as methyl groups are added and is more prone to undergo the 1,1-cycloaddition reaction. This is exactly what is observed. Placing electron withdrawing groups at C-3 (i.e., CF_3, H, etc.) will favor linearization of the nitrile ylide. As the dipole becomes less bent, the C_1N bond shortens and the NC_3 lengthens and the system prefers to undergo 1,3-dipolar cycloaddition. More recent calculations by Houk and Gandour[17] show that
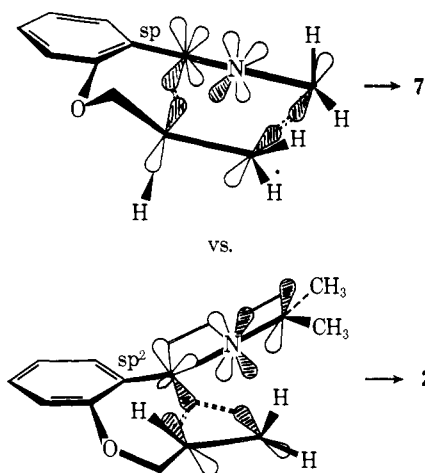
introduction of a phenyl or vinyl group at C_1 flattens the dipole considerably so that it is much more sensitive to C-3 substitution than the unsubstituted case. Thus, when the energy difference between the nonplanar bent and linear forms is small, substituent effects can play an extremely important role in determining the course of the intramolecular cycloaddition reactions of nitrile ylides.

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(9) Compound **5:** IR (neat) 6.05 μ; UV (methanol) 260 nm (ϵ 35 200); NMR (100 MHz, $CDCl_3$) τ 8.60 (ddd, 1 H, J = 12.0, 10.0, and 10.0 Hz), 7.20 (ddd, 1 H, J = 12.0, 6.0, and 6.0 Hz), 6.60 (m, 1 H), 6.08 (dd, 1 H, J = 12.0 and 10.5 Hz), 5.28 (dd, 1 H, J = 10.5 and 6.0 Hz), 4.80 (ddd, 1 H, J = 10.0, 6.0, and 2.0 Hz), 1.68–3.02 (m, 8 H).
(10) Compound **7:** IR (neat) 6.05 μ; m/e 173 (M^+), 145, 119, 91, and 77; NMR (100 MHz, $CDCl_3$) τ 8.48 (dddd, 1 H, J = 12.0, 10.0, 10.0, and 9.0 Hz), 7.78 (ddd, 1 H, J = 12.0, 8.0, and 7.0 Hz), 6.80 (m, 1 H), 6.24 (dddd, 1 H, J = 16.0, 10.0, 8.0, and 2.0 Hz), 619 (dd, 1 H, J = 13.0 and 10.0 Hz), 5.80 (ddd, 1 H, J = 16.0, 9.0, and 2.0 Hz), 5.38 (dd, 1 H, J = 10.0 and 6.0 Hz), 2.08–3.16 (m, 4 H).
(11) Compound **10,** mp 60–61 °C; NMR (100 MHz, $CDCl_3$) τ 8.62 (d, 3 H, J = 7.0 Hz), 8.30 (m, 1 H), 7.76 (pent., 1 H, 6.0 Hz), 6.80 (m, 1 H), 6.26 (dd, 1 H, J = 12.0 and 10.0 Hz), 6.0 (1 H, m), 5.40 (dd, 1 H, J = 10.0 and 6.0 Hz), and 2.1–3.3 (m, 4 H).
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(14) Compound **14;** NMR (100 MHz, $CDCl_3$) τ 8.12 (dd, 1 H, J = 14.0 and 9.0 Hz), 7.36 (dd, 1 H, J = 14.0 and 8.0 Hz), 6.52 (dddd, 1 H, J = 12.5, 9.0, 8.0, and 5.5 Hz), 6.08 (dd, 1 H, J = 12.5 and 9.5 Hz), 5.37 (dd, 1 H, J = 9.5 and 5.5 Hz), 2.6–3.28 (m, 3 H), and 2.0–2.20 (m, 1 H).
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Carbanions. 19. Reactions of Cesium or Cesium–Potassium–Sodium Alloy with Benzene and Toluene

