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PREPARATION AND REACTIONS OF [2,2-BIS(CARBETHOXY)PROPYL]-CYCLOPENTADIENYLDICARBONYLIRON

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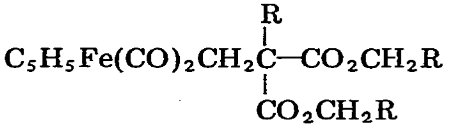
Summary

Although $\mathrm{FpCH_2\overset{CH_3}{C}(CO_2Et)_2}$, ($\mathrm{Fp} = \eta\text{-}\mathrm{C_5H_5Fe(CO)_2}$) (I) is stable and characterizable, the lower homologue $\mathrm{FpCH_2CH(CO_2CH_3)_2}$ (II) is not; this we attribute to a facile elimination reaction resulting from the relatively acidic β-hydrogen of II. Formation of I from $\mathrm{Fp^-}$ and $\mathrm{XCH_2CE_2CH_3}$ (X = Br, Cl; E = $\mathrm{CO_2CH_2CH_3}$) and cleavage of its Fe—C bonds (using $\mathrm{H^+}$, $\mathrm{Br_2}$, $\mathrm{Ce^{IV}}$ and $\mathrm{Hg^{II}}$) occur without major amounts of ester group migrations, even though $\mathrm{{\cdot}CH_2CE_2CH_3}$ radicals are involved in some of these reactions.

Introduction

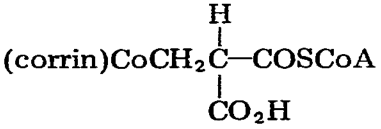
Interest in the extraordinary structural rearrangements of substrates brought about by enzymes containing coenzyme-$\mathrm{B_{12}}$ (5′-deoxyadenosylcobalamin) has resulted in many mechanistic studies [1,2]. Regrettably, the structural complexity of the corrin ligand in the cobalamins themselves prevents direct characterization of the attached organic ligands, thereby obscuring the timing and mechanism of rearrangement reactions. Many studies of (presumably) related organocobalt(III) species have been carried out as a consequence [3].

The extensive chemical similarities between the d^8-"supernucleophiles", cyclopentadienyldicarbonylferrate ($\mathrm{Fp^-}$) and cobal(I)amin ($\mathrm{B_{12s}}$) and between their alkylated derivatives led us to prepare compounds I and II, analogous to the intermediate III, invoked in proposals on the mechanism of the methylmalonyl—CoA to succinyl—CoA rearrangement [1,4].



$$\mathrm{C_5H_5Fe(CO)_2CH_2\overset{\displaystyle R}{\underset{\displaystyle CO_2CH_2R}{C}}{-}CO_2CH_2R}$$

(I, $\mathrm{R = CH_3}$;
II, R = H)



$$\mathrm{(corrin)CoCH_2\overset{\displaystyle H}{\underset{\displaystyle CO_2H}{C}}{-}COSCoA}$$

(III)

