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Improved One-Flask Preparations of Cyclopropanation Reagents: $(\eta^5\text{-}C_5H_5)(CO)_2FeCH_2S(CH_3)_2{}^+BF_4{}^-$ and $[\eta^5\text{-}C_5(CH_3)_5](CO)_2FeCH_2S(CH_3)_2{}^+BF_4{}^-$

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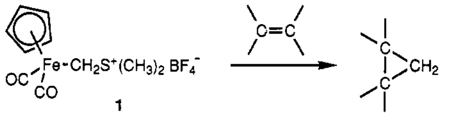
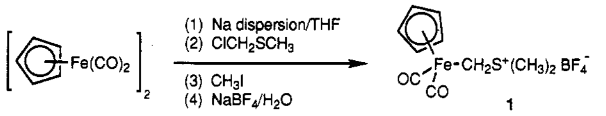
In earlier work, the organoiron sulfonium salt $(\eta^5\text{-}C_5H_5)(CO)_2FeCH_2S(CH_3)_2{}^+BF_4{}^-$ (1) was shown to be a very useful reagent for the direct cyclopropanation of alkenes (eq 1).[2] These reactions apparently proceed by dissociation of dimethyl sulfide to give the cationic iron carbene complex $[\eta^5\text{-}C_5H_5(CO)_2Fe{=}CH_2]^+$ as a reactive intermediate.[3] In addition to the favorable reactivity characteristics of 1 in this transformation, it is also especially attractive as a reagent because of its unusually high stability toward air and even hot water. However, as originally described, the preparation of this reagent entailed a rather long, cumbersome procedure. Among its disadvantages were the use of large amounts of sodium amalgam and highly reactive methylating agents such as trimethyloxonium salts and difficult manipulations of air-sensitive materials. In this brief note, we report a greatly simplified, practical, large-scale preparation of 1. We also report for the first time the preparation of the corresponding pentamethylcyclopentadienyl analogue $[\eta^5\text{-}C_5(CH_3)_5](CO)_2FeCH_2S(CH_3)_2{}^+BF_4{}^-$ (2), which also serves as a useful cyclopropanation reagent.



(1)

The preparation consists of a sequence of reactions all performed in one simple, round-bottom flask (eq 2). The starting material is the binuclear iron complex, $[\eta^5\text{-}C_5H_5(CO)_2Fe]_2$. This air-stable solid may be obtained commercially,[4] or it may be prepared very straightforwardly from iron pentacarbonyl and dicyclopentadiene.[5] It is converted into the very nucleophilic sodium ferrate, $Na[(\eta^5\text{-}C_5H_5)(CO)_2Fe]$, by reaction with a sodium dispersion as reported by Reger.[6] To the solution of this ferrate is added chloromethyl methyl sulfide, and to the resulting $(\eta^5\text{-}C_5H_5)(CO)_2FeCH_2SCH_3$ is added iodomethane; a small excess is used to destroy any unreacted sodium metal. The reaction mixture is then concentrated in vacuo, and the residue containing the sulfonium complex as the iodide salt, $(\eta^5\text{-}C_5H_5)(CO)_2FeCH_2S(CH_3)_2{}^+I^-$, is treated in the same flask with a hot aqueous solution of sodium tetrafluoroborate to effect anion exchange. Filtration of the resulting mixture and cooling of the filtrate provides the desired reagent as the tetrafluoroborate salt 1 in the form of a yellow, crystalline solid in 62% overall yield. As a test of the cyclopropanation reactivity of this material, its reaction with 1,1-diphenylethylene in nitromethane gives 1,1-diphenylcyclopropane in a yield of 97%.



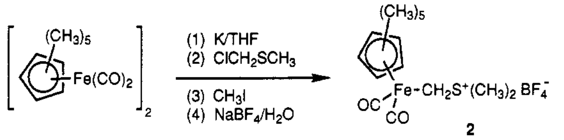
(2)

Table I. Relative Reactivity of 1 and 2 toward 1,1-Diphenylethylene[a]

reagent	% convn of 1,1-diphenylethylene to 1,1-diphenylcyclopropane[b] 20 min	60 min	240 min
1	38	70	97 (86)
2	76	98 (89)	–

[a] Reactions were run in nitromethane under standard conditions (see Experimental Section). [b] The percent conversions were measured by capillary GLC (HP-1 cross-linked methyl silicone gum column), but the values in parentheses are yields of isolated product.

