

STUDY OF THE REACTIVITY OF 2-(3-CHLOROBENZYLIDENE)[3]-FERROCENOPHANE-1,3-DIONE

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The addition of different C-nucleophiles to 2-(3-chlorobenzylidene)[3]ferrocenophane-1,3-dione has been studied. In most cases, the addition has led to expansion of the strained 3-membered bridge to the 7-membered one. An analogous bridge expansion has been observed also in the reaction of 2-(4-chlorobenzylidene)[3]ferrocenophane-1,3-dione with 1,3-cyclohexanedione. 2-(3-chlorobenzylidene)[3]ferrocenophane-1,3-dione reacts with vinyl ethyl ether as a heterodiene, yielding the 4 + 2 cycloadduct.

In our previous work¹ we reported on the synthesis of the strained ferrocene derivative, [3]ferrocenophane-1,3-dione, and examined its reactivity as an ambident nucleophile. In another work² we studied the reactivity of the dione in condensation reactions. We have found that in dependence on the aldehyde used, the reaction always yields 2-arylmethylene[3]ferrocenophane-1,3-diones, in some cases accompanied with products of the consecutive Michael addition of the starting [3]ferrocenophane-1,3-dione to the condensation product.

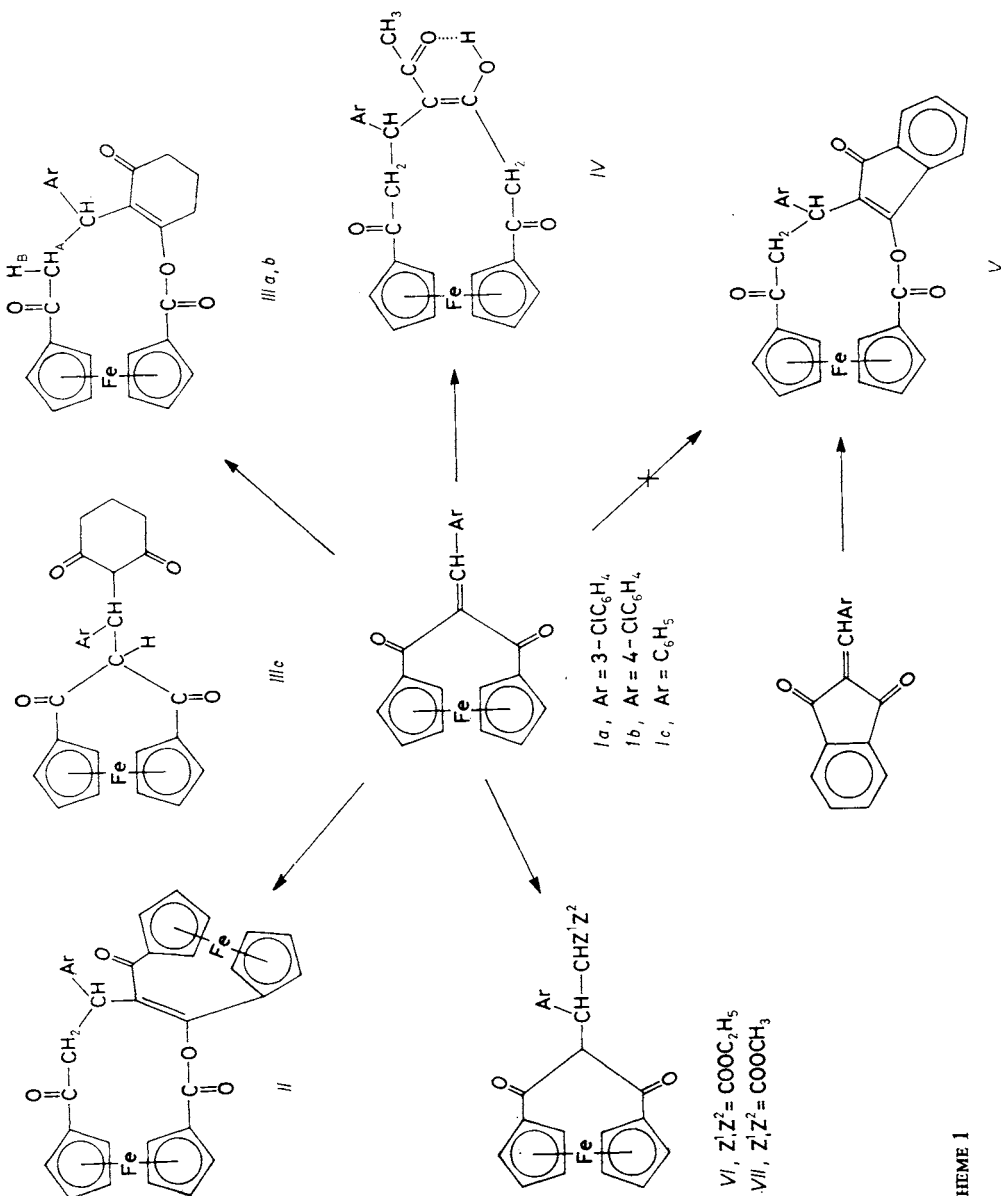
The aim of the present work was to study the reactivity of 2-(3-chlorobenzylidene)-[3]ferrocenophane-1,3-dione as the acceptor in Michael additions of different C-nucleophiles or as the heterodiene in the cycloaddition reactions. Another aim of the work was to compare the reactivity of 2-benzylidene[3]ferrocenophane-1,3-dione with an analogous 1,3-diketone, 2-benzylidene-1,3-indanedione.

