Decarbethoxylation and Ring-Opening Reactions of 2-Tetrahydrofuranyl-, 2-Tetrahydrothienyl-, and 2-(1,3-Dithianyl)-Substituted Esters[1]

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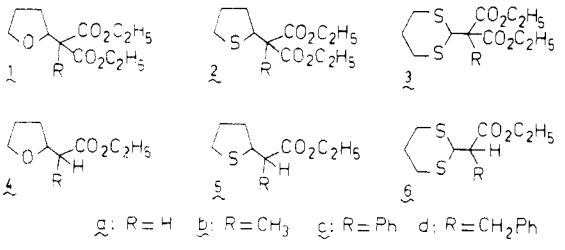
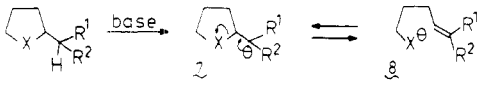
The course of decarbethoxylation reactions of 2-tetrahydrofuranyl-, 2-tetrahydrothienyl-, and 2-(1,3-dithianyl)-substituted malonic esters **1–3** with NaCl/H_2O in Me_2SO is shown to be dependent on the nature of the substituents at the α-carbon atom. In several instances, selective decarbethoxylation provides the monoesters **4–6**. In other cases, stereoselective ring-opening reactions take place, leading to mixtures of α,β- and β,γ-unsaturated esters. In the absence of H_2O, the cyclopropyl-substituted ester **13a** (R = H) is formed. Anions obtained by deprotonation of monoesters **4–6** and diesters **1–3** (R = H) undergo similar ring-opening reactions.

Recently, the preparation of 2-tetrahydrofuranyl (THF), 2-tetrahydrothienyl (THT), and 2-(1,3-dithianyl) (DT) geminal diesters **1–3** by reaction of the corresponding



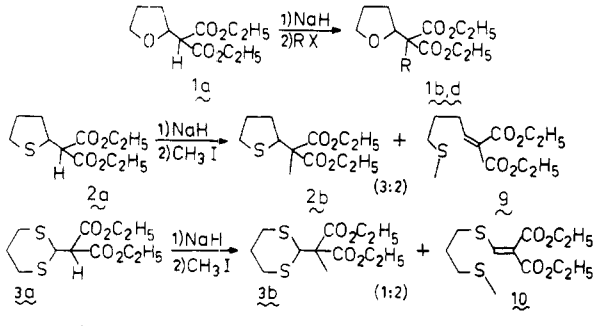
a: R = H **b**: R = CH_3 **c**: R = Ph **d**: R = CH_2Ph

α-chloro ethers and thioethers with malonic ester anions has been described.[1,2] Decarbethoxylation of these compounds was expected to provide the corresponding monoesters **4–6**.[3,4] The THF and THT moieties in esters **1**, **2**, **4**, and **5** could be envisioned as a potential four carbon synthon resulting from carbanionic ring-opening reactions (**7** → **8**).[5]



Results and Discussion

Anions of Malonic Esters 1a, 2a, and 3a. Anions **7** ($R^1 = R^2 = CO_2C_2H_5$) can be conveniently prepared by reaction of malonic esters **1a** and **2a** with sodium hydride



in THF.[6] The charge distribution within these anions and the position of the equilibrium **7** ⇄ **8** were studied by reactions with electrophiles.

Quenching **7** with H_2O afforded the starting malonic esters, indicating that the negative charge of these anions is mainly located in the geminal diester moiety and not at the heteroatom. Reaction of the anion derived from **1a** with methyl iodide and with benzyl bromide resulted in the exclusive formation of α-alkylated products **1b,d**, respectively.

On the other hand, reaction of the anions derived from **2a** and **3a** with methyl iodide afforded mixtures of α-methylated products **2b** and **3b** and ring-opened, *S*-methylated products **9** and **10**. This is not unexpected in view of the known affinity of sulfur toward alkyl iodides.

Decarbalkoxylation Reactions of Malonic Esters 1–3. The direct conversion of geminal diesters into monoesters by decarboxylation has been studied extensively

Table I. Decarbethoxylation Reactions of Geminal Diesters 1-3

substrate, R	t(95%),[a] h	product compn,[b] %	total yield,[b,c] %
1a, H[d]	1.5	**4a**, 25 **11a**, 30 **12a**, 45	76
1a, H[e]	1.5	**4a**, 30 **13a**, 15	50[e]
1b, CH_3[d]	30	**4b**, 40 **11b**, 50[f] **12b**, 6	76
1c, Ph[d]	10	**4c**, 50 **11c**, 25[g] **13c**, 5 **14** + **15**, 20	73
2a, H[h]	3	**5a**, 100	80
2b, CH_3[h]	8	**5b**, 100	80
2c, Ph[h]	5	**5c**, 90 **16**, 10	89
3a, H[h]	0.75	**6a**, 100	95
3b, CH_3[h]	4	**6b**, 10 **17**, 10 **18b**, 40 **19b**, 40	95
3c, Ph[h,i]	2	**6c**, 20 **17**, 10 **18c**, 40 **19c**, 20	85

[a] Reaction time needed for 95% conversion of the substrate. [b] Calculated from NMR and GC of crude products. [c] Yields after short-path distillation are ca. 10% lower. [d] Substrate and NaCl (0.7 M); H_2O (1.4 M). [e] Substrate and NaCl (0.7 M); diethyl malonate not isolated, since it is also rapidly decarbethoxylated. [f] *Z* isomer of **11b**, 4%. [g] Mixture of *E* (major) and *Z* isomer. [h] Substrate and NaCl (0.5 M); H_2O (1.0 M). [i] Ethyl phenylacetate was also identified.

