

Figure 2. A view of the $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\text{C}_{11}\text{H}_8)]^+$ ion. Selected bond lengths (angstroms): Fe-C(1) = 1.996 (2), C(1)-C(2) = 1.395 (3), C(2)-C(3) = 1.416 (3), C(3)-C(4) = 1.435 (3), C(4)-C(5) = 1.400 (3), C(5)-C(6) = 1.373 (3), C(6)-C(7) = 1.388 (3), C(7)-C(1) = 1.407 (3), C(3)-C(8) = 1.429 (3), C(8)-C(9) = 1.358 (3), C(9)-C(10) = 1.402 (4), C(10)-C(11) = 1.346 (4), C(11)-C(4) = 1.429 (3). Selected angles (degrees): Fe-C(1)-C(2) = 119.4 (1), Fe-C(1)-C(7) = 117.7 (2), C(2)-C(1)-C(7) = 122.6 (2).

from that predicated¹⁴ for the simplest carbene :CH₂ and observed in two Ta-CHR (R = H or Ph) complexes.^{15,16} Comparison of the Fe-C_{carb} distances of 1.979 (3) and 1.996 (2) Å in the cations of **1** and **4** with the Fe-C(sp²) distances of 2.025 (6) Å in cation $\{[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}\{\eta^1\text{-C}(\text{Ph}_3\text{P})\text{-CH}(\text{Ph})\}]^+\}$ ¹⁷ and 1.996 (8) Å in uncharged $(\eta^5\text{-C}_5\text{H}_5)\text{-}(\text{CO})_2\text{Fe}[\text{C}(\text{C}(\text{H}_3)\text{S}(\text{O})(\text{OCH}_2))]$ ¹⁸ suggests some degree of metal-ligand multiple bonding, particularly in **1**.

Acknowledgment. This work was supported by the Robert A. Welch Foundation (Grant No. F-223). We are also indebted to the National Science Foundation for purchase of a Syntex P2₁ diffractometer (Grant No. GP-37028). N.T.A. and W.M.J. also gratefully acknowledge partial support received from the National Science Foundation. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

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- Analytical and spectroscopic data for **8**: 26% yield; mp 114.5–115.5 °C dec; NMR (CDCl₃) δ 3.0 (saturated CH, d, J = 7 Hz, 2 H), 4.6 (Cp, s, 5 H), 5.6 (C₁, t, J = 7 Hz, 1 H), 6.62 (C₃, C₄, s, 2 H), 7.2 (aromatic, m, 4.5 H); IR (KBr) in carbonyl region 2010, 1935, 1960 cm⁻¹. Anal. Calcd for C₁₈H₁₄O₂Fe: C, 67.95; H, 4.44. Found: C, 67.99; H, 4.47.
- Analytical and spectroscopic data for **3**: 93% yield; mp 177–178 °C dec; ¹H NMR (0 °C, CD₃CN) δ 9.58 (C₂, C₁₁, d, J = 11 Hz, 2 H), 8.26 (C₃, C₁₀, d, J = 11 Hz), 8.58–8.08 (C₅–C₈, m) (total area of C₃, C₁₀, C₅–C₈, 6 H); ¹³C NMR (0 °C, CD₃NO₂) δ (from Me₄Si) 265.9 (C₁), 212.7 (CO), 158.5, 141.6, 140.3, 137.8, 137.1 (C₂–C₈), 89.5 (Cp); IR (CH₂Cl₂) in carbonyl region 2045, 2000 cm⁻¹; UV-visible (CH₂Cl₂) λ_{max} 500 (log ε 3.47), 468 (3.52), 330 (sh), 315 (sh), 282 (sh), 272 (4.21), 233 (4.20). Anal. Calcd for C₁₈H₁₄O₂FePF₆: C, 46.79; H, 2.84. Found: C, 46.78; H, 2.86.
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- Analytical and spectroscopic data for **18** and **19**: 37% yield; ¹H NMR (CDCl₃) δ 2.9, 3.45 (saturated CH, d, s, 2 H), 4.9 (Cp, s, 5 H), 5.35, 6.2, 6.7, 7.2 (olefinic and aromatic, all complex multiplets, 8 H); IR in carbonyl region 2020, 1950 cm⁻¹; high resolution mass spectrum of mixture, m/e 318.03302 (theory, 318.03410).
- Analytical and spectroscopic data for **4**: 88% yield; mp 176–177 °C dec; ¹H NMR (8 °C, CD₃NO₂) δ 10.4 (1 H, d, J = 2 Hz), 9.92 (1 H, d, J = 10.6 Hz), 9.23 (1 H, d of m, J = 10.6, 0.5 Hz), 8.50, 8.16 (5 H, m, J = 10.6 Hz); ¹³C NMR (0 °C, CD₃NO₂) δ (from Me₄Si) 215 (CO), 201 (C₁), 176, 174, 155, 145, 139, 138, 138, 137, 136, 133 (C₂–C₁₁), 89 (Cp); IR (CH₂Cl₂), carbonyl region 2037, 1992 cm⁻¹; UV-visible (CH₂Cl₂) λ_{max} 380 (log ε 3.52), 313 (sh), 380 (4.36), 232 (4.28). Anal. Calcd for C₁₈H₁₄O₂FePF₆: C, 46.79; H, 2.84. Found: C, 46.68; H, 2.86.
- Single crystals of **1** and **4** form from CH₂Cl₂ solutions at ca. -15 °C in space group P7 with a = 7.981 (4), b = 14.378 (3), c = 7.133 (1) Å, and α = 98.52 (1), β = 100.75 (1), γ = 93.33 (1)° for **1** and a = 8.2987 (6), b = 15.238 (2), c = 7.4361 (8) Å, and α = 90.509 (7), β = 104.396 (5), γ = 94.676 (6)° for **4**. The structures were solved by heavy-atom methods and refined by full-matrix least-squares procedures; R = Σ||F_o| - |F_c||/Σ|F_o| = 0.057 and 0.041 for **1** and **4**, respectively. Experimental procedures are essentially as previously delineated: Riley, P. E.; Davis, R. E. *Acta Crystallogr., Sect. B.* **1976**, *32*, 381.
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Received July 16, 1979

