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OXIDATIVE CYCLISATION OF A TRICARBONYLCYCLOHEXADIENEIRON COMPLEX USING FERRIC CHLORIDE ON SILICA GEL[1]

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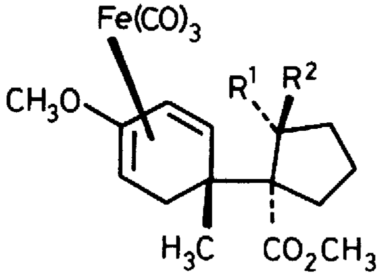
Summary: Treatment of the diene-Fe(CO)$_3$ complex (2) with dehydrated ferric chloride on silica gel support results in oxidative cyclisation of the alcohol function onto the diene ligand to give (3). This contrasts with the normal behaviour of both diene-Fe(CO)$_3$ complexes and alcohols toward ferric chloride.

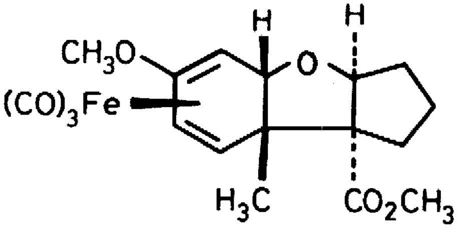
In the course of our investigations into the conversion of the readily prepared complex (1)[2] to trichothecane derivatives[3] we found it necessary to examine methods of further functionalising the 5-membered ring in the presence of the Fe(CO)$_3$ group as dienol ether protection. Our projected strategy involved the dehydration of alcohol (2), obtained quantitatively as a pale yellow crystalline single diastereoisomer, m.pt. 118-119^0, by sodium borohydride reduction of (1)[4]. In trying to optimise the dehydration of (2) we examined treatment with FeCl$_3$/silica gel, reported to effect such conversions in good yield[5]. We were sceptical about the outcome, since ethanolic ferric chloride is a reagent commonly employed to disengage Fe(CO)$_3$-complexes ligands[6]. To our surprise, exposure of (2) (100 mg) in dry tetrahydrofuran (5 ml) to 10% ferric chloride on silica gel (10 g, Merck 70-230 mesh Kieselgel 60), previously dehydrated at 70^{o}C/0.01 mm (5h), followed by evacuation at room temperature (40 min) and elution of the product through basic alumina with dichloromethane gave, in 90% yield, pure (3) as a pale yellow crystalline solid, m.p. 124-125^{o}C The structure was readily established from the n.m.r. spectrum,[4] which showed the well-known pattern for H-2, H-3, H-5[2], whilst the doublet due to H-6 collapsed to a singlet on irradiation of H-5[4].

In view of our recent finding[1b] that similar cyclised compounds may be opened with acid under mild conditions to give complexed cyclohexadienylium salts substituted at C-6, the present result is important in establishing the generality of oxidative cyclisations using a wide variety of reagents[7]. To date we have not pursued further transformations of (3), but it may be noted that the presence of the ester fuctionality provides a means of elaborating a lateral chain suitable for intramolecular reactions of a derived cation. The scope and synthetic utility of this reaction is currently under investigation.



(1) $R^1, R^2 = O$

(2) $R^1 = H$, $R^2 = OH$



(3)

References

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   (b) Part 8: A.J. Pearson, J.C.S. Chem. Comm., 1980, in press.
2. A.J. Pearson and P.R. Raithby, J.C.S. Perkin 1, 1980, 395.
3. Review: C. Tamm, Fortschr. Chem. Org. Naturst., 1974, <u>31</u>, 63.
4. All compounds were obtained as racemic mixtures. Spectral data are: (2): ν_{max}($CHCl_3$) 3620, 3600-3300, 2052, 1977, 1719, 1489 cm^{-1}. δ($CDCl_3$) 5.01 (1H, dd, $J_{2,3}$ 6.5, $J_{3,5}$ 2.5 Hz, H-3), 4.54 (1H, C<u>H</u>OH), 3.71 (3H, s, CO_2Me), 3.66 (3H, s, OMe), 3.30 (1H, m, H-5), 2.54 (1H, dd, J_{gem} 16, $J_{5,6}$ 3.5 Hz, H-6), 2.09 (1H, d, $J_{2,3}$ 6.5 Hz, H-2), 2.3 (1H, m) and 1.6 (6H, m) (3 x CH_2 + OH), 1.45 (1H, dd, J_{gem} 16, $J_{5,6}$ 2.5 Hz, H-6), 1.33 (3H, s, Me). m/e (%) 406 (15), 378 (27), 350 (5), 322 (45), 304 (100). Found: C 52.97, H 5.40. $C_{18}H_{22}FeO_7$ requires C 53.22, H 5.46%.
   (3): ν_{max}($CHCl_3$) 2040, 1960, 1710, 1490 cm^{-1}. δ($CDCl_3$) 5.06 (1H, dd, $J_{2,3}$ 6.5, $J_{3,5}$ 2.5 Hz, H-3), 4.54 (1H, d, br, J 4.5 Hz, H-8), 4.06 (1H, d, $J_{5,6}$ 4.0 Hz, H-6), 3.72 (3H, s, CO_2Me), 3.71 (3H, s, OMe), 3.08 (1H, dd, $J_{5,6}$ 4.0, $J_{3,5}$ 2.5 Hz, H-5), 2.21 (1H, d, $J_{2,3}$ 6.5 Hz, H-2), 2.0-1.2 (6H, m, 3 x CH_2), 1.23 (3H, s, Me). m/e (%) 404 (5), 376 (30), 348 (20), 320 (75), 262 (100). Found: M^+ 404.0556, $C_{18}H_{20}FeO_7$ requires M 404.0558.
5. E. Keinan and Y. Mazur, J. Org. Chem., 1978, <u>43</u>, 1020.
6. D.H.R. Barton, A.A.L. Gunatilaka, T. Nakanishi, H. Patin, D.A. Widdowson and B.R. Worth, J.C.S. Perkin I, 1976, 821, and references therein.
7. See also A.J. Birch, K.B. Chamberlain and D.J. Thompson, J.C.S. Perkin I, 1973, 1900.

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