## 1- AND 2-SUBSTITUTED 1,3-BUTADIENEIRON TRICARBONYLS

```
N. S. Nametkin, A. I. Nekhaev,
and V. D. Tyurin
```

UDC 547.1'13:547.315.2:546.725

One of the principal methods for the synthesis of the dienic  $\pi$ -complexes of the transition metals is based on the reaction of a dienic hydrocarbon with the appropriate metal compound. However, certain dienes, due to the known tendency to polymerize and oxidize, are difficult to isolate in the pure forms.

We found that the 1- and 2-ferrocenyl-1,3-butadienes, which are formed by heating 1-ferrocenyl-1buten-3-ol (I) and 2-ferrocenyl-3-buten-2-ol (II) with catalytic amounts of  $CuSO_4 \cdot 5H_2O$  in absolute benzene medium, without isolation, give 1-ferrocenyl-1,3-butadieneiron tricarbonyl (III) and 2-ferrocenyl-1,3butadieneiron tricarbonyl (IV) by reaction with the  $Fe_2(CO)_9$  present in the reaction mixture.



From the reaction products of (I), besides (III), was isolated the isomerization product of (I), namely 1-ferrocenyl-3-butanone (V) in 46% yield. The formation of (V) is in agreement with the data on the isomerization of allyl alcohol to propional dehyde in the presence of  $Fe(CO)_5$  [1], and also with the mechanism for the hydrolysis of  $\pi$ -allyliron tricarbonyl cations [1].

The isomerization of an  $\alpha$ ,  $\beta$ -unsaturated alcohol can be avoided if the dehydration of the alcohol is run in the absence of iron carbonyl, and the latter is added to the reaction after the formation of the diene, without isolating it from the reaction mixture, for example:



The structure of all of the obtained compounds was established on the basis of the NMR and IR spectral data in the  $400-3700 \text{ cm}^{-1}$  region.

## EXPERIMENTAL

<u>1-Ferrocenyl-1-buten-3-ol (I)</u>. With stirring and cooling to -5 to  $-10^{\circ}$ C, to a solution of 7.37 g (0.029 mole) of ferrocenalacetone in 150 ml of absolute ether was added a suspension of 1.10 g (0.029 mole) of LiAlH<sub>4</sub> in 100 ml of absolute ether in 30 min. The reaction mixture was decomposed with acidulated

A. V. Topchiev Institute of Petrochemical Synthesis, Academy of Sciences of the USSR, Moscow. I. M. Gubkin Institute of the Petrochemical and Gas Industry, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 890-892, April, 1974. Original article submitted May 30, 1973.

• 1974 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$15.00. water under ice cooling, and the ether layer was washed with water until neutral and then dried over MgSO<sub>4</sub>. After removal of the solvent we obtained 7.40 g (quantitative yield) of (I) as orange crystals, mp 87-88°C (from hexane). Infrared spectrum (v, cm<sup>-1</sup>): 3360 (OH), 1660 (C=C). Found: C 65.30; H 6.12; Fe 21.80%. C<sub>14</sub>H<sub>16</sub>FeO. Calculated: C 65.64; H 6.31; Fe 21.80%.

General Method for Dehydration of  $\alpha,\beta$ -Unsaturated Alcohols in Presence of Iron Carbonyl. With stirring, a mixture of the appropriate alcohol and iron nonacarbonyl in absolute benzene was refluxed in the presence of catalytic amounts of CuSO<sub>4</sub> · 5H<sub>2</sub>O until the green color disappeared. The reaction mixture was filtered, the solvent and Fe(CO)<sub>5</sub> were removed, and the residue was chromatographed on aluminum oxide, using petroleum ether for elution.