The results of our experiments concerning the reactions of different C-nucleophiles with 2-(3-chlorobenzylidene)[3]ferrocenophane-1,3-dione are summarized in Scheme 1 (compound *Ia*). The reactions were catalysed by potassium carbonate and 18-crown-6 as a co-catalyst or by triethylamine.

In the addition of [3]ferrocenophane-1,3-dione to 2-(3-chlorobenzylidene)[3]ferrocenophane-1,3-dione (*Ia*), we have isolated the product *II* which is identical with that obtained by the condensation of 3-chlorobenzaldehyde with [3]ferrocenophane-1,3-dione². This confirms our hypothesis about² *Ia* as the intermediate in the route leading to the 7-membered lactone bridge (compound *II*).

Attempts at addition of 1,3-cyclohexanedione and 2,4-pentanedione to the derivative *Ia* resulted in subsequent expansion of the 3-membered bridge in the starting

compound to the 7-membered one, which released the steric strain observed³ for the compound *Ia*. It is of interest that analogous products have not been formed. In the case of the reaction with 1,3-cyclohexanedione, the 3-membered bridge is



SCHEME 1

opened due to the O-attack on the carbonyl carbon, giving the lactone *IIIa*. In the reaction with 2,4-pentanedione, there proceeds the C-attack, yielding the carbocyclic derivative *IV* containing 7-membered bridge. The structure of the lactone *IIIa* was proved above all by ^1H NMR spectroscopy. The spectrum shows characteristic *ABC* system, $-\text{COCH}_2\text{Ar}$, which was found also for 2,3-disubstituted [5]ferrocenophane-1,5-diones⁴, in addition to the $\nu(\text{COO})$ band at 1740 cm^{-1} in the IR spectrum of the compound.

The highly probable structure of the derivative *IV* was assigned on the basis of the presence of typical *ABCD* system in the ^1H NMR spectrum of the compound and the OH chemical shift at δ 16.21. This shift indicates the strong intramolecular hydrogen bonding, which in the compound given exhibits stabilizing effect.

Our attempt at addition of another diketone, 1,3-indanedione, to the derivative *Ia* has not been successful. The reaction afforded a complex mixture of the products in which the product *V* with expanded bridge was detected only by thin layer chromatography. The product *V* has been obtained by the reverse procedure, *i.e.* by the addition of [3]ferrocenophane-1,3-dione to 2-(3-chlorobenzylidene)-1,3-indanedione. The unsuccessful attempt at the addition of 1,3-indanedione can be explained by autocondensation reactions of the compound in basic medium⁵⁻⁸.

From experiments it becomes clear that 2-benzylidene[3]ferrocenophane-1,3-dione differs in its reactivity towards nucleophilic reagents from its benzene analogue, 2-benzylidene-1,3-indanedione, for which compound the bridge opening has not been observed either during its synthesis^{9,10} or in attempted addition of C-nucleophiles, including 2,4-pentanedione¹¹.