(1) Part 8 of a series on the synthetic applications of cyclic α-chloro ethers and thioethers. Part 7: C. G. Kruse, E. K. Poels, and A. van der Gen, *J. Org. Chem.*, preceding paper in this issue.

(2) Part 6: C. G. Kruse, A. Wijsman, and A. van der Gen, *J. Org. Chem.*, **44**, 1847 (1979).

(3) With the exception of **4a** and the methyl ester corresponding to **6a** these compounds are unknown in the literature.

(4) Direct alkylation of monoester anions with α-chloro ethers[1] and thioethers[2] is not a selective reaction. Elimination was found to occur predominantly.

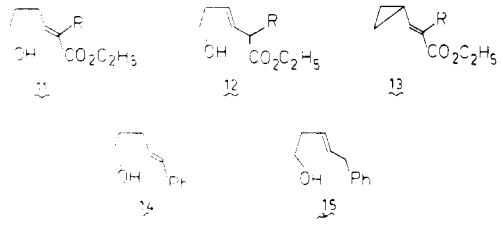
(5) P. E. Sum and L. Wieler, *J. Chem. Soc., Chem. Commun.*, 91 (1977).

(6) Sodium diethyl (2-tetrahydrofuranyl)malonate is poorly soluble in THF. Upon addition of HMPA (3 equiv) a clear solution is obtained.

0022-3263/79/1944-2916$01.00/0

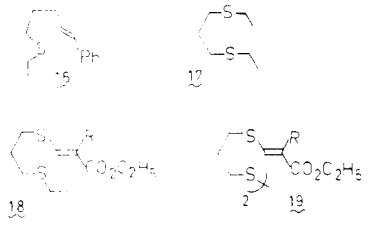
in recent years, in particular by Krapcho and co-workers.[7] In order to gain access to monoesters **4–6**, we subjected malonic esters **1–3** to decarbethoxylation conditions, using NaCl (1 equiv)/H_2O (2 equiv) in refluxing Me_2SO.[8] Examination of the results presented in Table I reveals a number of interesting facts both from a synthetic and from a mechanistic point of view.

In the case of the THT malonic esters **2a,b** and the DT malonic ester **3a**, selective decarbethoxylation was observed and the monoesters **5a,b** and **6a** were obtained, respectively, in high yields. However, decarbethoxylation of the THF malonic esters **1a–c** gave, besides the expected esters **4a–c**, a number of products resulting from ring opening.[9] The α,β-unsaturated hydroxy esters **11a–c** (*E* isomers)



were formed in considerable amounts. In the case of R = H, complete stereoselectivity was observed (see also Table I, notes *f* and *g*). Surprisingly, the major product of the decarbethoxylation of **1a** turned out to be the β,γ-unsaturated hydroxy ester **12a**.[10] Again, only the *E* isomer was found. When decarbethoxylation of **1a** was effected in the absence of H_2O, the product composition changed entirely. Apart from diethyl malonate and THF ester **4a**, the interesting cyclopropyl-substituted ester **13a** was formed (*E* isomer only). Reaction of the phenyl-substituted THF malonic ester **1c** yielded appreciable quantities of products **14** and **15**, presumably formed by two successive decarbethoxylation steps.[11]

In contrast to the results obtained with **3a**, decarbethoxylation of disubstituted DT malonic esters **3b,c** gave only small amounts of the corresponding monoesters **6**. It was observed that ring opening and S-ethylation occurred in this case, which ultimately led to products **17** and **18b,c** and disulfides **19b,c**.



(7) A detailed study of synthetic applications and mechanistic aspects, containing all leading references, has recently been published: A. P. Krapcho, J. F. Weimaster, J. M. Eldridge, E. G. E. Jahngen, A. J. Lovey, and W. P. Stephens, *J. Org. Chem.*, **43**, 138 (1978).

(8) (a) A. P. Krapcho and A. J. Lovey, *Tetrahedron Lett.*, 1091 (1974); (b) J. H. Markgraf, M. S. Ibsen, J. B. Kinney, J. W. Kuper, J. B. Lurie, D. R. Marrs, C. A. McCarthy, J. M. Pile, and T. J. Pritchard, *J. Org. Chem.*, **42**, 2631 (1977).

(9) Esters **4a** and **4b** could easily be separated from the higher boiling hydroxy esters by distillation of the crude products.

(10) The product composition changes as the reaction proceeds (GC), due to the isomerization of **12a** into **11a**, which in turn is converted into **4a** by an intramolecular Michael-type addition. After 6 h of refluxing an equilibrium mixture results: **4a**, 70%; **11a**, 20%; **12a**, 10%. A pure sample of **12a** was also converted into **11a** and **4a** when subjected to the same reaction conditions.

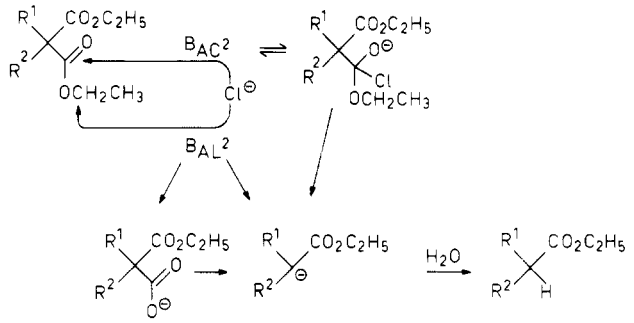
(11) (a) GC monitoring of the decarbethoxylation of **1c** reveals that **14** and **15** are secondary reaction products; (b) **4c** was shown to be stable under these conditions, indicating that the second decarbethoxylation step requires a more stabilized intermediate, such as **12c**; (c) in the case of diethyl phenyl(2-tetrahydrothienyl)malonate **2c**, small amounts of **16** were formed.

