Pergamon

Tetrahedron Letters, Vol. 37, No. 48, pp. 8763-8766, 1996
Copyright © 1996 Published by Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0040-4039/96 $15.00 + 0.00

PII: S0040-4039(96)02044-8

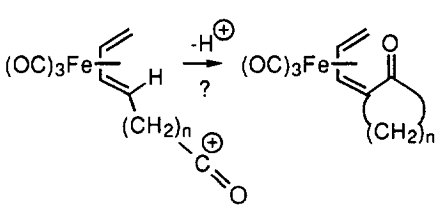
Intramolecular Friedel-Crafts Acylations of 1- and 2-Alkanoic Acid Diene Tricarbonyliron Complexes.

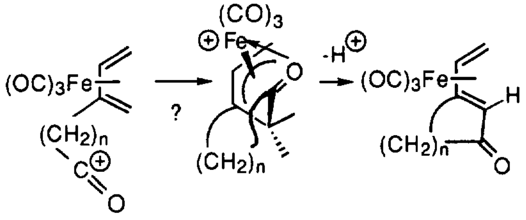
Michel Franck-Neumann*, Laurence Miesch-Gross, Olivier Nass

Laboratoire de Chimie Organique Synthétique, associé au CNRS, Institut de Chimie,
Université Louis Pasteur, 1, rue Blaise Pascal 67000 - Strasbourg (France)

Abstract : Upon treatment with $AlCl_3$, the acid chlorides of tricarbonyl [isoprene-4-butanoic acid] iron and of tricarbonyl [butadiene-2-propanoic acid] iron yield five membered cyclic ketones containing a portion of the metal bound diene. The intramolecular acylation is the main reaction.

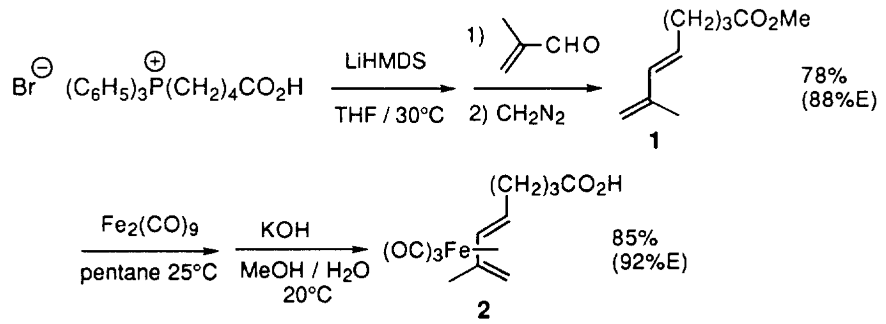
Diene tricarbonyliron complexes readily undergo Friedel-Crafts type acylation reactions[1]. The acylation always proceeds at the terminal position with formation of a complexed Z-dienone, the addition of the electrophile following an endo process where the intermediate cationic π-allyl complex is coordinatively saturated by the entering ketonic carbonyl oxygen[2]. The intramolecular Friedel-Crafts reaction of 1-alkanoic acid chloride substituted diene complexes ($n \geq 3$) on the same carbon atom 1 should be possible, since diene complexes substituted by alkyl groups at both terminal positions can be acylated[3]. Although intramolecular acylation of a 2-alkanoic acid substituted diene complex would not easily lead to a Z-dienone complex, the first step, i.e. the formation of a π-allyl iron cation, should work, since a stabilization by coordination with the ketonic carbonyl seems possible ($n \geq 2$)[4].

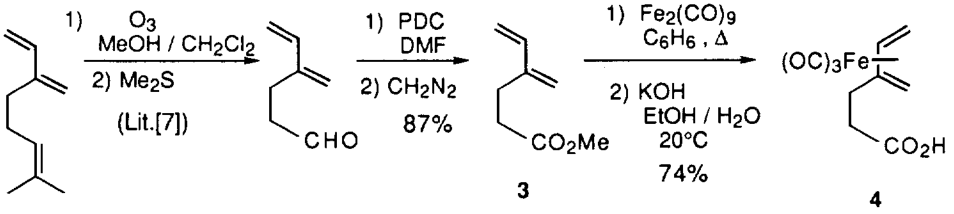




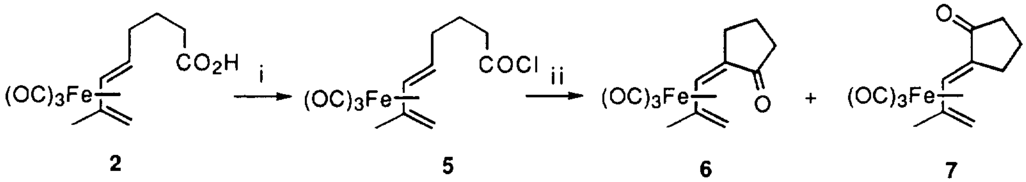
We investigated both possibilities, keeping in mind the formation of the reasonably most strained five membered ketone rings[5].

