Absolute Rates for Dimerization of Capto-dative Substituted Methyl Radicals in Solution: Absence of Kinetic Stabilization

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For three capto-dative substituted methyl radicals, t-butoxy(cyano)methyl radical (1), t-butylthio-(cyano)methyl radical (2), and methoxy(methoxycarbonyl)methyl radical (3), absolute rates for dimerization have been measured by e.s.r. spectroscopy and substantiated by product analysis. Values for the rate constants of 1.0×10^8—1.5×10^9 l mol^{-1} s^{-1} in the temperature range −60 to +60 °C support the diffusion-controlled nature of the dimerization. The comparison of Arrhenius activation parameters for dimerization with those for the bulk viscosity of the solutions does not provide evidence for noticeable intrinsic barriers to recombination, indicating the absence of kinetic stabilization for capto-dative substituted methyl radicals.

The factors which influence the ' stabilization ' of organic free radicals are of current interest in free radical chemistry. Whereas carbanions (carbenium ions) are effectively stabilized by electron acceptors (electron donors), radicals can be stabilized by electron donors as well as electron acceptors.[1] Dewar [2] was the first to suggest that the combined interaction of donor and acceptor substituents on the same radical centre should lead to an enhanced stabilization compared to donor–donor or acceptor–acceptor substitution. Along with contributions from others,[3] Viehe and his co-workers [4] have developed the concept of ' capto-dative ' (donor–acceptor) radical stabilization.

The term ' radical stabilization ', however, must be handled with caution. It has clearly been demonstrated,[5] that one has to distinguish between *stabilized* and *persistent* radicals. Delocalization of an unpaired electron produces thermodynamic stabilization (lowering of ground state energy) of the radical. Nevertheless, the radical can be transient, *i.e.* its lifetime under the same conditions is comparable with that of an undelocalized radical, and its rate of bimolecular termination in solution often approaches the diffusion-controlled limit.[6,7] Persistency, on the other hand, means kinetic stabilization, *i.e.* because of steric hindrance or other reasons, the termination rates of a persistent radical are much slower than those of a typical transient radical under similar conditions. The persistency of some donor–acceptor-substituted radicals [3f–i,4a,k] was assigned primarily to the synergetic capto-dative (cd) substituent effect.[4a,k] However, no quantitative or semiquantitative evaluation of the extent of such a stabilization was possible. We therefore decided to carry out studies in order to examine a possible kinetic and/or thermodynamic stabilization of capto-dative substituted radicals, and, if present, what their quantitative amount might be. Here we present the results of a kinetic study in which we have measured by e.s.r. spectroscopy the dimerization kinetics of capto-dative substituted methyl radicals. An investigation concerning the thermodynamic effects of cd-substitution of organic radicals will be presented in the near future.

For our investigation we have selected t-butoxy(cyano)-methyl radical (1), t-butylthio(cyano)methyl radical (2), and methoxy(methoxycarbonyl)methyl radical (3) for the following reasons. The substituents are common capto- or dative groups; suitable radical precursors are easily synthesized; a relatively high e.s.r. signal intensity is expected because of few hyperfine couplings; steric hindrance of bimolecular radical termination should be low; a different influence of oxygen and sulphur at the radical centre is possibly detectable from the comparison of radicals (1) and (2).

$(CH_3)_3C{-}O{-}\dot{C}H{-}CN$
(1)

$(CH_3)_3C{-}S{-}\dot{C}H{-}CN$
(2)

$CH_3O{-}\dot{C}H{-}CO_2CH_3$
(3)

$$Bu^tO{-}OBu^t \xrightarrow{h\nu} 2\ Bu^tO\cdot \qquad (1)$$

$$Bu^tO\cdot + RH \longrightarrow R\cdot + Bu^tOH \qquad (2)$$

$$2\ R\cdot \xrightarrow{2k_t} R{-}R \qquad (3)$$

Scheme 1

Results

t-Butoxy(cyano)methyl Radical (1).—*E.s.r measurements.* t-Butoxy(cyano)methyl radical (1) was generated by u.v. photolysis of a slow flowing solution containing 10 vol% t-butoxyacetonitrile, 30 vol% di-t-butyl peroxide (DTBP) and 60 vol% chlorobenzene (Scheme 1).†

Figure 1 displays e.s.r. spectra recorded at −52 and +26 °C. The unusual intensity distribution at −52 °C indicates the co-existence of two radicals, presumably the conformational isomers (1a) and (1b). Because of the very small differences in the coupling constants and *g* values of (1a and b) (comparable with the line width) we were only able to determine by computer simulation the parameters for the main isomer (see Table 1). At *ca.* +25 °C the interconversion of (1a and b) is fast compared to the e.s.r. time scale and an averaged spectrum is observed.