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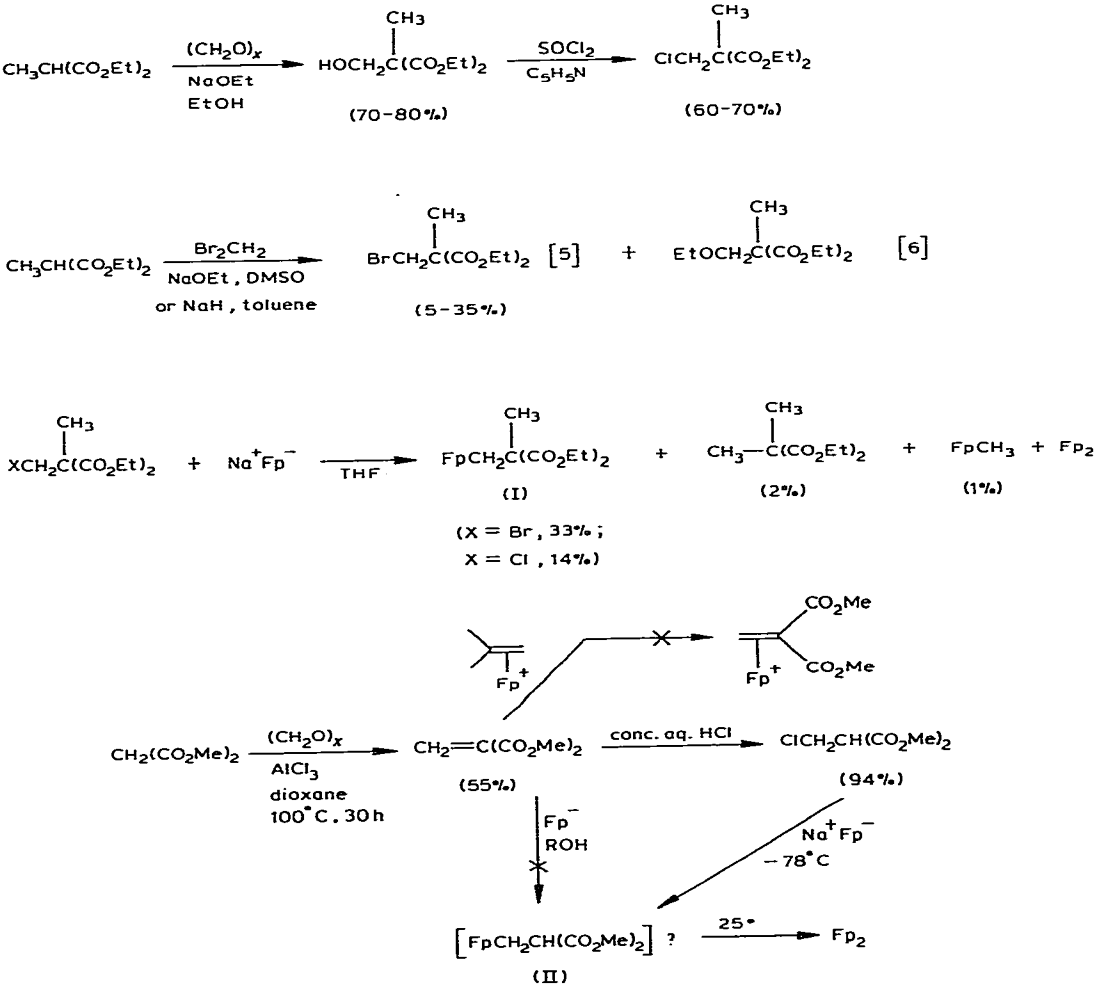
I and II were expected to be stable, characterizable compounds capable of undergoing Fe—C bond cleavages with appropriate reagents. Evidence of rearrangements in the organic products of such bond cleavages were sought in hope that these stable derivatives of d^6-Fe^{II} would provide insight into the unstable derivatives of d^6-Co^{III}.

Results

The routes followed in synthesis of I and II are outlined in Scheme 1. Displacement of halide from diethyl halomethylmethylmalonate by Fp^- proved to be a very slow process, requiring some 20 h at room temperature. This is presumably a consequence of the neopentyl-like structure of the halide. By-

SCHEME 1

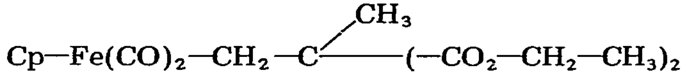
Syntheses of dicarbalkoxyalkyl derivatives of cyclopentadienyldicarbonyliron ($Fp = \eta$-$C_5H_5Fe(CO)_2$, $Et = C_2H_5$, $Me = CH_3$)



products which were isolated and identified included substantial amounts of dicyclopentadienyltetracarbonyldiiron (Fp_2), and small amounts of methylcyclopentadienyldicarbonyliron ($FpCH_3$), acetylcyclopentadienyldicarbonyliron ($Fp\overset{O}{\overset{\|}{C}}CH_3$), and diethyl dimethylmalonate. Diethyl methylsuccinate could not be detected by gas chromatography.

