Journal of Organometallic Chemistry, 117 (1976) C23—C26

Preliminary communication

ORGANOMETALLIC COMPOUNDS

XXII*. OXIDATIVE CYCLIZATION OF A 1,1'-DIVINYLFERROCENE DERIVATIVE WITH MOLECULAR OXYGEN IN THE PRESENCE OF LEWIS ACIDS

MASAO HISATOME, TAKAYUKI NAMIKI and KOJI YAMAKAWA*
Faculty of Pharmaceutical Sciences, Science University of Tokyo, Ichigaya-funagawara-machi, Shinjuku-ku, Tokyo 162 (Japan)

(Received May 25th, 1976)

Summary

Oxidative reaction of 1,1'-bis(1-phenylvinyl)ferrocene with molecular oxygen in the presence of various dia- or para-magnetic Lewis acids gave ferrocenophane peroxide and its derivatives. A possible mechanism for the oxidation is presented.

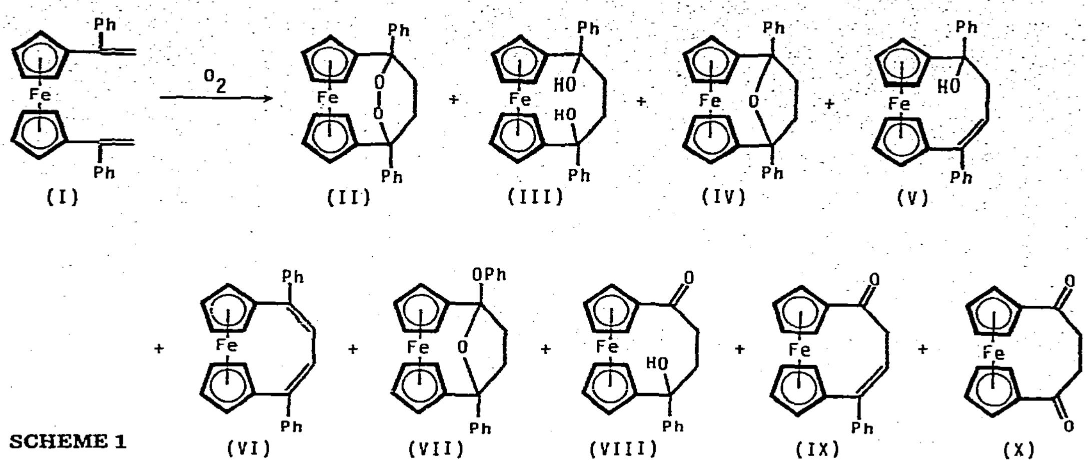
Previously, we reported the novel oxidative cyclization [2] and dimerization [3] of (1-hydroxyalkyl)ferrocene derivatives with molecular oxygen and hydrochloric acid or silica gel. However, Barton et al. [4] found that the formation of the peroxide of ergosteryl acetate occurred by 1,4-addition of triplet oxygen in the presence of diamagnetic electrophilic species under irradiation with light or with paramagnetic species in the dark.

The present communication describes the reaction of 1,1'-bis(1-phenylvinyl)ferrocene (I) with molecular oxygen, in the presence of dia- or paramagnetic Lewis acids without irradiation. The reaction produced ferrocenophane peroxide (II), by formation of a C—C bond, and its derivatives III—X. The results are summarized in Table 1. The products II, III, VI and VII were identified by comparison with the compounds described in a previous report [2b] (Scheme 1).

The chemical correlation among the novel ferrocenophanes IV, V, VIII, IX and X is shown in Scheme 2. Ether, IV (m.p. 193—196°C, M^+: m/e 406, ν(C—O—C): 1050—980 cm^{-1}) was obtained together with diene VI by treatment of diol III with $AlCl_3$ in CH_2Cl_2. Enol V (m.p. 179—180°C, M^+: m/e 406, ν(O—H): 3650 cm^{-1}, vinyl proton: δ 6.23 ppm (dd)) was easily converted into VI by treating with silica gel. The Grignard reaction of the diketone X (m.p. 182—183°C, M^+: m/e 268, ν(C=O): 1660 cm^{-1}) with PhMgBr afforded diol III and enol V. The

---

[*] For part XXI see ref. 1.