The starting diene complexes bearing the alkanoic acid side chains **2** and **4** were prepared, the former from the Wittig reaction product **1** of the ylid from (4–carboxybutyl) triphenylphosphonium bromide with α-methacroleine, which favours the E configuration, and the latter, from the known[6] product of the ozonolysis of myrcene[7] via the ester **3**. In both series it was advantageous to complex the diene ligands under the form of the easily saponifiable esters, since complexation of the free acids was not as straightforward.





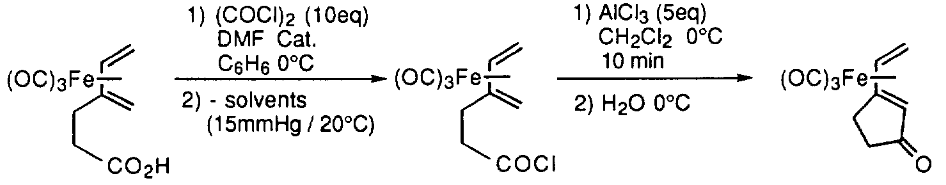
The acid **2** was transformed into its acid chloride **5** with oxalyl chloride after formation of the lithium salt. This procedure gave nearly pure acid chloride solutions with the best results in the following step. Upon addition of the Lewis acid $AlCl_3$ in dichloromethane at -20°C, a rapid reaction occurred, which yielded, after work-up with ice water, a mixture of the easily separable complexed dienones **6** (Z, more polar, 50 %) and **7** (E, less polar, ca. 5%)[8]. However, this result (# 1) could only be obtained on very small quantities (< 100 mg). On a larger scale difficulties were encountered, apparently not due to the reaction itself, which seemed to work well, but to the lability of the formed products in the highly acidic reaction conditions[9]. By changing the sense of the addition and using an attenuated form of $AlCl_3$, the results became reproducible on a larger scale. The aluminium trichloride (5 eq) in dichloromethane was deactivated with Et_3N (10 eq) and the solution of the acid chloride was added to this solution at -78°C, the reaction being rapidly completed at -30°C (# 2).



	i :	1) BuLi (1 eq). 2) $(COCl)_2$ (3 eq) ether. 3) - solvents 1 Torr/25° C, - LiCl (+ CH_2Cl_2, filtration).		
(# 1)	ii :	1) $AlCl_3$ (5 eq), CH_2Cl_2/-20° C 2) H_2O/0° C (addition of $AlCl_3$ to the acid chloride).	**6** (50 %)	**7** (5 %)
(# 2)	ii :	1) $AlCl_3$ (5 eq), Et_3N (10 eq), CH_2Cl_2/-78° C → -30° C. 2) Et_3N (15 eq), H_2O ($NaHCO_3$) (addition of the acid chloride to the Lewis acid).	**6** (58 %)	**7** (8 %)
(# 3)	ii :	1)$AlCl_3$ (5 eq), Et_3N (1 eq), ether/20° C. 2) H_2O ($NaHCO_3$)	**6** (41 %)	**7** (34 %).
(# 4) a)	ii :	$(CF_3CO)_2O$, CH_2Cl_2/25° C. 3 h	**6** (16%)	**7** (6%).
(# 4) b)	ii :	$(CF_3CO)_2O$, CH_2Cl_2/25° C. 48 h	**6** (13 %)	**7** (26 %).

