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Photochemistry of Carbanions. 1. Photoalkylation of Resonance-Stabilized Carbanions in Dimethyl Sulfoxide¹

Sir:

The photochemistry of carbanions has been a neglected topic in recent years, perhaps because of the complex mixtures encountered.² Our interest in this area was spurred by the conviction that use of low energy chromophores and visible light should minimize troublesome oxidation-reduction reactions. Recent developments have also made possible studies of solvent-separated highly delocalized carbanions in dimethyl sulfoxide.³ Ultimately, we hoped to investigate the relation of pK_a of the conjugate acid to any photoproducts observed. Confirming our original expectation, the visible light irradiation of several resonance-stabilized carbanions in dimethyl sulfoxide produced clean and in most cases high yield conversion to products. Unexpected, however, was the identification of the major product in each case as the result of methylation at the formal carbanionic center.

The objects of our preliminary investigation were the conjugate bases of various indicators used in spectrophotometric pK_a determinations.^{3,4} Thus, exposure of dimethyl sulfoxide solutions of triphenylmethyl anion to 0.1 M FeCl₃ filtered 450-W Hanovia light produced 1,1,1-triphenylethane as the major product (52%) along with ~5% of a minor product. Similarly, 9-phenylfluorenyl anion produced 9-methyl-9-phenylfluorene, 1,1,3,3-tetraphenyl-2-propenyl anion produced 1,1,3,3-tetraphenyl-1-butene, (4-diphenyl)diphenylmethyl anion produced 1-(4-diphenyl)-1,1-diphenylethane, and 9-methylfluorenyl anion produced 9,9-dimethylfluorene, although in low yield. These products along with yields and reaction times are listed in Table I.

These results bear a gross resemblance to the ground-state methylation of hydrocarbons with sodium methylsulfinylmethide reported by Argabright.⁵ However, photolysis of the carbanions in the presence of excess hydrocarbon failed to alter the product yields, conditions under which the presence of significant dimethyl sulfoxide concentration could be excluded.

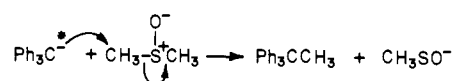
Table I. Results of Exploratory Photolysis of Carbanions^a

Anion ^b	pK_a^c	Product ^d	Reaction time, h	% yield ^e
Triphenylmethyl	31	1,1,1-Triphenylethane	3	52
Diphenyldiphenylmethyl	29	1-(4-Diphenyl)-1,1-diphenylethane	96	82
1,1,3,3-Tetraphenylpropenyl	26	1,1,3,3-Tetraphenyl-1-butene	12	80
9-Methylfluorenyl	22	9,9-Dimethylfluorene	48	1
9-Phenylfluorenyl	18	9-Methyl-9-phenylfluorene	18	66

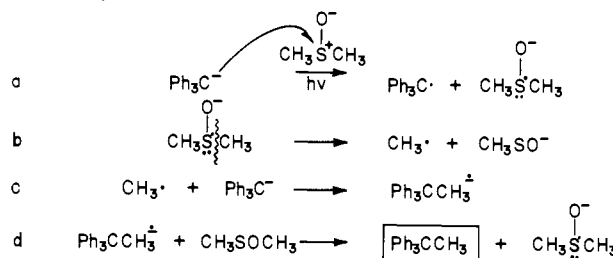
^a All data are for 10 mmol of anion in 200 mL of dimethyl sulfoxide. ^b Prepared according to the method of Bordwell et al.³ ^c As determined by Bordwell et al.³ ^d Determined by comparison with authentic material or independent synthesis. ^e Isolated yield by ether extraction. Actual yields were higher.

Chart I

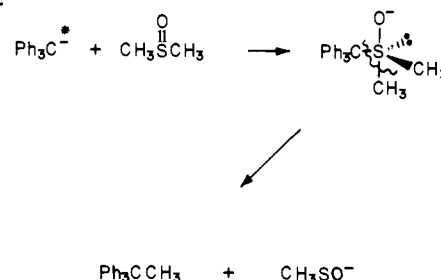
Mechanism I:



Mechanism II:



Mechanism III:



Further, the use of appropriate solution filters excluded any possible light capture either by dimethyl sulfoxide or parent hydrocarbon.