1-Ferrocenyl-1,3-butadieneiron Tricarbonyl (III). The reaction of 4.0 g (0.0157 mole) of (I) and 11.4 g (0.0314 mole) of Fe<sub>2</sub>(CO)<sub>9</sub> in 100 ml of absolute benzene in the presence of 0.2 g of CuSO<sub>4</sub> · 5H<sub>2</sub>O gave 0.6 g (10%) of (III) as orange crystals, mp 108-109°C (from pentane). Infrared spectrum ( $\nu$ , cm<sup>-1</sup>): 2055, 2010, 1985, 1965 (C = O). NMR spectrum (CCl<sub>4</sub>,  $\delta$ , ppm): 0.41 d (1, anti-H<sub>4</sub>); 1.56 m (1, H<sub>1</sub>); 1.79 m (1, syn-H<sub>4</sub>); 3.94 s (5, C<sub>5</sub>H<sub>5</sub>); 4.05 m (4, C<sub>5</sub>H<sub>4</sub>); 5.09 m (1, H<sub>3</sub>); 5.42 m (1, H<sub>2</sub>). Found: C 54.35; H 3.84; Fe 29.40%. C<sub>17</sub>H<sub>14</sub>Fe<sub>2</sub>O<sub>3</sub>. Calculated: C 54.01; H 3.74; Fe 29.55%. Elution with benzene gave (V) as yellow-orange crystals, mp 43-44°C (from hexane). Infrared spectrum ( $\nu$ , cm<sup>-1</sup>): 1712 (C=O). NMR spectrum (CCl<sub>4</sub>,  $\delta$ , ppm): 2.03 s (3, CH<sub>3</sub>); 2.54 s (4, CH<sub>2</sub>); 3.97 s (4, C<sub>5</sub>H<sub>4</sub>); 4.03 s (5, C<sub>5</sub>H<sub>5</sub>). Found: C 65.64; H 6.24; Fe 21.99%. C<sub>14</sub>H<sub>16</sub>FeO. Calculated: C 65.64; H 6.31; Fe 21.80%. Semicarbazone of (V), mp 184-185°C (decompn.) (from alcohol – water). Infrared spectrum ( $\nu$ , cm<sup>-1</sup>): 1697 (C=O), 3460 (N – H). Found: N 13.53%. C<sub>15</sub>H<sub>19</sub>FeN<sub>3</sub>O. Calculated: N 13.42%.

2-Ferrocenyl-3-buten-2-ol (II). This was obtained as described in [2] by the reaction of acetylfer-rocene with vinylmagnesium bromide.

 $\begin{array}{c} \underline{2-\text{Ferrocenyl-1,3-butadieneirontricarbonyl (IV).} & \text{From 5.84 g } (0.0228 \text{ mole}) \text{ of (II), 16.6 g } (0.0456 \text{ mole}) & \text{of Fe}_2(\text{CO})_9 \text{ and } 0.3 \text{ g of CuSO}_4 \cdot 5\text{H}_2\text{O in 120 ml of absolute benzene we obtained 1.55 g } (18\%) & \text{of (IV)} \\ \text{as orange crystals, mp 79-80°C (from pentane). Infrared spectrum } (\nu, \text{ cm}^{-1}): 2055, 1973 (C \equiv O). \text{ NMR} \\ \text{spectrum (CCl}_4, \delta, \text{ ppm): } 0.23 \text{ d } (2, \text{ anti-H}_{1,4}); 1.73 \text{ d } (1, \text{ syn-H}_4); 2.13 \text{ m (1, syn-H}_1); 4.09 \text{ s } (5, \text{ C}_5\text{H}_5); \\ 4.24 \text{ m (3, C}_5\text{H}_4); 4.58 \text{ m (1, C}_5\text{H}_4); 5.61 \text{ m (1, H}_3). \\ \text{Found: C 54.07; H 3.76; Fe 29.55\%. } \\ \text{Calculated: C 54.01; H 3.74; Fe 29.55\%.} \end{array}$ 

<u>1-(p-Fluorophenyl)-1-buten-3-one</u>. The compound was obtained in 67% yield by the condensation of p-fluorobenzaldehyde with acetone in the presence of 10% caustic solution as described in [3] for benzalace-tone; mp 31-32°C (petroleum ether – benzene). Infrared spectrum ( $\nu$ , cm<sup>-1</sup>): 1675 (C=O), 1620 (C=C). NMR spectrum (CCl<sub>4</sub>,  $\delta$ , ppm): 2.24 s (3, CH<sub>3</sub>); 6.55 d (1, H<sub>2</sub>); 7.26 m (4, C<sub>6</sub>H<sub>4</sub>); 7.41 d (1, H<sub>1</sub>), J<sub>1,2</sub> = 16.7 Hz. Found: C 73.00; H 5.80%. C<sub>10</sub>H<sub>3</sub>FO. Calculated: C 73.16; H 5.53%.

