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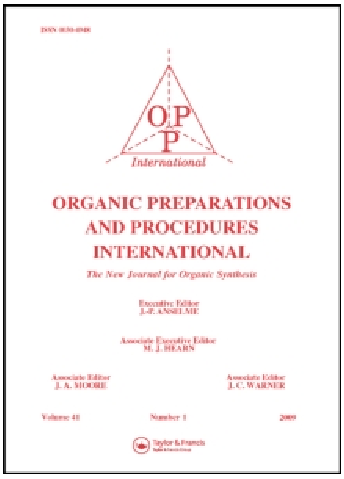

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AN IMPROVED SYNTHESIS OF 1-FERROCENYL-1,3-BUTADIENE

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ORGANIC PREPARATIONS AND PROCEDURES INT. 3(4), 171-175 (1971)

AN IMPROVED SYNTHESIS OF 1-FERROCENYL-1,3-BUTADIENE

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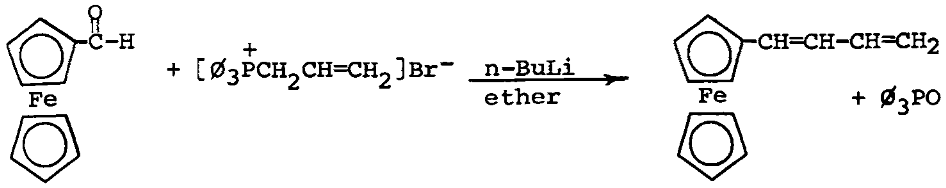

In conjunction with our study of the polymerization characteristics of several unsaturated ferrocene derivatives, a considerable quantity of 1-ferrocenyl-1,3-butadiene was required. Although the synthesis of this compound has been described previously,[1] most of these procedures do not lend themselves to the synthesis of 1-ferrocenyl-1,3-butadiene in appreciable quantity. One of these methods,[1d] the dehydration of 1-ferrocenyl-3-buten-1-ol, appeared at first to be readily adaptable to large scale synthesis. However, we found that the cupric ion catalyzed dehydration step of the synthesis gave very erratic results and was thus unsatisfactory for routine syntheses. We report a facile route to 1-ferrocenyl-1,3-butadiene by a modification of the Wittig procedure of Osgerby and Pauson[1a] which leads to a more than four-fold increase in yield over that reported previously. The starting materials, formylferrocene[2] and allyltriphenylphosphonium bromide,[3] are readily available and the reaction can conveniently be carried out on a molar scale.

From allyltriphenylphosphonium bromide (prepared in quantitative yield from the reaction of allyl bromide with triphenylphosphine) the ylid, allyltriphenylphosphorane, is generated in ethereal solution by the addition of *n*-butyl lithium; an ethereal solution of the aldehyde, containing a free-radical inhibitor, is then added over a period of 30 min. It is essential that all these reactions be carried out under an atmosphere of dry, oxygen-free nitrogen to prevent polymerization. Maximum yields were obtained when the entire reaction was carried out in a dry box. Suitable work-up of the reaction mixture after 5 hrs. and separation of the 1-ferrocenyl-1,3-butadiene on a silica gel column (to remove the last traces of triphenylphosphine oxide) gave a 52% yield of product suitable for use without further purification. The conversion of the aldehyde to 1-ferrocenyl-1,3-butadiene is very high, as evidenced by detection of only a trace of unreacted formylferrocene by glpc of the crude reaction mixture, but polymerization of the diene under the basic reaction conditions lowers the isolated yield appreciably.

EXPERIMENTAL[4]

Formylferrocene was prepared according to the method of Sato *et al.*,[2] mp 117-120° and allyltriphenylphosphonium bromide was obtained in essentially quantitative yield according to the method of Wittig and Schollkopf,[3] mp 210-211°.

1-Ferrocenyl-1,3-butadiene. - To 46.20 g. (0.120 mole) of allyltriphenylphosphonium bromide in 480 ml. of anhydrous ether, under a dry, oxygen-free nitrogen atmosphere, was added 75 ml. (0.120 mole) of 1.6 M n-butyllithium[5] and the reaction was stirred magnetically for 1.5 hrs. The appearance of a red color during this period of stirring was indicative of ylid formation. Then 16.4 g. (0.076 mole) of formylferrocene and 0.5 g. of di-ter-pentylhydroquinone dissolved in 160 ml. of anhydrous ether was added to the ylid over a period of 30 min. Stirring was continued for an additional 5 hrs.[6] during which time the reaction mixture turned a bright orange color. The ether was then evaporated by increasing the rate of flow of dry, oxygen-free nitrogen through the reaction flask. The resulting red-brown solid was immediately extracted[7] with two 160 ml. portions of dry benzene, and the combined benzene extract was filtered with suction to remove suspended insoluble material. Most of the benzene solvent was then removed by means of a rotary evaporator, and the resulting viscous solution placed on a 2.5 by 122 cm column of wet packed 60-200 mesh silica gel. Elution with approximately 1 ℓ. benzene afforded 9.48 g. (52%), mp[8] 62-67° 1-ferrocenyl-1,3-butadiene as the first material to be eluted. Recrystallization from methanol gave pure product, mp 80° [lit.[1a] mp 80°], which is completely stable to storage at room temperature for extended periods; ir ($CHCl_3$) 1600, 1640 (ν c=c), 1420 cm^{-1} (terminal) vinyl δ C-H); nmr ($CDCl_3$) δ 4.06 (s, 5, unsubstituted ring H), 4.20 (t, 2, substituted ring H), 4.32 (t, 2, substituted ring H), 5.05 (m, 2, C-4 H), 6.32 (m, 3, C-1, C-2, C-3 H).

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2. M. Sato, H. Kono, M. Shiga, I. Motoyama, and K. Hata, Bull. Chem. Soc., Japan, 41, 252 (1968).

3. G. Wittig and U. Schollkopf, Chem. Ber., 87, 1318 (1954).

4. Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. I. R. Spectra were obtained on a Perkin-Elmer Model 337 spectrophotometer, and nmr spectra we run on a Varian HA-100 spectrometer using $CDCl_3$ as solvent and tetramethylsilane as internal reference.

5. A 1.6 M solution of n-butyllithium in hexane may be obtained from Foote Mineral Company, Exton, Pennsylvania. We have also used other concentrations with equal success.

6. Longer stirring periods in the presence of n-butyllithium promotes polymerization and thus decreases the yield of desired product.

7. Once the solvent has been evaporated, the solid material must be extracted with benzene immediately. Delay makes the material difficult to handle, presumably because of extensive polymerization.

8. Infrared analysis of this material shows it to be a mixture of *cis* and *trans* isomers. Successive sublimations or recrystallization of this material leads to successively higher melting points until the pure *trans*, m.p. 97-98°, is reached.

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