I was obtained as a stable, slightly air-sensitive, yellow-brown oil, whose spectra were fully consistent with the expected structure. The proton and carbon NMR spectra, in particular, bespoke an unrearranged structure:

I,

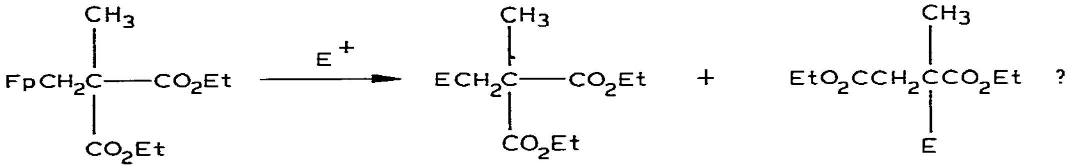


$$Cp{-}Fe(CO)_2{-}CH_2{-}\overset{CH_3}{C}{-}({-}CO_2{-}CH_2{-}CH_3)_2$$

PMR:	δ 4.78(s)	—	1.80(s)	—	1.30(s)	—	3.93(q)	1.20(t)
^{13}C NMR:	85.7	217.0	24.0	57.4	4.6	173.8	60.8	14.0

Unfortunately, a number of attempts to introduce the Fp group by displacement of chloride from dimethyl chloromethylmalonate at room temperature failed. Characterizable products included large quantities of the iron dimer, Fp_2, and consistent 2—3% yields of $FpCH_3$ and ferrocene. Running the reaction at —78° C gave reaction mixtures whose IR spectra, run immediately upon warming to room temperature, showed absorptions appropriate for II, at 2020, 1956, and 1738 cm^{-1}. But the compound decomposed quickly to Fp_2 and could not be isolated. Again, $FpCH_3$ and ferrocene were formed in small amounts, along with Fp_2 in major amounts. Thus II appears to be at best a short-lived species at room temperature.

Reactions of I with various electrophiles capable of cleaving the Fe—C bond were then studied, with the organic products being scrutinized for rearranged structures which resemble those in the methylmalonyl—CoA → succinyl—CoA rearrangements.



(IV, unrearranged)　　(V, rearranged)

(a E = H ;
b E = Br ;
c E = CO_2CH_3 ; (using Ce^{IV})
d E = HgCl)

Dissolution of I in trifluoroacetic acid gave cleanly diethyl dimethylmalonate (IVa), and cyclopentadienyldicarbonyl (trifluoroacetato)iron, $FpO\overset{O}{\overset{\|}{C}}CF_3$ [7].

No diethyl methylsuccinate (Va) was detectable by NMR or GC. Bromination of I under a variety of conditions produced complex reaction mixtures, which contained little of the expected diethyl (bromomethyl)methylmalonate (IVb). The principal products were IVa and the bromoiron compound, FpBr. Small amounts of diethyl methylmalonate were also formed. GC/MS analysis of reaction mixtures also revealed isomers of $C_5H_5Br_3$ and $C_5H_5Br_5$, arising from the cyclopentadienyl ring of I, and other components which arose from oxidation reactions, including diethyl 2-carbethoxy-2-methylsuccinate (IV, E = CO_2Et).

Reaction of I with Ce^{IV} in methanol produced, along with some IVa, a principal product whose IR and mass spectra were consistent with those expected for either IVc or Vc. Authentic IVc was synthesized by reaction of methyl chloroacetate with sodium diethyl methylmalonate. The reaction was bedeviled by concurrent transesterification reactions, but the principal component was isolated by preparative GC and shown to be IVc by an 80 MHz proton NMR, which showed sharp and equivalent ethyl ester groups. GC coinjection confirmed the identity of this material with the product of the Ce^{IV} oxidation of I. In two of three runs of the Ce^{IV} oxidation, a small GC peak (5—10% the area of IVc) with slightly shorter retention time than IVc and very similar mass spectrum was also observed. We ascribe this to a small amount of Vc formed by rearrangement of an ester group.

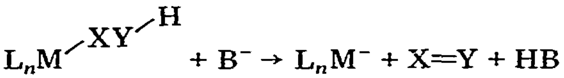
Reaction of I with mercuric chloride occurred cleanly so as to produce FpCl and RHgCl, as previously found for primary alkyl groups [8]. The proton NMR spectrum of the organomercurial indicated no ester group migration during the transmetalation reaction.