 $\frac{1-(p-Fluorophenyl)-1-buten-3-ol (VI)}{fluorophenyl)-1-buten-3-one with LiAlH_4 as described in [4] for cinnamyl alcohol; bp 128-133°C (10 mm).$ Infrared spectrum ( $\nu$ , cm<sup>-1</sup>): 3350 (OH), 1625 (C=C).

<u>1-(p-Fluorophenyl)-1,3-butadieneirontricarbonyl (VII).</u> A mixture of 11 g (0.067 mole) of 1-(p-fluorophenyl)-1-buten-3-ol and 0.5 g of CuSO<sub>4</sub> · 5H<sub>2</sub>O in 100 ml of absolute benzene was refluxed for 15 h. Then 16.6 g (0.033 mole) of Fe<sub>3</sub>(CO)<sub>12</sub> was added and the heating was continued for 3 h. We isolated 5 g (25%) of (VII) as yellow crystals, mp 81.5-82°C (from pentane). Infrared spectrum ( $\nu$ , cm<sup>-1</sup>): 2055, 1977 (C≡O). NMR spectrum (CCl<sub>4</sub>,  $\delta$ , ppm): 0.53 d (1, anti-H<sub>4</sub>); 1.92 m (2, syn-H<sub>4</sub> and H<sub>1</sub>); 5.40 m (1, H<sub>3</sub>); 5.84 m (1, H<sub>2</sub>); 7.09 m (4, C<sub>6</sub>H<sub>4</sub>). Found: C 54.35; H 3.19%. C<sub>13</sub>H<sub>9</sub>FeFO<sub>3</sub>. Calculated: C 54.20; H 3.16%.

 $\frac{1-(m-Fluorophenyl)-1-buten-3-one.}{10\% caustic solution as described in [3]; bp 97-98°C (2 mm).}$ Infrared spectrum ( $\nu$ , cm<sup>-1</sup>): 1680 (C=O), 1620 (C=C). NMR spectrum (CCl<sub>4</sub>,  $\delta$ , ppm): 2.30 s (3, CH<sub>3</sub>); 6.64 d (1, H<sub>2</sub>); 7.30 m (4, C<sub>6</sub>H<sub>4</sub>); 7.44 d (1, H<sub>1</sub>); J<sub>1.2</sub> = 16.7 Hz.

1-(m-Fluorophenyl)-1-buten-3-ol. The compound was obtained in 90% yield by the reduction of 1-(m-fluorophenyl)-1-buten-3-one with LiAlH<sub>4</sub> as described in [4]; bp 98-100°C (2 mm). Infrared spectrum ( $\mu$  cm<sup>-1</sup>): 3360 (OH); 1625 (C=C).

 $\frac{1-(m-Fluorophenyl)-1,3-butadieneirontricarbonyl (VIII)}{of 1-(m-fluorophenyl)-1-buten-3-ol in 100 ml of CCl<sub>4</sub> at ~20°C was added 4.5 ml (7.6 g; 0.05 mole) of POCl<sub>3</sub>. The mixture was heated for 40 min at 65-70°C, after which it was washed with 5% Na<sub>2</sub>CO<sub>3</sub> solution, then with water until neutral, the solvent was removed, and the residue was vacuum-distilled. We$ 

obtained 4.6 g of a colorless oil, bp 60-67°C (7 mm), which without purification was reacted with 15 g (0.03 mole) of Fe<sub>3</sub>(CO)<sub>12</sub> in 100 ml of absolute benzene. We isolated 0.15 g (1%) of (VIII) as yellow crystals, mp 54.5-55°C (from pentane). Infrared spectrum ( $\nu$ , cm<sup>-1</sup>): 2060, 1985 (C = O). NMR spectrum (CCl<sub>4</sub>,  $\delta$ , ppm): 0.54 d (1, anti-H<sub>4</sub>); 1.87 m (2, H<sub>1</sub>, syn-H<sub>4</sub>); 5.43 m (1, H<sub>3</sub>); 5.87 m (1, H<sub>2</sub>); 7.01 m (4, C<sub>6</sub>H<sub>4</sub>). Found: C 53.80; H 3.17%. C<sub>13</sub>H<sub>9</sub>FeFO<sub>3</sub>. Calculated: C 54.20, H 3.16%.

