was suspended in 250 ml methanol and stirred at 25° for 1 h. During this time the yellow color of the diolefin complex faded and a white solid formed. This mixture was then heated at reflux for 1 h. After 10 min at reflux there was extensive precipitation of palladium. The reaction mixture was then cooled and filtered. The filtrate was evaporated to small volume and the residue partitioned between benzene and water. The benzene solution was washed with three portions of water and then dried over sodium sulfate. After the benzene was evaporated the residue was distilled giving 2.51 g (36.4 %) of a fraction, b.p. 115–117° at 85 mm. A nuclear magnetic resonance spectrum on the neat liquid showed peaks at δ —5.7 (olefinic protons, relative intensity 3); —3.27 and —3.23 (OCH_3, total rel. intensity 3); —2.25 ($CH_2C{=}C$, rel. intensity 4); and —1.60 ppm ($C{-}CH_2{-}C$, rel. intensity 4) indicating the assigned structures (III) and (IV).

Monsanto Company, Hydrocarbons and Polymers Division, Research Department, St. Louis, Missouri (U.S.A.)
ROBERT G. SCHULTZ

1 J. CHATT, L. M. VALLARINO AND L. M. VENANZI, *J. Chem. Soc.*, (1957) 3413.
2 S. D. ROBINSON AND B. L. SHAW, *J. Chem. Soc.*, (1964) 5002.
3 J. K. STILLE, R. A. MORGAN, D. D. WHITEHURST AND J. R. DOYLE, *J. Am. Chem. Soc.*, 87 (1965) 3282.
4 J. TSUJI AND H. TAKAHASHI, *J. Am. Chem. Soc.*, 87 (1965) 3275.
5 R. B. KING, *Inorg. Chem.*, 3 (1963) 528.

Received March 22nd, 1966

The preparation of ferrocenylmethyl alkyl sulfides from alkyl ferrocenethiolcarboxylates

Esters of aromatic acids are reduced by lithium aluminum hydride to form two alcohols that correspond to the components of which the ester is composed (eqn. 1)[1]. Corresponding products have been obtained in the reduction of thiol esters by lithium aluminum hydride (eqn. 2). The alcohol is derived from the acyl fragment as before and the mercaptan is derived from the thiol portion[2]. In certain instances when the reduction of an aromatic ester is carried out in the presence of excess lithium aluminum

$$\mathrm{ArCO_2R} \xrightarrow{\mathrm{LiAlH_4}} \mathrm{ArCH_2OH} + \mathrm{ROH} \tag{1}$$

$$\mathrm{RCOSR'} \xrightarrow{\mathrm{LiAlH_4}} \mathrm{RCH_2OH} + \mathrm{R'SH} \tag{2}$$

hydride, the reduction of the acyl portion proceeds further with the formation of a methyl group[3,4,*]. Numerous reductions by lithium aluminum hydride have been

---

[*] The report that methylferrocene results from treatment of ferrocenoic acid or its methyl ester with excess lithium aluminum hydride[4] must be attributed to the *in situ* preparation of this latter reagent from lithium hydride and aluminum bromide. These reductions when carried out in our laboratories using commercially available lithium aluminum hydride (Metal Hydrides, Inc.) led only to the formation of ferrocenylmethanol. Methylferrocene was obtained only when added aluminum chloride was present in the reducing medium. These latter results are in agreement with the findings of Benkeser and Bach[5].

investigated in which the products can be varied profoundly by the addition of aluminum chloride to the reaction mixture*,[7]. When aromatic esters are reduced by a mixture of lithium aluminum hydride/aluminum chloride ("mixed hydrides")[6] the reaction products are identical to those obtained when lithium aluminum hydride itself is used[8]. Thus the addition of aluminum chloride is without effect upon the reduction of aromatic esters by lithium aluminum hydride. The reaction of thiol esters with the mixed hydrides reagent has not been reported.

Recently it has been shown that alkyl and aryl metallocenethiolcarboxylates can be prepared from the appropriate metallocene and an alkyl or aryl chlorothiolformate in the presence of aluminum chloride as a Friedel–Crafts catalyst[9]. The thiolesters thus obtained are versatile intermediates and provide one with a new route to ferrocenoic acid or substituted ferrocenoic acids, as well as to a variety of acid group derivatives. This report describes a number of further experiments with alkyl ferrocenethiolcarboxylates in which lithium aluminum hydride and mixed hydrides are employed.

In the course of these investigations methyl ferrocenethiolcarboxylate (I, $R = CH_3$) was reduced by mixed hydrides in an attempt to prepare methylferrocene.

$$\underset{(\mathrm{I})}{C_5H_5{-}Fe{-}C_5H_4{-}CO{-}SR} \xrightarrow[AlCl_3]{LiAlH_4} \underset{(\mathrm{II})}{C_5H_5{-}Fe{-}C_5H_4{-}CH_2{-}SR} + C_5H_5{-}Fe{-}C_5H_4{-}CH_3 \quad (3)$$

The reaction product, a light orange oil, was obtained in 87–95 % yield. Chromatography on a column of activity grade III alumina using hexane as an eluent led to the separation and removal of two bands. The first, an orange solid, was identified as methylferrocene by comparison with an authentic sample. The second material, also eluted with hexane, was an orange-yellow solid (m.p. 39–41°) identified as ferrocenylmethyl methyl sulfide (II, $R = CH_3$) by means of its infrared and NMR spectra in conjunction with microanalytical data. The NMR spectrum of this latter compound consisted of three sharp singlets at τ 5.82, 6.46, and 7.95 with relative areas 9, 2, and 3 respectively. Nesmeyanov and co-workers[10] have mentioned the synthesis of ferrocenylmethyl methyl sulfide (II, $R = CH_3$) from ferrocenylmethanethiol and dimethyl sulfate and reported only its melting point, 44–45°.