Sir:

1,1,1-Triphenylethane has been recently reported[1] to react with Cs–K–Na alloy of eutectic composition[2] at −70 °C in tetrahydrofuran (THF) to give an insoluble red organoalkali compound (**2**) which upon protonation gives 9-methyl-9-phenyl-2,4a,4b,7-tetrahydrofluorene (**3**). The reaction may be explained by Scheme I. The alloy has been now analyzed[3] before and after reaction[4] at −50 °C; the change in composition of the alloy and the number of hydrogen atoms added to the starting 1,1,1-triphenylethane are in agreement with **2** being formulated as a dicesium compound. This reaction of 1,1,1-triphenylethane caused us to wonder if benzene would give a similar reaction.

Hackspill[5] in 1912 reported that benzene reacts with cesium at 28 °C to give a black solid containing cesium in an amount near that expected for phenylcesium. He accordingly suggested that the substance was phenylcesium although it was said to be formed without evolution of hydrogen and gave biphenyl and hydrogen[6] upon hydrolysis. Hackspill[6] later questioned his assigned structure and noted that the product merited further study. Subsequently de Postis[7] came to the conclusion that the black compound had the empirical formula of $C_6H_6Cs_6$ and was a loose addition compound of benzene with cesium since it was attacked by water with evolution of hydrogen, did not react with gaseous CO_2, and failed to give "normal" alkylation products with alkyl halides. Clusius and Mollet[8] found that cesium reacts with benzene at 50–60 °C with steady evolution of hydrogen and that the black product reacts with water to give biphenyl and phenol.

We wish to report that reaction of excess benzene with finely divided cesium in THF at −70 °C gives a black precipitate which has a broad-line ESR spectrum indicative of a high yield of a radical anion in a doublet state. Quenching of the fine

Scheme I
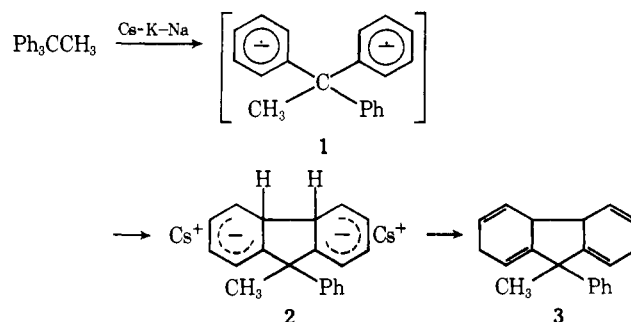
Scheme II
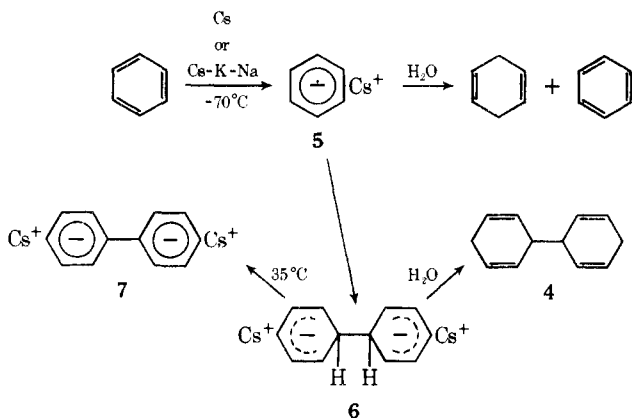
black precipitate after a reaction time of 1.5 h by forcing the suspension into ice water gave the products (in yields expressed as percent of starting cesium converted into the product) 1,4-dihydrobenzene (70%), cyclohexene (3%), and compound 4 (6%). With continued stirring at −70 °C for 4 h the yield of 4 increased to 12% with corresponding depletion in the quantity of 1,4-dihydrobenzene; with increase in temperature finally to 5 °C with stirring for some 2 h the yield of 4 was 39% and that of dihydrobenzene 36%. Compound 4 was a colorless oil of analytical and spectral properties[9] (^{1}H NMR (neat) δ 5.63 (8 H, m), 2.62 (6 H, m); mass spectrum, M+ m/e 158) in agreement with the structure of 1,1′,4,4′-tetrahydrobiphenyl. Further confirmation of this structure was by dehydrogenation of 4 over 5% Pd/C at 160 °C to give biphenyl. The thermal changes which brought about an increased yield of 4 were marked by a gradual change in the appearance of the reaction mixture from black to yellow-green (yellow precipitate in a pale blue solution) and a disappearance of the anion radical according to ESR measurements. The final yield of dihydrobenzene was frequently negligible but the yield of 4 did not, in our experience, exceed 40% (based on cesium). When the yellow precipitate was decomposed with D₂O, the product 4 had only four rather than six allylic hydrogens in its ^{1}H NMR spectrum and is assigned the structure of 1,1′-dihydro-4,4′-dideuteriobiphenyl.