Table II. Competitive Decarbethoxylations of THF and THT Malonic Esters[a]

substrates	NaCl[b] t(50%), h	NaCl[b] t(90%), h	$NaOC_2H_5$[b] t(50%), h	$NaOC_2H_5$[b] t(90%), h
1a / **2a**	0.5 / 1.0	1.1 / 2.0	0.25 / 0.65	0.5 / 1.5
1b / **2b**	6 / 3	15 / 7	4 / 2	11 / 5

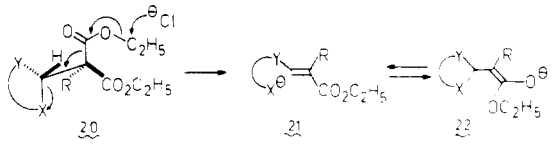
[a] Substrates, 0.25 M each; salt, 0.5 M; H_2O, 1.0 M; product composition is the same with NaCl and $NaOC_2H_5$. [b] Reaction times needed for 50 and 90% conversion were determined by plotting product composition (GC) against time.

Mechanistic Aspects. Monosubstituted malonic esters are supposedly decarboxylated mainly via the $B_{AC}2$ route, characterized by a tetrahydral intermediate, resulting from attack of the nucleophile at one of the ester carbonyl groups.[7] Due to steric hindrance in the case of disubstituted esters the $B_{AL}2$ pathway becomes the predominant process.[7]



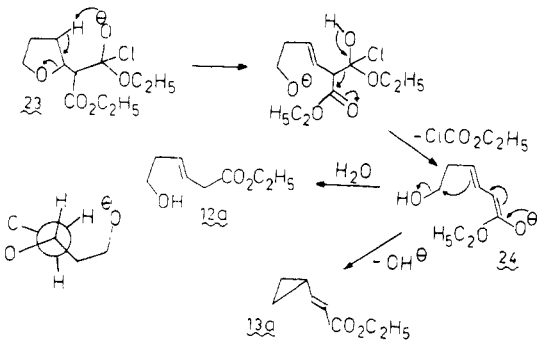
In either mechanism, the rate of decarbethoxylation is determined by the capacity of the substituents to stabilize the developing carbanion. In our decarbethoxylation reactions the rates of the THF, THT, and DT malonic esters decreased in the series R = H, R = Ph, and R = CH_3 (Table I).[12] These results are consistent with those observed by Krapcho and co-workers.[7] It was also observed that the DT malonic esters are decarboxylated more rapidly than the corresponding THF and THT esters. The relative reaction rates of THF and THT esters were determined more accurately by competition experiments. The results, summarized in Table II, show that $NaOC_2H_5$ is a more efficient decarboxylating agent than NaCl.

With respect to monosubstituted esters **1a** and **2a** it was found that the THF ester **1a** (Table II) reacted appreciably faster than **2a**. This is in agreement with the occurrence of a $B_{AC}2$ pathway, in which the stronger electron-withdrawing properties of a 2-tetrahydrofuranyl substituent are of major importance in determining the reaction rate. However, in the case of disubstituted malonic esters **1b** and **2b** the order of reactivity is reversed, indicating that a different mechanism is operating. This observation may be rationalized by assuming that a concerted reaction is operative as depicted in **20** (via a $B_{AL}2$ cleavage with concomitant ring opening) whereby the reaction rate is governed by the leaving group ability of X^-.



(12) In a competitive experiment it was also found that diethyl (*p*-methoxyphenyl)(2-tetrahydrothienyl)malonate was less easily decarbethoxylated than **1c** (40 and 55% conversion, respectively, after 3 h).

Scheme I



The anionic species formed by either a $B_{AC}2$ or a $B_{AL}2$ mechanism can be represented by the equilibrium **21** ⇄ **22**. Only in those cases where X = O were products resulting from protonation of **21** isolated. The selective conversion of THT-substituted malonic esters into their decarbethoxylated analogues (by protonation of **22**) reflects the tendency of thiolates and thiols to engage in Michael-type additions. It will be shown in the last section that the stereoselectivity observed in the formation of ring-opened products **11** may be regarded as an intrinsic property of anions of type **22**.

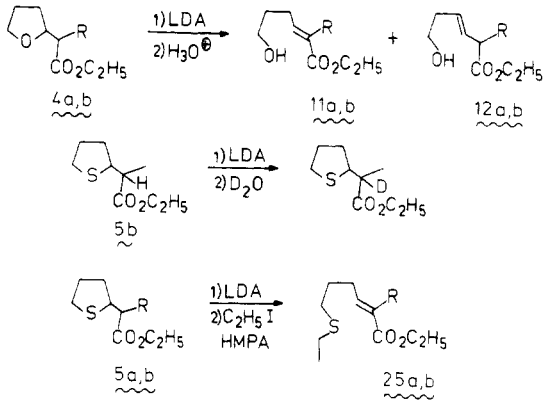
The formation of β,γ-unsaturated ester **12a** as the major product from decarbethoxylation of **1a** probably also results from the $B_{AC}2$ pathway. The rapidly formed intermediate **23** may engage in an intramolecular elimination reaction, as indicated in Scheme I. Upon decarbethoxylation the dienolate **24** is obtained and is in turn protonated to give **12a**. When the decarbethoxylation reaction is carried out in the absence of H_2O, intermediate **24** cannot be protonated and in this case ring closure with loss of hydroxide ion presumably occurs to produce the cyclopropyl ester **13a**.

An alternative mechanism for the formation of **12a** (decarbethoxylation followed by intramolecular proton abstraction in **22a**) seems less feasible, since this mechanism is not discriminating between mono- and disubstituted substrates (**12b** is a minor product in the decarbethoxylation of **1b**).