Discussion

Effect of acidic β-hydrogen

In our hands, II could not be obtained under conditions which led to I, apparently as a result of lability of II [9]. There is nothing inherently unstable about an organometallic group sharing a molecule with acidic hydrogens, $FpCH_2\overset{\overset{O}{\|}}{C}OH$ and analogous acids being well-characterized species [10]. Likewise, compounds with acidic malonate hydrogens α to an Fp group ($FpCH(CO_2R)_2$) [11] and γ to an Fp group ($FpCH_2CH_2CH(CO_2R)_2$) [12] are well-characterized. We infer that the specific structural feature which labilizes II is the acidic β-hydrogen.

From this perspective, II is a member of a class of organometallics which, though relatively unstable, are of considerable interest as possible reaction intermediates, including (α-hydroxyalkyl) metals, $L_nM\underset{/\ \backslash}{C}OH$ [13], and (hydroxycarbonyl) metals, $L_nM\overset{\overset{O}{\|}}{C}OH$ [14,15]. Although examples are isolable in special cases (especially where the metal group, L_nM, is CpRe(NO)CO) [16]) such substances appear generally to be labile toward base-induced elimination, analogous to the classical $E2$ elimination of organic chemistry. This provides a special mechanism for the general process of "β-hydride elimination", in cases in which



$$L_nM\diagup^{XY\diagup^{H}} + B^- \rightarrow L_nM^- + X{=}Y + HB$$

the "hydride" is actually protonic [17].

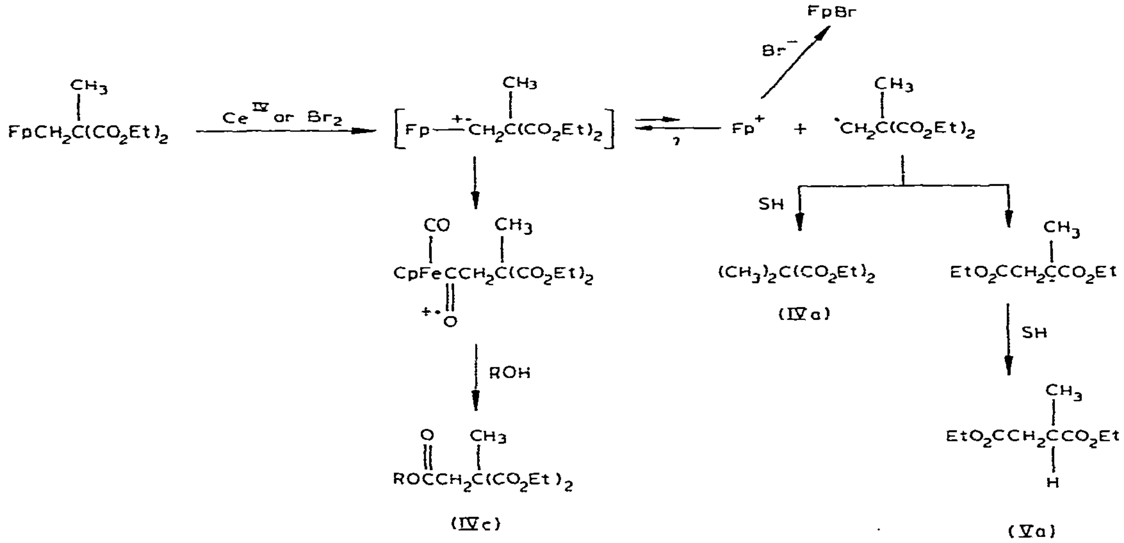
That the acidic β-hydrogen effect has not become evident during previous studies of organocobalt models for III is a consequence of the fact that most such studies [2,3] have used, for unstated reasons, methylated derivatives, $L_nCoCH_2\overset{CH_3}{\overset{|}{C}}(CO_2R)_2$. The proposed intermediate III, in which the carboxylate group would be ionized at physiological pH, would not suffer any instability as a consequence of its β-H.

