277. Structure and Chemistry of Malonylmethyl- and Succinyl-Radicals. The Search for Homolytic 1,2-Rearrangements

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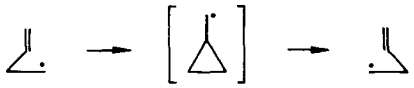
Summary

Malonylmethyl radical **I** [$\cdot CH_2CH(COOEt)_2$] and its thioester analogue **II** [$\cdot CH_2CH(COOEt)(COSEt)$] were generated by standard photolytic and thermolytic methods from perester and bromo precursors. The structures of **I** and **II** were examined by ESR spectroscopy and found to exist in preferred conformations. However, no indication for their rearrangement by 1,2-shift of either an ethoxycarboxyl or (ethylthio)carbonyl group to the corresponding succinyl radicals **III** and **IV**, respectively, was found at temperatures below -40 °C. At higher temperatures of up to 140 °C, the search for malonylmethyl → succinyl rearrangement was examined by thorough-product analysis of the perester decomposition. There is evidence for the rearrangement of the radical **I** to **III** by photolysis and of the radical **II** to **IV** by thermolysis at 130 °C in chlorobenzene to only a small extent.

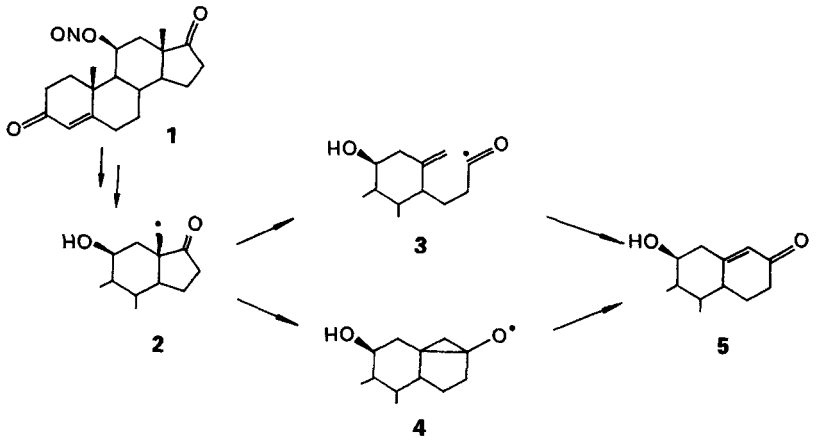
1. Introduction. – Many radicals with functional groups in the α-position have been investigated. Depending on the nature of the α-substituents, reactions such as eliminations, fragmentations and 1,2-rearrangements may occur. Mechanistically the 1,2-intramolecular migrations can either proceed *via* a three-membered cyclic transition state or by elimination/readdition process [1]. Aryl or vinyl groups are particularly noteworthy as α-substitutents. In these cases, rearrangements involving cyclopropylmethyl radicals as intermediates or transition states occur readily, even in conformationally non-rigid homoallyl radicals [1] *(Scheme 1)*.

Scheme 1



α-Substitutents with π-acceptor groups (*i.e.* C=N, C≡N or C=O) could in principle also rearrange, but only few of such migrations at the radical stage have been observed. Thus, the formation of **5** from the photolysis of the nitrite **1** [2] *(Scheme 2)* has been

Scheme 2

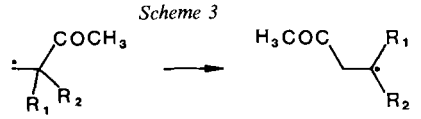


interpreted as occurring *via* an elimination/readdition process (**2** → **3** → **5**). Alternatively, it has been suggested that the C-centered radical adds to the adjacent carbonyl group, followed by ring cleavage and formation of the double bond (**2** → **4** → **5**) [3]. Also, the products formed by thermolysis of *tert*-butyl perlevulinates **6a–c** in cumene are thought to involve radicals which undergo an intramolecular 1,2-acyl shift to **7a–c** [4] *(Scheme 3)*. However, an elimination/readdition might be indicated, since it has been observed that acetyl radicals can be trapped in an apparent 1,2-acyl migration of **6d** [5].

More recently, it has been found that the reaction of **8** with $NaBH_4$ gives products, which are formed *via* **10** [6]. Since this reaction of alkylmercuric acetates proceeds *via* a radical chain [7], **9** is formed, and it subsequently leads to **10** by either a cyclopropoxy radical or by an elimination/readdition process *(Scheme 4)*.

Although such reactions have been studied, we are not aware of a report on a 1,2-shift of an ester or a thioester group in the literature. Thus, 3,3-bis(ethoxycarbonyl)valeraldehyde **11** is decarbonylated readily at 130 °C in the presence of di(*tert*-butyl)peroxide, and gives *via* radical **12** the unrearranged diester **13** in 92% yield [8] *(Scheme 5)*.

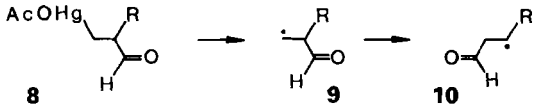
Scheme 3



6a $R_1 = R_2 = D$
b $R_1 = R_2 = CH_3$
c $R_1 = CH_3$, $R_2 = C_6H_5$
d $R_1 = CH_3$, $R_2 = H$

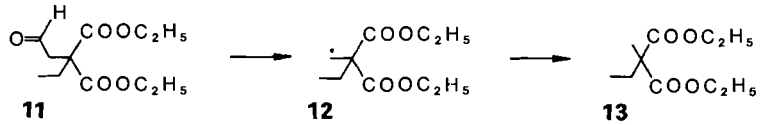
7a–d

Scheme 4



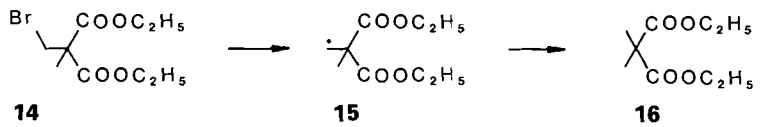
8 **9** **10**

Scheme 5



11 **12** **13**

Scheme 6

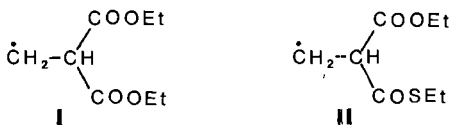


14 **15** **16**

Likewise, the reaction of **14** with Bu_3SnH gave only the malonate **16** and no succinate has been detected [9] *(Scheme 6)*. The failure to detect any rearranged product might be due to a slow rate of rearrangement in competition with a faster rate of which the radicals **15** abstract hydrogen from the relatively reactive Bu_3SnH.

In view of this ambiguous situation, we set out to investigate the chemistry of malonylmethyl and thiomalonylmethyl radicals in more detail, particularly regarding the possible 1,2-rearrangements to the corresponding succinyl and thiosuccinyl radicals, respectively. We may add that this specific interest is related to the malonylmethyl → succinyl rearrangement, which is efficiently catalyzed by vitamin B_{12} [10].

To elucidate the chemistry of the radicals **I** and **II**, and of the corresponding rearranged succinyl radicals **III** and **IV**, we first examined their structures by ESR spectroscopy. To study the rearrangement of **I** and **II** to **III** and **IV**, respectively, we further scrutinized the products of these radicals, generated either photolytically at room temperature or thermolytically at 125–140 °C from their *tert*-butyl peresters. For the ESR studies the corresponding bromo derivatives were also synthesized.



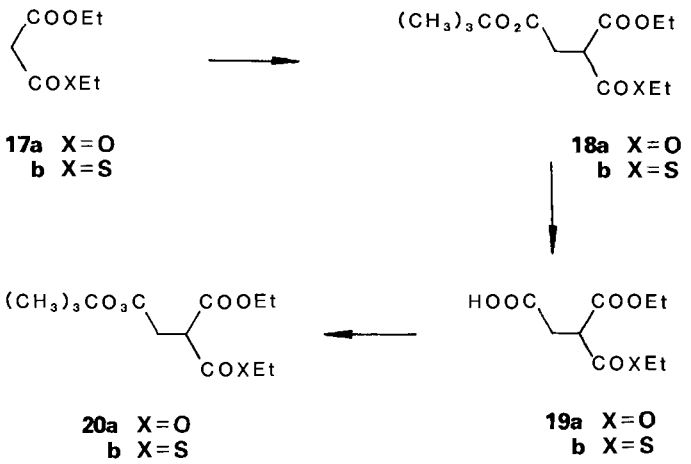
I **II**

III **IV**

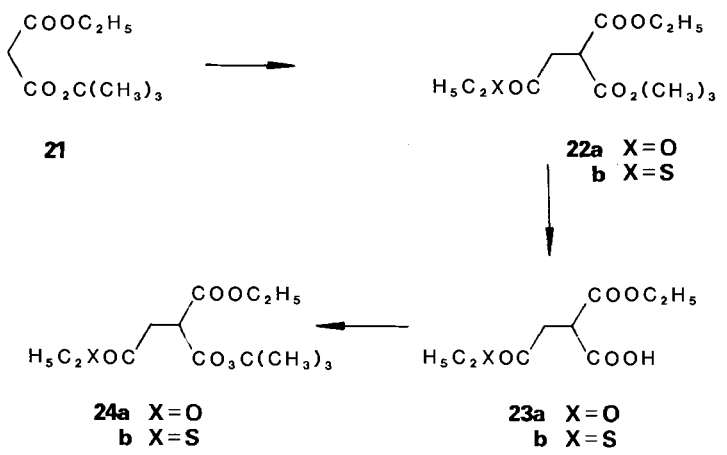
2. Results and Discussion.– 2.1. *Synthesis of the Radical Precursors.* Alkylation of the diethyl malonates **17a, b** with *tert*-butyl bromoacetate gave the triesters **18a, b** from which the acids **19a, b** were prepared by treatment with HBr in CH_2Cl_2. This method of cleavage of the *tert*-butyl esters, even in presence of thioester groups, was very efficient and afforded the acids **19a, b** in good to excellent yield *(Scheme 7)*.

Subsequent reaction of **19a, b** with *tert*-butyl hydroperoxide and dicyclohexyl carbodiimide according to the method of *Neises & Steglich* [11] gave the peresters **20a, b** in good yield. Similarly, the peresters **24a, b** with a succinate skeleton were prepared from *tert*-butyl ethyl malonate **21** *(Scheme 8)*.

Scheme 7

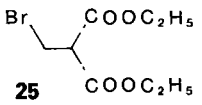


Scheme 8

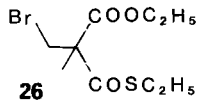


The bromomethylmalonates **25** and **26** needed as radical precursors were obtained according to the procedures in [12] [13].