General Method for Preparation of 2-Substituted m,p-Fluorophenyl-1,3-butadieneirontricarbonyls. With vigorous stirring and cooling in water, 220 ml of a 1 M solution of vinylmagnesium bromide in THF was added in 30 min to a solution of 27.6 g (0.2 mole) of m(p)-fluoroacetophenone in 100 ml of THF. The mixture was heated for 2 h, decomposed with water, extracted with ether, washed until neutral, and dried over MgSO<sub>4</sub>. After removal of the solvents the residue was vacuum-distilled. With stirring, a mixture of the crude distillate and 45 g (0.09 mole) of  $Fe_3(CO)_{12}$  was refluxed in absolute benzene until the green color disappeared. The reaction mixture was filtered, the solvent and  $Fe(CO)_5$  were removed, and the residue was chromatographed on aluminum oxide, using petroleum ether as the eluant.

2-(p-Fluorophenyl)-1,3-butadieneirontricarbonyl. We obtained 6.9 g (12% yield) of the compound as yellow crystals, mp 63-63.5 °C (from pentane). Infrared spectrum ( $\nu$ , cm<sup>-1</sup>): 2050, 1960 (C = O). NMR spectrum (CCl<sub>4</sub>,  $\delta$ , ppm): 0.31 s (2, anti-H<sub>1,4</sub>); 1.77 d (1, syn-H<sub>4</sub>); 2.23 s (1, syn-H<sub>1</sub>); 5.68 t (1, H<sub>3</sub>); 6.98 t (2, C<sub>6</sub>H<sub>4</sub>); 7.54 m (2, C<sub>6</sub>H<sub>4</sub>). Found: C 54.27; H 3.12; F 6.80%. C<sub>13</sub>H<sub>9</sub>FeFO<sub>3</sub>. Calculated: C 54.20; H 3.16; F 6.60%.

 $\begin{array}{c} 2-(\text{m-Fluorophenyl})-1,3-\text{butadieneirontricarbonyl.} \\ \text{yellow crystals, mp 32-32.5°C (from pentane). Infrared spectrum ($\nu$, cm^{-1}$): 2060, 1985 (C = O). NMR spectrum (CCl<sub>4</sub>, <math>\delta$ , ppm): 0.28 s (2, anti-H<sub>1,4</sub>); 1.82 d (1, syn-H<sub>4</sub>); 2.27 s (1, syn-H<sub>1</sub>); 5.75 t (1, H<sub>3</sub>); 7.15 m (4, C<sub>6</sub>H<sub>4</sub>). Found: C 54.10; H 3.02; F 7.03%. C<sub>13</sub>H<sub>9</sub>FeFO<sub>3</sub>. Calculated: C 54.20; H 3.16; F 6.60%. \end{array}

The authors express their gratitude to S. P. Gubin for his valuable advice and assistance in the work.

## CONCLUSIONS

1. A one-step method was proposed for the synthesis of the dienic  $\pi$ -complexes of iron tricarbonyl, starting with  $\alpha$ ,  $\beta$ -unsaturated alcohols.

2. 1-Ferrocenyl-1-buten-3-ol when reacted with  $Fe_2(CO)_9$  in the presence of  $CuSO_4 \cdot 5H_2O$  is isomerized to 1-ferrocenyl-3-butanone.

3. The 1- and 2-substituted 1,3-butadieneirontricarbonyls, containing ferrocenyl and m,p-fluoro-phenyl substituents, were synthesized.

## LITERATURE CITED

1. G. F. Emerson and R. Pettit, J. Am. Chem. Soc., 84, 4591 (1962).

2. R. W. Novak, T. E. Stevens, and M. Howard, J. Org. Chem., 36, 1699 (1971).

3. N. L. Drake and P. Allen, Jr., Organic Syntheses, Vol. 3, p. 17 (1923).

4. F. A. Hochstein and W. G. Brown, J. Am. Chem. Soc., 70, 3484 (1948).