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† No e.s.r. signals were detected if solutions of the radical precursors for (1)—(3) were photolysed in the absence of DTBP.

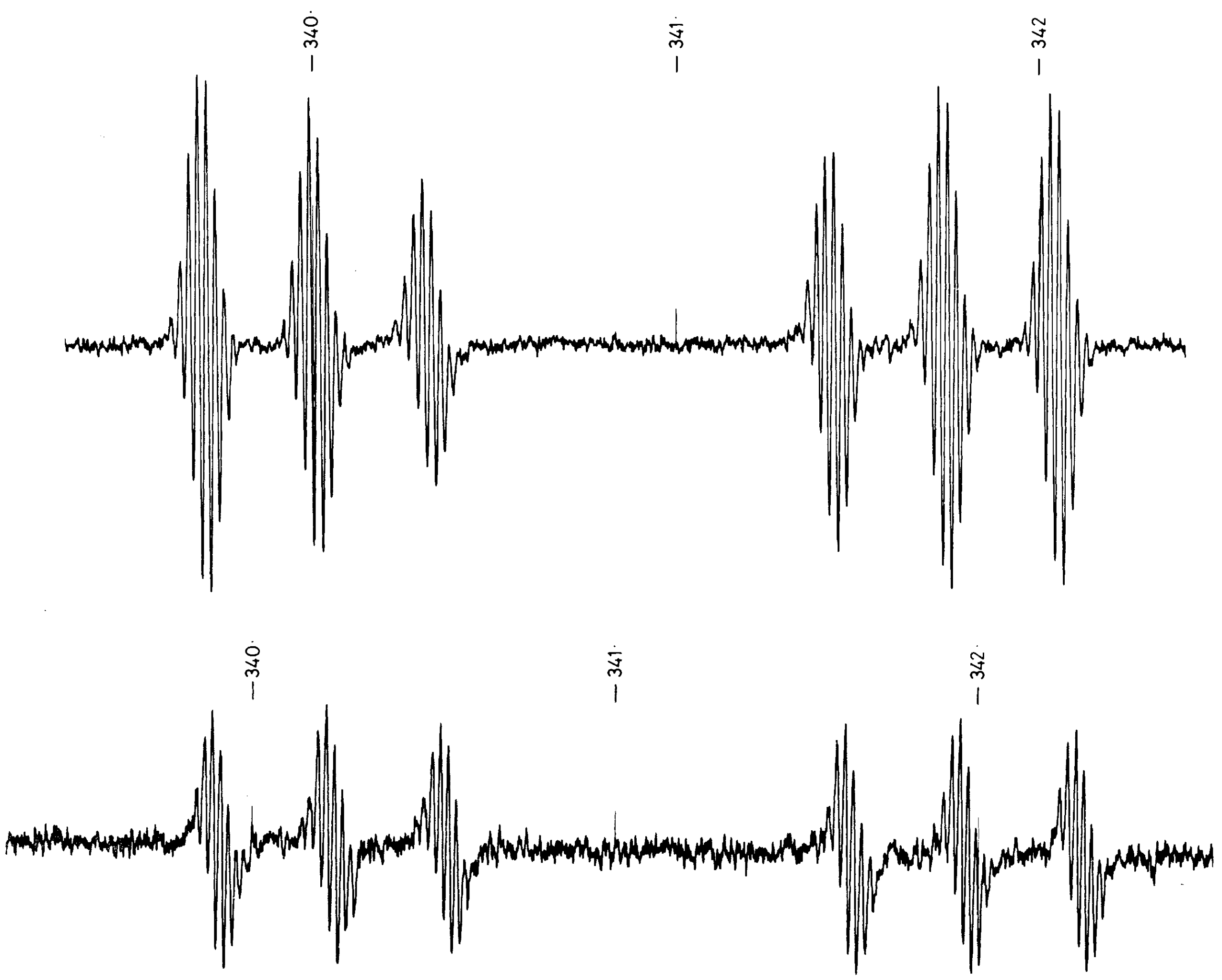


Figure 1. E.s.r. spectra of t-butoxy(cyano)methyl radicals (1) at −52 °C (top) and +26 °C (bottom). Radicals generated from t-butoxyacetonitrile by reaction with t-butoxyl radicals in chlorobenzene solution. Field markers in mT

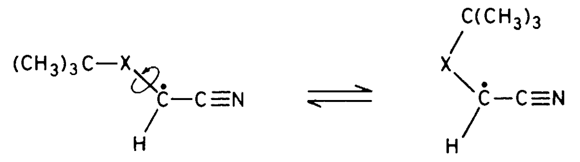
Kinetic measurements. The time-resolved measurements of the termination rate of radical (1) were performed by use of e.s.r. spectroscopy by the rotating-sector method of intermittent photolytic radical generation.[6,7] During the measurements, the solution, containing 10 vol% t-butoxyacetonitrile, 30 vol% DTBP, and 60 vol% chlorobenzene, was slowly pumped through a flat quartz cell inside the e.s.r. cavity (see Experimental section). The decay curves of the radical concentration were analysed in terms of a bimolecular self-termination of radical (1) according to equation (3). The data, collected in the temperature range from −66 to +59 °C, fit the second-order rate law (4) very well ($r^2 > 0.99$). Absolute rate constants are shown in Table 2. The values (1.1×10^8—1.8×10^9 l mol^{-1} s^{-1}) lie in the range for a diffusion-controlled radical self-termination.

$$[R] = [R]_0/(1 + 2k_t[R]_0t) \qquad (4)$$

The Arrhenius plot of the rate constants shows a slight degressive curvature. Because the scattering of the rate constants due to experimental error is too small to account for this effect, there must be an inherent influence of the medium on the radical recombination rate, which (relatively) decreases the rate constants with increasing temperature, or *vice versa.