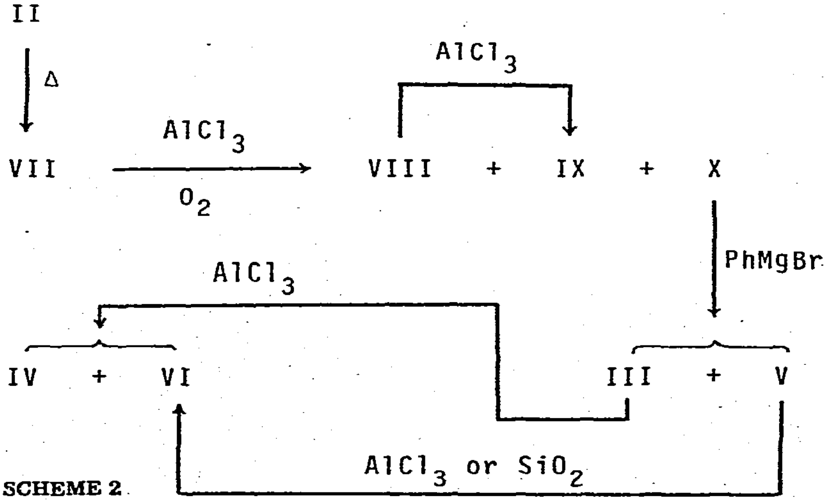
SCHEME 1

TABLE 1

THE REACTION OF I WITH O_2 IN THE PRESENCE OF LEWIS ACIDS AT ROOM TEMPERATURE; REACTION TIME: 1 h

Catalyst (mol equiv.)	Solvent	Yield (%)									
		II	III	IV	V	VI	VII	VIII	IX	X	Total
Diamagnetic Lewis acid											
$AlCl_3$ (4.7)	CH_2Cl_2	—	—	2	2	11	—	9	22	5	51.0
$AlCl_3$ (0.23)	CH_2Cl_2	45	6	—	2	0.5	2	1	0.5	—	57.0
$AlCl_3$ (2.5)[a]	CCl_4	67	2.6	0.2	0.8	—	5.8	0.6	0.2	—	77.2
BF_3-etherate (0.21)	CH_2Cl_2	28	12	0.6	5	0.3	1	2	0.4	—	49.3
$VOCl_3$ (0.20)	CH_2Cl_2	—	18	1.6	6.6	15	5.3	1.3	4.4	—	52.2
$VOCl_3$ (0.20)	CCl_4	31	4.4	3.6	2.6	4.7	5.9	2.9	0.3	—	55.4
CF_3COOH (0.23)	CH_2Cl_2	40	4	0.6	6	2	2	0.9	—	—	55.5
Paramagnetic Lewis acid											
$FeCl_3$ (0.20)	CH_2Cl_2	53	9.5	—	1.5	—	2.5	2.4	—	—	68.9
$VOCl_2$ (0.22)	CH_2Cl_2	84	1.3	—	0.2	—	3.8	0.4	—	—	89.7
$MoCl_5$ (0.20)	CH_2Cl_2	36	4.2	—	3.5	6.8	10	—	4.0	0.4	64.9

[a] At 4°C.



SCHEME 2

TABLE 2

THE REACTION OF PEROXIDE II AND KETAL VII WITH $AlCl_3$ (5.4 mol equiv.) IN CH_2Cl_2 AT ROOM TEMPERATURE; REACTION TIME: 1 h