The major Z-dienone complex **6** was always formed with the E-dienone **7**. This does not have its origin in a small contamination of the starting acid **2** (E) by minute amounts of the Z isomer, but is characteristic of the present reaction[10]. When the reaction was run in a more basic solvent (ether) with less Et_3N (1 eq), an enhanced overall yield of 75 % could be obtained, the ratio of Z to E dienone now reaching 5:4 (# 3). This is probably due to the longer reaction time needed (12-24 h), even at room temperature. Interestingly, the intramolecular acylation **2** → **6/7** could be performed directly and without $AlCl_3$ under the influence of trifluoroacetic anhydride at 25° C in dichloromethane (same evolution of the ratio 6:7 with the reaction time). Although the yields were modest (# 4a and # 4b), this is, to our knowledge, the first example of a Friedel-Crafts acylation reaction of an organic iron carbonyl complex directly with an acid, without Lewis acid activation[11]. The competitive formation of the two isomeric dienone complexes **6** and **7** and their easy interconversion under the influence of various reagents[12], led us to verify their structure by an X-ray analysis. This was done on the Z dienone complex **6**, and confirmed our structural attribution[13].

The 2-substituted butadiene acid complex **4** was transformed into its acid chloride **8** with an excess of oxalyl chloride in the presence of a catalytic amount of DMF. The solvents were eliminated under reduced pressure, dichloromethane was added and the mixture was treated with solid $AlCl_3$. After the rapid reaction, aqueous work-up yielded the complexed ketone **9**[8] along with small amounts of decomplexed vinylcyclopentenone[14].



4 **8** **9** (65%)

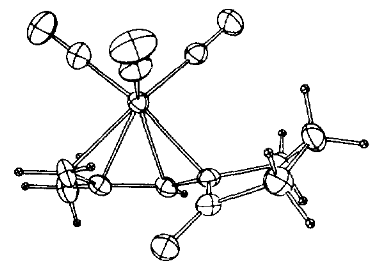
It appears in conclusion that intramolecular Friedel-Crafts acylations can be performed with diene-tricarbonyliron complexes leading to easily decomplexable[14] diene complexes, bearing 2-cyclopentenone or 2-methylenecyclopentanone substructures, but the scope of the reaction can most probably be extended to the formation of other cyclic ketones[15]. Competition with intermolecular acylation was a priori possible here, since the complexed dienes were not directly linked to electron withdrawing groups and were therefore not deactivated toward electrophilic substitution. It is noteworthy that under our conditions intermolecular reactions were not observed even with the relatively high concentrations used[16].

Acknowledgement : We are grateful to the Service Commun de rayons X de la Fédération de Recherche Chimie de l'Université Louis Pasteur for a crystal structure determination and to BASF for repeated gifts of $Fe(CO)_5$.

References and Notes:

1. Unfunctionalized diene complexes : Graf, R.E.; Lillya, C.P. *J. Organomet. Chem.* **1979**, *166*, 53-62 and ref. therein.
   Functionalized diene complexes : Franck-Neumann, M.; Sedrati, M.; Mokhi, M. *New J. Chem.*, **1990**, *14*, 471-480.

