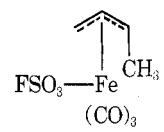
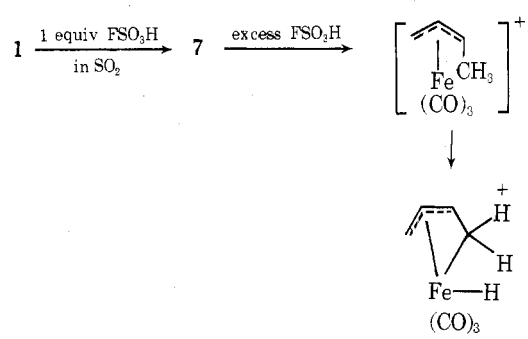
species 7 formed from 1 with 1 equiv of FSO_3H in SO_2 solution also seems to be covalently bonded because of the nearly identical nature of the ^{13}C NMR spectra for the species observed in both acid systems. Ionic species such as 3 and 4, even if intermediately formed, are not observable under the conditions as they would be rapidly quenched by the fluorosulfate acids. As the *syn*-methylallyl cation 4 was observed in HBF_4 or $HClO_4$ solution,[4,5] the covalent species 7 is assigned to be the *syn*-methylallylfluorosulfatoiron tricarbonyl complex.



7

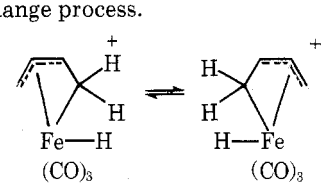
When the solution of 7 was treated with excess of FSO_3H, both the C_1 and the methyl carbon resonance were shielded by about 17 ppm. Although C_1 remains as a triplet (Figure 1D), the methyl quartet originally present in 7 now becomes a triplet of doublets indicating that the methyl carbon couples with two equivalent and a third different proton with J_{C-H} of 146.5 and 73.7 Hz, respectively. It is further noticed that the magnitudes of J_{C-H} for the methyl carbon, as well as C_2 and C_3, are substantially larger than those in 7. The increase in coupling constant and the shielding of the methyl carbon and that of C_1 thus agrees with the formation of 6 as the σ–π type complex in accordance with the suggestion of Brookhart and Harris.[7a,b] The observation of the geminal ^{13}C–Fe–^1H coupling (73.7 Hz) further substantiates the proposed structure.

The ^{13}C NMR observations are thus best interpreted in terms of initial formation (by 1 equiv of FSO_3H) of a covalent fluorosulfonic acid adduct 7 of butadieneiron tricarbonyl which upon treatment with excess of FSO_3H ionizes to give 6.



6

Protonation of butadieneiron tricarbonyl (1) with excess FSO_3D in SO_2 solution at −60 °C, based on the proton-coupled ^{13}C NMR spectrum (Figure 1E), gives an ion bearing deuterium on both C_1 and methyl carbon, but not on C_2 and C_3. This observation is thus in agreement with a slow intramolecular exchange process.



Our ^{13}C NMR spectroscopic studies reinforce the conclusions reached by Brookhart[7] and Whitesides[8] that butadieneiron tricarbonyl is monoprotonated in strong acids and not diprotonated as suggested previously by Kaesz.[6]

Experimental Section

Materials. Butadieneiron tricarbonyl (1) was obtained from Ventron Corp. Alfa Products, and was used without further purification. Both FSO_3H and FSO_3D (Cationics, Inc.) were freshly distilled under nitrogen.

Preparation of Ions. A weighed amount of 1 in SO_2 was placed in an NMR tube at dry ice–acetone bath temperature (ca. −78 °C) under nitrogen and was dissolved in SO_2 containing a known amount of acid (equimolar or fewfold excess FSO_3H) with stirring to give an about 10% solution. Samples were immediately transferred to a precooled NMR probe for spectroscopic study.

^1H and ^{13}C NMR Spectroscopy. Both ^1H and ^{13}C NMR spectra were obtained as previously reported.[1]

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Registry No.—1, 12078-32-9; 2, 12287-49-9; 6, 58904-55-5; 7, 58919-15-6; HCl, 7647-01-0; FSO_3H, 7789-21-1.

