Selective Dimerization of Alkyl Crotonates Catalyzed by Iron(0) Complexes Having 1,2-Bis(dimethylphosphino)ethane Ligands

Sanshiro Komiya,* Naohiko Oyasato, and Tomoyuki Furukawa
Department of Applied Chemistry, Tokyo University of Agriculture and Technology,
2-24-16 Nakamachi, Koganei, Tokyo 184

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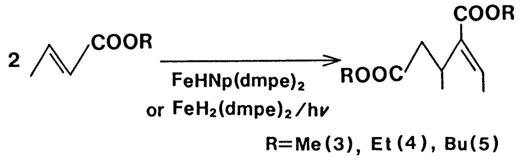
Synopsis. Highly selective dimerization of alkyl crotonates has been performed in the presence of a catalytic amount of $FeHNp(dmpe)_2$ or $FeH_2(dmpe)_2$/UV irradiation at room temperature.

Although metal-catalyzed dimerizations of olefins having functional groups under mild conditions have been expected to have wide applications to organic syntheses, only limited examples are known so far such as dimerizations of methyl acrylate[1)] and acrylonitrile[2)] by comparison with well known metal-catalyzed dimerizations of simple olefins or dienes.[3)] Unfortunately the most of these dimerizations in fact are not sufficiently selective and their yields are considerably low, in spite of their severe reaction conditions. We wish to report iron-catalyzed selective dimerization of alkyl crotonates under ambient conditions.

When methyl crotonate was treated with a catalytic amount of $FeHNp(dmpe)_2$, **1** (1 mol%)[4)] at room temperature, a methyl crotonate dimer was smoothly obtained in high yield in 2 h (dmpe=1,2-bis(dimethylphosphino)ethane, Np=2-naphthyl). $FeH_2(dmpe)_2$,[5)] **2** also catalyzed the dimerization under irradiation of UV light. Results of the catalytic dimerization of alkyl crotonates under various conditions are summarized in Table 1.



The dimerization is selective with high conversion. ¹H NMR, GC, and GCMS analyses reveal that the dimer consists of an only head-to-tail dimer (*E* isomer). Trace amounts of trimer and tetramer were detected in the reaction mixture (see experimental). The rate of the catalytic dimerization slightly decreased in the order of methyl, ethyl, and butyl esters, as shown in the time-yield curve of the reactions (Fig. 1). Unfortunately dimerization of other types of unsaturated esters such as methyl acrylate, methyl 3-butenoate and methyl methacrylate has failed.[6)] Addition of 1,2-bis(dimethylphosphino)ethane ligand (1 mol/l) severely retarded the reaction, suggesting that the formation of a coordinatively unsaturated intermediate such as $[Fe(dmpe)_2]$ is a key step in the catalytic dimerization. Such a coordinatively unsaturated species has been previously proposed in the C–H bond activations by **1**[4)] or by **2** under UV irradiation.[5)] Rate of the reaction was not significantly affected by changing the solvent from hexane to DMF, excluding the formation of ionic species as reaction intermediates. Thus, for the present catalytic Michael type

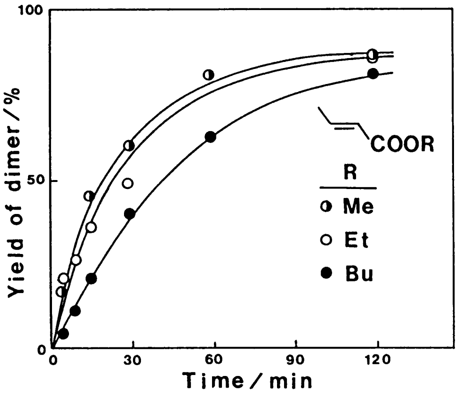
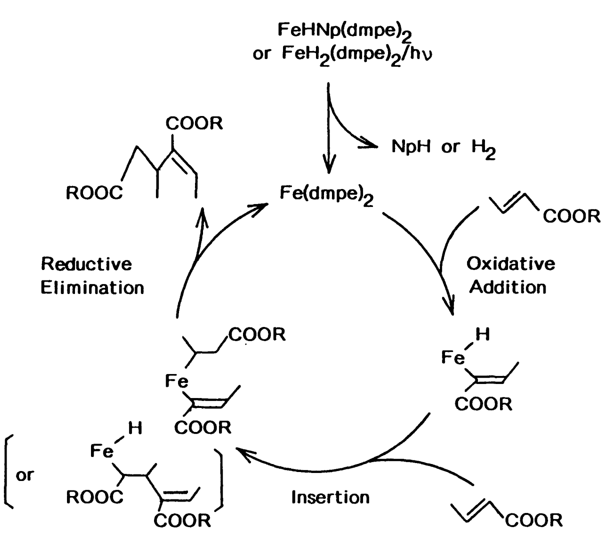


Fig. 1. Time-yield curve of the dimerization of alkyl crotonates by **1** (1 mol%) at r.t.

Table 1. Catalytic Dimerization of Alkyl Crotonates Promoted by Iron Complexes[a)]

Catalyst /mol%	Solvent	MeCH=CHCOOR /mmol	Conversion /%	Yield /%
$FeH_2(dmpe)_2$ (1.0)[b)]	None	R=Me(2.95)	93	89
(5.0)[b)]	None	(2.86)	99	95
$FeHNp(dmpe)_2$(1.0)	None	(2.89)	92	87
(5.0)	None	(2.85)	98	93
(1.0)[c)]	None	(3.72)	36	36
(0.4)	DMF	(2.95)	81	73
(0.4)	Hexane	(2.76)	80	78
(1.0)	None	R=Et (2.72)	88	85
(1.0)	None	R=Bu(2.28)	84	83

a) All the reactions were carried out for 2 h under N_2 at room temperature. b) UV irradiation with high-pressure Hg lamp. c) An equimolar amount of dmpe ligand (0.0372 mmol) per Fe was added.