The bromo-thiosuccinates **29** and **31** were prepared from ethylmaleate **27** by the sequence outlined in *Scheme 9*. Reaction of **27** with HBr in CH_2Cl_2 gave a 15 : 85 mixture of **28** and **30.** The structures of the regioisomers were established by the long-range C,H-coupling constants of the carboxyl C-atoms.

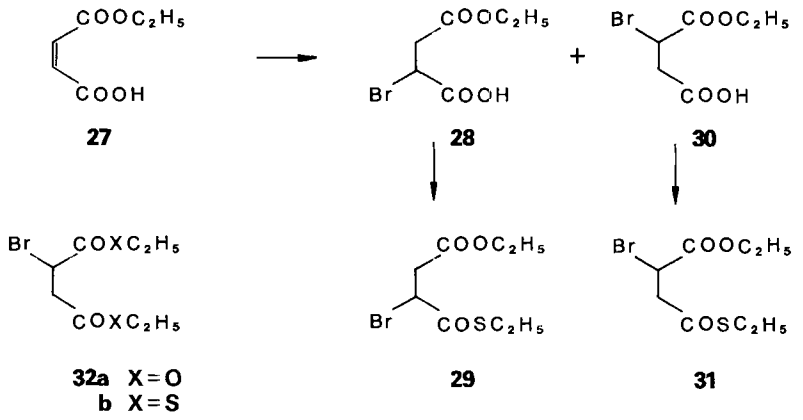


25



26

Scheme 9



After identification of the ester carbonylgroups by their $^3J(COOCH_2CH_3)$-values (**28**: 3.2 Hz; **30**: 2.9 Hz) comparison of the other long-range C,H-coupling constants of the carboxyl C-atoms allowed the structural assignment. Because coupling constants greater than 6 Hz (abs. value) are expected for $^2J(OOC\text{-}CH_2)$ [14], the *ddq*-pattern (J_d = 6.1, 4.6 Hz; J_q = 2.9 Hz) in the proton-coupled ^{13}C-NMR spectrum of the ester-carbonyl C-atom of the major isomer is only compatible with the structure **30**. This assignment is supported by the *td*-structure (J_t = 7.1 Hz; J_d = 2.4 Hz) of the corresponding acid-carboxyl C-atom and by the *ddd*-pattern (J_d = 6.1, 4.5, 3.1 Hz) of the proton-coupled ^{13}C-NMR spectrum for the same C-atom in the minor isomer. This conclusion has been confirmed by a selective C,H-decoupling experiment: irradiation of the CHBr-proton at 4.425 ppm in the ^{1}H-NMR spectrum of compound **30** eliminated the *d*-coupling of 2.4 Hz in the ^{13}C-NMR spectrum of the acid-carboxyl C-atom and the 6.1-Hz *d*-splitting in the ^{13}C-NMR spectrum of the ester-carboxyl C-atom. Therefore, the latter coupling constant must be assigned to $^2J(EtOOC\text{-}CHBr)$. The fact that $^2J(ROOC\text{-}CHBr)$ is about 1 Hz smaller than $^2J(ROOC\text{-}CH_2)$ is easily explained by the well-known electronegativity effect of the Br-substituent [15].

Because ^3J(C,H) as well as ^3J(H,H) coupling constants depend on the dihedral angle [15] [16], the observed values for ^3J(C,H) and ^3J(H,H) in **28** and **30** should agree with the most stable conformers of the two compounds. This is the case for the given assignment of **28** and **30**, but *not* for the alternative one.

2.2. *ESR Studies of Malonylmethyl and Succinyl Radicals together with their Thioester Analogues.* The photolysis of the bromomethylmalonate and bromosuccinate, **25** and **32a**, respectively, in the presence of a mixture of di(*tert*-butyl)peroxide and Et_3SiH provided a convenient method for the production of the radicals **I** and **III** for ESR study, *cf. e.g.* [17] *(Scheme 10)*.

Scheme 10

$$BuOOBu \xrightarrow{h\nu} 2BuO\cdot$$
$$BuO\cdot + Et_3SiH \longrightarrow BuOH + Et_3Si\cdot$$
$$Et_3Si\cdot + RBr \longrightarrow Et_3SiBr + R\cdot$$

2.2.1. *Structures of Radials* **I** *and* **III**. The well-resolved spectrum centered at $\langle g \rangle$ = 2.0022 in *Fig. 1* obtained from **25**, consists of a binomial *t* of *d*-splittings expected for the α- and β-protons of **I**. The magnitude of the *t*-splitting of 22.8 gauss for the α-protons is characteristic of that of primary alkyl radicals in which the radical center is

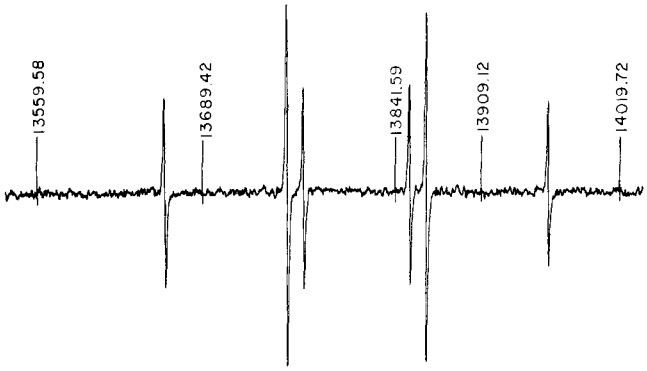


Fig. 1. *ESR spectra obtained from the photolysis of* **25** *with* Et_3SiH *in cyclopropane solution at* $-90°$. ^{1}H-NMR field markers are in kHz.

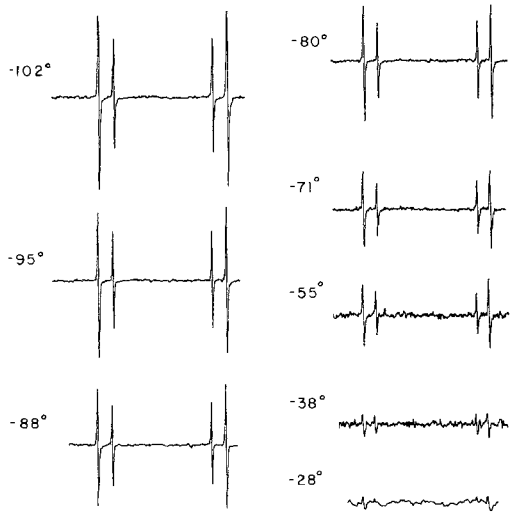
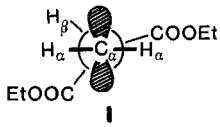


Fig. 2. *The temperature dependence of the central multiplet in* Fig. 1 *from* $-102°$ *to* $-28°$. Aside from the diminished signal intensity, there is no apparent line broadening at the higher temperatures.

more or less planar [17]. Furthermore, the magnitude of the *d*-splitting of 25.9 gauss for the β-proton is in the range expected for a conformation of the $C_\alpha - C_\beta$ bond in which the dihedral angle describing the $H_\beta - C_\beta$ and $H_\alpha - C_\alpha$ bonds is about $\pi/6$. It is noteworthy that the magnitude of the H_β-splitting $a_{\beta H}$ remains singularly unchanged over a temperature range of more than 60 °C. This conclusion is unmistakable in the central portion of *Fig. 2*, despite the poorer quality of the spectra obtained at the higher temperatures. The



I

Table. *ESR Parameters of Malonylmethyl and Succinyl Radicals together with their Thioester Analogues*

Precursor	Radical	T [°C]	⟨g⟩	Proton Hyperfine Splitting [gauss]		
				α	β	Others
25	$\dot{C}H_2CH(COOEt)_2$	−100	2.0022	22.8	25.9	
32a	$EtOOCCH_2\dot{C}HCOOEt$	− 95	2.0030	21.1	26.3	1.5
		− 40		21.1	25.2	1.5
20b	$\dot{C}H_2CH(COSEt)COOEt$	− 80	~ 2.003	22.3	18.0	
26	$\dot{C}H_2\overset{CH_3}{\overset{\vert}{C}}(COSEt)COOEt$	− 80	2.0023	22.2		
31	$EtOOC-\dot{C}H-CH_2COSEt$	− 93	2.0030	20.5	21.8	1.8

temperature invariance of $a_{\beta H}$ indicates that **I** is more or less 'locked' in the conformation shown above.

The ESR spectrum shown in *Fig. 3a* was obtained from the isomeric bromosuccinate **32a** at −95 °C. The magnitudes of the proton hyperfine splittings listed in the *Table* are consistent with those expected for the succinate radical **III**. Thus, the *d*- and *t*-splittings (21.1 and 26.3 gauss, respectively), arising from the α- and β-protons, respectively, are akin to those obtained for isomeric malonylmethyl radical **I**. However, there are several remarkable features in the ESR spectrum. First, the amplitudes of all the lines do not quite accord with the expected binomial intensity ratios, the $a_I = 0$ lines of the 1:2:1 triplet being slightly, but noticeably diminished at −95 °C relative to those at a higher temperature (see spectrum at −45 °C in *Fig. 3b*). This observation, coupled with the accompanying decrease in the magnitude of the β-triplet splitting, suggests the presence of temperature-dependent dynamics which exchange the β-protons in **III** between positions which are not quite equivalent.

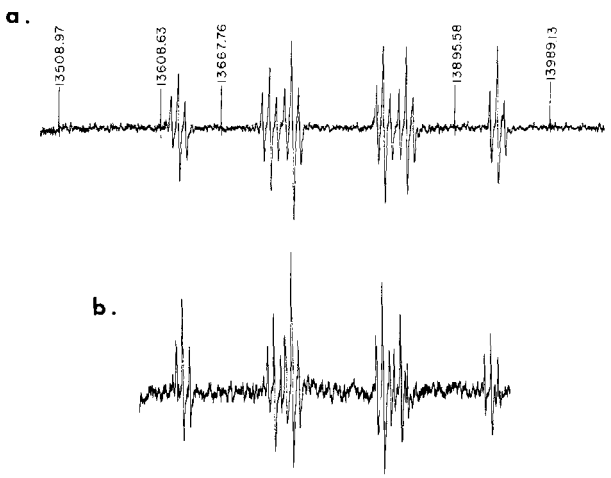
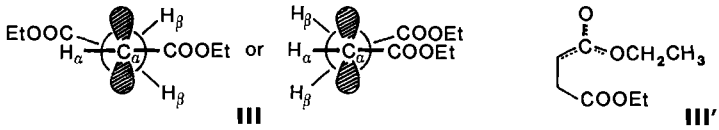


Fig. 3. *ESR spectrum obtained from the photolysis of* **32a** *with* Et_3SiH *in cyclopropane solution at* (a) −96° (b) −46°



III III'

A torsional motion about the $C_\alpha - C_\beta$ bond in either the conformations shown below, will qualitatively account for most of these observations [17]. We assign the additional *t*-splitting of 1.5 gauss in *Fig. 3* to the pair of CH_2-protons of the ethyl-ester function. Such an assignment together with the slight increase in the *g*-value of **III** is consistent with some spin delocalization into the α-ethoxycarbonyl group (see **III'**) which is similar to that observed earlier in the benzoylmethyl radical [18].

