Evidence for Organoironcarbonylate Anion Formation in Nucleophilic Addition to Tetracarbonyliron Complexes of Acrylate Esters

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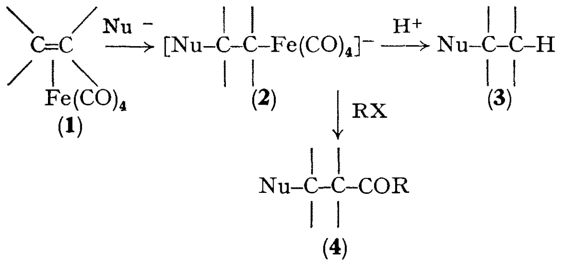
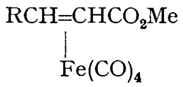
Summary Sequential addition of stabilized anions and alkyl iodides to tetracarbonyliron complexes of methyl acrylate and methyl crotonate affords products consistent with regiospecific generation and alkylation of an organoironcarbonylate anion intermediate

WE have previously reported[1] that nucleophilic addition to ethylene and methyl acrylate can be mediated through the corresponding tetracarbonyliron complexes As a working hypothesis we had assumed as shown in equation (1) that nucleophilic attack first produces a stable alkylirontetracarbonylate anion (2),[2] quenching of which with acid then yields addition product (3) [3] If this pathway is in fact followed, then it should be possible to alkylate (2) according to precedent[4,5] to give adducts of type (4) corresponding to the addition of the elements of NuCOR to alkene We report here results which confirm this prediction and thus establish that an intermediate which can be acylated is generated



(1)

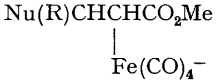


$$\underset{\mathrm{Fe(CO)_4}}{\mathrm{RCH{=}CHCO_2Me}}$$

(5) **a**, R = H
b, R = Me

Nu(R)CHCH$_2$CO$_2$Me
(6)

Nu(R)CHCH(COR′)CO$_2$Me
(7)



$$\mathrm{Nu(R)CH}\underset{\mathrm{Fe(CO)_4^-}}{\mathrm{CHCO_2Me}}$$

(8)

The results of treating complexes (**5a**)[6] and (**5b**)† ‡ with a number of stabilized anions under mild aprotic conditions followed by quenching with trifluoroacetic acid to give Nu(R)CHCH$_2$CO$_2$Me (**6**) are summarized in the Table These reactions were particularly clean, in each case a single product corresponding to regiospecific addition in the Michael sense being obtained in good yield The crotonate complex (**5b**) was somewhat less reactive than (**5a**), but addition took place with comparable efficiency

The addition of alkylating agents subsequent to nucleophilic addition was then explored as a probe for intermediates of type (**2**) Of a variety of agents examined, including dimethyl sulphate methyl tosylate methyl and n-butyl trifluoromethanesulphonate [7] methyl tresylate,¶[8] and 2-methoxy-3-ethylbenzothiazolium fluoroborate [9] only methyl iodide and lower primary alkyl iodides were effective in forming adducts Nu(R)CHCH(COR′)CO$_2$Me (**7**) §[10] These results are also given in the Table

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† Both (**5a**) and (**5b**) were prepared by a modification of the method described in ref 6, in 85 and 73% yields, respectively Compound (**5b**) is a new complex yellow needles m p 29 5—30 °C δ (CDCl$_3$ Me$_4$Si 100 MHz −15 °C) 1 77 (d 3H *Me*CH=, *J* 6 4 Hz), 3 29 (d 1H =C*H*CO$_2$Me *J* 11 1 Hz) 3 69 (s 3H Me) and 3 87 (m 1H MeC*H*–) ν (CHCl$_3$) 1712 (s ester C=O) 2019 (s broad, metal CO) and 2108 cm^{-1} (s metal CO) *m/e* 184 (*M* − 3CO) 168 [Fe(CO)$_4$] and 85 1 (MeCH=CHCO$_2$Me) Although it is reasonably stable in the crystalline state and in solution under argon, the lability of the compound has thus far prevented satisfactory combustion analysis