Earlier work of Astruc, Guerchais, and co-workers has demonstrated the stabilizing effect of the pentamethylcyclopentadienyl ligand in place of the parent cyclopentadienyl group in carbene complexes of iron.[7] Therefore, a logical extension of our work is the preparation of the pentamethylcyclopentadienyl derivative $[\eta^5\text{-}C_5(CH_3)_5](CO)_2FeCH_2S(CH_3)_2{}^+BF_4{}^-$ (2). A one-flask procedure (eq 3) is again used, with 2 being obtained in overall yields of 92–100%. The major difference in the procedure in this case is that the binuclear starting material, $\{[\eta^5\text{-}C_5(CH_3)_5](CO)_2Fe\}_2$,[8] is reductively cleaved to the corresponding ferrate with potassium rather than with sodium as in the parent system above. Use of sodium in the present case results in a very slow, inefficient cleavage. This observation is consistent with measurements of approximate reduction potentials of the two binuclear complexes; the pentamethylcyclopentadienyl derivative has a reduction potential that is approximately 0.4 V more negative than that of the parent compound.



(3)

This pentamethylcyclopentadienyl derivative 2 is also a useful cyclopropanation reagent. Indeed, it reacts somewhat more rapidly than 1 as indicated by the data compiled in Table I.

In conclusion, the cyclopropanation reagent 1 may be obtained by a much more convenient and practical procedure than originally reported. Furthermore, the pentamethylcyclopentadienyl derivative 2 may be obtained as well. The ready availability of these compounds should now contribute to their greater attractiveness as reagents for the synthesis of cyclopropanes.

Experimental Section

$(\eta^5$-Cyclopentadienyl)dicarbonyl[(dimethylsulfonio)methyl]iron Tetrafluoroborate (1). Into a single-neck 2-L round-bottom flask open to the air was placed a large magnetic stirring bar, cyclopentadienyldicarbonyl iron dimer (74.4 g, 0.210 mol), and sodium dispersion (40% by weight) in light mineral oil

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(27.4 g, 0.477 mol). The flask was then equipped with a reflux condenser topped with a three-way stopcock having a vertical tubulation capped with a septum through which solvents and reagents could be introduced with a syringe fitted with a long needle. By evacuation through the other tubulation of the stopcock, the apparatus was placed under vacuum (≤0.1 Torr) for 1–2 h to remove the bulk of the mineral oil. The flask was then filled with nitrogen, anhydrous tetrahydrofuran (850 mL; distilled from sodium benzophenone ketyl) was added, and the mixture was heated at reflux for 18 h. The mixture was cooled to 0 °C, chloromethyl methyl sulfide (35.2 mL, 0.420 mol) was added dropwise over 25 min, and the mixture was stirred for 1 h at 0 °C and for 1 h at 25 °C. Iodomethane (30.6 mL, 0.492 mol) was added over 5 min, the mixture was stirred for another 15 h at 25 °C, the volatile components were removed under vacuum (≤0.1 Torr), the vacuum was relieved with nitrogen, and the stopcock was removed from atop the condenser, thus exposing the mixture to the air. A solution of sodium tetrafluoroborate (277 g, 2.52 mol) in water (1200 mL) was prepared and was heated to 95 °C. Most of the solution (1000 mL) was slowly poured down the condenser into the flask while the reaction mixture was being stirred. The mixture was suctioned filtered through a preheated (hot water) 350-mL, medium-frit, sintered glass Büchner funnel containing a layer of diatomaceous earth and a layer of sand. The flask and the filter were rinsed with the remaining hot sodium tetrafluoroborate solution, and the combined filtrates were cooled slowly to 0 °C and placed in a freezer at ca. −10 °C for 1–3 h. The product was collected on a Büchner funnel, washed with cold water (150 mL) and cold ether (1500 mL), and dried in a stream of air overnight to give 89.2 g (62.4% overall yield) of **1** as amber-colored, flakelike crystals, identical with the previously reported compound.[2]