2.2.2. *Structures of Radicals* **II** *and* **IV**. The photolysis of peresters represents an alternative method for the production of transient organic radicals for ESR study [19] *(Scheme 11)*. Accordingly the photolysis of the thio-perester **20b** was carried out directly in the cavity of the spectrometer at $-100\,°C$.[1]) The resolved spectrum shown in *Fig. 4a* was observed initially upon photolysis, but continued irradiation for even a few minutes resulted in a more complex spectrum. Nonetheless the spectrum of **II** clearly consisted of the expected *t* of *d*'s with hyperfine splittings of 22.3 and 18.0 gauss, respectively. For comparison the ESR spectrum in *Fig. 4b* of the methyl analogue **II'** generated from **26**

Scheme 11

$$RCO_2t\text{-BuO} \xrightarrow{h\nu} RCO_2\cdot + t\text{-BuO}\cdot$$

$$RCO_2\cdot \xrightarrow{\text{fast}} CO_2 + R\cdot$$

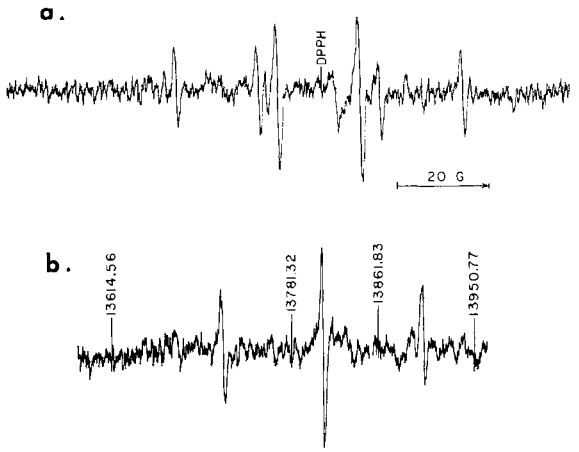
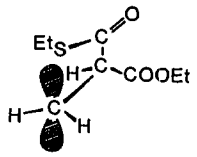


Fig. 4. *ESR spectrum obtained from the photolysis of* (a) **20b** *in cyclopropane solution at* $-100°$ *and* (b) **26** *in cyclopropane solution at* $-80°$

[1]) The perester method was chosen for the production of **II** since the corresponding organic bromide $BrCH_2CH(COSEt)(COOEt)$ could not be prepared in pure form.

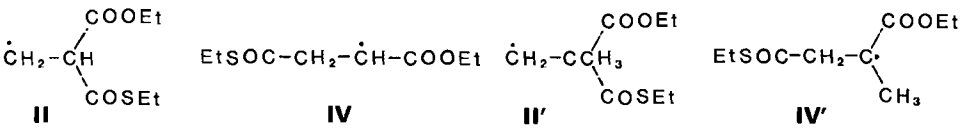
consisted of a single t with essentially the same H_α hyperfine splitting. No change was observed in the basic pattern upon warming the cavity temperature from $-80\,°C$ to $-25\,°C$, except for a decrease in the signal intensity.

The H_β-splitting of 18.0 gauss for **II** is unusually small for a primary alkyl radical. Indeed, hyperfine splittings of this magnitude have previously been observed only in primary alkyl radicals which are substituted on the $C(\beta)$-atom with a hetero-atom such



II

as chlorine or sulfur [17]. In these radicals, small values of $a_{\beta H}$ could arise from a slight distortion at $C(\beta)$-atom as a result of an incipient bridging by the heteroatom. As applied to **II**, a bridged structure could be accomodated by the observed ESR parameters. Whether such incipient bridging could lead to further reactions of **II**, as suggested by the photolytic studies, is not known. Whatever may be the case, however, the ESR studies provide no evidence for the 1,2-migration of the thioester group. Thus, the ESR spectrum of the rearranged radical **IV** shown in *Fig. 5* was readily obtained from the corresponding bromo-thioester **31**, and none of the features of **IV** were apparent in the ESR spectrum of **II**.



II **IV** **II'** **IV'**

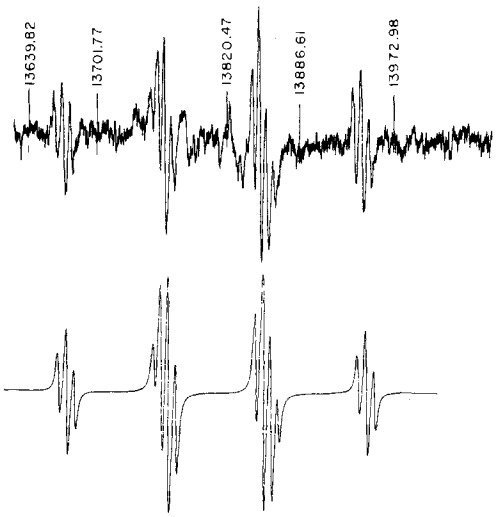


Fig. 5. (a) *ESR spectrum obtained from the photolysis of* **31** *in cyclopropane solution at* $-93°$. (b) *The computer-simulated spectrum in* (a) *using the ESR parameters in the* Table. Note that none of the features of **IV** are apparent in *Fig. 4a*.

Furthermore, the presence of an additional CH_3-group at *C(β)* as in **II'** did not facilitate such a migration [20], since there is no evidence in *Fig. 4b* for the rearranged methyl-thiosuccinyl radical **IV'**.

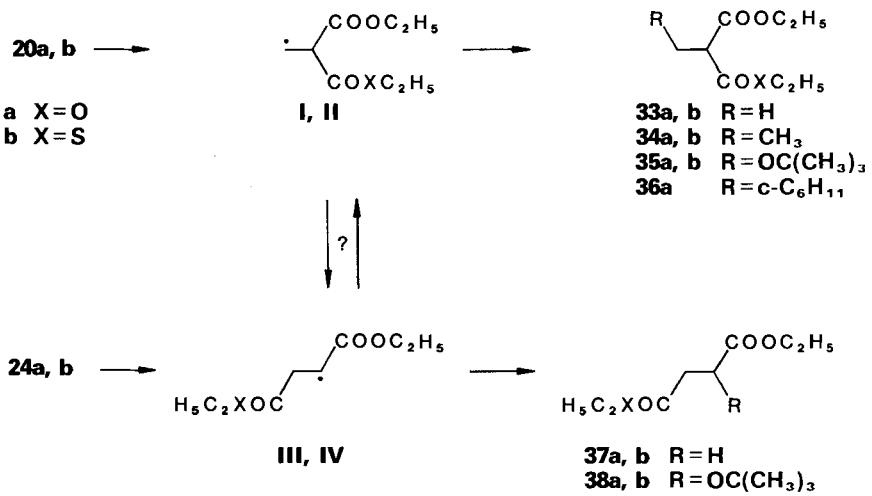
The ESR parameters for the thiosuccinyl radical **IV** are similar to those of the succinyl radical **III**, with the exception that the *t*-splitting arising from the β-protons in **IV** are significantly smaller than that in **III**. Incipient bridging analogous to that in the thiomalonylmethyl radical **II** provides a consistent pattern, especially if one considers a diminished driving force owing to the presence of an α-ethoxycarbonyl group (*cf.* structure **III'**).

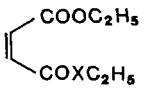
2.3. *Product Studies of Malonylmethyl and Succinyl Radicals* **I–IV**. – 2.3.1. For product studies of the radicals generated at room temperature, the peresters **20a, b** were photolyzed in cyclohexane. In each case, the GC/MS analysis of the reaction mixtures showed the presence of a variety of esters, which, according to the relative peak areas, were clearly dominated by **33a/35a** and **33b/35b.** Also, small amounts of **34a** and **34b** have been detected *(Scheme 12)*.

The structures of **33a/34a** and **33b/34b** were confirmed by comparison of their GC/MS spectra with those of the compounds prepared independently. The product **35a** could be distinguished from **38a**, prepared independently, by its slightly smaller GC retention time and its different MS fragmentation pattern. Two separate photolyses of **20a** yielded small amounts of **38a**, which could be detected in addition to **35a**. Since the GC retention time of methylmalonate **33a** differs from that of the succinate **37a** by more than 1 min, we should have been able to detect even small amounts of **37a**.

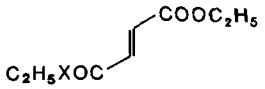
Similarly the thioperester **20b** gave the thiomalonates **33b** and **35b** in a ratio of 0.43 : 1. Although **35b** and **38b** have nearly identical GC retention times, they are readily distinguished by their MS fragmentation patterns. A careful screening of the relevant region in the GC/MS measurements indicated that no **38b** had been formed during the photolysis of **20b**. Likewise, photolysis of **24b** gave only **38b**. Other possible products

Scheme 12

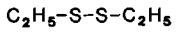




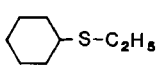
39a X=O
b X=S



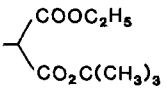
40a, b



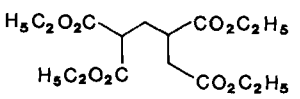
41



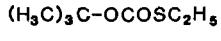
42



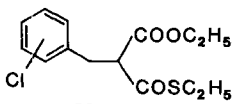
43



44



45



46

as the maleates **39a, b** and fumarates **40a, b** were absent according to the GC comparison of authentic esters with the mixtures obtained from photolysis of **20a** and **20b**.

In a control experiment, it was established that the suspected rearrangement product **37b**, decomposed only partially. Thus, after photolysis in cyclohexane for 2 h, 48% of the original **37b** could still be detected.

In addition to the esters described above, photolysis of the thioperester **20b** gave diethyl disulfide **41** and cyclohexyl ethyl sulfide **42** which could be identified by their MS. The disulfide **41** could have been formed in part from direct photocleavage. For instance, *S*-ethyl-thiodecanoate and *S*-ethyl-3-phenylthiopropionate each gave **41** upon photolysis in cyclohexane. However, **41** was also produced during the thermolysis of **20b** in chlorobenzene (see below).