The *E* configuration in product **12a** results from abstraction of the pseudo equatorial proton at C3 during the antiperiplanar process, as illustrated in Scheme I.[13]

The decarbethoxylation reactions of DT esters **3a–c** clearly demonstrate the different mechanisms followed by mono- and disubstituted malonic esters. Whereas **3a** is selectively converted into monoester **6a** via a $B_{AC}2$ mechanism, decarbethoxylation of **3b,c** results in formation of the *S*-alkylated products **18** and **19**. In these cases, intermediate **21** (X–Y = S–$(CH_2)_3$–S) can be alkylated by reacting with the ethyl chloride produced in the $B_{AL}2$ route or by competing with chloride ion as a decarbethoxylating agent. This assumption is supported by the observation that upon using $NaOC_2H_5$ as the decarbethoxylating agent for **3b** (no ethyl chloride can be produced), the formation of **18b** is still observed.

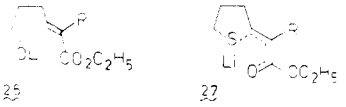
Anions of Monoesters 4–6. Anions of type **21** ⇄ **22**, which are intermediates in the decarbethoxylation of **1–3**, can be conveniently prepared by deprotonation of monoesters **4–6** with lithium diisopropylamide in THF at −78 °C.[14] The formation of the anion from THT ester **5b** was confirmed by incorporation of deuterium (ca. 50%) upon



quenching with D_2O.[15] Quenching the THF ester anions with aqueous ammonium chloride afforded the ring-opened hydroxy esters **11** and **12** (*E* isomers only). In similar quenching experiments the THT and DT esters were quantitatively recovered. Addition of HMPA (1 equiv) to the THF solutions of these anions did not alter these results.

However, when the lithium enolates of the THT esters **5a,b** and the DT ester **6a** were allowed to react with ethyl iodide in the presence of HMPA,[14] *S*-ethylated, ring-opened products **25a,b** and **18a**, respectively, were formed exclusively in yields of 80–90%.

These results can be explained by assuming an approximate structure for the lithiated THF and THT esters as indicated in **26** and **27**, respectively. The formation of



β,γ-unsaturated esters **12a,b** probably results from a second deprotonation of **26** to give a dienolate similar in structure to **24**.[16]

The pronounced nucleophilicity of sulfur and the less favorable formation of a lithium–sulfur bond are probably major factors in determining the ambident character of **27**.

Experimental Section

General Procedures. IR spectra (liquid film) were recorded on an Unicam SP-100 instrument. NMR spectra were recorded in $CDCl_3$ solutions on a JEOL PS-100 instrument, using tetramethylsilane as an internal standard (δ in parts per million, *J* in hertz). Mass spectra were obtained from an AEI-MS 902 apparatus, operating with an ionizing potential of 70 eV. Analytical and preparative GC studies were carried out using a 2-m, SE-30 (1, 3, or 5%) column and a 6-m, SE-30 (10 or 20%) column, respectively. Column chromatography was performed with silica gel G (Merck, 10–40 mesh).

Materials. Me_2SO, HMPA, and diisopropylamine were dried by refluxing with CaH_2 and distillation and stored over molecular 4A sieves. THF was distilled from $LiAlH_4$ prior to use. All other reagents used were high-grade commercial products.

Anions of Malonic Esters 1–3. A solution of the malonic ester **1a**, **2a**, or **3a** (1.0 equiv) in THF (25 mL/5 mmol) was added dropwise to a stirred suspension of NaH (1 equiv) in THF (10 mL/5 mmol). Stirring was continued until the evolution of hydrogen ceased (**1a** and **3a** at 20 °C, **2a** at reflux). Aliquots were quenched with H_2O and, after extraction with ether, analyzed by GC. Addition of the alkylating agent (MeI, 1.2 equiv; $PhCH_2Br$, 1.1 equiv) to the solution (**2a**, **3a**) or suspension (**1a**)[6] of the anion

(13) (a) J. F. Bunnett, *Angew. Chem., Int. Ed. Engl.*, 1, 225 (1962); (b) K Fukui and H. Fujimoto, *Tetrahedron Lett.*, 4303 (1965).

(14) R. J. Cregge, J. L. Herrmann, C. S. Lee, J. E. Richman, and R. H. Schlessinger, *Tetrahedron Lett.*, 2425 (1973).

(15) Trapping with D_2O of ester lithium enolates is known to result in only 45–75% D incorporation: M. W. Rathke and A. Lindert, *J. Am. Chem. Soc.*, **93**, 2318 (1971).

(16) See for anions of α,β-unsaturated esters: (a) M. W. Rathke and D. Sullivan, *Tetrahedron Lett.*, 4249 (1972); (b) J. L. Herrmann, G. R. Kieczykowski, and R. H. Schlessinger, *ibid.*, 2433 (1973). See also J. L. Herrmann and R. H. Schlessinger, *ibid.*, 2429 (1973).

caused a slightly exothermic reaction. After an additional 1 h of stirring at 20 °C and standard workup the products were obtained in the indicated yields (GC, NMR).

Diethyl Methyl(2-tetrahydrofuranyl)malonate (1b): 86%; spectral properties were identical with those reported previously.[1]

Diethyl Benzyl(2-tetrahydrofuranyl)malonate (1d): 89%; bp 115–120 °C (0.01 mm); n^{22}_D = 1.4980; NMR δ 7.18 (s, 5 H, aromatic), 4.19 and 4.12 (2 q, 4 H, OCH_2), 4.1 (m, 1 H, 2-H), 3.75 (m, 2 H, 5-H), 3.51 and 3.27 (AB, 2 H, ^2J = 13.8, benzylic), 2.05 and 1.8 (2 m, 4 H, 3- and 4-H), 1.22 and 1.18 (2 t, 6 H, CH_3).