* The Arrhenius activation energy therefore, could not be evaluated exactly from the plot. The forced linear regression including all experimental points yields E_a 13.82 ± 0.50 kJ mol^{-1} and log A 11.29 ± 0.09 (r^2 0.957), whereas the least-squares fit to the low-temperature values (−66 to +2 °C) which show better linearity (r^2 0.985), gives E_a 15.41 ± 0.42 kJ mol^{-1} and log A 11.95 ± 0.09.

The activation energy E_a of diffusion-controlled bimolecular radical terminations should be very similar to the energies of activation E_η for the bulk viscosities.[7-9] For our solution we found from the temperature dependence of the viscosity E_η 12.39 ± 0.38 kJ mol^{-1}. This value agrees well with the Arrhenius activation energy (E_a 15.41 kJ mol^{-1} can be regarded as an upper limit) and supports the diffusion-controlled or nearly diffusion-controlled self-termination of radical (1). The plot of log η *versus* $1/T$ according to Andrade's law shows a very slight, progressive curvature. This behaviour corresponds to the degressive curvature of the Arrhenius plot, *i.e.* the slower increase of the rate constants with increasing temperature is connected to a slower decrease of the solution viscosity. The latter effect, however, seems to be too small to explain the unusual temperature dependence of the rate constants.

Product analyses. The evaluation of kinetic parameters from the time profile of radical decay by a specific rate equation has to be justified by the product distribution. The



(1a) X = O (1b)
(2a) X = S (2b)