2.3.2. For product studies of radicals generated thermolytically, the peresters **20a, b** were decomposed in cumene at 140 °C. In both cases, the malonates **33a/35a** (5.6 : 1) and **33b/35b** (5.9 : 1) were formed as major products. Small amounts of **34a** and **34b** were also detected by the GC/MS analysis of the mixture. To be certain of its structure, **35a** was isolated from the mixture resulting from a scaled-up thermolysis. Its ^{1}H-NMR spectrum was easily distinguishable, and was free from the spectrum of **38a** which had been prepared independently from diethyl maleate. Among the other minor products formed by the thermolysis of **20a**, **43** could be identified by comparison of its MS with that of an authentic sample [21].

Another suspected product **44**, which could have been formed by the cross combination of the radicals **I** and **III** was excluded after this compound was prepared independently. Again, the major products expected from rearrangement, **37a** and **38a**, have not been detected.

Besides the products mentioned above, the thermolysis of **20b** in cumene gave a small amount of the thiocarbonate **45**. More important, however, is the detection of a small amount of *O*, *S*-diethyl succinate **37b**, which must have been formed after the rearrangement of **II** to **IV**. As mentioned above, **35a** and **38a** as well as **35b** and **38b** have very

similar GC retention times, whereas the esters **33a** and **37a** and the thioesters **33b** and **37b** can readily be distinguished. A careful screening of the GC/MS spectra showed the absence of **38a** and **38b** among the thermolysis products of **20a** and **20b**, respectively.

The thermolysis of the peresters **24a** and **24b** was much more selective than that observed with the methylmalonates **20a** and **20b**. As indicated by the GC-peak areas (neglecting response factors), the products **37a**/**38a** and **37b**/**38b** accounted for 98% and 90%, respectively, of the esters, with the succinates dominating over the *t*-butoxy-derivatives (*i.e.*, **37a**/**38a** 2.8 : 1; **37b**/**38b** 1.6 : 1). In each case, one additional product was observed in the GC/MS analysis, but the structures were not elucidated.

2.3.3. The search for products of radical rearrangement can be summarized as follows. The main products which are derived from the peresters **20a**, **b** and **24a**, **b** under a variety of conditions by way of the radicals **I**, **II** and **III**, **IV**, respectively, have been found to consist essentially of those products formed by H-abstraction and recombination of the intermediate radicals with *t*-BuO radicals. For those reactions carried out in cumene as solvent, H-abstraction products such as α-methylstyrene and dicumyl were also found. Based on the peak areas (assuming equal response factors) the two major components together with the minor products mentioned above, account for 89% – 98% of the esters in all the thermal decomposition reactions of the peresters studied. The selectivity decreased in the photoreactions, where these components constituted only 81% from **20a** and 67% from **20b**. Small amounts of products derived from a rearranged C-skeleton have been observed in photolysis and in the high-temperature experiments; *e.g.* photolysis of **20a** in cyclohexane gave 1.7% of **38a** and thermolysis of **20b** in cumene afforded less than 1% of **37b**. Control experiments have established that **37a** is stable under the conditions of thermolysis of **20a**. Likewise, **37b** was found to be stable during the thermal decomposition of **20b**.

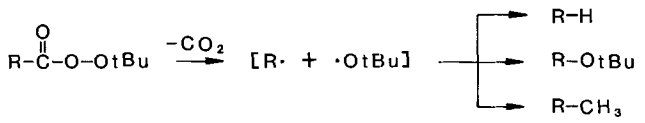
3. Conclusions. – Malonylmethyl radicals **I** have been generated unambigously in solution by standard photolytic and thermolytic methods. ESR studies show **I** to exist in a preferred conformation not unlike that of a variety of other primary alkyl radicals. The thiomalonylmethyl radicals **II** exist in a similar conformation, but there is evidence for incipient bridging of the β-(ethylthio)carbonyl group to the radical center. The ESR spectrum of the succinyl radical **III** and the thiosuccinyl radical **IV**, which are the rearrangement products of **I** and **II** *(Scheme 13)*, respectively, could also be determined. However, there is no evidence for the presence of **III** and **IV**, even in minor amounts, when **I** and **II**, respectively, were photolytically generated at temperatures below – 40 °C under the standard conditions of the ESR experiments. Thus, the ESR studies do not support the 1,2-rearrangement of an ethoxycarbonyl group in malonylmethyl radical **I** or of an (ethylthio)carbonyl group in **II**.

Scheme 13

I X=O **III** X=O
II X=S **IV** X=S

The rearrangement of malonylmethyl radicals was also scrutinized by identifying the products formed at higher temperatures. Photolysis of the peresters **20a** and **20b** at 20 °C afforded essentially products derived from the unrearranged radicals **I** and **II**, respectively. The principal products, which accounted for up to 98% of the esters, were formed by *a.* H-abstraction, and by recombination with *b.* *t*-BuO- and *c.* CH_3-radicals *(Scheme 14)*. Substitution reactions of the ester groups were also observed to a minor

Scheme 14



extent. The same products were also largely formed at the higher temperatures of 125–140 °C. The exceptions were diethyl *t*-butoxysuccinate **38a**, which was formed in photolysis of **20a** in *ca.* 1.7% yield and thiosuccinate ester **37b**, which was detected in *ca.* 0.1% yield, when the decomposition of **20b** was carried out at 140 °C in cumene.

The apparent lack of an extensive rearrangement of **I** → **III** and of **II** → **IV** could be an inherent feature of these radicals. However, we hasten to add that conclusions based on product distributions merely reflect differences in competing rate processes. As such, it is important to identify the nature of the competition. Thus the *t*-BuO-compounds **35a, b** (and **38a, b**) are likely to be products of the cage combination of the geminate radical pair, (see *Scheme 14*), for which the lifetime would be relatively short to observe rearrangement. Accordingly, the formation of only a small amount of **38a** from **I** in photolysis of **20a** and the absence of **38b**, resulting from possible rearrangement of **II**, indicates that rates of rearrangement are slower than recombination [22]. On the other hand, the hydrogen derivatives **33a, b** and **37a, b** are formed by H-abstraction largely from the solvent for which the rate processes are considerably slower than cage combination [23]. Indeed, when the thermolysis of **20b** was conducted in refluxing chlorobenzene, a poor H-donor, increased yields (*ca.* 2% each) of the rearranged products **37b** and **39b** were detected. As before, the unrearranged esters **33b** and **35b** as the major products, together with minor amounts of **34b** and the chlorobenzyl-thiomalonate **46** confirm the homolytic process extant. These results lead to the conclusion that homolytic 1,2-rearrangements of ethoxycarbonyl and (ethylthio)carbonyl groups in malonylmethyl radicals **I** and **II**, respectively, are relatively slow even under the best of the experimental conditions we could devise.

The work in Berne has been supported by the *Stipendienfonds der Basler Chemischen Industrie* and the *Swiss National Science Foundation*. HPLC equipment has partially been purchased by a grant form the *Stiftung zur Förderung der wissenschaftlichen Forschung an der Universität Bern*. The help of Mrs. *V. Meyer* with separation problems and of Mr. *H. Gfeller* with GC/MS measurements is gratefully acknowledged. We also thank the *National Science Foundation* (USA) for financial support of the research carried out in Indiana.

Experimental Part

General. Silica gel used for prep. separations was *Merck* Silica gel *60*; silica gel plates *Merck 60 F-254* were used for TLC (R_f-values are ratio of fronts). For HPLC *Merck* Silica gel 7 µm was used; if not stated otherwise, hexane/*t*-butyl methyl ether 4:1 or 9:1 was used. UV spectra were measured on *Perkin-Elmer 554* UV/VIS spectrophotometer. IR spectra [cm^{-1}] were measured in $CHCl_3$ on *Perkin-Elmer 257* and *457* instruments; only bands with medium or strong absorption are reported. NMR spectra were obtained in $CDCl_3$ using *Varian EM 360*, *Bruker WP 80* and, for ^{13}C, *Varian XL 100 FT* (25.2 MHz) instruments. Chemical shifts are recorded in δ [ppm] downfield from TMS as an internal standard (s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet, stack = heavily overlapping signals), coupling constants are reported in Hz. Mass spectra (MS) were recorded on *Varian MAT CH5-DF* and *CH-7*, signals are recorded as m/z in % of the base peak. For GC/MS analyses see below. Elemental analyses were performed by *M. Manser*, Mikroanalytisches Labor, ETH, Zürich.

Reactions have not been optimized. If not stated otherwise, reactions were worked up by pouring the reaction mixture on ice/water extracting three times with Et_2O. After treatment with base or acid and neutralization with $NaHCO_3$ as indicated, the org. phase was dried over $MgSO_4$ and concentrated in vacuo (*i.v.*) on a rotatory evaporator at temperatures < 40°. As solvents were used: CH_2Cl_2 (*Fluka, puriss.*), hexane (*Fluka*, HPLC-quality), *t*-butyl methyl ether (*Fluka*, HPLC-quality), THF (distilled over K), hexamethylphosphortriamide (*Fluka, puriss.*).

General Procedure for the Cleavage of *t*-Butylesters. – HBr was bubbled through a solution of the *t*-butylester in CH_2Cl_2 for 1 h. The mixture was extracted with $NaHCO_3$-solution, the aq. layer was subsequently acidified with H_3PO_4 and worked up.

General Procedure for the Formation of *t*-Butylpercarboxylates [11]. – To a solution of the carboxylic acid and 0.5–4 mol% of 4-(dimethylamino)pyridine in anh. CH_2Cl_2 was added *t*-butylhydroperoxide (2 mol-equiv.) in di(*t*-butyl)peroxide at 0°. Dicyclohexylcarbodiimide (1 mol-equiv.) was either added in small portions or as a solution in CH_2Cl_2. After stiring for 5 h at r.t., the suspension was filtered, concentrated *i.v.* and the residue dissolved in Et_2O. Extraction with 2N H_2SO_4 and workup gave an oil, which was freed from di(*t*-butyl)peroxide *i.v.* (0.1 mm). Subsequent flash chromatography [24] (mobile phase hexane/*t*-butyl methyl ether 4:1) yielded the perester, which for analytical purposes was further purified by HPLC.