Several mechanistic possibilities exist and are outlined in Chart I. Mechanism I involves direct nucleophilic attack on dimethyl sulfoxide. Mechanism II involves electron transfer to dimethyl sulfoxide followed by homolytic cleavage of the carbon-sulfur bond in the resulting radical anion to form methyl radical, which in turn recombines with triphenylmethyl radical or triphenylmethyl anion. This mechanism is equivalent to the $S_{RN}1$ mechanism of photostimulated aromatic substitution.⁶ Mechanism III involves exciplex formation followed by decomposition via a double α scission from an oxysulfurane-like intermediate.⁷

Of the three mechanistic possibilities, mechanism I is least likely, involving as it does a nucleophilic process unknown in sulfoxides. Further, simple Hückel calculations show the excited state of triphenylmethyl anion to have near zero charge density at the central atom. Mechanism II has a great deal of precedent,⁶ which is further supported by the tendency of dimethyl sulfoxide to produce methyl radicals upon dissociative electron capture⁸ or oxidative addition of hydroxyl radical.⁹ Furthermore, the electron-donating ability of triphenylmethyl anion is well established.¹⁰ The long reaction times, however, suggest the nonintervention of a chain mechanism, and pho-

tolysis in the presence of methyl radical scavengers such as cyclohexane failed to alter product yields. The variation in reaction times required correlates roughly with the electron affinities of the products,¹¹ which may reflect the electron-transfer aspects of the mechanism. However, we also note that the presence of such electron traps might merely divert another mechanism. Mechanism III has some precedent in the known decomposition of σ -sulfuranes to yield sulfides,⁷ but attempts to produce oxysulfuranes directly have been unsuccessful.¹² Finally, more exotic pathways cannot at this time be completely ruled out.

A complete understanding of the exact mechanism of this new photoreaction must await a quantitative study of the role structure, pK_a , electron affinities, ionization potentials, and excited-state energies play in the excited-state reactivities of the anions involved. Such studies are in progress and will be reported at a later date.

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An Iron-Bridged Diborane(6) Derivative.

Preparation of $K^+[\mu\text{-Fe}(\text{CO})_4\text{B}_2\text{H}_5^-]$

Sir:

The formation of metal-boron bonds through reaction of transition metal carbonylate ions with BH_3 has been relatively unexamined except for the preparation of species¹ such as $\text{H}_3\text{BRe}(\text{CO})_5^{1-}$, and $\text{H}_3\text{BMn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3^{1-}$. Only reactions of monoanions have been reported, and the products were simple BH_3 adducts. A possible exception¹ is $(\text{H}_3\text{B})_2\text{-Re}(\text{CO})_5^{1-}$ which might be $\text{H}_3\text{BHBH}_2\text{Re}(\text{CO})_5^{1-}$.

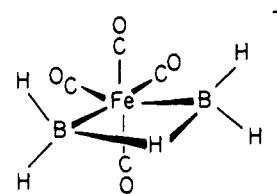
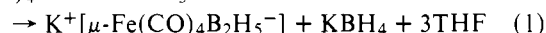
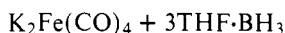


Figure 1. The proposed structure of $[\mu\text{-Fe}(\text{CO})_4\text{B}_2\text{H}_5^-]$.