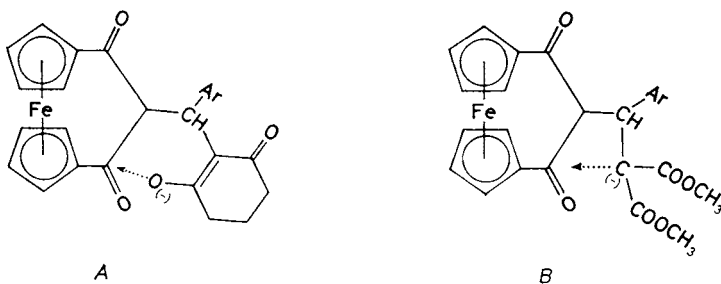
It is of interest that in ^1H NMR spectra of all the products with [7]ferrocenophane system, the chemical shift of one ferrocene hydrogen (likely H_a) is in the markedly lower field- at around δ 5.10. In the spectra of the products of the addition of ethyl and methyl malonates (*VI*, *VII*) two signals are located in the lower field compared to the other ferrocene hydrogens. As the ^1H NMR spectrum of these adducts measured at 80 MHz shows two multiplets at δ 5.3 and 5.0, the assignment of which is not unambiguous and as the chemical shift of CHC_6H_5 proton cannot be differentiated, we have measured the spectrum of the derivative *VI* at 300 MHz. The spectrum showed the following chemical shifts: 7.5–7.2 (Ar, m, 4 H), 5.54 (CHCO, d, 1 H, $J = 11.1$ Hz), 5.27 (Fc, m, 1 H), 4.97 (Fc, m, 1 H), 4.7–4.5 (Fc, m, 6 H), 4.558 (CHAr, dd, 1 H, $J = 11.1$ and 6.1 Hz), 4.177, 4.120 and 4.105 (OCH_2 , q, 4 H), 3.962 (d, 1 H, $J = 6.1$ Hz), 1.253 and 1.210 (CH_3 , t, 6 H). The unambiguous assignment of the chemical shifts of CH—CO, CH—COOR, and CH—Aryl group protons as well as hydrogens of the ferrocene skeleton at δ 5.27 and 4.97 was made by the double resonance method.

The structure of the derivative *VI* was confirmed also by the interpretation of its ^{13}C NMR spectrum by the off-resonance method. The spectrum did not show the signal of the quarternary sp^2 carbon but only signals of three CH sp^3 carbons at

δ 69.3 (CHCO), 54.4 (CHCOOR), and 41.1 (CHAr). The chemical shifts of the carbonyl carbons as well as of all C_{α} and $C_{\alpha'}$ carbons are nonequivalent, similarly to the starting 2-benzylidene[3]ferrocenophane-1,3-diones¹².

We have been interested in whether the structure of the product of the addition of ethyl malonate to the compound *Ia* depends on the catalyst used. We have found that with both $K_2CO_3/18$ -crown-6 and KF/Al_2O_3 , the same product *VI* is formed in 52 and 25% yield, respectively. The reaction has not proceeded in the presence of triethylamine as the catalyst.

It is therefore of interest why in the addition of malonic acid esters, the reaction stops at the stage of Michael adduct, while in the case of 1,3-dicarbonyl compounds it proceeds *via* subsequent expansion of the ferrocene bridge. We presume that the cleavage-off of proton from 1,3-dicarbonyl compounds results in formation of the delocalized, resonance-stabilized anion, which allows bridge expansion to proceed *via* 6-membered transition state. In the case of malonic acid derivatives, such a delocalized anion is not formed and the bridge expansion would require a 4-membered transition state (*A* or *B*). The great difference between the stability and thus also

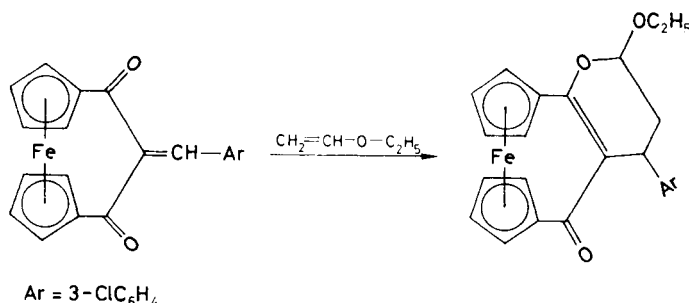


delocalization of carbanions derived from 2,4-pentanedione and of ethyl malonate is indicated also by pK_a values which are 9.00 and 13.3 in water¹³ or 14.20 and 17.22 in methanol¹⁴.

