Tetrahedron Letters, Vol. 33, No. 24, pp. 3447-3448, 1992
Printed in Great Britain

0040-4039/92 $5.00 + .00
Pergamon Press Ltd

A NEW REACTION INVOLVING $Cp(CO)_2Fe^-K^+$ AND CARBOXONIUM SALTS FOR SYNTHESIS OF CARBENE PRECURSORS

Ronald D. Theys and M. Mahmun Hossain*
Department of Chemistry, University of Wisconsin-Milwaukee,
Milwaukee, Wisconsin 53201

Abstract: The synthesis of electrophilic iron carbene precursors from Fp anion and carboxonium salts of acetals is described.

Due to their usefulness in generating highly reactive, nonheteroatom-stabilized carbenes, preparation of precursors for electrophilic iron carbenes has received much attention recently.[1] These carbenes are produced in-situ from their precursors for transfer to alkenes in cyclopropanation reactions.[1c] Conversely, heteroatom-stabilized carbenes are less reactive and instead are often used as intermediates to the more reactive secondary, nonheteroatom-stabilized carbenes.[2] In pursuing various routes to carbene precursors we have discovered a new reaction for Fp anion **3** with carboxonium salts **2** of acetals for the synthesis of both heteroatom and nonheteroatom-stabilized iron carbene precursors.

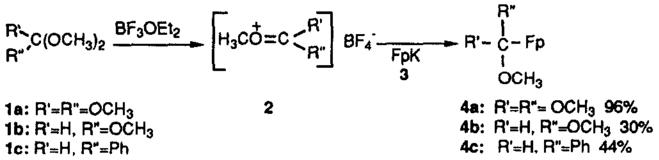
Synthesis of **2a**[3] and **2b**[4] was achieved by dropwise addition of borontrifluoride etherate to a slight excess of acetal **1a,b** in dried diethyl ether over a one hour period at 0°C (Scheme I). A white solid precipitated as the acid was added. The solvent was discarded by transfer via filter stick, the carboxonium salt **2** washed three times with fresh solvent, and the salt dried under vacuum. A solution of excess potassium cyclopentadienylirondicarbonyl (FpK) **3** in dried and degassed THF at -78°C was transferred via canula to the salt flask held at -78°C. Within 30 minutes of the addition of anion, the reaction was complete as judged by disappearance in the IR of the anion carbonyl peaks. In-vacuo removal of the solvent and extraction using pentane at 0°C to -23°C gave the precursors **4a** and **4b** in fair to excellent yield.[5] The precursor **4b** was identified by its ^1H NMR spectrum.[6] Precursor **4a** was characterized by spectroscopic methods.[7]

The carboxonium salt **2c**[8] was synthesized using a similar procedure as above but with a 3 mole excess of acetal **1c** to reduce the possiblity of the presence of free acid. Since **2c** is soluble in ether it was transferred as a solution at -78°C to the FpK solution held at -78°C. The reaction was determined to be complete within 30 minutes of addition. In-vacuo removal of the solvent and separation from the acetal on an activity I alumina column using a 0-50% ether in pentane mixture allowed the isolation of precursor **4c**.[9]

The complex **4a** is the first reported synthesis of such a precursor. To demonstrate the utility of **4a** in generating its carbene, a -78°C solution of **4a** in methylene chloride was treated with trimethylsilyl triflate and warmed to room temperature. A yellow solid precipitated immediately upon addition of pentane. Recrystallization from pentane and methylene chloride resulted in a 90% yield of the carbene $[Fp{=}C(OCH_3)_2]^+\ SO_3CF_3^-$.[10]

Nucleophilic addition of the Fp anion to carboxonium salts represents the first example of reaction involving these two species.[11] Hegedus effected a nucleophilic addition to the carboxonium salt **2a** using chromium pentacarbonyl dianion.[3c] However, he failed to observe any reaction with the carboxonium salt **2b** observing only that decomposition of the reagents resulted upon reaction.

Scheme I



Not only is our new reaction using Fp anion successful with carboxonium salt **2a** but also with the carboxonium salts **2b** and **2c** of secondary and tertiary acetals, respectively. This reaction represents a simple entry into the synthesis of precursors **4b**[6] and **4c**.[2a,c,12] Future investigation will focus on expanding this new reaction to a general method including a larger variety of acetals for synthetically important carbene precursors.

References and Notes

1. (a) Vargas, R. M.; Theys, R. D.; Hossain, M. M. *J. Am. Chem. Soc.* **114**, 777 (1992). (b) O'Connor, E. J.; Brandt, S.; Helquist, P. *Ibid.* **109**, 3739 (1987). (c) Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **87**, 411 (1987). (d) Casey, C. P.; Miles, W. H.; Tukada, H. *J. Am. Chem. Soc.* **107**, 2924 (1985).
2. (a) Bodnar, T.; LaCroce, S. J.; Cutler, A. R. *J. Am. Chem. Soc.* **102**, 3292 (1980). (b) Brookhart, M.; Tucker, J. R.; Husk, G. R. *Ibid.* **103**, 979 (1981). (c) Casey, C. P.; Miles, W. H. *J. Organometal. Chem.* **254**, 333 (1983).
3. (a) Meerwein, H. *Angew. Chem.* **67**, 374 (1955). (b) Meerwein, H.; Bodenbenner, K.; Borner, P.; Kunert, F.; Wunderlich, K. *Liebrigs Ann. Chem.* **632**, 38 (1960). (c) Imwinkelried, R.; Hegedus, L. S. *Organometallics* 7, 702 (1988).
4. (a) Borch, R. F. *J. Am. Chem. Soc.* **90**, 5303 (1968). (b) Borch, R. F. *J. Org. Chem.* **34**, 627 (1969).
5. Unoptimized yields based on carboxonium salt as the limiting reagent.
6. (a) Casey, C. P.; Tukada, H.; Miles, W. H. *Organometallics* **1**, 1083 (1982). (b) Forschner, T.; Menard, K.; Cutler, A. *J. Chem. Soc., Chem. Commun.* 121 (1984).
7. Precursor **4a**: IR (CH_2Cl_2): 1952.7, 2011.3 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ 3.20 (s, 3H), 4.80 (s, 5H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ 50.3, 86.6, 136.8, 216.6. MS(EI): 282 (M) (not observed), 105, 121, 152, 166, 180, 195, 208, 223, 251.
8. Rabinovitz, M.; Bruck, D. *Tetrahedron Letters* **3**, 245 (1971).
9. Carboxonium salt **2c** was not isolated. The unoptimized yield of **4c** was based on BF_3OEt_2 as the limiting reagent for complete reaction.
10. McCormick, F. B.; Angelici, R. J. *J. Inorg. Chem.* **20**, 1111 (1981).
11. A control reaction between **2c** and Fp anion **3** produced no precursor **4c**, only starting material remained.
12. (a) Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* **99**, 6099 (1977). (b) Brookhart, M.; Humphrey, M. B.; Kratzer, H. J.; Nelson, G. O. *Ibid.* **102**, 7802 (1980).

(Received in USA 27 February 1992)