4-t-Butyl 1-ethyl 2-(ethoxycarbonyl)butanedioate (**18a**). A solution of diethylmalonate (**17a**) (2.0 g, 124 mmol) and *t*-butyl bromoacetate (1,82 ml, 2.42 g, 12.4 mmol) in 10 ml CH_2Cl_2 was added to a solution of NaOH (0.97 g, 24.8 mmol) and tetrabutylammoniumhydrogen sulfate (4.21 g, 12.4 mmol) in 15 ml H_2O was stirred for 3 h. From the org. layer crude product **18a** (3.5 g) was obtained, which contained 20% diethyl malonate. For analysis, a small sample was purified by HPLC. IR 2980, 1728, 1368, 1200, 1152. ^{1}H-NMR: 1.25 (2t, J = 7.2, 6H); 1.42 (s, 9H); 2.8 (d, J = 7.2, 2H); 3.72 (t, J = 7.2, 1H); 4.17 (2q, J = 7.2, 4H) [17]. MS: 219 (6, $M^+ - (CH_3)_2C=CH_2 + H$), 201 (31), 173 (44), 145 (18), 128 (16), 127 (13), 57 (100), 56 (13), 41 (15).

$C_{13}H_{22}O_6$ Calc. C 56.92 H 8.08% Found C 56.78 H 8.14%

The crude material was used for the preparation of *3-bis(ethoxycarbonyl)propionic acid* (**19a**) (1.86 g, 68%).

4-O,O-t-Butyl 1-ethyl 2-(ethoxycarbonyl)monoperoxybutanedioate (**20a**). The acid **19a** (2.06 g, 9.4 mmol) was treated with *t*-butyl hydroperoxide and gave **20a** (2.33 g, 85% yield) as an oil. IR: 2983, 1770, 1730, 1390, 1370, 1332, 1275, 1245, 1175, 1155, 1125, 1030. ^{1}H-NMR: 1.26 (t, J = 7.2, 6H); 1.30 (s, 9H); 2.92 ($\approx d$, J = 7.6, 2H); 3.83 ($\approx t$; J = 7.6, 1H); 4.20 (q, J = 7.2, 4H). MS: 201 (42), 174 (11), 173 (100), 155 (14), 145 (25), 129 (11), 128 (14), 127 (46), 115 (11), 101 (16), 100 (17), 99 (25), 73 (38), 59 (47), 57 (16), 55 (21), 43 (21).

$C_{13}H_{22}O_7$ Calc. C 53.78 H 7.64% Found C 53.62 H 7.73%

4-t-Butyl 1-ethyl 2-[(ethylthio)carbonyl]butanedioate (**18b**). To a mixture of ethyl (ethylthio)carbonylacetate (**17b**) [13] (1.2 g, 6.8 mmol) and *t*-butyl bromoacetate (1.33 g, 6.8 mmol) in 7 ml of CH_2Cl_2 at 0° was added a solution of NaOH (0.544 g, 13.6 mmol) and tetrabutylammonium hydrogensulfate (2.3 g, 6.8 mmol) in 7 ml H_2O. After stirring (3 h, then r.t.), the org. layer was separated, dried and distilled (bulb-to-bulb) (64°–93°, 0.05 Torr) to give pure **18b** (1,05 g, 55%). An analytically pure sample was obtained by repeated HPLC purification. IR 2980, 1730, 1678, 1370, 1153. ^{1}H-NMR: 1.27 (t, J = 7, 6H); 1.45 (s, 9H); 2.95 (q, J = 7) and 2.82 (q, J = 7.8, 4H); 3.97 ($\approx t$, $J \approx$ 7.8, 1H); 4.21 (q, J = 7, 2H) [25]. MS: 229 (57), 217 (93), 155 (73), 145 (93), 128 (72), 118 (88), 101 (46), 58 (44), 57 (100), 56 (38), 55 (69), 41 (57).

$C_{13}H_{22}O_5S$ Calc. C 53.78 H 7.64% Found C 53.93 H 7.82%

3-(Ethoxycarbonyl)-3-[(ethylthio)carbonyl]propionic acid (**19b**). The diester **18b** (7.24 g, 25.8 mmol) was cleaved as described and gave **19b** (4.94 g, 81.7%) as an oil.

4-O,O-t-Butyl 1-ethyl 2-[(ethylthio)carbonyl]monoperoxybutanedioate (**20b**). The acid **19b** (4.94 g, 21.09 mmol) was reacted with *t*-butyl hydroperoxide and gave **20b** (2.24 g, 34.6% of 99.6% activity [26]. IR: 2985, 2937, 1769, 1735, 1676, 1410, 1390, 1370, 1295, 1185, 1127. ^{1}H-NMR: 1.05–1.4 (stack, 15H); 3.93 ($\approx q$, 4H); 4.03 ($\approx t$, 1H); 4.23 (q, J = 7.0, 2H) [25]. MS: 217 (25, $M^+ - COSC_2H_5$), 189 (23), 155 (31), 128 (38), 99 (24), 73 (100), 59 (25), 55 (26).

$C_{13}H_{22}O_6S$ Calc. C 50.97 H 7.24 S 10.47% Found C 51.08 H 7.44 S 10.31%

Diethyl 2-(t-butoxycarbonyl)butanedioate (**22a**). A solution of t-*butyl ethyl malonate* (**21**) (1.65 g, 8.8 mmol) in 10 ml THF was added slowly at 3° to a suspension of KH (free from oil, 0.35 g, 8.8 mmol) in 30 ml THF. After completion of the deprotonation, a solution of ethyl bromoacetate (1.47 g, 8.8 mmol) and hexamethylphosphortriamide (1.58 g, 8.8 mmol) in 5 ml THF was added, and stirred overnight at r.t. After addition of a few drops of EtOH, the mixture was concentrated and worked up with 2N HCl and $NaHCO_3$ to give 1.51 g (62.8%) of crude **22a**. For analysis a small sample was purified by HPLC. IR: 2985, 1725, 1370, 1155, 1145, 1028, 910. ^{1}H-NMR: 1.23 (t, J = 7.0, 3H); 1.26 (t, J = 7.0, 3H); 1.45 (s, 9H); 2.87 ($\approx d$, J = 7.2, 2H); $\approx$ 3.75 ($\approx t$, J = 7.2, 1H); 4.15 (q, J = 7.0, 2H); 4.20 (q, J = 7.0, 2H) [25]. MS: 219 (2), 201 (3), 173 (11), 145 (8), 128 (13), 100 (11), 73 (6), 57 (100), 56 (9), 55 (19).

$C_{13}H_{22}O_6$ Calc. C 56.92 H 8.08% Found C 56.96 H 7.94%

Diethyl 2-t-butylperoxycarbonylbutanedioate (**24a**). *2,3-Bis(ethoxycarbonyl)propionic acid* (**23a**) was prepared from **22a** (3.26 g, 14.9 mmol) and reacted with *t*-butyl hydroperoxide as described. HPLC-purification gave pure **24a** (0.91 g, 21%) as a colorless oil. IR: 2980, 1775, 1735, 1368, 1260, 1200, 1110, 1025. ^{1}H-NMR: 1.22 (t, J = 7.2, 3H); 1.26 (t, J = 7.2, 3H); 1.32 (s, 9H); 2.92 ($\approx d$, J = 7.2, 2H); 3.83 (t, J = 7.2, 1H); 4.17 (q, J = 7.2, 2H); 4.2 (q, J = 7.2, 2H) [25]. MS: 201 (22), 173 (56), 145 (13), 127 (26), 115 (100), 101 (17), 99 (14), 87 (88), 73 (29), 69 (33), 59 (41), 57 (75), 55 (24), 43 (60).

$C_{13}H_{22}O_7$ Calc. C 53.78 H 7.64% Found C 53.70 H 7.61%

t-*Butyl ethyl [(ethylthio)carbonylmethyl]malonate* (**22b**). A solution of **21** (3.85 g, 30.5 mmol) in 10 ml THF was added slowly to a suspension of KH – previously treated with pentane to remove the oil – (0.85 g, 21.3 mmol) in 30 ml THF at 0°. After stirring for 15 min, a solution of *S*-ethyl bromothioacetate (3.85 g, 21 mmol) prepared from bromoacetic acid and ethanethiol according to [11] in a yield of *ca.* 73% after bulb-to-bulb distillation (b.p. 60–70°, 0.1 Torr), and HMPT (3.76 g, 21 mmol) in 30 ml THF was dropped in. After stirring over night, the mixture was worked up and gave after distillation **22b** as a slightly yellow oil (2.6 g, 42.7%). Pure (**22b**) was obtained by HPLC. IR: 2975, 2930, 1720, 1680, 1369, 1300–1195, 1145, 1090, 995. ^{1}H-NMR: 1.23 (t, J = 7, 3H); 1.25 (t, J = 7.2, 3H); 1.43 (s, 9H); 2.87 (q, J = 7.2, 2H); 3.07 ($\approx d$, J = 7.6, 2H); 3.75 ($\approx t$, J = 7.6, 1H); 4.15 (q, J = 7, 2H) [25]. MS: 229 (4), 217 (5), 189 (5), 173 (21), 117 (10), 99 (5), 57 (100), 41 (10).

$C_{13}H_{22}O_5S$ Calc. C 53.77 H 7.64% Found C 53.47 H 7.56%

Ethyl 2-(t-butylperoxycarbonyl)-3-[(ethylthio)carbonyl]propionate (**24b**). The ester **22b** (1.38 g, 4.78 mmol) was cleaved with HBr in CH_2Cl_2 as described above and treated with *t*-butyl hydroperoxide according to the general procedure. After workup, crude **24b** was obtained as a yellow oil (0.49 g, 44%). For analysis a sample was purified by HPLC. IR: 2987, 2935, 1775, 1738, 1681, 1452, 1405, 1390, 1370, 1327, 1265, 1180, 1090, 1030, 1000, 910. ^{1}H-NMR: 1.2 (t, J = 7.6, 3H); 1.25 (t, J = 7, 3H); 1.3 (s, 9H); 2.88 (q, J = 7.6, 2H); 3.18 ($\approx d$, J = 7, 2H); 3.93 ($\approx t$, J = 7.6, 1H); 4.19 (q, J = 7, 2H) [25]. MS: 245 (1), 217 (22), 201 (46), 189 (29), 173 (87), 155 (46), 145 (31), 127 (100), 101 (26), 99 (42), 89 (16), 73 (86), 59 (27), 55 (35).

$C_{13}H_{22}O_6S$ Calc. C 50.96 H 7.24% Found C 50.76 H 7.31%

Ethyl 3-bromo-2-(ethoxycarbonyl)propionate (**25**). The procedure in [12] was modified. Diethyl methoxymethylmalonate (2,5 g, 12.2 mmol) was added to a solution of HBr in EtOH (50%) and stirred for 48 h. After workup, a bulb-to-bulb distillation gave a colorless liquid (2.02 g, 65%). ^{1}H-NMR: 1.30 (t, 6H); 3.75 (s, 3H); 4.25 (q, 4H). ^{13}C-NMR: 166.6 (s); 62.0 (t); 54.8 (d); 26.9 (t); 14.0 (q). MS: 252 (1, M^+), 181 (30), 179 (31), 127 (99), 101 (79), 99 (80), 82 (30), 73 (67), 55 (89), 29 (100).