2. Greaves, E.O.; Knox, G.R.; Pauson, P.L.; Toma, S. *J.C.S. Chem. Comm.* **1974**, 257-258 and ref. therein.
3. Franck-Neumann, M.; Sedrati, M.; Abdali, A. *J. Organomet. Chem.* **1988**, *339*, C9-C12.
4. This is probably the case for the carbonylative annulation of myrcene tricarbonyliron by reaction with oxalyl chloride (35-40 % mixture of cyclic six-membered diastereomers) : Birch, A.J.; Pearson, A.J. *J.C.S. Chem. Comm.* **1976**, 601-602.
5. Five membered cyclic ketones condensed with conjugated diene units can be valuable intermediates for the synthesis of polyquinanes and related structures. In this context, decomplexation with cyclocarbonylation of adequately substituted diene tricarbonyliron complexes may be useful :
   Franck-Neumann, M.; Vernier, J.M. *Tetrahedron Lett.*, **1992**, *33*, 7361-7364
   Franck-Neumann, M.; Vernier, J.M. *Tetrahedron Lett.*, **1992**, *33*, 7365-7368.
6. Bertele, E.; Schudel, P. *Helv. Chim. Acta*, **1967**, *50*, 2445-2456.
7. Alternatively, we checked that the ester **3** could be obtained directly from chloroprene by a copper catalyzed 1,4-addition of its Grignard reagent with methyl acrylate. This one-pot reaction worked well only when done in the presence of trimethylchlorosilane to trap the enolate (cf. [17]).
8. Selected data :
   6 : $C_{12}H_{12}FeO_4$ ($\underline{C}$, $\underline{H}$), yellow crystals F = 73° C ; **9** : $C_{10}H_8FeO_4$ ($\underline{C}$, $\underline{H}$), yellow crystals F = 80° C ;
   IR (CCl_4, cm^{-1}) υ (C≡O) **6** : 2050, 1985 and 1978; **9** : 2062, 1999 and 1978 ; υ (C=O) **6** : 1684; **9** : 1717;
   ^1H-NMR ($CDCl_3$, 200 MHz, ppm/TMS, Hz) :
   6 : δ = 1.42-1.65 (m, 3H), 1.66 (s, 3H), 1.80 (m, 1H), 1.83 (t, 1H, J = 2.2), 1.89 (dd, 1H, J = 18.4 and 9.5), 2.33 (ddm, 1H, J = 18.9 and 9.8), 2.49 (d, 1H, J = 2.3), 4.79 (s, 3H);
   9 : δ = 0.37 (dd, 1H, J = 8.8 and 2.4), 1.98 (dd, 1H, J = 6.6 and 2.4), 2.03 (s, 1H), 2.35-2.50 (m, 2H), 2.92 (ddd, 1H, J = 16.0, 6.8 and 4.0), 3.21 (ddt, 1H, J = 16.0, 8.0 and 8.0), 5.70 (dd, 1H, J = 8.7 and 6.7);
   ^{13}C-NMR ($CDCl_3$, 50 MHz, ppm/TMS) : **6** : δ = 20.7, 24.4, 38.0, 48.4, 70.3, 88.0, 107.2, 209.7;
   9 : δ = 27.9, 35.5, 39.4, 60.2, 80.5, 120.8, 209.3, 213.8.
9. Under these conditions, on a 1 g scale the yield of isolated dienone complexes dropped to 20-30 % while decomplexed and isomerized secondary products were obtained. The use of only catalytic quantities of $AlCl_3$ was however not the solution, since the reaction stopped then far from completion.
10. An almost pure sample of the Z isomer of the acid **2**, prepared by Wittig reaction of α-methacroleine with the ylid from (4-carboethoxybutyl) triphenyl phosphonium bromide, gave only poor yields of intramolecular acylation products, the major isomer formed being anew the Z dienone complex **6** (25 % at best, under the favourable influence of a CO atmosphere) !
11. Recently a reaction of the opposite type, i.e. the acylation of allylsilanes with the acid chloride of 2,4-hexadienoic acid $Fe(CO)_3$, also without a Lewis acid has been described : Nakanishi, S.; Kumeta, K.; Otsuji, Y. *Tetrahedron Lett.*, **1994**, *35*, 3727-3728.
12. For instance the pure Z dienone complex **6** yields mixtures of **6** and the E dienone complex **7** when treated with AcCl or CF_3CO_2H (followed by work-up with H_2O) or MeTi $(Oipr)_3$ (75 % isomerization Z → E, without reaction).
13. The details of the X-ray structure determination will be given in the full paper. Ortep view **6** :



14. With cerium ammonium nitrate (CAN) in dry acetone the complexes **6** and **7** led respectively to the corresponding relatively unstable Z-dienone (67 % + 19 % SM, 4 h at -50° C) and very stable E-dienone (87 %, 5 min at 25° C). Similarly the complex **9** gave 3-vinyl-2-cyclopentenone (95 %).
15. An interesting intramolecular Friedel-Crafts reaction has been described in the cyclobutandiene tricarbonyliron series, leading to 1,2 "ortho" and 1,3"para" (major) cyclizations : Adams, C.M.; Crawford, E.S.; Salim, E. *Tetrahedron Lett.*, **1992**, *33*, 3963-3966.
16. The Friedel-Crafts reaction of butadiene tricarbonyliron with ω-diacid dichlorides led only to consecutive intermolecular acylations : Sapienza, R.S.; Riley, P.E.; Davis, R.E.; Pettit, R. *J. Organometal. Chem.*, **1976**, *121*, C35-C40.
17. Corey, E.J.; Boaz, N.W. *Tetrahedron Lett.*, **1985**, *26*, 6019-6022.
    Magot-Cuvru, A.; Blanco, L.; Drouin, J. *Tetrahedron*, **1991**, *47*, 8331-8338.

(*Received in France* 15 *July* 1996; *accepted* 16 *October* 1996)