In our previous work we observed formation of the products containing expanded bridge only when condensation of [3]ferrocenophane-1,3-dione was made with the benzaldehyde substituted with electron-accepting substituents (*m*-Cl, *p*-CN, *p*-NO₂). We have therefore made an attempt to perform the addition of 1,3-cyclohexanedione also to other derivatives such as 2-(4-chlorobenzylidene)[3]ferrocenophane-1,3-dione (*Ib*) and 2-benzylidene[3]ferrocenophane-1,3-dione (*Ic*).

In the case of the derivative *Ib*, we have obtained the expected product *IIIb*, which was confirmed by ¹H NMR and IR spectra and by elemental analysis. On the other hand, in the reaction of 1,3-cyclohexanedione to the compound *Ic*, the addition proceeded obviously only to the C=C bond without opening and the subsequent expansion of the 3-membered ferrocenophane bridge. This is supported above all

by the IR spectrum of the product *IIIc*, in which the characteristic $\nu(\text{COO})$ band at 1740 cm^{-1} is absent. The presence of $\nu(\text{OH})$ band at 3100 cm^{-1} speaks for the stabilization of the product by intramolecular hydrogen bonding. As the compound is very insoluble, we have not succeeded in measuring its $^1\text{H NMR}$ spectrum (compound decomposes in DMSO).



SCHEME 2

With the aim to compare the reactivity of 2-benzylidene-1,3-indanedione and its ferrocene analogue *Ia* also in other reactions, we made an attempt to accomplish Diels–Alder addition of ethyl vinyl ether to the compound *Ia*. As shown in Scheme 2, we have obtained the expected product, *i.e.* the substance analogous to the compound formed by the reaction of ethyl vinyl ether with 2-benzylidene-1,3-indanedione¹⁵. It is worth mentioning, however, that the ferrocene derivative *VIII* so obtained undergoes easily decomposition to the starting compounds even at room temperature.

EXPERIMENTAL

Starting 2-benzylidene[3]ferrocenophane-1,3-diones were prepared by the reported procedure². Melting points were determined on a Kofler hot plate apparatus and are not corrected. $^1\text{H NMR}$ spectra were recorded on Tesla 487 (80 MHz) instrument in CDCl_3 if not stated otherwise. The 300 MHz spectrum of the compound *VI* was recorded on Bruker AM 300 instrument in CDCl_3 , using tetramethylsilane as internal reference. $^{13}\text{C NMR}$ spectrum of the compound was recorded on JEOL-100 FT spectrophotometer working at 25 MHz (CDCl_3 , TMS). IR spectra were recorded on Specord 75 IR spectrophotometer.

Addition of [3]ferrocenophane-1,3-dione to *Ia*

To a stirred mixture of 0.5 g of K_2CO_3 and 0.3 g of 18-crown-6 in 40 ml of dry benzene was added under nitrogen 0.2 g (0.72 mmol) of [3]ferrocenophane-1,3-dione and 0.27 g (0.72 mmol) of *Ia*. After 36h-stirring at room temperature, K_2CO_3 was removed by filtration and the solvent by vacuum distillation. The residue was chromatographed on SiO_2 using benzene–ethyl acetate (4 : 1) as the eluent. The compounds obtained from the first two bands in small amounts were

not identified. The third band afforded 0.05 g (11%) of the product *II*; yellow crystals not melting up to 360°C (crystallized from benzene). For $C_{33}H_{23}ClFe_2O_4$ (630.76) calculated: 62.84% C, 3.68% H, 17.71% Fe; found: 62.08% C, 3.56% H, 17.08% Fe. 1H NMR spectrum was identical with that reported². IR spectrum: $\nu(COO)$ 1740 cm^{-1} (s), $\nu(CO)$ 1675 cm^{-1} (s), and 1620 cm^{-1} (s).

Attempted addition of 1,3-indanedione to *Ia*

A total of 0.3 g (0.8 mmol) of *Ia* were added to a mixture of 0.5 g of K_2CO_3 , 0.3 g of 18-crown-6 and 0.12 g (8 mmol) of 1,3-indanedione in 40 ml of dry benzene. After 24 h-stirring at room temperature, the reaction mixture was worked up as in the preceding paragraph. Three substances were detected by TLC, one of which was the addition product (see the experiment below). However, no compound has been isolated by chromatography on SiO_2 in the amount sufficient for identification (decomposition).