2-Bromo-3-(ethoxycarbonyl)propionic acid (**28**) *and 3-bromo-3-(ethoxycarbonyl)propionic acid* (**30**). Ethyl maleate (**27**) was prepared by heating a 1:1 mixture of maleic anhydride and EtOH for 2 h at 90°; subsequent removal of anhydride and diethyl maleate by distillation gave pure **27**. HBr was feeded into a solution of **27** (4.72 g,

32.7 mmol) in 40 ml CH_2Cl_2 at r.t. After 1 h the solution was washed with H_2O and extraced twice with $NaHCO_3$. After acidification with H_3PO_4, extraction with Et_2O and subsequent bulb-to-bulb distillation gave 6.65 g (90%) of a 15:85 mixture of **28** and **30**. Flash chromatography [24] of 1-g portions gave 1.82 g of pure **30** and 3.17 g of a 1.1:1 mixture of **28** and **30**. Low-pressure chromatography [27] (*Merck* silica gel, 40–63 μm, mobile phase CH_2Cl_2/AcOH 20:1 gave pure **28** and **30**.

28: b.p. 125° (0.01 Torr); R_f (CH_2Cl_2/AcOH 20:1) 0.32. IR: 1735S, 1727, 1373, 1300, 1260, 1180, 1150, 1020. ^{1}H-NMR (80 MHz): 1.26 (*t*, *J* = 7.2, 3H); 2.99 (*A*-part of *ABX*, *J* = 17.4, 5.9, 1H); 3.23 (*B*-part of *ABX*, *J* = 17.4, 8.1, 1H); 4.20 (*q*, *J* = 7.2, 2H); 4.60 (*X*-part of *ABX*, *J* = 5.9, 8.1, 1H); 9.17 (*s*, 1H); impurity at 6.87. ^{13}C-NMR (25.2 MHz, (D_6)benzene): 13.9 (*q*, $-CH_3$); 38.4 (*d*, > CHBr); 39.7 (*t*, $-CH_2-$CHBr); 61.7 (*t*, OCH_2); 170.1 (*s*, *C*OOEt); 173.0 (*s*, $-$COOH); long-range coupling pattern of the carboxyl signals: 170.1 (*tq*, ^2J (EtOO*C*$-CH_2$) = 7.2 [av. of 2*J* (EtOO*C*$-CH_A$) and ^2J (EtOO*C*$-CH_B$)]); ^3J (EtOO*C*$-CH_2-CH$Br) = 2.9, ^3J (*C*OO$-CH_2$) = 2.9); 173.0 (*ddd*, ^2J (HOO*C*$-CH$Br) = 6.1; ^3J (HOO*C*$-$CHBr$-CH_2$) = 4.5 and 3.1). MS: 226 (1), 224 (1, M^+), 181 (59), 180 (40), 179 (61), 178 (38), 73 (100), 71 (73), 55 (60), 45 (41).

30: b.p. 125° (0.01 Torr), R_f (CH_2Cl_2/AcOH 20:1) 0.38. IR: 1740, 1720, 1400, 1373, 1305, 1280, 1180, 1150. ^{1}H-NMR (80 MHz): 1.29 (*t*, *J* = 7.2, 3H); 3.03 (*A*-part of *ABX*, *J* = 17.8, 5.9, 1H); 3.32 (*B*-part of *ABX*, *J* = 17.8, 8.7, 1H); 4.25 (*q*, *J* = 7.2, 2H); 4.52 (*X*-part of *ABX*, *J* = 8.7, 5.9, 1H); 9.66 (*s*, 1H). ^{13}C-NMR (25.2 MHz, (D_6)benzene) 13.7 (*q*, CH_3); 37.9 (*d*, > CHBr); 39.4 (*t*, CH_2-CHBr); 62.3 (*t*, OCH_2); 168.9 (*s*, $-$*C*OOEt); 175.7 (*s*, COOH); long-range coupling pattern of the carboxyl signals: 168.9 (*ddq*, ^2J (EtOO*C*$-CH$BR) = 6.4, ^3J (EtOO*C*$-$CHBr$-CH_2$) = 4.6 and 3.2, ^3J (O=*C*$-$O$-CH_2$) = 3.2), 175.7 (*td*, ^2J (HOO*C*$-CH_2$) = 7.1 [av. of ^2J (EtOO*C*$-CH_A$) and ^2J (EtOO*C*$-CH_B$)], ^3J (HOO*C*$-CH_2-CH$Br) = 2.4); irradiation at 4.425 ppm in the ^{1}H-NMR spectrum (selective decoupling of *CH*Br) removes *d* of HOO*C*. MS: 208 (3), 206 (3), 181 (6), 179 (6), 154 (18), 152 (20), 73 (100), 71 (35), 55 (76), 45 (44).

$C_6H_9BrO_4$ Calc. C 32.02 H 4.03 Br 35.51% Found C 31.70 H 4.01 Br 34.82%

Ethyl 3-bromo-3-[(ethylthio)carbonyl]propionate (**29**) *and ethyl 2-bromo-3-[(ethylthio)carbonyl]propionate* (**31**). A mixture of **28** and **30** (3.38 g, 15 mmol) was esterified with ethanethiol as described above and chromatographed. As partial elimination of HBr had occurred, the combined fractions were treated in CH_2Cl_2 with HBr. Further separation by HPLC gave pure **29** and **31**.

29: R_f (pentane/Et_2O): 0.50. IR: 1730, 1680, 1378, 1268, 1145, 1095, 1030, 990, 960. ^{1}H-NMR: 1.25 (*t*, *J* = 7.0, 3H); 1.28 (*t*, *J* = 7.3, 3H); 2.93 (*q*, *J* = 7.3, 2H); 3.05 (*A*-part of *ABX*, *J* = 16.4, 7.6, 1H); 3.20 (*B*-part of *ABX*, J_{BX} = 7.6, 1H); 4.13 (*q*, *J* = 7.0, 2H); 4.74 (*X*-part, 1H). ^{13}C-NMR: 14.1; 14.25; 24.34; 39.78; 46.07; 61.22; 169.0; 194.74. MS: 225 (15), 223 (15), 209 (98), 207 (100), 181 (95), 179 (97), 99 (81), 71 (37), 55 (54).

$C_8H_{13}BrOS$ Calc. C 35.70 H 4.87 Br 29.69 S 11.91% Found C 35.93 H 5.13 Br 29.60 S 11.63%

Alternatively **29** was prepared from *2-Bromo-3-(ethoxycarbonyl)propionic acid* (**28**) (0.4 g, 1.9 mmol) by esterification with ethanethiol as described above. Pure **29** was obtained by HPLC (0.41 g, 80%). ^{1}H-NMR spectrum of **29**, prepared from pure **28**, is identical with that of **29** obtained from the mixture of **28** and **30**.

31: R_f (pentane/Et_2O): 0.56. IR: 1735, 1680, 1378, 1318, 1295, 1268, 1175, 1090, 995. ^{1}H-NMR: 1.24 (*t*, *J* = 7.3, 3H); 1.29 (*t*, *J* = 7.0, 3H); 2.9 (*q*, *J* = 7.3, 2H); 3.19 (*A*-part of *ABX*, *J* = 16.4, 6.5, 1H); 3.44 (*B*-part of *ABX*, J_{BX} = 8.0, 1H); 4.20 (*q*, *J* = 7.0, 2H); 4.62 (*X*-part of *ABX*, 1H). ^{13}C-NMR 13.85 (*q*); 14.55 (*q*); 23.51 (*t*); 38.34 (*d*); 48.08 (*t*); 62.26 (*t*); 168.51 (*s*); 195.33 (*s*). MS: 225 (6), 223 (6), 209 (79), 207 (81), 181 (97), 179 (100), 127 (28), 99 (92), 71 (40), 55 (31).

$C_8H_{13}BrO_3S$ Calc. C 35.70 H 4.87 Br 29.69 S 11.91% Found C 35.82 H 4.95 Br 29.41 S 11.85%

S,S-*Diethyl bromobutanebis(thioate)* (**32b**). HBr was bubbled through a solution of S,S-diethyl dithiofumarate (2.06 g, 9,8 mmol) [28] in 50 ml CH_2Cl_2 for 2 h. After stirring for additional 20 h, the mixture was extracted with $NaHCO_3$ to give a reddish oil, from which pure yellow **32b** (1.27 g, 45%) was obtained by repeated HPLC. IR: 1677, 1263, 1050, 1010, 970. ^{1}H-NMR: 1.25 (*t*, *J* = 7.5, 3H); 1.26 (*t*, *J* = 7.5, 1H); 2.94 (*q*, 2H); 2,95 (*q*, 2H); 3.27 (*A*-part of *ABX*, J_{AB} = 16, J_{AX} = 6.9, 1H); 3.39 (*B*-part of *ABX*, J_{BX} = 6.5, 1H); 4.79 (*X*-part of *ABX*, 1H). MS: 225 (100), 223 (99, $M^+ - SC_2H_5$), 143 (51), 115 (50), 89 (33), 55 (61);

$C_8H_{13}BrO_2S_2$ Calc. C 33.68 H 4.59 Br 28.02 S 22.48% Found C 34.07 H 4.75 Br 27.99 S 22.19%

The Production of Radicals in the ESR Cavity. – The quality of the ESR spectra presented in *Fig. 1–5* are typical for the systems examined in this study. The presence of minor components in the spectra were examined carefully. In particular, the presence of the prominent lines associated with the ESR spectrum of **III** (generated

independently from **32a**) was scrutinized in the spectrum of **I** as it was generated from **25** at various temperatures. Similarly, evidence for the lines arising from **IV** was sought in the spectrum of **II** at various temperatures. In general, those radical precursors which contained the β-(ethylthio)carbonyl group such as **20b**, **26** and **29** afforded ESR spectra of poorer quality, but were nonetheless assignable. Those radical precursors which contained an α-(ethylthio)carbonyl group such as **29** and **32b** did not afford the spectrum of the parent radical. We tentatively ascribe the latter to a unimolecular fragmentation process leading to the corresponding ketene and ethylthiyl radical. Unfortunately no evidence was found for the latter by carrying out the photolysis in the presence of alkenes to trap the thiyl radicals as β-(ethylthio)ethyl adducts (*c.f.* [29]).