In a more effective procedure, reaction of 7.36 g of cesium alloy of composition (atom percent) 42.1% Cs, 48.9% K, and 9.0% Na with 13.41 mmol of benzene in THF gave after 2 h of vigorous stirring at −43 ± 2 °C an alloy of composition 33.9% Cs, 55.7% K, and 10.4% Na. Jetting of the green organic phase containing a fine suspension of yellow precipitate into ice water yielded according to a quantitative GLPC analysis 1.20 mmol of 1,4-dihydrobenzene, 5.08 mmol of 4, and 1.96 mmol of benzene. On the assumption that for each proton appearing in the organic products beyond that in benzene, one cesium atom is consumed, the calculated final composition of the cesium alloy would be 33.3% Cs, 55.4% K, and 10.3% Na. The calculated result agrees closely with that found. In this experiment the ratio of cesium atoms extracted from the liquid alloy to molecules of benzene initially present was 0.88 to 1, while the ratio of hydrogen atoms added after quenching with water to initial molecules of benzene was 0.94 to 1; thus only a small amount of additional reduction of benzene by the alloy occurs during quenching.

Our experiments with benzene are in accord with Scheme II. Reaction with cesium, or Cs–K–Na alloy, at −70 °C gives initially a black precipitate which evidently is cesium benzenide 5 since hydrolysis gives primarily 1,4-dihydrobenzene (and benzene). Warming of the black precipitate to as high as 5 °C or better carrying out the reaction with excess Cs–K–Na alloy at about −43 °C gives a yellow precipitate 6 which upon protonation gives 1,1′,4,4′-tetrahydrobiphenyl 4 (in 76% yield with

the alloy). Warming of 6 to 35 °C gives finally a black precipitate 7 which is dicesium biphenylide according to its reaction with iodine which gives biphenyl or with water which gives a mixture of hydrocarbons like that obtained from a sample[10] of dicesium biphenylide prepared by reaction of biphenyl with excess cesium in THF. Dicesium biphenylide is of the same empirical composition as phenylcesium; evidently the compound prepared by Hackspill[5] was largely dicesium biphenylide, likely containing some of its precursors 5 and 6.

Toluene has been reported to react with cesium[7,11] in the vicinity of its melting point (28.6 °C) or with cesium in THF[12] at 20 °C with evolution of hydrogen to give benzylcesium. We find that at −45 ± 5 °C in THF toluene (14.79 mmol) reacts upon vigorous stirring with 7.77 g of cesium alloy of composition 48.3% Cs, 44.5% K, and 7.2% Na to give a black precipitate which after some 45 min was converted into a yellow precipitate in a blue solution (overall color, green). After a reaction time of 4 h, the liquid alloy had a composition of 37.8% Cs, 53.2% K, 9.0% Na. The calculated composition based upon extraction from the alloy of 1 g-atom of cesium per mole of toluene is 38.1% Cs, 53.3% K, and 8.6% Na. The data agree well with cesium being the alkali metal preponderantly reacting with toluene and can be calculated to show 1.03 atoms of cesium reacting per molecule of toluene present. Jetting the organic phase containing the yellow precipitate into ice water gave 4.7 mmol of 2,5-dihydrotoluene, 3.2 mmol of toluene, and 3.5 mmol of tetrahydrodimethylbiphenyls. The average number of hydrogen atoms appearing in the organic product beyond that in toluene is 1.11 atoms per molecule of toluene; hence again a little additional reduction occurs during quenching.