Formation and cleavage of C—Fe bonds

Reactions of the diethyl (halomethyl)methylmalonates with Na^+Fp^- in THF consistently yielded 1—3% of diethyl dimethylmalonate (IVa), along with the desired product I. This bespeaks some portion of the reaction occurring by an electron-transfer pathway [18], with the radical $\cdot CH_2CE_2CH_3$ picking up a hydrogen from a solvent molecule. The electron-transfer pathway may be favored in these substrates by their considerable reluctance to undergo S_N2 displacement. No diethyl methylsuccinate, from rearrangement of the presumed radical, could be detected by GC. Winstein likewise found no rearrangement during the peroxide-induced decarbonylation of $H\overset{O}{\overset{\|}{C}}CH_2CE_2CH_2CH_3$ [19].

Reaction of I with trifluoroacetic acid and with mercuric chloride at room temperature were rapid and clean, only unrearranged IVa and IVd being formed. Likewise, the principal product of reaction with Ce^{IV} in methanol was the unrearranged methyl ester IVc. However, GC/MS analysis of reaction mixtures from the latter reaction showed a small amount of an isomeric product with a mass spectrum very similar to that of IVc, which we believe to be due to the rearranged compound Vc. Likewise, a trace of diethyl methylsuccinate (Va), accompanied the principal product IVa, upon reaction of I with bromine in methylene chloride. Failure of this reaction to produce significant amounts of the expected bromide IVb (or Vb) is puzzling; however, the formation of IVa again suggests radical intermediates.

Electrophilic cleavages of C—Fe bonds of alkyl Fp compounds have generally been found to proceed with preservation of stereochemical integrity of the alkyl group [20]. It is thus not surprising to find complete maintenance of structural integrity of the organic moiety of I in the protonolysis and mercuration reactions, and predominant maintenance in all cases. In the reactions with oxidizing agents, some evidence that structural rearrangements occur to a small extent has been found. These results are consistent with outer sphere electron-transfer mechanisms previously suggested for these oxidation reactions [20,21]. Dissociation of the organic moiety of I as a radical seems most likely, since the alternative carbonium ion appears to be quite unstable. In the case of the bromination reaction, most of the product derives from this dissociation rather than from metal-to-carbonyl migration (so-called "insertion") of the alkyl group, which predominates with Ce^{IV}. Notwithstanding the small amounts of



rearranged products in these latter cases, substantial similarities between the chemical reactions of I and those imputed to III have not been revealed in this study.

Experimental section

All solvents were reagent grade or redistilled technical grade. All organometallic reactions and manipulations were conducted under a nitrogen atmosphere with use of degassed solvents.

Diethyl (chloromethyl)methylmalonate

Diethyl (hydroxymethyl)methylmalonate [22] (93.3 g, 0.46 mol) was treated with 66 ml (0.92 mol) of thionyl chloride and 18.5 ml (0.23 mol) of pyridine. After 20 h reflux, the liquid product was separated from the solid and the latter was washed with ether. The organic liquids were washed with 3 × 100 ml of water, dried ($MgSO_4$), and evaporated. Distillation (b.p. 107—111°C/20 mmHg) gave 54.01 g (53%) of pure diethyl (chloromethyl)methylmalonate [22], NMR: δ (ppm) 1.2 (t, 6H); 1.4 (s, 3H); 3.8 (s, 2H); 4.1 (q, 4H).

[2,2-Bis(carbethoxy)propyl]cyclopentadienyldicarbonyliron (I)

A 250-ml three-neck flask having a stopcock attached to the bottom was fitted with dropping funnel and Nujol bubbler, mechanical stirrer and nitrogen inlet adapter, and charged with 9 ml of mercury. An amalgam was formed by addition of 0.564 g of sodium (24.5 mmol) in small pieces. After cooling, a solution of 2.54 g of dicyclopentadienyltetracarbonyldiiron (Fp_2) (7.17 mmol) in 125 ml of tetrahydrofuran was added, and the mixture was stirred for 2 h. The mercury was drained out through the stopcock, and 3.56 g (14.0 mmol) of diethyl bromomethylmethylmalonate [5] (IVb), was added to the mixture. After 18 h of stirring, the mixture was poured into 100 ml of water and extracted with 100 ml of ether. A second ether extract of 50 ml was combined with the first, and they were dried (Na_2SO_4) and evaporated. The semisolid brown residue was triturated with several portions of hexane, and the concentrated hexane extracts were chromatographed on neutral alumina, under nitrogen. Hexane eluted methyldicarbonylcyclopentadienyliron ($FpCH_3$, 2—13%). Increasing amounts of dichloromethane in hexane eluted diethyl dimethylmalonate (1—3%), starting halomethyl compound, Fp_2 dimer, and then, using 60—100% methylene chloride, the product I, as a yellow-brown oil.

