previous assignment based on the band width of the proton adjacent to the hydroxyl group.[4b] Ketols **2** and **3** (Table I) were prepared from *cis*-hydroxy ester **1a** by the corresponding Grignard reactions followed by Jones oxidation. Six-membered homologs **7** and **8** were preferentially prepared from *trans*-2-hydroxycyclohexanecarboxylic esters by the same sequence. 2-Benzhydrylcyclopentanone **6** was obtained by dehydration of hydroxy ketone **2** to 2-benzylidenecyclopentanone and subsequent hydrogenation. *cis*- and *trans*-2-benzoyl- and -2-acetylcyclopentanols (**20a**, **20b**, **21a**, and **21b**, Table II) were prepared from *cis*-2-hydroxycyclopentanenitrile and MeMgBr or PhMgBr, respectively, followed by the hydrolysis of formed imines. Equilibration occurred during these reactions and the mixture of cis and trans ketols was separated by chromatography. Compounds **20a** and **20b** were also obtained from the reaction of *trans*-hydroxy ester **1b** with PhMgBr (see Experimental Section). Stereochemical assignments in this series were based on the differences in hydroxyl stretching frequencies in the infrared spectra: unlike *cis*-2-acylcyclopentanols, the trans isomers do not show the presence of intramolecular hydrogen bonding (Table III). Independent synthesis of diols **24a** and **27a** from *cis*-hydroxy ester **1a** served as an additional proof for the cis configuration of compounds **20a** and **21a**.

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