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Alkylation of the Carbanion from Methyl Bis(ethylthio)acetate with Alkyl and Aralkyl Halides[1]

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Treatment of dithioacetals with strong base can result in carbanions capable of reacting with alkyl halides to give moderate to poor yields of products.[2] Corey and Seebach improved considerably upon this reaction with the introduction of the lithium salts of dithiane and its derivatives.[3] The importance of these reactions in addition to the formation of new carbon–carbon bonds stems from the convenience of utilizing the resulting bis(alkylthio)ketals to obtain ketones after hydrolysis, or methylene groups following reduction with Raney nickel. Recently a need arose in this laboratory for a two-carbon fragment that could be alkylated and act as a precursor to α-keto esters. A few years ago, a preparation of α-keto esters was reported using the carbanion from ethyl 1,3-dithiane-2-carboxylate in condensations with alkyl halides.[4] In this work ethyl 1,3-dithiane-2-carboxylate was prepared by a boron trifluoride catalyzed reaction of 1,3-propanedithiol with ethyl diethoxyacetate.

In the present report it is demonstrated that the activating effect of the ester group on the acidity of the neighboring proton is such that a simple bis(alkylthio)acetal will work equally well. Moreover, the cost of preparing the reagent as performed below is a small fraction of that required to prepare the dithiane derivative. Methyl bis(ethylthio)acetate (1) was

Table 1. Preparation and Properties of Bis(ethylthio)ketals of α-Keto Esters (2)[a]

RX	Registry no.	Product	Registry no.	Yield %	Bp, °C (Torr)	$n^{19}D$	NMR (CCl_4, Me_4Si), δ ppm
CH_3I	74-88-4	**2a**	59054-68-1	100	49–50 (0.01)	1.5032	1.17 (t, 6 H, J = 7 Hz, $-SCH_2CH_3$), 1.65 (s, 3 H, $>CCH_3$), 2.60 (q, 4 H, J = 7 Hz, $-SCH_2CH_3$) 3.67 (s, 3 H, $-CO_2CH_3$)
CH_3CH_2Br	74-96-4	**2b**	59054-69-2	94	53–55 (0.02)	1.5022	0.60–1.37 (m, 9 H, CH_3), 1.87 (q, 2 H, $-CCH_2CH_3$), 2.22 (q, 4 H, $-SCH_2CH_3$), 3.67 (s, 3 H, $-CO_2CH_3$)
$(CH_3)_2CHI$	75-30-9	**2c**	59054-70-5	91	57–59 (0.01)	1.5029	1.05 (d, 6 H, $-CH(CH_3)_2$), 1.18 (t, 6 H, J = 7 Hz, $-SCH_2CH_3$), 2.00–3.00 (m, 5 H, $-SCH_2CH_3$ and $-CH(CH_3)_2$), 3.67 (s, 3 H, $-CO_2CH_3$)
$CH_3(CH_2)_2CH_2I$	542-69-8	**2d**	59054-71-6	91	67–70 (0.02)	1.4966	0.90–2.00 (complex m, 15 H, $-CH_2CH_2CH_2CH_3$ and $-SCH_2CH_3$), 2.22 (q, 4 H, $-SCH_2CH_3$), 3.67 (s, 3 H, $-CO_2CH_3$)
$PhCH_2Br$	100-39-0	**2e**	59054-72-7	99	101–105 (0.05)	1.5560	1.15 (t, 3 H, J = 7 Hz, $-SCH_2CH_3$), 2.55 (q, 4 H, J = 7 Hz, $-SCH_2CH_3$), 3.22 (s, 2 H, benzyl CH_2), 3.57 (s, 3 H, $-CO_2CH_3$), 7.06 (s, 5 H, phenyl)

[a] Satisfactory analytical data (±0.2% for C and H) for all products were submitted for review.

$$Cl_2CHCO_2Me + 2Na^+SEt^- \longrightarrow \underset{1}{(EtS)_2CHCO_2Me}$$

the compound chosen for study. It was easily prepared by treatment of methyl dichloroacetate with sodium ethylmercaptide in methanol by a procedure somewhat similar to that used to prepare the corresponding ethyl ester.[5]

Compound **1** was previously prepared by reductive thiolation of methyl trichloroacetate.[6] In addition to the ready commercial availability and low cost of methyl dichloroacetate, another advantage of using the methyl ester rather than the ethyl ester is that the NMR spectra of the condensation products discussed below are greatly simplified.