This unexpected course of reaction, the formation of alkyl ferrocenylmethyl sulfides, was found to be independent of the identity of the alkyl group R (eqn. 3). Under identical conditions homologues of (I) (R = ethyl, n-propyl, isopropyl, n-butyl, n-octyl) provided the corresponding alkyl ferrocenylmethyl sulfides (II). These were characterized by their infrared and NMR spectra. The infrared spectra of the alkyl ferrocenylmethyl sulfides are highly reminiscent of alkyl ferrocenes in that they exhibit only aliphatic and ferrocene absorptions.

Reductions of (I) ($R = CH_3$) with unmodified lithium aluminum hydride provided ferrocenylmethanol and methanethiol as would be expected from eqn. (2). Thus the addition of aluminum chloride to the reducing medium alters the reaction pathway and leads to a novel reduction with the formation of ferrocenylmethyl methyl sulfide and methylferrocene. Further investigation of this reduction of thiol esters to produce sulfides is currently in progress and will be reported at a later date.

---

[*] A summary of the uses of mixed hydrides can be found in ref. 6.

Experimental

Ferrocenylmethyl methyl sulfide. To a stirred suspension of 2.0 g (0.053 mole) lithium aluminum hydride in 100 ml ether there was added slowly a solution containing 6.0 g (0.045 mole) aluminum chloride in 75 ml ether. The reaction mixture was stirred at reflux for ½ h to insure complete reaction, followed by dropwise addition of a solution of 2.0 g (0.0077 mole) methyl thiolferrocenoate in 50 ml ether. The reaction mixture was stirred for 2 h at reflux then hydrolyzed by careful addition of wet ether followed by water and finally dilute hydrochloric acid. Evaporation of the ether phase provided a light orange oil which was taken up in hexane and chromatographed on activity grade III alumina (Alcoa F-20) using hexane as eluent.

Evaporation of the eluate containing the first yellow band provided 0.4 g (26 %) of methylferrocene identified by its infrared and NMR spectra. Evaporation of the hexane containing the second band provided 1.3 g (69 %) of yellow crystals m.p. 39–41°. (Found: C, 58.72; H, 5.84; S, 12.90. $C_{12}H_{14}FeS$ calcd.: C, 58.65; H, 5.73; S, 13.02 %.) Similar reduction of ethyl, n-propyl, isopropyl, n-butyl, and n-octyl thiolferrocenoate provided the corresponding alkyl ferrocenylmethyl sulfide.

When the reduction of methyl thiolferrocenoate was carried out using only excess lithium aluminum hydride, the products were ferrocenylmethanol (88 %) and bis(ferrocenylmethyl) ether (10 %), in addition to methyl mercaptan.

Western Division Research Laboratories, DONALD E. BUBLITZ
The Dow Chemical Company, Walnut Creek, California (U.S.A.)

1 R. F. NYSTROM AND W. G. BROWN, *J. Am. Chem. Soc.*, 69 (1947) 1197.
2 M. S. NEWMAN, M. W. RENOLL AND I. AUERBACH, *J. Am. Chem. Soc.*, 70 (1948) 1023.
3 L. H. CONOVER AND D. S. TARBELL, *J. Am. Chem. Soc.*, 72 (1950) 3586.
4 A. N. NESMEYANOV, E. G. PEREVALOVA, L. S. SHILOVTSEVA AND Z. A. BEINORAVICHUTE, *Dokl. Akad. Nauk. SSSR*, 121 (1958) 117; *Chem. Abstr.*, 53 (1959) 323.
5 R. A. BENKESER AND J. L. BACH, *J. Am. Chem. Soc.*, 86 (1965) 890.
6 M. N. RERICK, *Selective Reduction of Organic Compounds with Complex Metal Hydrides*, Metal Hydrides Inc., Beverly, Mass.
7 E. L. ELIEL AND M. N. RERICK, *J. Am. Chem. Soc.*, 82 (1960) 1367;
E. L. ELIEL, V. G. BADDING AND M. N. RERICK, *J. Am. Chem. Soc.*, 84 (1962) 2371 and other papers in this series.
8 E. WIBERG AND A. JAHN, *Z. Naturforsch.*, 7b (1952) 580.
9 D. E. BUBLITZ AND G. H. HARRIS, *J. Organometal. Chem.*, 4 (1965) 404.
10 A. N. NESMEYANOV, E. G. PEREVALOVA, L. I. LEONT'EVA AND U. A. USTYNYUK, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, (1965) 1696; *Chem. Abstr.*, 63 (1965) 18146.

Received January 18th, 1966

J. Organometal. Chem., 6 (1966) 436–438

Organogermanium compounds

VII.* Hydrogen-exchange in germanium- and silicon-substituted acetylenes

To obtain further information about electronic effects of trialkylsilyl and trialkylgermyl groups we have measured the rates of detritiation at 25° in a mixture of

---

* For Part VI see ref. 1.