Diethyl Methyl(2-tetrahydrothienyl)malonate (2b) and Diethyl 4-(Methylthio)butylidenemalonate (9): 90%; 3:2 mixture; NMR δ(H) from **2b** identical with those reported[1]; δ(H) from **9** includes 6.97 (t, 1 H, ^3J = 8, 1-H), 2.07 (s, 3 H, SCH_3).

Diethyl Methyl[2-(1,3-dithianyl)]malonate (3b) and Diethyl [3-(Methylthio)propyl]thiomethylidenemalonate (10): 93%; 1:2 mixture, separated by column chromatography (ethyl acetate–hexane 1:2). **3b**: R_f 0.3; spectra identical with those reported.[2] **10**: R_f 0.2; n_D^{20} = 1.5376; IR 1710, 1690 (C=O); 1540 (C=C); 1240, 1060 (COC) cm^{-1}; NMR δ 8.35 (s, 1 H, olefinic), 4.29 and 4.24 (2 q, 4 H, OCH_2), 3.00 (t, 2 H, 1-H), 2.62 (t, 2 H, 3-H), 2.08 (s, 3 H, SCH_3), 1.99 (p, 2 H, 2-H), 1.33 and 1.30 (2 t, 6 H, CH_3).

Decarbethoxylation Reactions. Stirred mixtures of the requisite geminal diesters **1–3**, with NaCl or $NaOC_2H_5$ in Me_2SO and H_2O, were heated at reflux. The concentrations are indicated in Tables I and II. The temperature of the reaction mixtures was 170–175 °C in the case of NaCl and 165–170 °C in the case of $NaOC_2H_5$. Reaction times, *t*, given in Tables I and II were taken from the beginning of reflux until external heating was removed. In most cases, but not with DT esters **3**, the color of the reaction mixture changed to dark brown upon refluxing for several hours. If the reactions were monitored with GC (Table II), aliquots were quenched with H_2O and extracted with ether. In the case of the preparative runs (Table I), workup consisted of pouring the reaction mixture into a mixture of H_2O (reactions with $NaOC_2H_5$–0.1 N HCl) and ether, washing the combined ether extracts with brine, drying ($MgSO_4$), and concentrating in vacuo. The crude products thus obtained contained more than 90% of the compounds mentioned in Table I, in the indicated yields.

Monoesters **4a,b**, **5a–c**, and **6a** were purified by distillation in vacuo. Monoester **4c**, unsaturated (hydroxy) esters **11a,b**, **12a,b**, and **13a,b**, and the 5-(hydroxy or ethylthio)alkenes **14–16** were isolated in a pure state by preparative GC. Decarbethoxylation reaction mixtures of **3b,c** were subjected to column chromatography (ethyl acetate–hexane (5:2)) to effect partial separation of products **17–19**. Thioether **17** was further purified by preparative GC. Propylthiopropenoate **18b** was obtained in ca. 90% purity, but products **6b,c**, **18c**, and **19b,c** were only present in fractions containing mixtures of several other products.

The structures of all reaction products were determined by careful analysis of their GC, IR, NMR, and, where needed, mass spectra. Compounds **4b,c**, and **5b,c** were present as a mixture of two diastereoisomers. The configuration of double bonds in **11**, **13–16**, **18**, and **19** was elucidated by considerations of chemical shift and coupling constant values observed for vinylic protons.[17] The *E* configuration of **12a** followed from IR (975 cm^{-1}, strong, (*E*)-HC=CH); careful GC analysis of **12a,b** revealed only one peak under a wide range of conditions and sharp NMR signals were observed.

Ethyl (2-Tetrahydrofuranyl)acetate (4a): bp 50 °C (0.04 mm); n^{23}_D = 1.4345 (lit.[18] n^{20}_D = 1.4369); IR 1750 (C=O); 1160, 1060 (COC) cm^{-1}; NMR δ 4.26 (m, 1 H, 2-H), 3.82 (m, 2 H, 5-H), 2.56 and 2.44 (dAB, 2 H, ^3J = 6.5 and ^2J = 15.0, α-H), 2.1–1.9 and 1.6 (m, 4 H, 3- and 4-H).

Ethyl α-(2-Tetrahydrofuranyl)propionate (4b): bp 40–55 °C (0.15 mm); n^{24}_D = 1.4372; IR 1740 (C=O); 1250, 1180, 1060 (COC) cm^{-1}; NMR δ 4.0–3.75 (m, 3 H, 2- and 5-H), 2.49 and 2.47 (p, 1 H, α-H), 1.9–1.6 (m, 4 H, 3- and 4-H), 1.22 and 1.12 (d, 3 H, ^3J = 7.2, α-CH_3).

Ethyl Phenyl(2-tetrahydrofuranyl)acetate (4c): IR 1740 (C=O); 1600, 1480, 730, 695 (phenyl); 1150, 1070, 1030 (COC) cm^{-1}; NMR δ 7.31 (s, 5 H, aromatic), 4.5 (m, 1 H, 2-H), 3.8 (m, 2 H, 5-H), 3.62 and 3.52 (d, 1 H, ^3J = 9, α-H), 2.0–1.6 (m, 4 H, 3- and 4-H).

Ethyl (2-Tetrahydrothienyl)acetate (5a): bp 78 °C (0.2 mm); n^{23}_D = 1.4878; IR 1740 (C=O); 1250, 1180, 1150, 1020 (COC) cm^{-1}; NMR δ 3.72 (p, 1 H, 2-H), 2.85 (m, 2 H, 5-H), 2.59 (d, 2 H, ^3J = 7, α-H), 2.05–1.65 (m, 4 H, 3- and 4-H).