Scheme 1. A possible mechanism for the iron-catalyzed dimerization of alkyl crotonates.

dimerization, the following concerted mechanism involving C-H bond oxidative addition followed by insertion of alkyl crotonate and reductive elimination of the dimer has been proposed (Scheme 1).7) The vinylic C-H bond oxidative addition process as an initial step is reasonable, since the hydrido-(vinyl)-metal complexes were isolated from the reactions of zero-valent iron and ruthenium complexes with alkyl methacrylates.5,8)

Experimental

General. All the reactions were carried out under nitrogen. Solvents used were dried by usual procedure, distilled, and stored under nitrogen. Reagent grade of unsaturated esters were dried with CaH_2 and distilled before use. $FeH_2(dmpe)_2$ and $FeHNp(dmpe)_2$ were prepared according to the literature methods.4,5)

Dimerization of Methyl Crotonate. A typical procedure of the dimerization is described below: $FeHNp(dmpe)_2$ (14.0 mg, 0.0289 mmol) was placed in a Schlenk tube under nitrogen and a settled amount of methyl crotonate (0.304 cm^3, 2.89 mmol) was added by using a microsyringe. After stirring the solution for 2 h, the solution was analyzed by GC and GCMS. The results were summarized in Table 1. The dimer was purified by column chromatography (alumina/hexane) and characterized mainly by NMR. **3**, GCMS: m/z=200, ^{1}H NMR ($CDCl_3$): δ=1.20 (Me, d, 7.1 Hz), 1.85 (Me, d, J=7.3 Hz), 2.59 (H, dd, J=7.1, 15.4 Hz), 2.75 (H, dd, J=7.8, 15,4 Hz), 3.30 (H, ddq, J=7.1, 7.8, 7.1 Hz), 3.63 and 3.72 (OMe, s), 6.83 (H, q, J=7.3 Hz). Traces of trimers (m/z=300, yield=0.7%) and tetramers (m/z=400, yield=2.8%) were also detected, but the detail structure of these oligomers was not characterized. Other reactions were performed analogously. **4**, ^{1}H NMR ($CDCl_3$): δ=0.93 (Me, t, J=7.2 Hz), 0.97 (Me, t, J=7.1 Hz), 1.28 (Me, d, J=7.1 Hz), 1.57 (Me, d, J=7.3), 2.63 (H, dd, J=6.8, 15.4 Hz), 2.94 (H, dd, J=8.1, 15.4 Hz), 3.37 (H, ddq, J=6.8, 8.1, 7.1 Hz), 3.92 (CH_2, q, J=7.2 Hz), 3.99 (CH_2, q, J=7.1 Hz), 6.84 (H, q, J=7.3 Hz); **5**, δ=0.92 (Me, t, J=7.1 Hz), 0.95 (Me, t, J=7.1 Hz), 1.21 (Me, d, J=7.1 Hz), 1.3—1.7 (CH_2, m), 1.84 (Me, d, J=7.3 Hz), 2.57 (H, dd, J=7.3, 15.4 Hz), 2.74 (H, dd, J=8.1, 15.4 Hz), 3.30 (H, ddq, J=8.1, 7.3, 7.1 Hz), 4.03 (CH_2, t, J=5.6 Hz), 4.12 (CH_2, t, J=6.6 Hz), 6.82 (H, q, J=7.3 Hz). When $FeH_2(dmpe)_2$ was used as a catalyst, UV irradiation with a high-pressure Hg lamp was applied during the reaction. In these cases hydrogen gas was detected in the gas phase after the reaction.

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6) In these reactions unreacted esters were recovered. In the reaction of $FeH_2(dmpe)_2$ with methyl acrylate and methyl methacrylate under UV irradiation, stable hydrido-(alkenyl)- and/or methyl(carboxylato)iron complexes, which are not catalytically active and are tentatively characterized by only in situ ^{1}H NMR (in C_6D_6), were formed. $FeH(CH=CHCOOMe)(dmpe)_2$: 10.3 ppm (d of qui, J(HH)=18.3 Hz, J(PH)=7.3 Hz, $FeC\underline{H}=CH-$), 6.26 (d, J(HH)=18.3 Hz, $FeCH=C\underline{H}-$), −16.76 (qui, J(PH)=45.2 Hz, FeH). $FeH(CH=C(Me)COOMe)(dmpe)_2$: 10.18 (br, FeCH=), −12.91 (d of q, J(PH)=42, 55 Hz). $FeMe(O\text{-}COC(Me)=CH_2)(dmpe)_2$: 5.06 and 5.56 (br, CH_2), −3.23 (qui, J(PH)=7.3 Hz, FeMe). Other signals are obscured due to extensive overlapping with the signals of large free ester.

7) At present we prefer the above mechanism involving C-H bond oxidative addition followed by insertion of methyl crotonate into Fe-H bond, since other mechanisms involving successive insertion into Fe-H bond and β-elimination are not suitable for interpreting the high selectivity of the reaction.

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