The reaction of toluene with cesium may be explained by a process analogous to that shown for benzene in Scheme II. Of particular interest is the composition of the tetrahydrodimethylbiphenyl fraction. The elemental analysis and spectral properties (^{1}H NMR (CCl₄) δ 1.66 (6 H, s), 2.53 (6 H, m), 5.2–5.9 (6 H, m); ^{13}C NMR (CDCl₃) with all absorptions at about equal intensities δ 131.5 (s), 126.6 (d of d), 124.4 (d), 121.6 (d of d), 41.6 (d), 31.4 (t), 23.2 (q)) are in agreement with this product having predominantly structure 9, containing
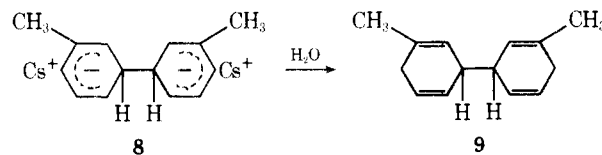
evidently about a one to one mixture of disastereomers (as implied by the splitting of the δ 126.6 and 121.6 peaks in the ^{13}C NMR spectrum). Further confirmation of structure 9 was supplied by dehydrogenation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in benzene at reflux; the product consisted of 99.1% 3,3′-dimethylbiphenyl along with 0.2 and 0.7% of 2,2′- and 2,3′-dimethylbiphenyl, respectively. The high regioselectivity in dimerization may be explained by the charge distribution in the toluene radical anion (deduced from analysis of its ESR spectrum[13]) wherein the odd electron is located primarily on the carbons ortho and meta to the methyl group. If these carbons bearing the highest density of the odd electron are the only carbons which couple, then the reaction would lead solely to the 2,2′, 2,3′, and 3,3′ isomers as found. That the 3,3′ isomer is most favored is reasonable since only in this isomer are both of the methyl groups in the intermediate 8 located at nodal carbons in the highest filled molecular orbitals of the pentadienyl anion systems of 8.

The formation of high yields of radical anions and derived products from reaction of benzene and toluene with cesium or cesium alloys is perhaps unexpected.[1,14] Thus benzene in 2:1

Communications to the Editor

by volume of THF to 1,2-dimethoxyethane with Na–K alloy at −83 °C is converted[15] at equilibrium to radical anion only to the extent of about 0.1%; toluene under similar conditions forms a radical anion to an even lesser extent.[16] The present results can be rationalized on the basis of the superior reducing power in THF of cesium and cesium alloys over the other alkali metals or alloys. The reaction is evidently promoted by strong electrostatic interaction between cesium cations and benzene or toluene radical anions and the association of ions into insoluble aggregates. These reactions seem to constitute the simplest synthesis of 1,1′,4,4′-tetrahydrobiphenyl and derivatives; dehydrogenation of the latter may in some cases provide a convenient synthesis of certain derivatives of biphenyl. The generality of these reactions is under investigation.

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Novel Bimetallic Products from Iron Carbonyls and Methylaminobis(difluorophosphine): an Example of Square Pyramidal Pentacoordinate Iron(0)

Sir:

Recently we reported reactions of $CH_3N(PF_2)_2$ with $Co_2(CO)_8$ to give bimetallic products of the type $[CH_3N(PF_2)_2]_3Co_2L_2$ ($L = CO$ and CH_3NHPF_2) containing a cobalt–cobalt bond supported by three bridging $CH_3N(PF_2)_2$ groups.[1] This communication reports the preparation and structural characterization of bimetallic iron carbonyl deriv-
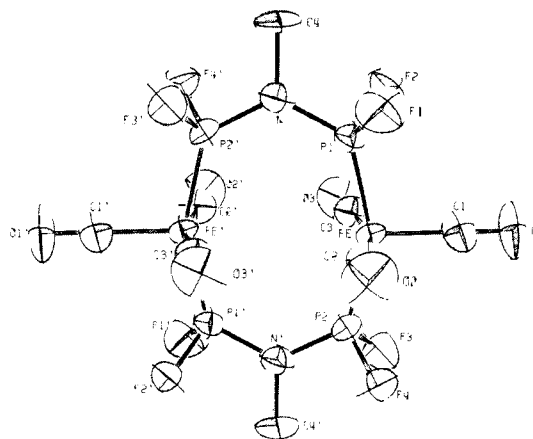
atives containing pairs of iron atoms bridged by one or two $CH_3N(PF_2)_2$ ligands. Of particular interest is the unambiguous identification by x-ray crystallography of a pentacoordinate iron(0) derivative in which the iron coordination polyhedron is best represented as a square pyramid rather than the more usual trigonal bipyramid.