Addition of [3]ferrocenophane-1,3-dione to 2-(3-chlorobenzylidene)-1,3-indanedione

A total of 0.3 g (1 mmol) of 2-(3-chlorobenzylidene)-1,3-indanedione were added to a mixture of 0.5 g of K_2CO_3 , 0.3 g of 18-crown-6 and 0.28 g (1 mmol) of [3]ferrocenophane-1,3-dione in 40 ml of dry benzene. After 24 h-stirring at room temperature, the reaction mixture was worked up as mentioned above. Chromatography on SiO_2 with the use of benzene-ethyl acetate (8.5 : 1.5 to 7 : 3) afforded small amounts of substances from the first, third, fourth and fifth band, which were not identified. The second band yielded 0.22 g (36%) of the compound *V*; yellow crystals which did not melt after recrystallization from benzene up to 360°C. For $C_{29}H_{19}ClFeO_4$ (523.74) calculated: 66.63% C, 3.67% H, 10.68% Fe; found: 66.27% C, 3.45% H, 10.32% Fe. IR (Nujol): $\nu(COO)$ 1725 cm^{-1} (w), $\nu(CO)$ 1680 cm^{-1} (s), and 1747 cm^{-1} (s).

Addition of 1,3-cyclohexanedione to *Ia*

A total of 0.33 g (0.9 mmol) of *Ia* were added to a mixture of 0.14 g of K_2CO_3 , 0.26 g of 18-crown-6 and 0.2 g (17 mmol) of 1,3-cyclohexanedione in 40 ml of dry benzene. After 24 h-stirring at room temperature, the reaction mixture was worked up as above. Chromatographic separation afforded 0.2 g (46.5%) of the product *IIIa*; m.p. 239–241°C (benzene). For $C_{26}H_{21}ClFeO_4$ (488.73) calculated: 63.89% C, 4.33% H, 11.43% Fe; found: 63.35% C, 4.31% H, 10.82% Fe. 1H NMR ($CDCl_3$): δ 7.3–7.0 (3- ClC_6H_4 , m, 4 H), 5.10 (Fc, m, H_x , 1 H), 4.88 (Fc, m, 3 H), 4.50 (Fc, m, 4 H), 3.86 (H_A , dd, 1 H) J_{AB} = 18.7 Hz, J_{AC} = 12.7 Hz, 3.2 (H_C , m, 1 H), 2.81 (H_B , dd, 1 H) J_{BC} = 4 Hz, 2.40 (CH_2 , m, 4 H), 1.98 (CH_2 , m, 2 H). IR ($CHCl_3$): $\nu(COO)$ 1740 cm^{-1} (s), $\nu(CO)$ 1675 cm^{-1} (s), and 1655 cm^{-1} (m). Mass spectrum, m/z = 488. The compounds were used in the same amounts as indicated above in an attempt to effect the reaction with triethylamine (0.5 ml). After refluxing the mixture for 7 h, 0.07 g (21%) of the starting compound and 0.2 g (46%) of the product were isolated by chromatography.

Addition of 1,3-cyclohexanedione to *Ib*

The procedure and weighed amounts of the compounds were the same as in the addition of *Ia*. The product *IIIb* was isolated in 39% yield (0.12 g); m.p. 228.5–232°C (benzene-petroleum ether). For $C_{26}H_{21}ClFeO_4$ (488.73) calculated: 63.89% C, 4.33% H, 11.43% Fe; found: 64.41% C, 4.72% H, 11.43% Fe. 1H NMR ($CDCl_3$): δ 7.25 (4- ClC_6H_4 , s, 4 H), 5.10 (Fc, H_x , m, 1 H), 4.88 (Fc, m, 3 H), 4.50 (Fc, m, 4 H), 3.86 (H_A , dd, 1 H), J_{AB} = 18.7 Hz, J_{AC} = 12.7 Hz, 3.2 (H_C , m,

1 H), 2.81 (H_B , dd, 1 H) $J_{BC} = 4$ Hz, 2.40 (CH_2 , m, 4 H), 1.98 (CH_2 , m, 2 H). IR ($CHCl_3$): $\nu(COO)$ 1730 cm^{-1} (s), $\nu(CO)$ 1670 cm^{-1} (s), and 1645 cm^{-1} (m).