‡ All new compounds reported herein except as noted in the previous footnote afforded satisfactory combustion analyses

§ The ^{1}H n m r spectra of adducts (**7**) corresponded to replacement of an α-proton in (**6**) with –COR′

¶ Tresylate = 2,2,2-trifluoroethanesulphonate

TABLE Addition of NuH and NuCOR′ to $(RCH{=}CHCO_2Me)Fe(CO)_4$

R	Nucleophile[a]	(6)[b] Solvent,[c] conditions	(6)[b] Yield/%	(7) Solvent,[c] R′,[d] conditions[e]	(7) Yield/%
H	$NaCH(CO_2Et)_2$	A, 0 °C, 20 h	92	2·1 A–B, Me, 25 °C/1 h	85
				2:1 A–B, Et, 45—50 °C, 72 h	54
				2:1 A–B, Pr^n, 45—50 °C, 72 h	40
	$NaCH(COMe)CO_2Et$	A, 0 °C, 21 h	95	2.1 A–B, Me, 25 °C, 1 h	43
				2:1 A–B, Et, 25 °C, 144 h	42
	$NaCH(CN)CO_2Et$	4:1 A–B, 0 °C, 20 h	88	2:1 A–B, Me, 25 ° C, 24,h	43
	$Na^+\{CO_2Me\overline{C[CH_2]_4CO}\}^-$	1:1 A–C, 0 °C, 20 h	88	4.3·2 A–B–C, Me, 25 °C, 24 h	46
Me	$NaCH(COMe)CO_2Et$	1 1 A–C, 25 °C, 48 h	78	1 2 1 A–B–C, Me, 40 °C, 96 h	61
	$NaCH(CN)CO_2Et$	4.1 A–B, 0 °C, 20 h	93	2:1 A–B, Me, 40 °C, 120 h	16

[a] 1 5—2 0 equiv of nucleophile, generated from NuH and NaH, were used [b] Reaction quenched with CF_3CO_2H [c] A = tetrahydrofuran, B = 1-methyl-2-pyrrolidinone, and C = hexamethylphosphoramide [d] R′I complex = 4—5 1 [e] Conditions for alkylation. Addition of nucleophile was carried out as for formation of (**6**), after which solvent composition was adjusted for alkylation

The reaction of complex (**5a**) with diethyl sodiomalonate–methyl iodide was remarkably clean and efficient, adduct (**7**) [Nu = $CH(CO_2Et)_2$, R = H, R′ = Me] being obtained rapidly and in high yield as the only product In all other cases, however, the corresponding Michael adduct (**6**) was a significant co-product In addition, the rate of alkylation and yield of (**7**) decreased with increasing chainlength of R′I These yields did not increase with various changes in reaction conditions, *i e*, temperature, CO atmosphere, solvent, and alkylating agent

The formation of adducts (**7**) strongly supports the intermediacy of (**8**) or a functionally equivalent species Identification of the intermediate as (**8**) finds indirect support in the work of Mitsudo *et al*[5] who identified the anionic intermediate from reaction of $[HFe(CO)_4]^-$ with methyl acrylate as $\{MeCH[Fe(CO)_4]CO_2Me\}^-$ and found that it reacted with some lower primary alkyl iodides to give hydroacylated products, $MeCH(COR)CO_2Me$ The similarity of this work to the present work is noteworthy, and the restriction of effective alkylating agents suggests that at least one pathway other than S_N2 displacement is playing a major role in product formation Since the reaction of sodium cyclopentadienyldicarbonyliron with reactive alkyl halides has been shown to generate free radicals[11] and since there is good evidence that some reactions of $[RFe(CO)_4]^-$ involve electron transfer,[12] is seems likely that one or more electron transfer processes is also involved here

Notwithstanding this limitation on alkylating agent, these results demonstrate that the tetracarbonyliron group can serve as a control element for effecting regiospecific introduction of two carbon–carbon bonds into an acrylate ester

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