The ability of $CH_3N(PF_2)_2$ to function as a biligate monometallic ligand[2] as indicated by the formation of $CH_3N(PF_2)_2M(CO)_4$ ($M = Cr$, Mo, and W)[3] and $[CH_3N(PF_2)_2]_3M$ ($M = Cr$, Mo, and W)[4] suggested that the iron carbonyl system might form a $CH_3N(PF_2)_2Fe(CO)_3$ complex. In this connection reaction of 2.0 g (4 mmol) of $Fe_3(CO)_{12}$ with 2.0 g (12 mmol) of $CH_3N(PF_2)_2$ in 75 mL of boiling tetrahydrofuran for 20 min followed by rapid removal of solvent and crystallization from dichloromethane gave 0.77 g (20% yield) of yellow crystalline $[CH_3N(PF_2)_2Fe(CO)_3]_n$.[5] mp 128–129 °C; infrared $\nu(CO)$ in hexane 2040 (w), 2037 (m), 2033 (m), 2011 (s), 2005 (s), and 1974 (m) cm^{-1}. Molecular weight determinations on freshly prepared benzene solutions of $[CH_3N(PF_2)_2Fe(CO)_3]_n$ by vapor pressure osmometry consistently indicated formulation as a dimer (calcd mol wt for $n = 2$, 614; found, 627, 583, 618, 572).

The iron complex $[CH_3N(PF_2)_2Fe(CO)_3]_2$ (**I**) forms monoclinic crystals from *n*-hexane at −20 °C for 3 h: space group $P2_1/n$; $a = 10.473$ Å, $b = 10.825$ Å, $c = 9.035$ Å; $\beta = 100.127°$; $Z = 4$. Because of crystal decomposition, three crystals were required for collection of x-ray intensity data. Least-squares refinement using the 893 observed reflections ($R = 0.0839$, $R_w = 0.0511$) indicates the structure depicted in Figure 1. This structure uses the inversion center. The iron–iron distance is 3.90 Å, clearly a nonbonding distance. The coordination geometry of each iron atom (Figure 1) is best represented as a square pyramid with successive angles between adjacent pairs of the basal ligands of 88.5 (5)°, 88.3 (4)°, 87.4 (4)°, and 88.3 (4)° as compared with 90° for an idealized square pyramid. The successive angles between the apical carbonyl group and the four basal ligands are 98.8 (7)°, 102.6 (4)°, 97.6 (7)°, and 103.5 (4)° corresponding to α values[6] of −9°, −13°, −8°, and −13°, respectively.

The complex $[CH_3N(PF_2)_2Fe(CO)_3]_2$ (**I**) is unstable upon standing in solution at room temperature with respect to evolution of carbon monoxide to form orange $[CH_3N(PF_2)_2]_2Fe_2(CO)_5$ (**II**),[5] mp 192–193 °C; infrared $\nu(CO)$ in hexane 2066 (w), 2026 (s), 1992 (s), 1978 (m), and 1786 (m) cm^{-1}. The relatively stable red-orange $[CH_3N(PF_2)_2]_2$-$Fe_2(CO)_5$ (**II**) is also obtained presumably via $[CH_3N(PF_2)_2Fe(CO)_3]_2$ (**I**) from the reaction of $Fe_3(CO)_{12}$ with $CH_3N(PF_2)_2$ in boiling diethyl ether or tetrahydrofuran for several hours or in hexane at room temperature for 60 h. The diiron pentacarbonyl **II** is also obtained in 40% yield by