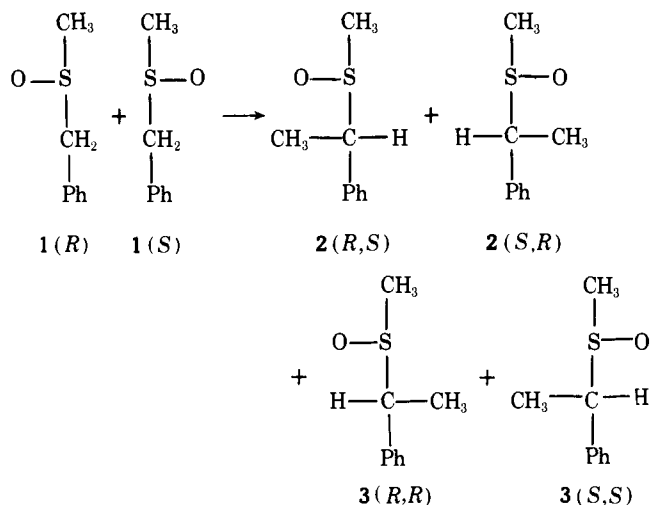
Stereospecific Alkylation of a Carbanion in the Solid State

Sir:

Reactions in organic compounds are more selective when performed in the solid state rather than in solution.¹⁻³ For instance, the elimination in some halides is highly stereospecific when performed in the crystalline state.^{4,5} The regioselectivity is drastically altered when the alkylation of some phenolate anions is performed in heterogeneous medium.⁶⁻⁸ Similar findings have been described for the alkylation of pyrazole anion.⁹ Optical induction has been observed during the reaction of chiral monocristals of chalcone with bromine,¹⁰ and the higher reactivity of one enantiomer of a crystalline carboxylic acid with an optically active amine has been noted.¹¹

The stereoselectivity of the lithiated carbanion derived from methyl benzyl sulfoxide¹²⁻¹⁴ has been proposed to be due to internal chelation of the lithium cation by sulfoxide oxygen.¹⁵⁻¹⁸ This chelation favors one of the diastereoisomeric carbanions and the reaction of these carbanions has been proposed to occur with inversion at the carbanionic center for nonchelating reagents such as alkyl halides and with retention in the case of chelating reagents such as water.¹⁶ However, further studies are difficult because of the rapid equilibration of the species present in solution. We thought that in the solid state the reactivity may be more selective owing to the presence of a single diastereoisomer and to a fixed solvation state.

When a 1.1 M solution of the lithiated carbanion derived from racemic benzyl methyl sulfoxide **1** in tetrahydrofuran (THF) was cooled from -78 to -100 °C, a white precipitate was obtained. After removal of the solvent and washing several times with pentane (-100 °C), the solid was dried under vacuum. At 25 °C, liquid methyl iodide was added to the solid and after workup the ratio of the diastereoisomeric methylated products [$r = 2(R,S) + 2(S,R)/3(R,R) + 3(S,S)$] was determined by ¹H NMR¹⁹ to be 5:1. However, if a mixture of



methyl iodide vapor and nitrogen was passed over the dispersed solid at 25 °C, one single diastereoisomer was formed which was shown by ^1H NMR to be identical with the major isomer (*R,S* and *S,R*) formed above and in solution (in THF at 25 °C, the ratio *r* was 5).²⁰ If the solid is not dispersed, a liquid phase appears and most likely the reaction with methyl iodide occurs in this liquid phase; the ratio *r* was 5. When methyl iodide was added to the mother liquors at -78 °C or to the solid dissolved in THF at -78 °C, the ratio *r* was found to be 15. This is because equilibration of the diastereoisomeric carbanions has taken place in solution. When the solid was treated with heavy water or O-deuterated ethanol as liquids, there was only very slight preference for one diastereoisomer.