Addition of 1,3-cyclohexanedione to *Ic*

A total of 0.24 g (0.7 mmol) of *Ic* were added to a solution of 0.16 g (1.4 mmol) of 1,3-cyclohexanedione and 0.5 ml of triethylamine in 35 ml of dry benzene. After 2h-stirring and heating to the boiling point of the solvent, 0.30 g (94%) of the product *Ic* were obtained. The product did not melt up to 360°C. For $C_{26}H_{22}FeO_4$ (454.29) calculated: 68.73% C, 4.90% H, 12.29% Fe; found: 69.20% C, 4.92% H, 12.45% Fe. IR (Nujol): $\nu(OH)$ 3100 cm^{-1} , $\nu_{as}(CO)$ 1688 cm^{-1} , $\nu(CO)$ 1684 cm^{-1} , $\nu_s(CO)$ 1679 cm^{-1} , and $\nu(C=C)$ 1600 cm^{-1} .

Addition of 2,4-pentanedione to *Ia*

A total of 0.5 g (1.3 mmol) of *Ia* were added to a mixture of 0.49 ml (5 mmol) of 2,4-pentanedione, 1.5 ml of triethylamine and 100 ml of dry benzene. The reaction mixture was refluxed with stirring for 7.5 h. After solvent removal by vacuum distillation, the residue was chromatographed on SiO_2 (benzene-ethyl acetate (9 : 1-7 : 3)). The first band gave 0.12 g (24%) of the starting dione. Small amounts of unidentified compounds were obtained from the second and third band. The last band yielded 0.35 g (70%) of the product *IV*; m.p. 202.5-206°C (benzene-petroleum ether). For $C_{25}H_{21}ClFeO_4$ (476.72) calculated: 62.98% C, 4.44% H, 11.91% Fe; found: 62.30% C, 4.47% H, 11.38% Fe. 1H NMR ($CDCl_3$): δ 16.21 (OH, 2, 1 H), 7.3-7.0 (3- ClC_6H_4 , =CH, m, 5 H), 4.7 (Fc, m, 2 H), 4.5 (Fc, m, 4 H), 4.1 (Fc, m, 2 H), 3.70 (H_D , d, 1 H) $J_{DC} = 10.1$ Hz, 3.15 (H_C , m, 1 H), 3.04 (H_A , dd) $J_{AB} = 18.8$ Hz, 2.55 (H_B , d, 1 H) $J_{BC} \sim 1$ Hz, 1.73 (CH_3 , s, 3 H). IR ($CHCl_3$): $\nu(CO)$ 1640 and 1720 cm^{-1} , $\nu(C=C)$ 1590 cm^{-1} . Mass spectrum, $m/z = 476$.

Addition of ethyl malonate to *Ia*

A) Catalysis by $K_2CO_3/18$ -crown-6. A total of 0.3 g (0.8 mmol) of *Ia* was added to a mixture of 0.5 g of K_2CO_3 , 0.3 g of 18-crown-6 and 0.12 ml (0.8 mmol) of ethyl malonate in 40 ml of benzene. After 24 h-stirring at room temperature, the reaction mixture was worked up as usual. Chromatography afforded 0.22 g (5%) of the product *VI*; m.p. 140-143°C (benzene). For $C_{27}H_{25}ClFeO_6$ (536.73) calculated: 60.41% C, 4.70% H, 10.41% Fe; found: 60.91% C, 4.26% H, 10.26% Fe. 1H NMR ($CDCl_3$, 80 MHz): δ 7.46-7.10 (3- ClC_6H_4 , m, 4 H), 5.50 (CHCO, d, 1 H), 5.34 (Fc, m, 1 H), 4.95 (Fc, m, 1 H), 4.72-4.30 (Fc, CHC_6H_4Cl , m, 7 H), 4.2-3.85 (OCH_2CHCOO , m, 5 H), 1.25-1.00 (CH_3 , t, 6 H). ^{13}C NMR ($CDCl_3$): δ 191.6 and 190.3 (CO), 168.5 and 168.3 (COOR), 141.4 (C_1Ar), 134.1 (C_3Ar), 129.7 (C_5Ar), 129.2 (C_2Ar), 127.7 (C_6Ar), 127.5 (C_4Ar), 90.8 and 90.6 ($C_{1,1}$, Fc), 74.1 and 73.4 ($C_{\beta,\beta}$, Fc), 73.2, 72.9, 69.9 and 69.6 ($C_{\alpha,\alpha}$, Fc), 69.3 (CHCO), 61.60 (OCH_2), 54.4 (CHCOOR), 41.1 (CHAr), 13.9 (CH_3). IR (Nujol): $\nu(COOR)$ 1740 cm^{-1} (m) and 1707 cm^{-1} (s), $\nu(CO)$ 1680 cm^{-1} (s) and 1647 cm^{-1} (m).

