Intramolecular Alkyne–Alkyne and Alkyne–Alkene Couplings Promoted by Iron Carbonyls

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The first examples of iron carbonyl-promoted intramolecular coupling of alkyne and alkene, giving rise to cyclopentenones, are described.

There has been considerable interest in the development of methods for the construction of five-membered carbocyclic rings, owing to their occurrence in a diverse range of natural product molecules.[1] In recent years, several approaches *via* transition metal-promoted coupling of alkenes and/or alkynes have been discovered.[2] One of these, the Pauson–Khand reaction, utilizes a cobalt-promoted coupling of alkyne and alkene, with carbonyl insertion, to generate cyclopentenones.[3] This reaction can be carried out inter- or intramolecularly, and the latter approach has been used in the synthesis of biologically active terpenoids such as coriolin.[4] We describe herein preliminary results showing that high-yielding intramolecular carbonylative coupling of alkyne with alkene can be carried out using iron carbonyls, which are less expensive than cobalt carbonyl.

It has been known for many years that alkynes can be converted to cyclopentadienone–$Fe(CO)_3$ complexes by their reaction with pentacarbonyliron.[5] A report in 1977 showed that nona-2,7-diyne could be converted to the complex **1** by reaction with $Fe(CO)_5$ in toluene at 110 °C for 24 h, but the yield was low (14%).[6] We now report that **1** is obtained in 87% yield by a simple modification of these reaction conditions, as shown in eqn. (1). The trimethylsilylsubstituted derivative **2** is similarly obtained in 80% yield.†

Based on these results, as well as previous experience with iron carbonyl-promoted diene–alkene couplings,[7] we felt that conversion of enyne derivatives to cyclopentenones should be possible. Accordingly, the allyl prop-2-ynyl ether[8] **3** was treated with excess of pentacarbonyliron under the above conditions to give the cyclopentenone **4** in 47% yield. After some experimentation it was found that high yields (87%) of **4** could be obtained using the following procedure [eqn. (2)]. To 10 ml of distilled, degassed acetone was added 0.342 g (0.94 mmol) of nonacarbonyldiiron. The mixture was stirred at room temperature for 6 h under argon to give a burgundy-coloured solution. The solvent and any volatile compounds were removed by bulb-to-bulb distillation *in vacuo* to give an air-sensitive dark-red solid, assumed‡ to be (acetone) $Fe(CO)_4$. This was dissolved in 2 ml of acetone and mixed with a toluene solution of **3** (0.152 g, 0.88 mmol, in 3 ml). The solution was stirred for 13 h under Ar at room temperature in a Fischer–Porter bottle, after which time it was pressurized under 55 psi of CO and heated at 145 °C for a total of 60 h. The

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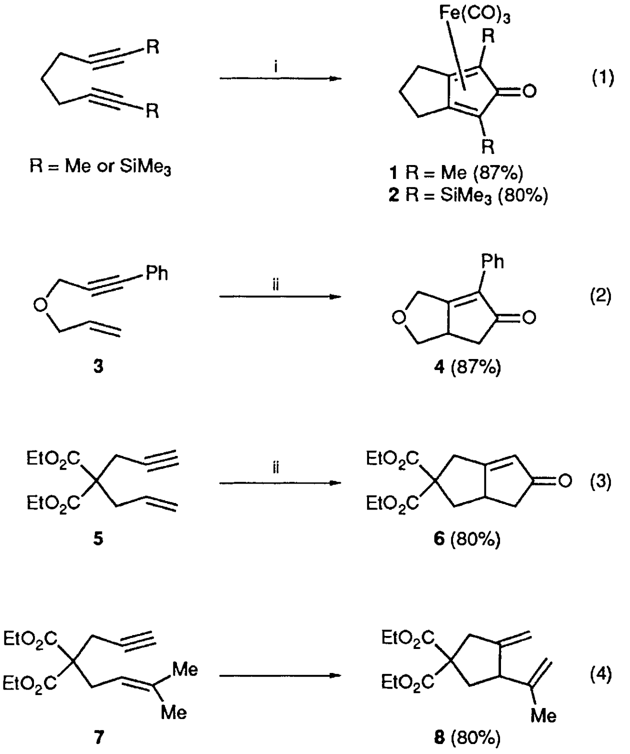
† Pentacarbonyliron is toxic and appropriate precautions should be taken during its use.

‡ Further characterization of this compound is being pursued. It is well known that $Fe_2(CO)_9$ reacts with ligands to give $Fe(CO)_5$ and products of structure $Fe(CO)_4L$ and $Fe(CO)_3L_2$. See: D. F. Shriver and K. H. Whitmire, *Comprehensive Organometallic Chemistry*, ed. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon Press, Oxford, 1982, vol. 4, ch. 31.1.