Measurement of the ESR Spectra. – All ESR spectra were measured with a *Varian E-112* spectrometer equipped with a *Hewlett-Packard 5248L* electronic counter and a *5255A* frequency converter together with a *Harvey Wells G502* gaussmeter. The samples were cooled in a quartz *Dewar* located directly in the ESR cavity with a flow of cold N_2. Photolysis was performed with a medium-pressure (*Hanovia*, 1 kW) mercury-xenon lamp focussed into the ESR cavity. All g-values were corrected relative to perylene radical ($\langle g \rangle = 2.00257$) as the standard.

The radicals were generated by continuous photolysis of the perester (*Scheme 11*) or the appropriate bromo compound in the presence of di(*t*-butyl) peroxide and (Et_3SiH (*Scheme 10*) directly in the ESR cavity at low temperatures. Cyclopropane was used as the solvent in all cases. In the experiments with the bromo compounds (RBr), a 1:1:1 mixture by volume of di(*t*-butyl) peroxide, Et_3SiH and RBr was diluted with an equal volume of cyclopropane in a 4 mm ID suprasil quartz tube, which was sealed *i.v.* after three freeze-pump-thaw cycles. The peresters (*ca.* 0.1M) were dissolved in cyclopropane and the suprasil tube degassed as described above.

Decomposition of Peresters 20a, b and 24a, b. – The peresters (*ca.* 20 mmol) were heated in 0.5 ml cumene or chlorobenzene to 140° and 125°, respectively, for 3 h. The peresters **20a** and **20b** were dissolved in cyclohexane and photolyzed with a 125-W high-pressure Hg-lamp in a quartz vessel for 2 h.

Synthesis of Reference Compounds. – *Ethyl 2-[(ethylthio)carbonyl]propionate* (**34b**). This ester was prepared from **17b** (1 g, 5.7 mmol) and EtBr (0.62 g, 5.7 mmol) according to [13] in a yield of 66%. An analytically pure sample was obtained by GC (*Carbowax 20M*, 20%). IR: 2975, 1735, 1680, 1455, 1368, 1265, 1200, 1025, 990. ^{1}H-NMR: 0.95 (*t*, *J* = 7.2, 3H); 1.25 (2*t*, *J* = 7.2, 6H); 1.92 (*dq*, *J* = 8.0, 7.2, 2H); 3.42 (*t*, *J* = 8.0, 1H); 4.15 (*q*, *J* = 7.2, 2H). MS: 204 (16, M^+), 159 (10), 143 (100), 115 (12), 89 (22), 87 (16), 73 (75), 43 (32).

$C_9H_{16}O_3S$ Calc. C 52.92 H 7.89% Found C 53.02 H 7.98%

Ethyl 3-[(ethylthio)carbonyl]propionate (**37b**). A solution of ethyl succinate (1.46 g, 9.8 mmol) in 7 ml CH_2Cl_2 was treated with ethanethiol (1.24 g, 20 mmol) according to the general procedure given for formation of peresters. After workup a bulb-to-bulb distillation (57°, 0.05 Torr) gave **37b** as a colorless oil (1.4 g, 74%).

Diethyl 2-(t-butoxy)succinate (**38a**). A mixture of diethyl maleate (2.02 g, 10.5 mmol), isobutylene (3.87 g, 69 mmol) and conc. H_2SO_4 (0.31 g, 3.2 mmol) was shaken in a pressure bomb at 60° for 1 h. After cooling, Et_2O was added and the org. phase was worked up. Distillation and HPLC purification gave 1.7 g of **38a** as a colorless oil in a yield of 65%. IR: 2980, 1732, 1392, 1370, 1260, 1176, 1105, 1070, 1030. ^{1}H-NMR: 1.0–1.5 (stack, 15H); 2.66 (*d*, *J* = 6.6, 2H); 4.0–4.44 (stack, 5H) [25]. MS: 173 (5), 145 (3), 117 (78), 89 (8), 71 (13), 57 (100), 41 (28).

$C_{12}H_{22}O_5$ Calc. C 58.51 H 9.00% Found C 58.49 H 8.88%

Ethyl (Z)-3-[(ethylthio)carbonyl]-2-propenoate (**39b**). Ethyl maleate (2.0 g, 13.9 mmol) was esterified with ethanethiol as described for **37b** and gave after chromatography (hexane/*t*-butyl methyl ether 4:1) pure **39b** (1.26 g, 47.4%).

Ethyl (E)-3-[(ethylthio)carbonyl]-2-propenoate (**40b**). A solution of fumaroyl dichloride [28b] (2 g, 13.1 mmol) in 15 ml dry benzene was treated at 0° with ethanethiol (0.81 g, 13.1 mmol), Et_3N (2.55 g, 25.2 mmol) and stirred for 1 h. After addition of EtOH (0.6 g, 13.1 mmol) the mixture was stirred for 17 h. After workup, the crude **40b** was chromatographed (hexane/*t*-butyl methyl ether 4:1) to give pure **40b** (0.76 g, 30%).

t-Butyl ethyl methylmalonate (**43**). A mixture of *t*-butyl ethyl malonate (2 g, 10.6 mmol) and MeI (0.66 ml, 10.64 mmol) in 10 ml CH_2Cl_2 was stirred vigourously with a solution of tetrabutylammonium hydrogensulfate (3.6 g, 10.6 mmol) and NaOH (0.85 g, 21.3 mmol) in H_2O at 5–10° for 2 h. After workup of the org. phase, crude **43** (1.89 g, 88%) was purified twice by GC. n_D^{20}: 1.4142 ([21]: 1.4133). IR: 2880, 1735 (sh), 1720, 1450, 1370, 1150. ^{1}H-NMR: 1.2–1.55 (*m* with sharp *s* at 1.50, 15H); 3.4 ($\approx q$, *J* = 7.0, 1H); 4.2 (*q*, *J* = 7.0, 2H). MS: 147 (3), 129 (18), 101 (89), 57 (100), 56 (35), 55 (13), 44 (16), 41 (69), 39 (24).

Diethyl 2,4-bis(ethoxycarbonyl)adipate (**44**). To a solution of NaOMe (6.1 mmol) in 20 ml anh. EtOH was added diethyl malonate (1.72 g, 10.7 mmol) and then slowly diethyl methylidenesuccinate (2 g, 10.7 mmol). After stirring for 50 h at r.t., the dark brown solution was neutralized with aq. H_2SO_4, concentrated i.v. and worked up. Repeated bulb-to-bulb distillation gave pure **44** (2.24 g, 60.5%). IR: 2980, 1745, 1370, 1045. ^{1}H-NMR: 1.13–1.38 (*m*, 12H), 2.0–3.0 (*m*, 5H), 3.3–3.6 (*m*, 1H), 3.9–4.35 (*m*, 8H). MS: 301 (44), 272 (10), 255 (100), 227 (19), 213 (11), 187 (33), 181 (44), 180 (25), 174 (24), 173 (66), 140 (44), 128 (33), 127 (27).

$C_{16}H_{26}O_8$ Calc. C 55.48 H 7.57% Found C 55.37 H 7.56%

S-*Ethyl decanethioate* (**47**). Decanoic acid (4.5 g, 26.1 mmol) was esterified with ethanethiol (1.62 g, 26.1 mmol) as described above for the preparation of peresters and gave after HPLC-purification 4.56 g (80%) of the product. IR: 2935, 2860, 1675. ^{1}H-NMR: 0.75–1.0 (*m*, 3H); 1.1–2.0 (stack, 17H); 2.53 (*t*, *J* = 7.4, 2H); 2.87 (*q*, *J* = 7.0, 2H). MS: 187 (5), 155 (25), 95 (18), 85 (21), 81 (21), 71 (45), 57 (48), 55 (18), 43 (65), 41 (35), 28 (100).

$C_{12}H_{24}OS$ Calc. C 66.61 H 11.18 S 14.82% Found C 66.38 H 10.96 S 14.71%

S-*Ethyl 3-phenylpropanethioate*. 3-Phenylpropionic acid (4.5 g, 30 mmol) was esterified with ethanethiol (2.2 ml, 30 mmol) as described for **37b** to give 4.9 g (92%) of the product in a purity of 95%. For analysis the product was purified by HPLC. IR: 2970, 2918, 1680, 1450, 1050, 970. ^{1}H-NMR: 1.22 (*t*, *J* = 7.4, 3H); 2.65–3.1 (stack, 6H); 7.2 (stack, 5H). MS: 194 (17, M^+), 155 (7), 133 (22), 106 (100), 105 (42), 91 (86), 77 (23).

$C_{11}H_{14}OS$ Calc. C 68.00 H 7.26 S 16.50% Found C 68.11 H 7.39 S 16.40%

GC/MS Studies. – *General.* After photolysis or thermolysis of the *t*-butyl percarboxylates, the volatile products formed were analyzed by GC/MS (*Varian MAT 44S*, capillary GC column *SE 52*). A capillary GC column *CW 20M* was used in the separate search for the isomeric *t*-butoxy products. As shown by one separate experiment, about 80% of the reaction mixture is volatile. The products are listed according to increasing retention time (t_R). The structure of the products were assigned either *a*) by comparison with MS of compounds prepared independently, or *b*) by comparison with MS published [30] [31] or *c*) by fragmentation pattern or *d*) by t_R (capillary-GC) of the product mixtures to which the suspected compounds had been added. Esters, to which a structure has not been assigned, are labelled by their assumed parent peak. For the estimate of ratio of products, the peak areas of the GC signals (capillary GC with FID, *Varian Integrator CDS 111*) without correction for response factors [32] are used. Only those products are taken into account, which, according to their MS fragmentation pattern are formed from the peresters.

