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NOTE

CONDENSATION OF FERROCENE WITH 1,1,3,3-TETRAMETHOXYPROPANE

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While the alkylation of ferrocene with formaldehyde alone or as a component in the Mannich reaction is well known[1], the use of acetals as alkylating agents has not been examined. We have found that the reaction of ferrocene with malondialdehyde dimethyl acetal in the presence of boron trifluoride etherate gives 3-ferrocenylpropenal (III) in 50% yield. The reaction provides an expeditious synthesis of this aldehyde which had previously been prepared from ferrocenecarboxaldehyde either by condensation with acetylene and Rupé rearrangement of the resulting acetylenic carbinol or by Knoevenagel condensation with malonic acid, decarboxylation, reduction of the carboxylic acid to 3-ferrocenylallyl alcohol and subsequent oxidation of this substance with manganese dioxide[2]. The cation (II) rather than (I) is apparently the final product of this reaction since the unsaturated aldehyde (III) is isolated under basic as well as acid workup conditions.

$$\mathrm{FcH + (CH_3O)_2CHCH_2CH(OCH_3)_2 \xrightarrow[CHCl_3]{BF_3 \cdot Et_2O} \underset{(I)}{Fc\overset{+}{C}HCH_2CH(OCH_3)_2}} \rightarrow$$

$$\rightarrow \mathrm{\underset{(II)}{FcCH{=}CH\overset{+}{C}HOCH_3} \xrightarrow{H_2O} \underset{(III)}{FcCH{=}CHOCH_3}}$$

Several attempts to extend this reaction to cyclic acetals such as 2,5-dimethoxytetrahydrofuran and 2,5-dimethoxy-2,5-dihydrofuran were unsuccessful. With these reagents extensive decomposition occurred in the presence of a variety of acid catalysts.

EXPERIMENTAL

A solution prepared from 2.0 g of ferrocene and 2.0 g of 1,1,3,3-tetramethoxypropane in 45 ml of chloroform was cooled, in a nitrogen atmosphere, to 2°. Freshly distilled boron trifluoride etherate (20 ml) was added dropwise over a period of 0.5 h. The resulting purple solution was allowed to stir at 2° for 15 min, at room temperature for 1 h and finally at 64° for an additional hour. The solution was then poured into

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100 ml of water, extracted with ether several times, and the combined extracts were washed to neutrality, dried over magnesium sulfate and finally concentrated to a red oil. This was placed on a chromatographic column prepared from 100 g of Camag alumina (activity 2). Elution with ether gave one major band, which afforded 1.29 g of 3-ferrocenylpropenal (50.5%). Recrystallization from ether gave red needles, m.p. 97–98°; IR (KBr) 1660 (C=O), 1612 (C=C); NMR ($CDCl_3$) δ 4.22 (S, 5, C_5H_5), 4.59 (S, 4, C_5H_4R), 6.39 (q, 1, $J_{12}=8$ Hz, $J_{23}=16$ Hz, C=CH–C=O), 7.48 (d, 1, $J_{23}=16$Hz, CH=C–C=O), 9.65 (d, 1, $J_{12}=8$ Hz, CHO). (Found: C, 65.03; H, 5.02. $C_{13}H_{12}FeO$ calcd.: C, 65.06; H, 5.00%.)

The same product was obtained when the reaction solution was worked up by pouring into excess 10% aqueous sodium hydroxide solution and immediately extracted with ether.

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