Table 1. E.s.r. parameters of capto-dative substituted methyl radicals

Radical	T/K	g Factor [a]	Hyperfine splitting (mT) [b]
(1)	221	2.003 80	1.738 (1H$_\alpha$) 0.024 (3H$_\delta$) 0.310 (1N)
(1)	299	2.003 43	1.744 (1H$_\alpha$) 0.022 (3H$_\delta$) 0.315 (1N)
(2a)	209	2.005 71	1.502 (1H$_\alpha$) [c] 0.268 (1N)
(2b)	209	2.005 67	1.495 (1H$_\alpha$) [c] 0.277 (1N)
(2)	298	2.005 61	1.482 (1H$_\alpha$) [c] 0.268 (1N)
(3a)	215 [e]	2.003 98	1.762 (1H$_\alpha$) 0.285 (3H$_\gamma$) 0.159 (3H$_\delta$)
(3b)	215	2.004 07	1.740 (1H$_\alpha$) 0.282 (3H$_\gamma$) 0.112 (3H$_\delta$)
(3a)	278 [f]	2.003 99	1.755 (1H$_\alpha$) 0.280 (3H$_\gamma$) 0.155 (3H$_\delta$)
(3b)	278	2.004 11	1.740 (1H$_\alpha$) 0.278 (3H$_\gamma$) 0.105 (3H$_\delta$)

[a] ±0.000 02. [b] ±0.002 mT. [c] Peak-to-peak line width 0.03 mT. [d] (2a) Tentatively assigned to *s-trans*-conformer, (2b) assigned to *s-cis*-conformer; ratio (2a) : (2b) 2.5. [e] Ratio (3a) : (3b) 2.2. [f] Ratio (3a) : (3b) 1.3.

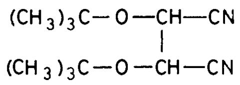
neglect of this requirement can lead to serious errors in the kinetic parameters as the detection of complex radical termination reactions from the time profile of radical concentration may be very difficult.[10]

To confirm the assumed second-order self-termination, we have analysed the solutions used in the kinetic measurements by g.l.c. and spectroscopic methods. The g.l.c. analysis of the solution after irradiation indicates *ca.* 5% conversion of the radical precursor t-butoxyacetonitrile during the kinetic measurements. Two main products in the ratio 1 : 1 and only one minor side-product were detected. To achieve greater conversion of the substrates, we irradiated equal amounts of the stock solution for 0.5 h under the conditions of the e.s.r. experiment in the temperature range −60 to +42 °C. G.l.c. analysis leads to the following results: the two main products account for 85—89% of all new material (except t-butyl alcohol) and show a constant ratio of 1.02 ± 0.12; the relative amount of the side-product changes from 4.2% at −60 °C to 5.5% at −35 °C and to 2.1% at +42 °C; the remaining 8.6 ± 2.3% of the photolysis products contain more than nine compounds in nearly equal amounts. These products are partly due to secondary photolytic reactions of the primary products, because their relative amount increases with increasing photolysis time. The main products, isolated by preparative g.l.c. and characterized by spectroscopic methods, are the expected *meso*- and DL-dimers (4) (2,3-di-t-butoxysuccinonitrile) of radical (1). The yield of the side-product was too low to allow isolation. Its mass spectrum (g.l.c.–m.s.-coupling) shows no peak which can be assigned to a molecular ion but clearly indicates the $(CH_3)_3COCHCN$ unit. Therefore this substrate seems to be a recombination product of radical (1) with some other radical, which could not be identified unambiguously by the mass spectral data.

Table 2. Absolute rate constants of t-butoxy(cyano)methyl radical (1)

T/K [a]	$2 \times 10^{-8}k_t^{exp}$/ l mol^{-1} s^{-1} [b]	η/cP [c]	$2 \times 10^{-8}k_t^{D}$/ l mol^{-1} s^{-1} [d]	$2k_t^{exp} : 2k_t^{D}$
208	1.10 ± 0.05			
221	2.03 ± 0.03	6.65	1.84	1.10
228	3.25 ± 0.14	4.81	2.63	1.24
238	3.75 ± 0.19	3.21	4.11	0.91
241	4.46 ± 0.32	2.95	4.52	0.99
248	5.21 ± 0.18	2.26	6.09	0.86
255	6.19 ± 0.35	1.90	7.43	0.83
261	7.12 ± 0.45	1.63	8.87	0.80
269	9.78 ± 1.13	1.36	10.96	0.89
276	10.09 ± 0.21	1.19	12.88	0.78
285	11.70 ± 1.71	1.01	15.73	0.74
290	11.42 ± 0.47	0.92	27.48	0.65
300	12.94 ± 0.80	0.78	21.52	0.60
311	14.29 ± 2.41	0.68	25.26	0.57
332	17.67 ± 1.47	0.54	34.30	0.52