Ethyl α-(2-Tetrahydrothienyl)propionate (5b): bp 70–80 °C (0.4 mm); n^{23}_D = 1.4818; IR 1740 (C=O); 1240, 1150 (COC); 725 cm^{-1}; NMR δ 3.5 (m, 1 H, 2-H), 2.83 (m, 2 H, 5-H), 2.44 (dq, 1 H, ^3J = 9.5 and 7, α-H), 2.05–1.65 (m, 4 H, 3- and 4-H), 1.24 (d, 3 H, ^3J = 7, α-CH_3).

Ethyl Phenyl(2-tetrahydrothienyl)acetate (5c): n^{20}_D = 1.5476; IR 1750 (C=O), 1490, 695 (phenyl); 1160, 1020 (COC) cm^{-1}; NMR δ 7.31 (s, 5 H, aromatic), 4.05–4.15 (m, 3 H, 2-H and OCH_2), 3.54 (d, 1 H, ^3J = 12, α-H), 2.85 (m, 2 H, 5-H), 2.05–1.55 (m, 4 H, 3- and 4-H).

Ethyl [2-(1,3-Dithianyl)]acetate (6a): bp 78 °C (0.04 mm); n^{20}_D = 1.5337; IR 1740 (C=O); 1220, 1140, 1020 (COC); 900 (DT) cm^{-1}; NMR δ 4.39 (t, 1 H, ^3J = 7.5, 2-H), 2.88 (m, 4 H, 4- and 6-H), 2.75 (d, 2 H, ^3J = 7.5, α-H), 2.05–1.95 (m, 2 H, 5-H).

(*E*)-Ethyl 6-Hydroxyhex-2-enoate (11a):[19] NMR δ 6.98 (dt, 1 H, 3-H), 5.83 (dt, 1 H, 2-H), 3.64 (t, 2 H, 6-H), 2.95 (s, 1 H, OH), 2.30 (q, 2 H, 4-H), 1.74 (p, 2 H, 5-H), $^3J_{2,3}$ = 15.4, $^3J_{3,4}$ = 6.7 and $^4J_{2,4}$ = 1.5.

(*E*)-Ethyl 2-Methyl-6-hydroxyhex-2-enoate (11b):[20] n^{24}_D = 1.4672; IR 3450 (OH); 1710 (C=O); 1650 (C=C); 1260, 1120, 1080, 1050 (COC); 740 (HC=C) cm^{-1}; NMR δ 6.78 (tq, 1 H, 3-H), 3.65 (t, 2 H, 6-H), 2.9 (s, 1 H, OH), 2.27 (q, 2 H, 4-H), 1.83 (d, 3 H, 2-CH_3), 1.70 (p, 2 H, 5-H), $^3J_{3,4}$ = 7.5 and $^4J_{3,2\text{-}CH_3}$ = 1.2.

(*E*)-Ethyl 6-Hydroxyhex-3-enoate (12a): IR 3400(OH); 1740 (C=O); 1190, 1160, 1040 (COC); 975 ((*E*)-HC=CH) cm^{-1}; NMR δ 5.60 (m, 2 H, 3- and 4-H), 3.61 (t, 2 H, 6-H), 3.18 (s, 1 H, OH), 3.03 (d, 2 H, 2-H), 2.29 (q, 2 H, 5-H).

(*E*)-Ethyl 2-Methyl-6-hydroxyhex-3-enoate (12b): NMR δ 5.58 (m, 2 H, 3- and 4-H), 3.65 (t, 2 H, 6-H), 3.13 (p, 1 H, 2-H), 2.3 (m, 2 H, 5-H), 1.3–1.2 (m, 6 H, 2-CH_3 and ester CH_3).

(*E*)-Ethyl 3-Cyclopropylpropenoate (13a): *m/e* 140 (M^+), 125, 112, 97, 95, 84, 67; IR 1725 (C=O); 1655 (C=C); 1270, 1150, 1045 (COC); 950 ((*E*)-HC=CH) cm^{-1}; NMR δ 6.43 (dd, 1 H, 3-H), 5.88 (d, 1 H, 2-H), 1.55, 0.9 and 0.6 (3 m, 5 H, cyclopropyl-H), $^3J_{2,3}$ = 15.2 and $^3J_{3,\text{cyclopropyl-H}}$ = 9.7.

(*E*)-Ethyl 2-Phenyl-3-cyclopropylpropenoate (13c): IR 1690 (C=O); 1620 (C=C); 1490, 700 (phenyl); 1220, 1180, 1030 (COC) cm^{-1}; NMR δ 7.35 (s, 5 H, aromatic), 6.42 (d, 1 H, 3-H), 1.4, 0.9 and 0.7 (3 m, 5 H, cyclopropyl-H), $^3J_{3,\text{cyclopropyl-H}}$ = 10.5.

(*E*)-1-Phenyl-5-hydroxypentene-1 (14): IR 3400 (OH); 1610, 1500, 1460, 740, 690 (phenyl); 1050 (CO); 695 ((*E*)-HC=CH) cm^{-1}; NMR δ 7.29 (s, 5 H, aromatic), 6.44 (d, 1 H, 1-H), 6.24 (dt, 1 H, 2-H), 3.70 (t, 2 H, 5-H), 2.32 (q, 2 H, 3-H), 1.76 (p, 2 H, 4-H), 1.68 (s, 1 H, OH), $^3J_{1,2}$ = 18.

(*E*)-1-Phenyl-5-hydroxypentene-2 (15): IR 3400 (OH); 1610, 1500, 1460, 735, 695 (phenyl); 1050 (CO); 965 ((*E*)-HC=CH) cm^{-1}; NMR δ 7.22 (s, 5 H, aromatic), 5.75 and 5.55 (tAB, 2 H, ^3J = 16, 2- and 3-H), 3.63 (t, 2 H, 5-H), 3.37 (d, 2 H, 1-H), 2.31 (q, 2 H, 4-H), 1.8 (s, 1 H, OH).