The carbanion of **1** was prepared by treatment with sodium hydride in dry *N,N*-dimethylformamide. When tetrahydrofuran was the solvent only a very slow reaction was noted. In dimethoxyethane the reaction was quite vigorous, but upon aqueous workup hydrolysis of the ester group occurred. Treatment of the carbanion of **1** in *N,N*-dimethylformamide with D_2O demonstrated a complete conversion to the carbanion as noted by the disappearance of the singlet at δ 4.25 in the NMR spectrum. The reaction of this carbanion with the halides used here appear to give nearly quantitative yields of a new group of bis(ethylthio) compounds derived from α-keto esters (**2a–e**).

$$1 \xrightarrow{NaH} \underset{Na^+}{(EtS)_2\bar{C}CO_2Me} \xrightarrow{RX} \underset{\underset{R}{|}}{(EtS)_2CCO_2Me}$$
$$2$$

The physical properties of these new compounds are summarized in Table I. Work is in progress to condense the carbanion of **1** with glycosyl halides in order to prepare α-keto ester derivatives for use in the synthesis of *C*-nucleosides.

Experimental Section[7]

Methyl Bis(ethylthio)acetate (1). Sodium (4.6 g, 0.2 mol) was placed in a three-neck flask equipped with a dropping funnel and a condenser under a nitrogen atmosphere. The flask was chilled in an ice bath and 100 ml of methanol was slowly added. When all of the sodium had reacted, 12.4 g (0.2 mol) of ethanethiol was added slowly. The ice bath was removed and 14.3 g (0.1 mol) of methyl dichloroacetate was added, dropwise. The mixture was stirred at room temperature for 48 h and then treated with 75 ml of water and 150 ml of ethyl ether. The ether layer was separated, washed with water (50 ml) and saturated sodium chloride solution (50 ml), and dried over magnesium sulfate. Evaporation of the solvent gave a colorless oil which was distilled to yield 14.8 g (76%): bp 125–127 °C (5 Torr); $n^{19}D$ 1.5038; ir (film) 1735 cm^{-1} (ester); NMR (CCl_4) δ 1.26 (t, 6 H, J = 7 Hz, $-SCH_2CH_3$), 2.68 (q, 4 H, J = 7 Hz, $-SCH_2CH_3$), 3.70 (s, 3 H, $-CO_2CH_3$), 4.25 (s, 1 H, –CH–) [lit.[6] bp 122° (11 Torr)].

General Procedure for Alkylation. Sodium hydride (0.480 g, 57% oil dispersion) was placed in a dropping funnel fitted to a three-neck reaction flask in an atmosphere of dry nitrogen. It was washed twice with hexane (dried over sodium wire) and the washings were removed with a pipet. Ice-cold *N,N*-dimethylformamide (25 ml) was added to the funnel and the suspension was passed into the flask. A solution of methyl bis(ethylthio)acetate (**1**, 1.94 g, 0.01 mol) dissolved in 25 ml of *N,N*-dimethylformamide was added dropwise to the sodium hydride suspension which was stirred and chilled to 0 °C. Evolution of hydrogen was observed throughout this period. An additional drop or two of **1** was usually added to be certain that no sodium hydride remained. After an additional 5–10 min of stirring a slight excess of the halide was added and the reaction mixture was stirred at room temperature overnight. The mixture was diluted with 100 ml of water (pH was neutral) and the oil which separated was extracted with 50 ml of ethyl ether. The aqueous layer was further extracted with ether (2 × 25 ml) and the combined extracts were washed with water (5 × 100 ml) and dried over magnesium sulfate. The solvent was removed by evaporation under reduced pressure to yield nearly quantitative amounts of the desired products as oils. These appeared to be sufficiently pure for further reactions as determined by the NMR spectra. For purposes of elemental analysis, samples were distilled under high vacuum.

Registry No.—**1**, 38564-39-5; ethanethiol, 75-08-1; methyl dichloroacetate, 116-54-1.

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