[a] ±1.5 K. [b] Average of 8 decay curves. [c] Extracted from the plot log η *versus* 1/*T*. [d] Calculated by equation (7).



$$\begin{array}{c}(CH_3)_3C-O-CH-CN\\ \quad\;\;|\\ (CH_3)_3C-O-CH-CN\end{array}$$

(4)

The results confirm the assumption of an almost pure bimolecular self-termination of radical (1), The detected side-reaction seems to be too low for altering the order of magnitude of the determined rate constants significantly.

t-*Butylthio*(*cyano*)*methyl Radical* (2).—*E.s.r. measurements.* U.v. photolysis of a solution containing 10 vol% t-butylthioacetonitrile, 30 vol% DTBP, and 60 vol% chlorobenzene produces an intense e.s.r. spectrum of the t-butylthio(cyano)methyl radical (2) (Figure 2). The e.s.r. spectrum recorded at −64 °C indicates the presence of two conformational isomers (2a and b) (ratio 2.5 : 1), just as for radical (1). Computer simulation leads to the spectral parameters listed in Table 1. The more intense component of the e.s.r. spectrum was tentatively assigned to the *s-trans*-conformer (2a). At +25 °C a nearly undistorted spectrum is observed, indicating rapid interconversion of the two conformers.

Kinetic measurements. For radical (2) the time-resolved e.s.r. measurements were carried out in the temperature range −53 to +25 °C, using a solution of the same composition as for the above steady-state e.s.r. measurement. The kinetic analysis yields excellent least-squares fits ($r^2 > 0.99$) of the second-order rate law (4) to the time profile of radical concentration in the dark period of the rotating sector. The rate constants (Table 3) range from 0.95×10^8 to 1.62×10^9 l mol^{-1} s^{-1}, suggesting a diffusion-controlled rate of bimolecular radical termination. The second-order decay of radical (2)

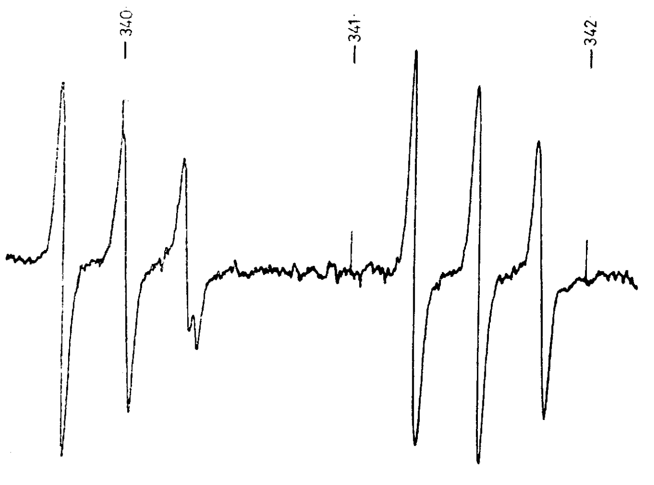


Figure 2. E.s.r. spectrum of t-butylthio(cyano)methyl radicals (2) at −64 °C, generated from t-butylthioacetonitrile by reaction with t-butoxyl radicals in chlorobenzene solution. Field markers in mT

Table 3. Absolute rate constants of t-butylthio(cyano)methyl radical (2)

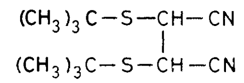
T/K [a]	$2 \times 10^{-8}k_t^{exp}$/ l mol^{-1} s^{-1} [b]	η/cP	$2 \times 10^{-8}k_t^{D}$/ l mol^{-1} s^{-1} [c]	$2k_t^{exp} : 2k_t^{D}$
210	0.95 ± 0.11	7.46	1.56	0.82
220	1.35 ± 0.05	5.35	2.88	0.59
221	1.10 ± 0.05	5.26	2.32	0.47
233	2.29 ± 0.11	3.59	3.60	0.64
234	2.25 ± 0.13	3.53	3.67	0.61
239	3.40 ± 0.14	3.05	4.34	0.78
253	5.04 ± 0.27	2.12	6.61	0.76
257	6.09 ± 0.55	1.92	7.41	0.82
263	7.42 ± 0.28	1.68	8.66	0.86
270	8.72 ± 0.61	1.44	10.38	0.84
277	10.01 ± 0.30	1.22	12.61	0.79
291	14.10 ± 1.59	0.93	17.37	0.81
299	16.18 ± 1.74	0.82	20.18	0.80