Photolysis of **20a** *in Cyclohexane.* The following esters have been detected: *diethyl methylmalonate* **33a** (*a*) (37%); *ethyl 2-(ethoxycarbonyl)butyrate* (**34a**) (*b*) [32] (1.3%); *ethyl 3-(*t*-butoxy)-2-(ethoxycarbonyl)propionate* (**35a**) (*c*) (40.8%); *diethyl 2-(*t*-butoxy)succinate* (**38a**) (1.7%) see thermolysis of **20a**; *diethyl cyclohexylmethylmalonate* (**36a**) (*c*);*(M$^+$ = 206)* (1%), *m/z*: 206 (1), 173 (24), 127 (15), 115 (9), 99 (9), 87 (12), 86 (9), 69 (14), 59 (21), 58 (10), 57 (100), 56 (9), 55 (14), 45 (12), 43 (40), 42 (12), 41 (26); *(M$^+$ = 218)* (7%), *m/z*: 219 (1), 218 (1), 174 (18), 173 *(100)*, 172 (43), 155 (11), 154 (9), 145 (25), 129 (9), 128 (38), 127 (44), 126 (42), 117 (11), 101 (23), 100 (44), 99 (42), 73 (30), 55 (57), 45 (11), see *(M$^+$ = 218)* of thermolysis of **20a**; *(M$^+$ = 200)* (1%), *m/z*: 197 (8), 161 (22), 160 (100), 159 (21), 133 (59), 132 (23), 127 (9), 115 (43), 114 (25), 105 (26), 104 (18), 99 (13), 95 (19), 88 (35), 87 (23), 86 (32), 81 (17), 79 (7), 67 (19), 59 (10), 58 (8), 57 (9), 55 (37), 54 (10), 53 (11), 45 (13), 44 (11), 43 (19), 41 (26); *(M$^+$ = 274)* (1.7%); *m/z* = 274 (1), 183 (7), 174 (82), 173 (16), 129 (9), 128 *(100)*, 110 (23), 109 (64), 100 (61), 95 (9), 83 (10), 82 (11), 81 (30), 79 (14), 67 (44), 56 (10), 55 (11), 54 (11), 53 (12), 43 (20), 41 (40), 39 (14); *(M$^+$ = 210)* (6%): *m/z*: 211 (1), 173 (26), 160 (23), 133 (22), 127 (20), 119 (23), 114 (11), 109 (10), 105 (11), 101 (20), 99 (11), 95 (22), 94 (11), 88 (24), 86 (19), 83 (11), 81 (18), 79 (15), 73 (41), 68 (8), 67 (43), 57 (12), 56 (8), 55 *(100)*, 54 (19), 53 (13), 45 (16), 43 (19), 42 (10), 41 (55); *(M$^+$ = 292)* (1%); *m/z*: 299 (1), 294 (1), 265 (5), 264 (8), 242 (8), 174 (11), 173 (100), 172 (25), 127 (26), 109 (9), 99 (10), 95 (11), 81 (11), 79 (9), 57 (14), 55 (26), 44 (11), 41 (14).

Photolyses of **20b** *in Cyclohexane. Diethyldisulfide* (**41**) (*a*); S-*ethyl 2-ethoxythiopropionate (?)* (*c*) (3%): *m/z*: 162 (9), 102 (45), 101 (23), 89 (100), 88 (19), 74 (22), 73 (10), 61 (58), 60 (16), 59 (14), 55 (16).

Cyclohexyl ethyl sulfide (**42**) (*c*) (4.7%): *m/z* = 144 (16), 83 (19), 82 (69), 81 (25), 67 (100), 66 (20), 59 (13), 55 (74), 44 (39), 53 (13), 45 (12), 41 (43), 39 (20).

Ethyl 2-[(ethylthio)carbonyl]propionate (**33b**) (*a*) (20%); *ethyl 2-[(ethylthio)carbonyl)butyrate* (**34b**) (*a*) (1.4%); *(M$^+$ = 149)* (10%), *m/z*: 149 (4), 99 (10), 83 (61), 82 (100), 81 (28), 67 (91), 66 (18), 47 (56), 56 (16), 55 (72), 54 (48), 53 (14), 44 (24), 43 (23), 42 (12), 41 (43), 40 (12), 39 (26).

*Ethyl 3-(*t*-butoxy)-2-[(ethylthio)carbonyl]propionate* (**35b**) (*c*) (46%): *(M$^+$ = 232)* (2.6%), *m/z*: 217 (1), 203 (2), 189 (6), 187 (26), 159 (100), 158 (42), 141 (21), 131 (29), 127 (36), 114 (10), 113 (70), 112 (32), 99 (16), 98 (20),

55 (21). *(M^+ = 232)* (12.5%), *m/z*: 216 (2), 200 (7), 189 (9), 173 (80), 172 (35), 150 (26), 154 (11), 145 (26), 144 (11), 128 (12), 127 (100), 126 (24), 117 (13), 100 (13), 99 (40), 98 (26), 89 (13), 73 (16), 55 (38). *(M^+ = 255)* (4.8%); *m/z*: 255 (1), 217 (2), 189 (8), 173 (72), 172 (30), 155 (10), 145 (69), 144 (21), 127 (35), 117 (10), 100 (11), 99 (20), 83 (54), 82 (22), 67 (16), 55 (100), 54 (19), 41 (19).

Thermolysis of **20a** *in Cumene.* The following esters were obtained: **33a** (*a*) (67%); *t*-butyl ethyl methylmalonate (**43**) (*a*) (2.1%); **34a** (*b*) [33] (1.6%); **35a** (*c*) (18%); *m/z*: 231 (0.7), 173 (5), 145 (4), 118 (6), 117 (78), 89 (8), 73 (7), 71 (13), 57 (100), 56 (12), 55 (10). This fragmentation pattern is different from **38a** (see below). In a preparative run, **35a** was enriched by destillation *i.v.* and subsequently chromatographed (mobile phase hexane *t*-butyl methyl ether 4:1). HPLC preparation yielded a impure sample of **35a**. ^{1}H-NMR: 1.17 (*s*, 9H); 1.28 (*t*, *J* = 7.2, 3H); 1.38 (*X*-part of *ABX*, *J* = 6.5, 1H); 3.57 (*B*-part of *ABX*, *J* = 7.09, 6.5, 1H); 3.82 (*A*-part of *ABX*, *J* = 7.09, 6.5, 1H); 4.2 (*q*, *J* = 7.2, 4H). Three additional esters have been observed: *(M^+ = 218)* (3.7%), *m/z*: 218 (1), 201 (11), 200 (6), 174 (18), 173 (100), 172 (39), 155 (10), 154 (9), 145 (25), 129 (9), 128 (41), 127 (59), 126 (32), 117 (10), 101 (24), 100 (44), 99 (40), 73 (30), 72 (9), 55 (60), 45 (11); *(M^+ = 200)* (0.5%, *m/z*: 200 (2), 174 (4), 173 (26), 172 (12), 146 (11), 145 (54), 128 (30), 127 (50), 117 (16), 101 (32), 100 (84), 99 (56), 73 (46), 72 (19), 55 *(100)*, 54 (10), 45 (28); *(M^+ = 346)* (0.5%), *m/z*: 300 (5), 281 (1), 254 (10), 201 (20), 174 (10), 173 (100), 172 (52), 171 (8), 155 (16), 145 (21), 144 (14), 128 (10), 127 (51), 126 (49), 101 (12), 100 (13), 99 (50), 98 (75), 97 (14), 83 (16), 73 (15), 70 (14), 67 (11), 56 (75), 55 (75), 54 (10), 43 (13), 41 (24).

Thermolysis of **20b** *in cumene:* **33b** (*a*) (83%); *t-butoxy-S-ethyl thiocarbonate* (**45**) (*c*) (2%), *m/z*: 162 (8), 157 (5), 145 (9), 118 (4), 101 (6), 89 (10), 83 (3), 61 (4), 58 (5), 57 (00), 56 (23), 41 (23). **34a** (*a*) (0.5%); **37b** (*a*) (0.1%); **35b** (*c*) (14%); *m/z* = 247 (1), 205 (6), 173 (10), 145 (10), 127 (27), 118 (11), 117 (22), 116 (10), 115 (16), 101 (14), 100 (14), 99 (44), 89 (34), 87 (14), 75 (29), 73 (11), 59 (54), 58 (56), 57 (100), 56 (23), 55 (58), 54 (11), 43 (24), 41 (44).

Thermolysis of **20b** *in chlorobenzene:* **41** (*a*); **33b** (*a*) (41%); *ethyl(Z)-3-[(ethylthio)carbonyl]-2-propenoate* (**39b**) (*a, b*) (2%); **34b** (*a*) (7%); **37b** (*a*) (2%); **35b** (27%); *ethyl 3-(chlorophenyl)methyl-2-[(ethylthio)-carbonyl]propionate* (**46**) (*c*) (22%), *m/z*: 249 (4), 239 (3), 215 (9), 211 (21), 195 (16), 194 (8), 193 (48), 175 (11), 165 (21), 147 (11), 127 (32), 126 (13), 125 (100), 103 (29), 102 (16), 101 (14), 89 (26), 77 (16), 55 (14).

Thermolysis of **24a** *in Cumene:* **37a** (*a*) (72%); **38a** (*a*) (26%); *(M^+ = 218)* (2.3%), *m/z*: 218 (3), 202 (4), 201 (20), 200 (10), 174 (22), 173 (100), 172 (13), 155 (14), 154 (10), 145 (29), 129 (8), 128 (50), 127 (68), 117 (12), 101 (23), 100 (46), 99 (38), 73 (30), 55 (58), 45 (13), see thermolysis of **20a**; (**41**) could not be found by computer search of all spectra recorded.

Thermolysis of **24b** *in cumene:* **37b** (*a, c*) (55%); **38b** (*c*) (35%); *m/z*: 201 (4), 189 (3), 173 (5), 133 (38), 117 (16), 89 (14), 71 (9), 59 (10), 57 (100), 56 (11), 55 (9), 43 (11), 41 (28). *(M^+ = 232)* (9.8%), *m/z*: 217 (5), 202 (4), 201 (33), 189 (11), 174 (8), 173 (80), 172 (10), 155 (27), 145 (29), 128 (11), 127 (100), 126 (13), 117 (11), 101 (10), 100 (10), 99 (44), 73 (13), 55 (41), 45 (16).

Stability of **37a** *and* **37b** *during Thermolysis of Peresters.* Perester (**20a**) (0.039 g, 0.14 mmol) was heated in 0.5 ml of solvent in the presence of 60 µl of a mixture of **37a** and tridecane for 3 h. Ratios of these two compounds were determined before (and after) reaction by capillary GC; with cumene as solvent 30.5 : 69 : 5 (27.6 : 72.4), with chlorobenzene as solvent 27.8 : 71.2 (27.1 : 72.9). Similarly, perester **20b** (0.048 g, 0.15 mmol) was heated in the presence of 60 µl of a mixture of **37b** and tridecane. Solvent: cumene: ratio = 23.5 : 76.5 (17.8 : 82.2); chlorbenzene: ratio = 22.8 : 77.2 (22.1 : 77.9).

Stability of **37b** *in Photolysis.* Thioester **37b** (0.017 g) and tridecane (0.016 g) were photolyzed in 1 ml cyclohexane for h (125-W high-pressure lamp, quartz vessel). The ratio of the two compounds was determined before (and after) reaction by capillary GC and revealed 52% decomposition of **37b**.

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