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# OXIDATIVE DIMERIZATION OF (1-HYDROXYALKYL)FERROCENE WITH OXYGEN(1)

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Treatment of (1-hydroxy-1-phenylethyl)ferrocene (III) in hexane with $O_2$ in the presence of $SiO_2$ or acidic $Al_2O_3$ gave several oxidative dimerization products: butadiene (VIII), 1,4-dihydroxybutane (IX), and tetrahydrofuran derivatives (Xa and b). Production of these compounds suggests formation of an unisolated peroxide (XII) as an intermediate.

Oxidative intramolecular cyclization of several 1,1'-bis(1-hydroxyalkyl)ferrocenes (I) with oxygen and acidic catalyst to produce 1,1'-(1,2-dioxane-3,6-diyl)-ferrocenes (II), peroxide derivatives of [4]ferrocenophane, and their derivatives has already been reported by us.(2-4) The present paper describes oxidative dimerization of (1-hydroxy-1-phenylethyl)ferrocene (III) by intermolecular reaction analogous to the above cyclization.

Alcohol (III)(mp 112-114°C) was prepared by the Grignard reaction of benzoylferrocene (V) with $CH_3MgI$ or acetylferrocene (VI) with PhMgBr. Bozak *et al.*(5,6) have reported that no alcohol (III) but a butene derivative (VII) resulted in the Grignard reaction of V. By re-examination of the reaction of V, we obtained the alcohol (III) (12%) and ethylene (IV) (47%) but no butene (VII). The ethylene (IV) should be produced by dehydration of III. The butene (VII) was produced either on digestion of the Grignard intermediate(5,6) with aq. HCl (74%), or on treatment of alcohol (III) or ethylene (IV) with aq. HCl (see Table 1). The dimerization possibly proceeded *via* the addition of the intermediately formed ferrocenylcarbonium ion to ethylene (IV).

Alcohol (III) was treated with $O_2$ gas and 6N HCl in benzene under the same conditions as the cyclization of I to give ethylene (IV), butene (VII) and benzoylferrocene (V).[7] However, treatment of III under an $O_2$ gas or air atmosphere in the presence of silica gel in hexane afforded butadiene (VIII), 1,4-dihydroxybutane (IX) and tetrahydrofuran (Xa and b). The products VIII, IX and X were obtained on treatment with acidic alumina but not with neutral alumina. VIII, IX and X were also produced on treatment of ethylene (IV) with silica gel or acidic alumina in hexane. The reaction of III or IV with oxygen did not occur in benzene even when silica gel or acidic alumina was used.[8]

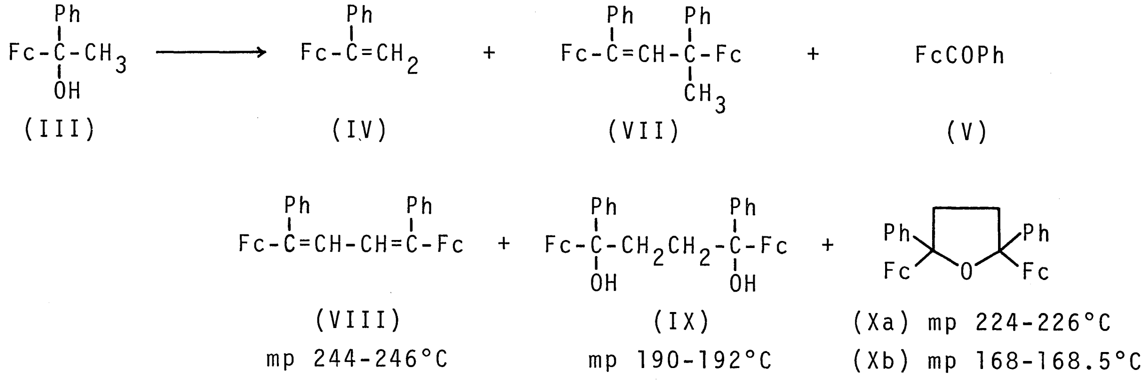
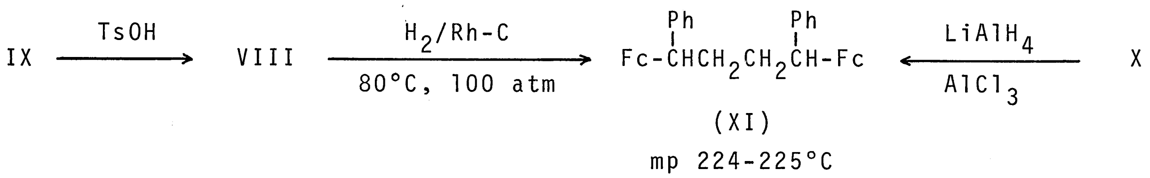