[a] ±1.5 K. [b] Average of 8 decay curves. [c] Calculated by equation (7).

was supported by the linear dependence of the e.s.r. signal intensity on the square-root of the incident light intensity, measured at −51 and +8 °C.

From the corresponding linear (r^2 0.988) Arrhenius plot of the rate constants an activation energy of E_a 18.51 ± 0.67 kJ mol^{-1} (log A 12.51 ± 0.14) was calculated. Whereas the rate constants lie in the range expected for diffusion-controlled reactions, the determined activation energy is higher than the activation energy E_η for the viscosity of the solution. The latter, evaluated from the linear plot of log η *versus* $1/T$ amounts to E_η 13.11 ± 0.13 kJ mol^{-1}. The difference $E_a - E_\eta$ of 5.4 kJ mol^{-1} seems to be too high to be attributed solely to experimental errors.

Product analyses. The g.l.c. analysis of the photolysed solutions used in the kinetic runs showed the build-up of two main products with concentration ratio 1 : 1. The relative conversion of the radical precursor t-butylthioacetonitrile was *ca.* 1.5—2%. The two main products count for 94.8 ± 2.1% of all new material (except t-butyl alcohol) and their relative amount remains constant (1.0 ± 0.1) in the temperature range from −63 to +50 °C, as was determined by stationary photolyses (0.5 h) of a freshly prepared solution. After isolation by column and thin layer chromatography, the products were identified as *meso*- and DL-dimers (5) of radical (2). Thus, bimolecular recombination at the radical centre is essentially the only way for termination of radical (2).



$$\begin{array}{l}(CH_3)_3C-S-CH-CN\\ \qquad\qquad\quad\ |\\ (CH_3)_3C-S-CH-CN\end{array}$$

(5)

Methoxy(methoxycarbonyl)methyl Radical (3).—*E.s.r. measurements.* During u.v. photolysis of a solution of 20 vol% methyl methoxyacetate, 30 vol% DTBP, and 50 vol% chlorobenzene at −58 °C the e.s.r. spectrum displayed in Figure 3 was recorded. The spectrum results from the superposition of three individual spectra in the ratio 2.2 : 1 : 0.25, which we attribute to conformational isomers (3a and b) of the methoxy(methoxycarbonyl)methyl radical (3) and to radical (6) generated by hydrogen abstraction from the ether methyl group of methoxyacetate. The hyperfine splittings (Table 1) were determined by computer simulation; the assignment to conformers (3a and b), respectively, is arbitrary. An assignment to conformers resulting from rotation about the $CH_3O-\dot{C}H$ bond may also be possible. Justification for the assignment of the minor spectrum [a_H 1.748 (2H), a_H 0.183 mT (2H), g 2.00315] to radical (6) and not to the analogous radical derived from hydrogen abstraction at the ester methyl group is given by product analysis (see below).

To avoid the formation of radical (6) which would disturb the kinetic measurements, we generated radicals (3a and b) by photolysis of a solution containing 23 vol% methyl α-bromo-α-methoxyacetate, 23 vol% DTBP, 23 vol% triethylsilane, and 31 vol% chlorobenzene according to Scheme 2. In this case, at −54 °C the ratio (3a) : (3b) amounts to 2 : 1 and no other radical is observed.