(*E*)-1-Phenyl-5-(ethylthio)pentene-1 (16): NMR δ 7.3 (s, 5 H, aromatic), 6.30 (d, 1 H, 1-H), 6.09 (dt, 1 H, 2-H), 2.53 (q, 2 H, 3-H), 2.49 (t, 2 H, 5-H), 2.31 (q, 2 H, SCH_2), 1.75 (p, 2 H, 4-H), 1.24 (t, 3 H, CH_3), $^3J_{1,2}$ = 16.

1,3-(Diethylthio)propane (17): n^{20}_D = 1.5050 (lit.[21] n^{20}_D = 1.5052); IR 2950, 1440 (CH); 1240 cm^{-1}; NMR δ 2.61 (t, 4 H, 1- and 3-H), 2.52 (q, 4 H, SCH_2), 1.84 (p, 2 H, 2-H), 1.25 (t, 6 H, CH_3).

(*E*)-Ethyl 2-Methyl-3-[3′-(ethylthio)propylthio]propenoate (18b): *m/e* 248 (M^+), 219, 203, 135; IR 1700 (C=O); 1590 (C=C);

(17) (a) Good agreement between observed and calculated values of chemical shifts of vinylic protons was found, according to R. M. Silverstein, G. C. Bassler, and T. C. Morrill in "Spectrometric Identification of Organic Compounds", 3rd ed., Wiley, New York, 1974, p 223; (b) T. H. Kinstle and B. Y. Mandanas, *Chem. Commun.*, 1699 (1968).

(18) P. M. Frearson, D. G. Hardy, and E. S. Stern, *J. Chem. Soc.*, 2103 (1960).

(19) After preparative GC, 10% of **12a** was still present.

(20) Spectral data of the *Z* isomer include the following NMR data: δ 5.92 (tq, 1 H, 3-H), 3.61 (t, 2 H, 6-H), 3.1 (s, 1 H, OH), 2.54 (q, 2 H, 4-H), 1.90 (d, 3 H, 2-CH_3), 1.69 (p, 2 H, 5-H), $^3J_{3,4}$ = 7.9, $^4J_{3,2\text{-}CH_3}$ = 1.1.

(21) T. L. Jacobs and G. E. Illingworth, *J. Org. Chem.*, **38**, 2692 (1963).

1220, 1100 (COC); 730 cm^{-1}; NMR δ 7.49 (q, 1 H, 3-H), 2.94 (t, 2 H, 1'-H), 2.62 (t, 2 H, 3'-H), 2.51 (q, 2 H, SCH_2), 1.93 (p, 2 H, 2'-H), 1.83 (d, 3 H, 2-CH_3), 1.23 (t, 3 H, CH_3), $^4J_{3,2\text{-}CH_3}$ = 1.0.

Some spectral data of the other products include the following. **6b**: IR 1750 cm^1 (C=O); *m/e* 220 (M^+), 119. **6c**: IR 1740 (C=O); 1220, 1020 (COC); 1470, 730, 695 (Ph); 905 cm^{-1} (DT); NMR δ 4.52 (d, 1 H, 2-H), 3.91 (d, 1 H, α-H); $^3J_{2,\alpha}$ = 11. **18c**: IR 1700 (C=O); 1560 (C=C); 1600, 1480, 730, 700 (Ph); 1220, 1030 cm^{-1} (COC); NMR 7.80 (s, 1 H, 3-H). **19b**, main absorptions in IR identical with those of **18b**; NMR 7.45 (q, 1 H, 3-H), 1.84 (d, 3 H, 2-CH_3), $^4J_{3,CH_3}$ = 1; *m/e* 219 ($^1/_2M^+$), 197, 135, 103. **19c**: IR as for **18c**; NMR 7.70 (s, 1 H, 3-H).

Common spectral data for $CO_2C_2H_5$ groups of all ethyl esters: IR 2980, 1440 (CH) cm^{-1}; NMR δ 4.1–4.2 (q, 2 H, OCH_2), 1.2–1.3 (t, 3 H, CH_3).

Anions of Monoesters 4–6. A solution of the requisite ester in THF (5 mmol in 2 mL) was added dropwise at −78 °C to a stirred solution of lithium diisopropylamide[14] in THF (5.5–6.5 mmol in 8 mL). The slightly yellow solutions were stirred at −78 °C for 20 min in the case of monosubstituted esters **4a**, **5a**, and **6a** and for 1 h in the case of disubstituted esters **4b** and **5b**. Aliquots were quenched with a mixture of aqueous ammonium chloride and ether. GC analysis of the organic layer revealed that ring opening had occurred only in the case of THF esters **4a,b**. Workup afforded in 95% yield of a mixture of **4a,b** (20%), **11a,b** (65%), and **12a,b** (15%) as determined with GC and NMR. In the case of THT esters **5a,b** and DT ester **6a**, a mixture of ethyl iodide (6.5 mmol) and HMPA (5 mmol) was added. The reactions with monosubstituted esters were quenched after 5 min of stirring at −78 °C, and in the case of **5b** after 30 min of stirring at −78 °C and then at 20 °C. Standard workup yielded crude products containing 5–10% of starting esters **5a,b** and **6a** and 80–90% of products **25a,b** and **18a**, respectively. The yields were calculated from NMR and GC. Pure samples were obtained by preparative GC (**25a,b**) or column chromatography (**18a**).