IR: 2010s, 1965s, 1745br cm^{-1}; MS: m/z 364, (0.4%, P), 308 (35.8, $P-2CO$), 235 (35.7, $P-2CO-CO_2Et$), 234 (31.4), 170 (42.5), 164 (38.4), 149 (17.2, $CpFeCO^+$), 136 (20.5), 121 (100.0, $CpFe^+$), 69 (39.9, $C_3H_5CO^+$), 56 (15.6, Fe^+). Methanol/dichloromethane mixtures eluted acetyldicarbonylcyclopentadienyliron ($\mathrm{Fp\overset{\overset{O}{\|}}{C}CH_3}$, 3—6%). The methyl- and acetyl- compounds were identified by IR, NMR and GC comparisons to authentic samples. The hexane-insoluble material was essentially pure dimer, Fp_2.

Dimethyl chloromethylmalonate

A mixture of dimethyl methylenemalonate [23] (3.3 g, 23 mmol) and conc. aq. HCl (6.7 g, 68 mmol) was stirred at room temperature for 2 h, then extracted with chloroform. The solvent was evaporated at reduced pressure, giving essentially pure product. ^1H NMR: δ (ppm) 3.8 (s+m); ^{13}C NMR: δ (ppm) 40.0 (CH_2), 52.6 (CH_3), 54.1 (CH), 166.7 (CO). The bromomethylmalonate could be made analogously.

Reaction with sodium cyclopentadienyldicarbonylferrate

A solution of dimethyl chloromethylmalonate (2.0 g, 14 mmol) in 15 ml THF was added to a solution of 14 mmol of Na^+Fp^- prepared as above. Mild warming occurred. After stirring overnight, the solvent was evaporated under reduced pressure, and the mixture remaining was extracted with 3 × 2 ml hexane. Chromatography on basic alumina yielded CH_3Fp (0.09 g, 2%), an unstable yellow band, IR 2023 and 1967 cm^{-1}, and the dimer Fp_2, which was also the major component of the hexane-insoluble material.

In another instance, a solution of 20 mmol Na^+Fp^- in 120 ml THF was very slowly added to a solution of dimethyl chloromethylmalonate (2.80 g, 16 mmol) in 20 ml THF, in a —78°C bath. Thirty minutes after completion of addition, the solution was allowed to warm to room temperature. The solvent was evaporated at reduced pressure, and the residue extracted with hexane and chromatographed on basic alumina. After a trace of $FpCH_3$, a bright yellow band believed to be II eluted from the column with 15% dichloromethane/hexane. IR: 2016, 1965, 1738 cm^{-1}; a solid-probe mass spectrum showed only Fp_2, and a satisfactory NMR spectrum could not be obtained.

Reaction of I with trifluoroacetic acid

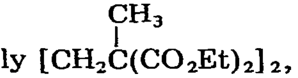
Trifluoroacetic acid (0.8 g, 7 mmol) was added to 0.100 g (0.27 mmol) of I at room temperature, and an NMR spectrum was taken after 20 min. Only four resonances were visible; those at δ (ppm) 1.31 (t), 1.72 (s), and 4.21 (q) due to diethyl dimethylmalonate and one at 5.24 (s) due to cyclopentadienyldicarbonyl (trifluoroacetato)iron [7]. The metal carbonyl region of the IR showed two strong peaks at 2022 and 2066 cm^{-1} due to the latter [7]. Gas chromatography confirmed the identity of the product as diethyl dimethylmalonate. A trace ($<1\%$) of diethyl methylmalonate was also revealed, but no diethyl methylsuccinate [24].