Kinetic measurements. Because the e.s.r. spectra reveal the formation of radical (6) if methyl methoxyacetate is the radical precursor, we have chosen the method of halogen abstraction by triethylsilyl radicals (Scheme 2) for producing radical (3) in the kinetic investigations. The decay of (3) was followed e.s.r. spectroscopically using the above solution in the temperature range from −14 to +33 °C. Fairly good second-order fits (r^2 0.933—0.999) were obtained; the rate constants range from 5.5 × 10^8 to 2.5 × 10^9 l mol^{-1} s^{-1}. Whereas the rate constants are reasonable for a diffusion-controlled bimolecular decay, the Arrhenius parameters E_a 20.85 ± 1.13 kJ mol^{-1} and log A 12.96 ± 0.21 are exceedingly high. The temperature dependence of the solution viscosity only gives E_η 11.51 ± 0.17 kJ mol^{-1}. This discrepancy suggests some complication in the assumed radical reactions, which is supported by the increasing ratio $2k_t^{exp} : 2k_t^{D}$ with increasing temperature (see Table 4 and Discussion section). An explanation for the discrepancy was given by the product studies: during the photolysis an additional decay reaction of radical (3) takes place to an appreciable extent. Therefore, the second-order rate law (4) is no longer valid.

In order to get an additional estimate of the kinetic parameters, we also used methyl methoxyacetate as radical precursor. Using a solution composed from 20 vol% $CH_3OCH_2CO_2CH_3$, 30 vol% DTBP, and 50 vol% chlorobenzene the decay of (3) was measured in the temperature range −58 to −6 °C. The kinetic parameters were evaluated on the basis of a pure bimolecular self-termination of radical (3) neglecting the additional decay reaction Rate constants from 3.0 × 10^8 to 1.6 × 10^9 l mol^{-1} s^{-1} were obtained (Table

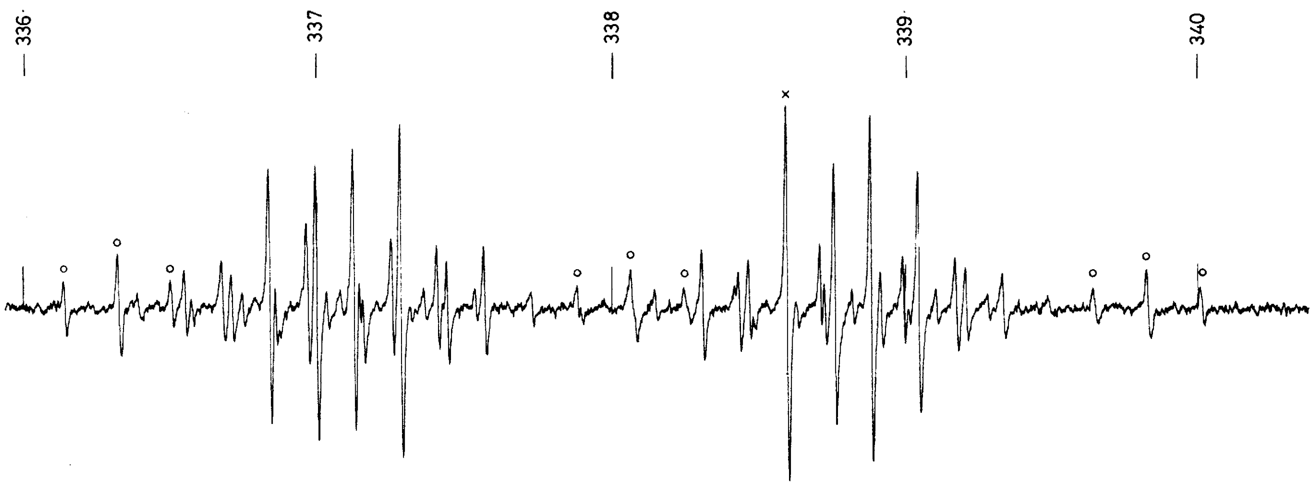
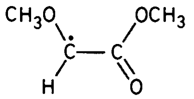
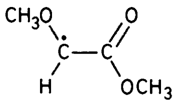


Figure 3. E.s.r. spectrum of methoxy(methoxycarbonyl)methyl radicals (3) at −58 °C, generated from methyl methoxyacetate by reaction with t-butoxyl radicals in chlorobenzene solution. Signals of $\cdot CH_2OCH_2CO_2CH_3$ radicals (6) are denoted by circles. The cross marks the hyperfine splitting line used in the kinetic measurements. Field markers in mT



(3a)



(3b)

