Academician A. N. NESMEYANOV, V. D. VIL' CHEVSKAYA, N. S. KOCHETKOVA

1963

SovietRxiv

Abstract

Full Text

Chemistry

Academician A. N. NESMEYANOV, V. D. VIL’ CHEVSKAYA, N. S. KOCHETKOVA

SYNTHESIS OF 1-FERROCENOYL-2-CARBOMETHOXYETHYL

By acylation of ferrocene with the acid chloride of the monomethyl ester of maleic acid in the presence of anhydrous $AlCl_3$ in methylene chloride, we obtained 1-ferrocenoyl-2-carbomethoxyethylene, m.p. 99.5-100°. Its structure was demonstrated: 1) by catalytic hydrogenation, which led to the β-carbomethoxypropionylferrocene previously synthesized by us (^{1}); 2) by IR spectra; 3) by determination of the molecular weight.

In the IR spectrum of 1-ferrocenoyl-2-carbomethoxyethylene there is a band in the region of 1610 cm^{-1}, corresponding to a double bond conjugated with a carbonyl group. The presence of intense bands at 1280 cm^{-1} and 1310 cm^{-1} confirms the presence of a double bond; moreover, it may be assumed that the product obtained is the trans isomer. Apparently, isomerization occurs under the reaction conditions. By changing the ratio of the starting materials to 1 : 2 : 4 (ferrocene : acid chloride : $AlCl_3$), we obtained 1,1′-di(1-keto-2-carbomethoxyethylene)ferrocene, m.p. 164°. In some cases, under the conditions for synthesis of the monosubstituted compound, a hydrogenated product was unexpectedly obtained—β-carbomethoxypropionylferrocene, which after hydrolysis with alkali gave β-carboxypropionylferrocene (^{1}).

In a recently published work, Sujama and Teitei (^{2}) report that, in attempting to obtain unsaturated products of acylation of ferrocene with fumaryl chloride (or citraconyl chloride), they isolated only hydrogenated products: for example, 1,2-diferrocenoylethane and β-carboxypropionylferrocene. In an attempt to acylate ferrocene with maleic anhydride, no definite products were obtained (^{3}).

Reaction of ferrocene with carbomethoxymaleic acid chloride

A. To a mixture of 10 g (0.05 mole) of ferrocene in 75 ml of methylene chloride and 8 g (0.05 mole) of carbomethoxymaleic acid chloride, with stirring, a solution of 7.2 g (0.05 mole) of aluminum trichloride in 15 ml of abs. ether was added dropwise. After heating for 1 hr 30 min at 50°, the reaction mixture was decomposed with ice. The methylene chloride layer was separated, washed with water, and poured into a dish. From the aqueous layer, after reduction with stannous chloride, ferrocene was isolated, and from the methylene chloride an oily substance was obtained, which was chromatographed from petroleum ether on alumina. In this process an insignificant amount of ferrocene was isolated and violet crystals, m.p. 94-96°. After 5-min boiling in a solution of petroleum ether with charcoal and filtration through a thin layer of alumina, shiny dark-violet crystals of 1-ferrocenoyl-2-carbomethoxyethylene were isolated in the form of needles, m.p. 99.5-100°. They are readily soluble in ordinary organic solvents and in alkalis.

Found, %: C 60.36; 60.45; H 4.87; 4.89; Fe 18.69; 18.63
$C_{15}H_{14}O_3Fe$. Calculated, %: C 60.40; H 4.70; Fe 18.79

Molecular weight (cryoscopy, benzene) found 278, calculated 298.

B. A solution of 15 g (0.08 mole) of ferrocene in 150 ml of carbon disulfide was mixed with 12 g (0.08 mole) of carbomethoxymaleic acid chloride and, at···

with stirring, a solution of 10.8 g (0.08 mole) of aluminum trichloride in 15 ml of abs. ether was added dropwise. The mixture was heated for 1 hr 40 min at 50°. After the usual workup, a yellow crystalline product was isolated. It was dissolved in 20% KOH and heated on a water bath at 50-60°. It was then filtered and precipitated with HCl. The precipitated solid was separated, washed with water, and dried, m.p. 160-162°. After two recrystallizations from aqueous methyl alcohol, it melted at 167°. A mixed sample with deliberately prepared β-carboxypropionylferrocene gave no depression of the melting point.

Found, %:	C 58.68; 58.80;	H 4.95; 4.99;	Fe 19.20; 19.37
$C_{14}H_{14}O_3Fe$. Calculated, %:	C 58.74;	H 4.89;	Fe 19.57

Small amounts of ferrocene and an oily product were isolated from the carbon disulfide. The latter was dissolved in alkali and precipitated with HCl. An insignificant precipitate formed. Ferrocene was isolated from the aqueous layer upon reduction with stannous chloride.

B. A solution of 10 g (0.05 mole) of ferrocene in 100 ml of carbon disulfide was mixed with 15.9 g (0.107 mole) of carbomethoxymaleic acid chloride anhydride, and, with stirring, 28.8 g (0.216 mole) of $AlCl_3$ was added to the mixture over 25 min. After heating for two hours at 45°, the carbon disulfide was decanted, and the residue was decomposed with ice. A small amount of ferrocene was isolated from the carbon disulfide. Dark-violet oily crystals precipitated from the aqueous layer. They were chromatographed from benzene on alumina. A little ferrocene was eluted with heptane, and benzene washed out a dark-violet substance with m.p. 158-160°. 1,1′-Di-(1-keto-2-carbomethoxyethylene)ferrocene, recrystallized twice from a mixture of petroleum ether with benzene (1:1), melted at 164°. Weight 2.4 g (22% of theory, calculated on reacted ferrocene).

Found, %:	C 58.17; 58.18;	H 4.49; 4.61;	Fe 13.72; 13.92
$C_{20}H_{18}O_6Fe$. Calculated, %:	C 58.50;	H 4.39;	Fe 13.66

The substance is soluble in ordinary organic solvents and in alkali. After separation of the oily solid product, the aqueous solution was reduced with stannous chloride and extracted with ether. 4.8 g of ferrocene was isolated.

Catalytic hydrogenation of 1-ferrocenoyl-2-carbomethoxyethylene

In a solution of 0.5 g of 1-ferrocenoyl-2-carbomethoxyethylene in 50 ml of abs. alcohol, in the presence of platinum oxide, 97 ml of H_2 was absorbed. The catalyst was separated, and from the alcoholic solution, after removal of the solvent, a yellow product with m.p. 58° was isolated. After recrystallization from a mixture of petroleum ether with benzene (3:1), it melted at 60°. A mixed sample with β-carbomethoxypropionylferrocene gave no depression of the melting point.

Institute of Organoelement Compounds
Academy of Sciences of the USSR

Received
18 VI 1963

REFERENCES

1. A. N. Nesmeyanov, N. A. Vol' kenau, V. D. Vil' chevskaya, DAN, **118**, No. 3, 512 (1958).

2. N. Sugiyama, T. Teitei, Bull. Chem. Soc. Japan, **35**, No. 8, 1423 (1962).

3. R. Dabord, B. Gautheron, C. R., No. 11, 2015 (1962).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.