We have examined the reaction of $\text{Fe}(\text{CO})_4^{2-}$ with $\text{THF}\cdot\text{BH}_3$,

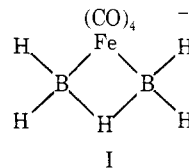


and report the preparation of the $[\mu\text{-Fe}(\text{CO})_4\text{B}_2\text{H}_5^-]$ ion, the first example of a substituted diborane(6) with a transition metal occupying a bridge site. Working on a 1-mmol scale, $\text{K}^+[\mu\text{-Fe}(\text{CO})_4\text{B}_2\text{H}_5^-]$ was obtained in yields as high as 98% when reactants were employed in $3\text{THF}\cdot\text{BH}_3/\text{K}_2\text{Fe}(\text{CO})_4$ ratio. Unreacted $\text{K}_2\text{Fe}(\text{CO})_4$ and diminished yields of $\text{K}^+[\mu\text{-Fe}(\text{CO})_4\text{B}_2\text{H}_5^-]$ were obtained when this ratio was $<3/1$. Solid $\text{K}^+[\mu\text{-Fe}(\text{CO})_4\text{B}_2\text{H}_5^-]$ is dark brown in appearance. It is stable at room temperature for several hours, sealed under vacuum. In THF solution, no decomposition of $\text{K}^+[\mu\text{-Fe}(\text{CO})_4\text{B}_2\text{H}_5^-]$ is noted in NMR spectra obtained after several hours at 50°C . Anal. Calcd for $\text{KFe}(\text{CO})_4\text{B}_2\text{H}_5$ (percent by weight): H, 2.16; C, 20.6; B, 9.21; Fe, 23.9. Found: H, 2.07; C, 20.7; B, 8.93; Fe, 23.6.

^{11}B and ^1H NMR spectra are consistent with the molecular structure shown in Figure 1. A triplet of doublets is observed upfield of $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ ($\delta -15.4$ ppm) in the ^{11}B NMR spectrum. (Note. A negative chemical shift denotes a resonance which occurs at higher field than the reference.)² The triplet arises from coupling of two terminal ^1H atoms with each ^{11}B atom, $J_{\text{BH}_t} = 112$ Hz. Each component of this triplet is split into a doublet owing to spin coupling of a single ^1H atom bridging two ^{11}B atoms ($J_{\text{BH}\mu} = 25$ Hz). ^1H decoupling causes collapse of the ^{11}B NMR spectrum to a singlet. This spectrum is independent of temperature in the range studied ($+50$ to -80°C). The ^1H NMR spectrum (^{11}B decoupled) consists of resonances at τ 8.20 and 15.17 ($(\text{CH}_3)_4\text{Si}$, τ 10.00) with relative areas of 4.1/1.0, respectively. These spectra are consistent with those of other bridge substituted diboranes (μ -amino-,³ μ -thio-,⁴ and μ -selenodiboranes⁵).

The infrared spectrum of $\text{K}^+[\mu\text{-Fe}(\text{CO})_4\text{B}_2\text{H}_5^-]$ (THF solution) shows a doublet in the BH terminal stretching region at 2450 (w) and 2400 (w) and BH bridge stretches at 1845 (vw) and 1655 (vw). Similar bands are observed in the infrared spectra of $\mu\text{-Se}(\text{CH}_3)\text{B}_2\text{H}_5^{5-}$ and $\mu\text{-NR}_2\text{B}_2\text{H}_5^{3a}$. The CO stretches of $\text{K}^+[\mu\text{-Fe}(\text{CO})_4\text{B}_2\text{H}_5^-]$ occur at 2030 (w), 1943 (vs), and 1927 (s). These bands fall in the same region as the CO stretches⁶ of $\text{HFe}(\text{CO})_4^-$, as expected for a single negatively charged species, and are at significantly higher frequencies than the CO stretches of $\text{K}_2\text{Fe}(\text{CO})_4^{6-}$.

The $\text{Fe}(\text{CO})_4^{2-}$ ion is the conjugate dibase of $\text{H}_2\text{Fe}(\text{CO})_4$. It is a potential four-electron donor in the formation of the $[\mu\text{-Fe}(\text{CO})_4\text{B}_2\text{H}_5]^{1-}$ ion from $\text{THF}\cdot\text{BH}_3$. One representation of the valence structure of this anion is I in which the iron is



formally d^2sp^3 hybridized and is bonded to the B_2H_5 system through two 2-center Fe-B bonds. This representation is analogous to the commonly held valence description of bonding of nitrogen to the B_2H_5 system in a μ -aminodiborane(6), μ -