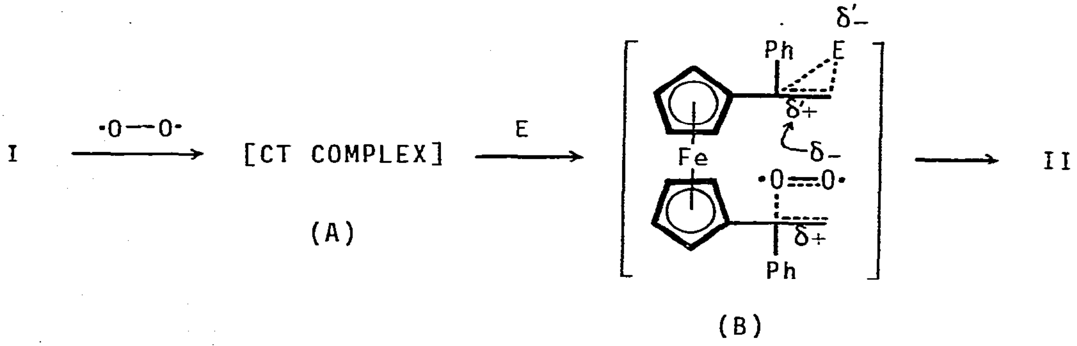
Starting material	Atmosphere	Yield (%)						
		III	V	VI	VII	VIII	IX	X
II	O_2	2	2	—	6	2	39	9
II	N_2	—	1	2	4	6	51	1
VII	O_2	—	—	—	1	8	41	9
VII	N_2	—	—	—	1	8	61	1

reaction of ketal VII with excess $AlCl_3$ under an atmosphere of oxygen gave ketol VIII (m.p. 195—198°C, M^+: m/e 346, ν(O—H): 3280 cm^{-1}), enone IX (m.p. 188—189°C, M^+: m/e 328, ν(C=O): 1660 cm^{-1}, ν(C=C): 1630 cm^{-1}, vinyl proton: δ 6.58 ppm (t)) and diketone X. However, production of the diketone X decreased significantly under an atmosphere of nitrogen (Table 2). Treatment of peroxide II with excess $AlCl_3$ gave similar results to that of the ketal except for formation of small amounts of III, V and VI. Ketal VII was also derived from the peroxide II by thermal reaction at 150°C.

From consideration of these results the following process is proposed. A part of peroxide II initially formed by oxidation is converted by Lewis acid into diol III and ketal VIII via homolytic cleavage of the O—O bond followed by abstraction of hydrogen and rearrangement. Ferrocenophanes IV—VI and VIII—X are derived from the diol and ketal, respectively. Diketone X should be an oxidation product of ketal VII with molecular oxygen.

The catalytic activity of diamagnetic Lewis acids in the oxidation of I could not be distinguished from that of paramagnetic Lewis acids. The divalent iron (diamagnetic) of the ferrocene nucleus was not oxidized into trivalent (paramagnetic) by any catalyst. Neither irradiation nor the presence of radical species was required for this reaction.

An alternative mechanism to the spin exchange and pairing process proposed by Barton et al. [4c] should be considered for the oxidation of ferrocene derivatives. The reaction behaviour can be explained in terms of the mechanism shown in Scheme 3; the oxidation proceeds via a charge transfer complex A [5, 6], of the ferrocene derivative (a strong electron donor) with triplet oxygen (an



E;Electrophilic Lewis acid

SCHEME 3

electron acceptor), and with the complex B having a superoxide ion character [6]. Further experiments are in progress to confirm this mechanism.

References

1 M. Hisatome, T. Sakamoto and K. Yamakawa, J. Organometal. Chem., 107 (1976) 87.
2 (a) M. Hisatome and K. Yamakawa, J. Chem. Soc. Chem. Commun., (1973) 199; (b) M. Hisatome, S. Minagawa and K. Yamakawa, J. Organometal. Chem., 55 (1973) C82; (c) M. Hisatome, T. Namiki and K. Yamakawa, J. Organometal. Chem., 96 (1975) C55.
3 M. Hisatome, S. Koshikawa and K. Yamakawa, Chem. Lett. (Tokyo), (1975) 789.
4 (a) D.H.R. Barton, G. Leclerc, P.D. Magnus and I.D. Menzies, J. Chem. Soc. Chem. Commun., (1972) 447; (b) D.H.R. Barton, R.K. Haynes, P.D. Magnus and I.D. Menzies, J. Chem. Soc. Chem. Commun., (1974) 511; (c) D.H.R. Barton, R.K. Haynes, G. Leclerc, P.D. Magnus and I.D. Menzies, J. Chem. Soc. Perkin I, (1975) 2055.
5 H. Tsubomura and R.S. Mulliken, J. Amer. Chem. Soc., 82 (1960) 5966.
6 M.J.A. McGrath, Tetrahedron, 32 (1976) 377.