(η^5-1,2,3,4,5-Pentamethylcyclopentadienyl)dicarbonyl[(dimethylsulfonio)methyl]iron Tetrafluoroborate (2). Freshly cut potassium (0.15 g, 3.9 mmol) was cleaned by melting in warm, anhydrous THF (10 mL) under an argon atmosphere. After the potassium was cooled to 25 °C, the solvent was replaced by fresh THF (30 mL), $\{[\eta^5\text{-}C_5(CH_3)_5](CO)_2Fe\}_2$ (0.84 g, 1.7 mmol) was added, and the argon atmosphere was reestablished. The slurry was heated in an oil bath at 65–70 °C while being vigorously stirred for 4 h, after which only a small amount of particulate potassium remained. The red solution was cooled in an ice bath, and $ClCH_2SCH_3$ (0.33 mL, 3.9 mmol) was slowly added via syringe. The mixture was stirred for 45 min in the ice bath and for an additional hour at 25 °C. Iodomethane (1 mL, 16 mmol) was added, and the mixture was stirred at 25 °C for 16 h. The solvent was removed on the rotary evaporator from the resulting yellow slurry. The residue was taken up in a hot solution of $NaBF_4$ (1 g, 9 mmol) and water (40 mL), and the mixture was filtered to remove a dark oily substance. The product crystallized upon cooling, giving 1.1–1.2 g (92–100%) of **2** as yellow-orange crystals: mp 152–156 °C; IR (KBr) 1997 and 1945 (CO str) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.85 (s, 6 H), 2.14 (s, 2 H), 1.80 (s, 15 H).

Standard Procedure for Cyclopropanation of Alkenes. 1,1-Diphenylcyclopropane. Into a 5-mL round-bottom flask were placed a magnetic stirring bar, reagent **1** or **2** (2.00 mmol), and 1,1-diphenylethylene (0.180 g, 1.00 mmol). The flask was fitted with a reflux condenser, atop of which was placed a stopcock, and a nitrogen atmosphere was established within the apparatus. Nitromethane (0.50 mL)[9] was added, and the mixture was heated at reflux (oil bath temperature 116 °C) for up to 4 h while being stirred. The reaction mixture was cooled, and the product was isolated with hexane as a workup solvent and ferric chloride to destroy ferrocene as reported previously.[2b] Obtained was 0.167–0.173 g (86–89%) of 1,1-diphenylcyclopropane.[2b]

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Registry No. 1, 72120-26-4; 2, 120120-19-6; $[\eta^5\text{-}C_5H_5(CO)_2Fe]_2$, 12154-95-9; $\{[\eta^5\text{-}C_5(CH_3)_5](CO)_2Fe\}_2$, 35344-11-7; $ClCH_2SCH_3$, 2373-51-5; 1,1-diphenylethene, 530-48-3; 1,1-diphenylcyclopropane, 3282-18-6.

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(9) The nitromethane (Eastman Kodak) was dried first over anhydrous $MgSO_4$ and then over anhydrous $CaSO_4$ overnight. The solvent was filtered into a flask containing activated 3-Å molecular sieves and was heated at 60 °C for 8 h while being stirred. The nitromethane was distilled from the powdered molecular sieves under reduced pressure (bp 58 °C, 150 Torr; Lit.[10] bp 58 °C, 160 Torr) directly into a flask containing additional 3-Å molecular sieves. The purified solvent was stored in the dark. When "wet" nitromethane from commercial sources is used directly as a reaction solvent, the percent conversions of alkenes to cyclopropanes are reduced substantially. **CAUTION:** Distillations of nitromethane and reactions using this solvent at elevated temperature should be conducted behind a safety shield.

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1-Amino-3,5,7-trinitroadamantane: An Unexpected Oxidation Product of 1,3,5,7-Tetraaminoadamantane. An Improved Synthesis of 1,3,5,7-Tetranitroadamantane

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Recent investigations in our laboratories have focused on the synthesis of strained polycyclic hydrocarbons possessing multiple nitro groups in order to establish their potential as useful energetic materials.[1] Many of the currently available methods for the preparation of these molecules introduce the requisite nitrogens as amino groups, which are subsequently oxidized.[2] The often modest yields obtained from the oxidations, using classical oxidizing agents,[2] has prompted us to devise new strategies for effecting the amino to nitro conversion.

It has recently been demonstrated that a biphasic system of ethyl acetate or dichloromethane and water containing sodium percarbonate (SPC), sodium bicarbonate, and *N,N,N′,N′*-tetraacetylethylenediamine (TAED) oxidized primary amines to the corresponding *C*-nitroso compounds in good to excellent yields via the agency of in situ generated peroxyacetic acid.[3,4] This observation and the well-known fact that *C*-nitroso monomers are smoothly converted to nitro compounds on treatment with ozone[5] suggested that this two-step sequence might serve as a useful method to accomplish the desired amine to nitro oxidation (Scheme I).

1-Aminoadamantane (**1a**) was selected as a model compound because 1-nitrosoadamantane maintains a favorable equilibrium concentration of its monomeric form **1b** in solution as judged by the presence of the intense blue color characteristic of aliphatic nitroso monomers. It appears that the dissociation of the nitroso dimer **1c** into its mo-

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