Scheme 1 *Reagents and conditions*: i, $Fe(CO)_5$, toluene, 135 °C, CO (75–80 psi), sealed tube, 23–24 h; ii, $Fe(CO)_4$(acetone), toluene; 145 °C, sealed tube, CO (55 psi), 60 h

usual isolation and chromatographic purification afforded **4** in 87% yield.§

Similar treatment of the enyne **5** gave the cyclized compound **6** in 80% yield [eqn. (3)]. However, the *gem*-dimethyl substituted alkene **7** gave **8**, the product of an intramolecular ene reaction, in 80% yield [eqn. (4)]. When the latter reaction was carried out in the *absence* of iron carbonyl, several products including **8** were obtained. While the reaction appears to be cleaner in the presence of iron carbonyl, there is no reason to believe at the present time that this is due to an iron-promoted ene reaction. Despite these limitations, the potential for an iron-promoted enyne to cyclopentenone conversion is established. Future work will be aimed at determining the scope and synthetic utility of these processes.

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§ All new compounds were characterized by 200 MHz ^1H NMR and IR spectroscopy, and high-resolution mass spectrometry; ^1H NMR data for **4**: $\delta(CDCl_3)$ 7.7–7.3 (5H, m, ArH), 5.0 (1H, d), 4.65 (1H, d), 4.42 (1H, t), 3.38 (1H, m), 3.3 (1H, dd), 2.9 (1H, dd) and 2.38 (1H, dd).

References

1 P. F. Schuda, H. L. Ammon, M. R. Heimann and S. Battacharjee, *J. Org. Chem.*, 1982, **47**, 3434; S. Nozoe, J. Furakawa, V. Sanakawa and S. Shibata, *Tetrahedron Lett.*, 1976, 195; R. L. Funk and G. L. Bolton, *J. Org. Chem.*, 1984, **49**, 5021; D. P. Curran and D. M. Rakievicz, *J. Am. Chem. Soc.*, 1985, **107**, 1448; S. Danishefsky, M. Hirama, K. Gombatz, T. Harayana, E. Berman and P. F. Schuda, *J. Am. Chem. Soc.*, 1978, **101**, 7020.

2 B. M. Trost and D. C. Lee, *J. Am. Chem. Soc.*, 1988, **110**, 7255; E. Negishi, *Acc. Chem. Res.*, 1987, **20**, 65; T. V. Rajanbabu, W. A. Nugent, D. F. Taber and P. J. Fagan, *J. Am. Chem. Soc.*, 1988, **110**, 7128; J. M. Takacs, L. G. Anderson, G. V. Bindu Madhavan, M. W. Creswell, F. L. Seely and W. F. Devroy, *Organometallics*, 1986, **5**, 2395.

3 I. Khand, R. K. Knox, P. L. Pauson, W. E. Watts and M. I. Foreman, *J. Chem. Soc., Perkin Trans. 1*, 1973, 977; M. C. Croudace and N. E. Schore, *J. Org. Chem.*, 1981, **46**, 5357; S. W. Brown and P. L. Pauson, *J. Chem. Soc., Perkin Trans. 1*, 1990, 1205; I. U. Khand and P. L. Pauson, *J. Chem. Soc., Perkin Trans. 1*, 1976, 30.

4 P. Magnus and P. A. Quagliato, *Organometallics*, 1982, **1**, 1243; C. Exon and P. Magnus, *J. Am. Chem. Soc.*, 1983, **105**, 2477.

5 E. Weiss, R. G. Merenyi and W. Hubel, *Chem. Ind. (London)*, 1960, 407; *Chem. Ber.*, 1962, **95**, 1170.

6 R. S. Dickson, C. Mok and G. Connor, *Aust. J. Chem.*, 1977, **30**, 2143.

7 A. J. Pearson, M. Zettler and A. A. Pinkerton, *J. Chem. Soc., Chem. Commun.*, 1987, 264; A. J. Pearson and M. W. Zettler, *J. Chem. Soc., Chem. Commun.*, 1987, 1233; *J. Am. Chem. Soc.*, 1989, **111**, 3908.

8 K. Tamao, K. Kobayashi and Y. Ito, *J. Am. Chem. Soc.*, 1988, 110, 1286. These authors reported a Ni^0-promoted conversion of enyne **3** to the 2,6-dimethylphenylimino derivative of **4** in 62% yield.