Table 1. Yields of the products in the reaction of alcohol (III) and ethylene (IV) with $O_2$ and acidic catalysts.

| Conditions | | | | Yields (%) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | IV | VII | V | VIII | IX | Xa | Xb |
| III | 6N HCl | $O_2$ | benzene | 82 | 1.6 | 2.2 | — | — | — | — |
| IV | 6N HCl | air | benzene | 74 | 5.3 | 1.9 | — | — | — | — |
| III | $SiO_2$ | air | hexane | 51 | — | 2.8 | 15 | — | — | — |
| III | $SiO_2$ | $O_2$ | hexane | 48 | — | 4.8 | 23 | 0.8 | 5.5 | 6.8 |
| III | $H^+$-$Al_2O_3$ | $O_2$ | hexane | 49 | — | 5.7 | 5.9 | 5.0 | 1.0 | — |
| III | $SiO_2$ | air | benzene | 70 | — | 2.3 | — | — | — | — |
| III | $SiO_2$ | $N_2$ | hexane | 84 | — | 2.2 | — | — | 1.4 | — |
| IV | $SiO_2$ | $O_2$ | hexane | 22 | — | 7.9 | 11 | 3.1 | 1.6 | — |

These products were isolated by column-chromatography on neutral alumina. Butadiene derivative (VIII) showed a $\nu_{C=C}$ band at 1599 $cm^{-1}$, an olefinic proton signal at $\delta$ 6.51 (2H, s), and an $M^+$ at m/e 574.1028 ($C_{36}H_{30}Fe_2$), respectively, in its Raman, PMR and high-resolution mass spectra. The spectra of 1,4-dihydroxybutane (IX) indicated $\nu_{OH}$ bands at 3520 and 3370 $cm^{-1}$ (IR), a singlet of two hydroxyl protons at ca. δ 3.4 and an $M^+$ at m/e 610.1287 ($C_{36}H_{34}O_2Fe_2$). Tetrahydrofuran derivative ($C_{36}H_{32}OFe_2$) was separated into two stereoisomers Xa (mp 224-226 °C; $M^+$, 592.1154) and Xb (mp 168-168.5°C; $M^+$, 592.1179). The methylene protons (4H) of Xa and Xb appeared as an AA'XX' system at δ 2.2-2.9 and an AA'BB' system at δ 2.5-2.65, respectively. The configuration of the two isomers was not yet confirmed.

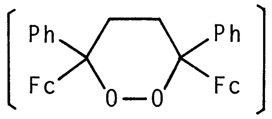
The structure of VIII, IX and X was also confirmed by the following reactions. Butane derivative (XI) showed an $M^+$ at m/e 578.1325 ($C_{36}H_{34}Fe_2$) and a methine proton signal at δ 3.53 (2H, m).



$$\text{IX} \xrightarrow{\text{TsOH}} \text{VIII} \xrightarrow[80°\text{C, 100 atm}]{H_2/\text{Rh-C}} \text{Fc-}\overset{\text{Ph}}{\text{CH}}\text{CH}_2\text{CH}_2\overset{\text{Ph}}{\text{CH}}\text{-Fc} \xleftarrow[\text{AlCl}_3]{\text{LiAlH}_4} \text{X}$$

(XI)
mp 224-225°C

The compounds VIII, IX and X produced in the present reaction should be oxidatively dimerized via a different mechanism from that of formation of butene (VII). The peroxide (XII) expected could not be isolated in the oxidative reaction. However, it is reasonable to assume that the products VIII, IX and X were produced _via_ the peroxide (XII), since the structure of those was analogous to that of the by-products in the oxidative cyclization of I.



(XII)

It is shown that the formation of C-C bond in the reactions of (1-hydroxyalkyl)ferrocene derivatives with oxygen⁹⁾ and acidic catalysts occurs also intermolecularly. Further experiments are in progress to investigate the mechanism of the present and previous reactions.

## References and Notes

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5) R.E. Bozak, H.M. Sorensen, and R.G. Riley, Chem. Commun., 520 (1969).

6) R.E. Bozak, R.G. Riley, W.P. Fawns, and H. Javaheripour, Chem. Lett., 167 (1974).

7) The benzoylferrocene (V) was not a contaminant in the starting materials, because V was also obtained when III and IV prepared from acetylferrocene were used. V was possibly formed by oxidation of V.

8) The reaction seems to depend on solubility of the starting materials to solvents.

9) The oxidative reactions occurred in the dark. The reactions seem to be not participated by singlet-state oxygen, since the reaction system would appear to have no species for excitation of $O_2$.

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