Thus the reaction of methyl iodide vapors with the dispersed solid occurs stereospecifically. The stereoselectivity was lost with chelating reagents like deuterium oxide and ethanol. This is reminiscent of the effect of lithium halides on the stereoselectivity of the reaction in solution²¹ and could be due to catalysis by lithium cation.¹⁶ Quite clearly, in the solid state, one diastereoisomer is present and its reactivity is highly stereoselective with a nonchelating reagent.

This now opens up the possibility of investigating the stereochemical course of an electrophilic substitution by the structural analysis of this solid. In the solid state, asymmetric induction may be intramolecular as in the present case, or intramolecular in the presence of an asymmetric ligand. This line of work is worthy of further investigation.

Acknowledgment. We acknowledge the financial support of the CNRS through Grant ATP Structures Chirales (No. 3824).

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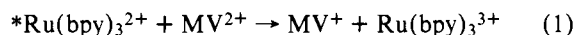
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Received November 27, 1979

Light-Induced Charge Separation by Functional Micellar Assemblies

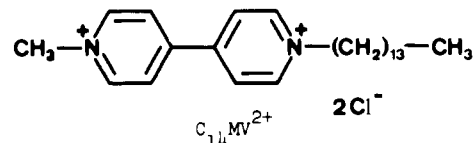
Sir:

In the field of photochemical energy conversion, particular attention has been paid to the reduction of methylviologen by the charge-transfer excited state of $\text{Ru}(\text{bpy})_3^{2+}$:



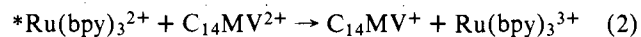
This reaction was first investigated by Whitten et al.¹ after Gafney and Adamson² discovered that the excited ruthenium complex can serve as a powerful one-electron reductant. Important with respect to light energy conversion is that the reaction products MV^+ and $\text{Ru}(\text{bpy})_3^{3+}$ are capable of producing hydrogen³ and oxygen⁴ from water. Moreover, simultaneous H_2 and O_2 generation from water by visible light has recently been observed with the same redox system.⁵ To improve the quantum efficiency of this device, it is necessary to retard the back-reaction between MV^+ and $\text{Ru}(\text{bpy})_3^{3+}$ which in water occurs at a rate of $2.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.⁶ A micellar system which achieves this goal is now described in detail.

Instead of simple methylviologen, we employed the amphiphilic derivative $\text{C}_{14}\text{MV}^{2+}$ as an electron acceptor. This



surfactant micellizes at concentrations above $\sim (7) \times 10^{-3} \text{ M}$ as determined from surface tension measurements.⁷ Throughout the work it was employed at concentrations considerably below the cmc. A frequency doubled Nd laser (λ 530 nm, pulse width 15 ns) was used for excitation and the behavior of transient species monitored by kinetic spectroscopy.⁸

The oxidative quenching process



was found to occur with a specific rate of $(8 \pm 0.8) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ at 10^{-4} M $\text{Ru}(\text{bpy})_3^{2+}$ and $5 \times 10^{-4} \text{ M}$ $\text{C}_{14}\text{MV}^{2+}$ (ionic strength $1.4 \times 10^{-3} \text{ M}$). This is somewhat faster than the reduction^{3b} of MV^{2+} in water ($k_1 = (2) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$). The kinetic salt effect induces a slight acceleration of the reaction with increasing ionic strength. For example, in the presence of 10^{-2} M NaCl (total ionic strength $1.14 \times 10^{-2} \text{ M}$) the rate constant is $(1.1 \times 10^9) \text{ M}^{-1} \text{ s}^{-1}$.

Cationic micelles do not affect the kinetics of reaction 2. This was carefully checked by measuring the quenching rate in the presence of increasing amounts (up to $5 \times 10^{-2} \text{ M}$) of cetyltrimethylammonium chloride (CTAC) in solutions containing $5 \times 10^{-4} \text{ M}$ $\text{C}_{14}\text{MV}^{2+}$ and 10^{-4} M $\text{Ru}(\text{bpy})_3^{2+}$. Fluctuations in the k_2 values were within 10% of $(8) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ over the whole concentration range. In particular no systematic change in k_2 was observed when the CTAC concentration passed