(*E*)-Ethyl 6-(Ethylthio)hex-2-enoate (25a): 80%; n^{23}_D = 1.4843; IR 2940, 1440 (CH); 1650 (C=C); 1720 (C=O); 1250, 1180, 1030 (COC); 970 cm^{-1} ((*E*)-HC=CH); NMR δ 6.92 (dt, 1 H, 3-H), 5.82 (dt, 1 H, 2-H), 4.16 (q, 2 H, OCH_2), 2.52 (t, 2 H, 6-H), 2.51 (q, 2 H, SCH_2), 2.36 (dq, 2 H, 4-H), 1.74 (p, 2 H, 5-H), 1.28 (t, 3 H, OCH_2CH_3), 1.24 (t, 3 H, SCH_2CH_3), $^3J_{2,3}$ = 16, $^3J_{3,4}$ = 7, $^4J_{2,4}$ = 1.5.

(*E*)-Ethyl 2-Methyl-6-(ethylthio)hex-2-enoate (25b): 88%; n^{20}_D = 1.4865; IR 2950, 1440 (CH); 1720 (C=O); 1650 (C=C); 1250, 1100 (COC); 740 cm^{-1}; NMR δ 6.72 (tq, 1 H, 3-H), 4.17 (q, 2 H, OCH_2), 2.53 (t, 2 H, 6-H), 2.52 (q, 2 H, SCH_2), 2.29 (q, 2 H, 4-H), 1.85 (d, 3 H, 2-CH_3), 1.72 (p, 2 H, 5-H), 1.29 (t, 3 H, OCH_2CH_3), 1.25 (t, 3 H, SCH_2CH_3), $^3J_{3,4}$ = 7.5, $^4J_{3,CH_3}$ = 1.5.

(*E*)-Ethyl 3-[3'-(Ethylthio)propylthio]propenoate (18a): 70%; n^{20}_D = 1.5338; IR 2950, 1440 (CH); 1700 (C=O); 1570 (C=C); 1240, 1150, 1025 (COC); 940 ((*E*)-HC=CH), 825 cm^{-1}; NMR δ 7.70 and 5.80 (AB, 2 H, ^3J = 15.2, 3- and 2-H), 4.18 (q, 2 H, OCH_2), 2.94 (t, 2 H, 1'-H), 2.64 (t, 2 H, 3'-H), 2.53 (q, 2 H, SCH_2), 1.95 (p, 2 H, 2'-H), 1.28 (t, 3 H, OCH_2CH_3), 1.26 (t, 3 H, SCH_2CH_3).

Registry No. **1a**, 70398-41-3; **1b**, 70398-42-4; **1c**, 70398-43-5; **1d**, 70576-34-0; **2a**, 70398-46-8; **2b**, 70398-47-9; **2c**, 70398-48-0; **3a**, 63822-64-0; **3b**, 69178-02-5; **3c**, 69178-04-7; **4a**, 2434-02-8; **4b**, 70562-10-6; **4c**, 70562-11-7; **5a**, 65102-19-4; **5b**, 70562-12-8; **5c**, 70562-13-9; **6a**, 70562-14-0; **6b**, 70562-15-1; **6c**, 70562-16-2; **9**, 70562-17-3; **10**, 70562-18-4; **11a**, 13038-15-8; (*E*)-**11b**, 70562-19-5; (*Z*)-**11b**, 70562-20-8; (*E*)-**11c**, 70562-21-9; (*Z*)-**11c**, 70562-22-0; **12a**, 70562-23-1; **12b**, 70562-24-2; **13a**, 21014-26-6; **13c**, 70562-25-3; **14**, 13159-16-5; **15**, 58927-91-6; **16**, 70562-26-4; **17**, 33672-52-5; **18a**, 70562-27-5; **18b**, 70562-28-6; **18c**, 70562-29-7; **19b**, 70562-30-0; **19c**, 70562-31-1; **25a**, 70562-32-2; **25b**, 70562-33-3; MeI, 74-88-4; $PhCH_2Br$, 100-39-0.

Ferrocenyl Carbocations. The Stability of Some [4]Ferrocenophane 6- and 7-Carbocations

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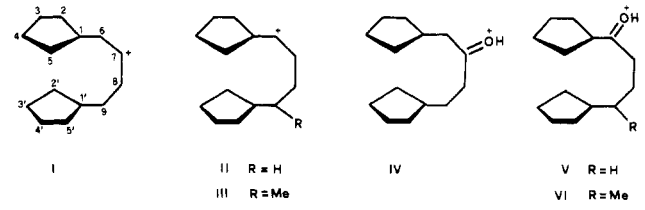
The equilibrium constants for the protonation of [4]ferrocenophan-7-one and -6-one and for the ionization of the corresponding alcohols in aqueous sulfuric acid, as well as the behavior of these molecules as acid–base indicators, suggest that the [4]ferrocenophane 7-carbocations are strongly stabilized by the ferrocenyl group, despite the distance of the positive center from the Cp ring.

The structure and the stability of the α-ferrocenyl carbocations have been extensively debated on the basis of their physical properties,[1-6] reactivity,[7,8] and equilibria.[9,10]

It seemed of interest to measure the stability of the β-ferrocenyl carbocations, since the investigation of substrates, where the direct conjugation between the positive carbon and the Cp ring is absent, appeared useful for a deeper insight on the role played by the ferrocenyl group in the stabilization of the α-carbocations. [4]-Ferrocenophan-7-ol was taken as a convenient substrate, whose carbocation was found to possess a sufficiently high stability[11] by NMR spectral measurements.

The work reported in this paper concerned the formation of carbocations as obtained from the ionization of [4]ferrocenophan-7-ol (I) and the protonation of [4]-ferrocenophan-7-one (IV) in aqueous H_2SO_4. The cations derived from [4]ferrocenophan-6-ol (II) and -6-one (V) and from their 9-methyl derivatives (III and VI) were also



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