Reaction of I with mercuric chloride

In a 50 ml three-neck flask fitted as above were placed 0.40 g (1.09 mmol) of I, 0.297 g (1.09 mmol) of $HgCl_2$, and 6 ml of THF. After 45 h, IR showed both I and FpCl, so an additional equivalent of $HgCl_2$ was added. After an additional 22 h the IR showed only FpCl (2053, 2005 cm^{-1}) in the carbonyl region. After evaporation of the THF, ^1H NMR of the residue showed a singlet due to FpCl at δ 5.0 and the unrearranged organomercurial IVd: δ (ppm) 1.2 (q, 6H), 1.4 (s, 3H), 1.9 (s, 2H), and 4.1 (q, 4H). Purification of IVd by chromatography on neutral alumina was not successful.

Reaction of I with bromine

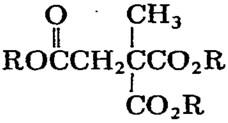
A solution of I (0.101 g, 0.27 mmol) in 3 ml CH_2Cl_2 at 0°C was treated with 0.27 ml of a 1 *M* solution of bromine in CH_2Cl_2. Gas chromatographic analysis (NPGS column, 125°C) showed diethyl dimethylmalonate (r.t., 1.5 min) to be the principal volatile product, with a small amount of diethyl methylmalonate (r.t., 1.8 min) also present. Neither bromomethyl compound (r.t., 7.0 min) nor diethyl methylsuccinate (r.t., 3.5 min) was detectable. Evaporation of the solution left a residue whose ^1H NMR spectrum (in CS_2) also revealed predominantly diethyl dimethylmalonate and FpBr.

Other bromination attempts, involving use of bromine in two-fold excess, gave very complex reaction mixtures, having at least eight GC peaks. In addition to the products described above, a room temperature run in carbon disulfide revealed a small amount of diethyl (bromomethyl)methylmalonate, an isomer of $C_5H_5Br_3$, and other, unidentified, products. A run at −80°C in CH_2Cl_2 also produced ethyl bromide, tri- and penta-bromocyclopentanes, a trace of diethyl methylsuccinate (based on both MS and GC retention time as compared with an authentic sample), and diethyl 2-carbethoxy-2-methylsuccinate (based on MS comparison with authentic sample). Both of these reactions also produced an incompletely identified material, possibly  $[\mathrm{CH_2}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}(\mathrm{CO_2Et})_2]_2$, based on MS peaks at *m/z* 243, 215, 187, 174, 141, 128, and 113.

Reaction of I with ceric ammonium nitrate in methanol

A solution of 0.424 g of I (1.16 mmol) in 10 ml of methanol was treated with 3.18 g (5.80 mmol) of solid $Ce(NH_4)_2(NO_3)_6$. After 1 h the solvent was evaporated, and the residue dissolved in water and methylene chloride. The organic layer was dried, filtered, and evaporated, leaving a brown oil. GC showed a trace of diethyl methylmalonate, the same unknown described above, and two isomers whose mass spectra were consistent with structures IVc and Vc. The principal isomer ($\geqslant 90\%$) was identical by GC coinjection with authentic IVc (see below).

Synthesis of IVc, methyl 3,3-bis(carbethoxy)butyrate

In a three-neck flask fitted as above were placed 7.00 g (40 mmol) of diethyl methylmalonate, 10 ml of toluene, and 1.98 g 50% sodium hydride (41 mmol). After 1 h stirring, 3.02 g (27.8 mmol) of methyl chloroacetate was added. The reaction was monitored by GC, which showed mixtures of triesters which formed simultaneously. After 2 h, water was added to quench the reaction, the layers were separated, and the organic layer dried ($CaCl_2$) and evaporated, leaving 6.1 g of product. Distillation at 1—2 mm gave: (1) a mixture of diethyl methylmalonate and methyl ethyl methylmalonate, b.p. 35—38°C, identified by ^1H NMR; (2) a mixture of triesters,  $\mathrm{RO\overset{\overset{O}{\|}}{C}CH_2\underset{CO_2R}{\overset{CH_3}{C}}CO_2R}$, with all possible combinations of $R{=}CH_3$ and CH_2CH_3, identified by GC/MS. The principal component was isolated by preparative GC (10′ × 3/8″ SE-30 column) and shown to be IVc by its 80 MHz ^1H NMR spectrum: δ (ppm) 1.25 (t, 6H), 1.54 (s, 3H), 2.94 (s, 2H), 3.67 (s, 3H), 4.20 (q, 4H).

Acknowledgments

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