B) Catalysis by KF/Al_2O_3 . To 40 ml of acetonitrile, 0.2 g (0.5 mmol) of *Ia*, 0.1 ml (0.6 mmol) of ethyl malonate and 0.1 g of KF/Al_2O_3 (prepared according to ref.¹⁶) were added. After 24h-stirring at room temperature, the catalyst was removed by filtration and the solution was poured into water. The organic material was extracted with dichloromethane. After drying over Na_2SO_4 and solvent evaporation, 0.07 g (25%) of the product *VI* were obtained by chromatography.

Addition of methyl malonate to *Ia*

A total of 0.26 g (0.7 mmol) of *Ia* were added to a mixture of 0.1 g of K_2CO_3 , 0.21 g of 18-crown-6 and 0.1 g (0.7 mmol) of methyl malonate in 40 ml of dry benzene. After 24 h-stirring at room temperature, the reaction mixture was worked up as usual. Chromatography afforded 0.12 g (34%) of the product melting at 167–170°C (benzene–petroleum ether). For $C_{25}H_{21}ClFeO_6$ (508.70) calculated: 59.02% C, 4.17% H, 6.97% Cl, 10.98% Fe; found: 61.20% C, 4.36% H, 6.43% Cl, 11.10% Fe. 1H NMR ($CDCl_3$): δ 7.4–7.1 (3- ClC_6H_4 , m, 4 H), 5.50 (CHCO, d, 1 H) $J = 11.1$ Hz, 5.23 (Fc, m, 1 H), 4.91 (Fc, m, 1 H), 4.7–4.4 (Fc, CHAr, m, 7 H), 3.92 (CHCOOR, d, 1 H) $J = 6.1$ Hz, 3.66 and 3.61 (OCH_3 , s, 3 H, s, 3 H). IR (Nujol): $\nu(COOR)$ 1750 cm^{-1} (s), 1730 cm^{-1} (m), $\nu(CO)$ 1680 cm^{-1} (s), 1640 cm^{-1} (m).

Cycloaddition of *Ia* to ethyl vinyl ether

An ampoule containing 40 ml of dry benzene was charged with 0.5 g (1 mmol) of *Ia* and 0.72 g (10 mmol) of ethyl vinyl ether. After sealing, the ampoule was heated in water bath to 70°C for 20 h. Then the ampoule was cooled, opened and the solvent evaporated *in vacuo*. The residue was chromatographed on SiO_2 using benzene–ethyl acetate (9.8 : 0.2) as the eluent. The first, red band afforded only trace amounts of an unidentified substance, the second, violet band yielded traces of the starting compounds. The product *VII* (0.34 g, 59.6% yield) was isolated from the third band. The compound crystallized with difficulty from petroleum ether and melted at 153–170°C (decomposition of the product to starting compounds). For $C_{24}H_{21}ClFeO_3$ (448.7) calculated: 64.25% C, 4.73% H, 7.90% Cl, 12.45% Fe; found: 64.35% C, 6.68% H, 7.76% Cl, 12.62% Fe. 1H NMR ($CDCl_3$): δ 7.5–7.0 (3- ClC_6H_4 , m, 4 H), 5.26 (OCHO, m, 1 H), 4.7–4.1 (Fc, m, 8 H), 3.84 (OCH_2 , q, 2 H), 3.6 (CHAr, m, 1 H), 2.2 (CH_2 , m, 2 H), 1.19 (CH_3 , t, 3 H). IR ($CHCl_3$): $\nu(CO)$ 1730 and 1600 cm^{-1} , $\nu(C=C)$ 1597 cm^{-1} .

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