$\cdot CH_2O{-}CH_2{-}CO_2CH_3$

(6)

$$Bu^tO{-}OBu^t \xrightarrow{h\nu} 2\ Bu^tO\cdot \quad (5)$$

$$Bu^tO\cdot + Et_3SiH \longrightarrow Et_3Si\cdot + Bu^tOH \quad (6)$$

$$Et_3Si\cdot + RX \longrightarrow R\cdot + Et_3SiX \quad (7)$$

$$2R\cdot \xrightarrow{2k_t} R{-}R \quad (8)$$

Scheme 2

4). The Arrhenius plot (r^2 0.987) gives E_a 15.95 ± 0.92 kJ mol^{-1} and log A 12.32 ± 0.20. The comparison of the activation energy with the temperature coefficient E_η 14.03 ± 0.04 kJ mol^{-1} of the viscosity manifests good correspondence. According to product analysis (see below) *ca.* 15% of radical (3) is destroyed by recombination with radical (6). Thus, the effect on the kinetic parameters is close to the standard deviation. The data demonstrate the diffusion control of the reaction.

Table 4. Absolute rate constants of methoxy(methoxycarbonyl)methyl radical (3)

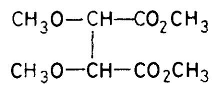
	T/K [a]	$2 \times 10^{-8}k_t^{exp}$/ l mol^{-1} s^{-1} [b]	η/cP	2×10^{-8} k_t^D/ l mol^{-1} s^{-1} [c]	$2k_t^{exp}$: $2k_D$
d	260	5.5 ± 0.3	1.80	8.0	0.69
	264	6.7 ± 0.8	1.63	9.0	0.74
	268	8.2 ± 0.2	1.51	9.9	0.83
	276	11.3 ± 0.4	1.30	11.8	0.96
	285	14.0 ± 1.3	1.11	14.2	0.99
	291	16.3 ± 2.4	1.00	16.1	1.01
	296	21.6 ± 1.3	0.94	17.5	1.23
	297	17.9 ± 0.7	0.90	18.0	1.00
	306	25.1 ± 1.4	0.80	21.2	1.18
e	215	3.01 ± 0.18	7.13	1.67	1.80
	235	6.31 ± 0.35	3.65	3.57	1.77
	251	9.15 ± 0.66	2.29	6.08	1.50
	267	16.10 ± 0.88	1.54	9.60	1.68

[a] ±1.5 K. [b] Average of 8 decay curves. [c] Calculated by equation (7). [d] Solution 23% methyl bromomethoxyacetate, 23% DTBP, 23% triethylsilane, 31% chlorobenzene. [e] Solution 20% methyl methoxyacetate, 30% DTBP, 50% chlorobenzene

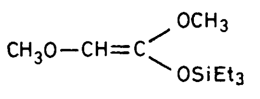
Product analyses. As mentioned above, the e.s.r. spectrum recorded during photolysis of a $CH_3OCH(Br)CO_2CH_3$–DTBP–Et_3SiH–chlorobenzene mixture only displays the signals of radicals (3a and b). Analysis of the photolysed solution, however, some days after the kinetic measurements yielded methyl dimethoxyacetate, hexaethyldisiloxane, and t-butyl bromide as main products, besides a broad spectrum of other compounds in lesser amounts. G.l.c., g.l.c.–m.s., and ^1H n.m.r. analysis after photolysis of freshly prepared solutions at +30 °C under the conditions of the e.s.r. experiments for 0.5 h, immediately and some time after having finished the photolysis gave different results: the overall yield of products was 15—16% in good correspondence with the consumption of the starting material (14—15%); >20 compounds in different amounts accounted for the products. Six minutes after termination of the photolysis the main products were Bu^tOH (19.5%), Bu^tBr (6%), $BrSiEt_3$ (40%), the *meso*- and DL-dimer (7) of radical (3) (7%), and a product which constitutes the sum of a methoxy(methoxycarbonyl)methyl group and a triethylsilyl group. It may formally derive from a radical recombination reaction of (3) and triethylsilyl radical. The mass spectrum can be interpreted in terms of structure (8).

G.l.c. runs of the same solution after prolonged periods of time reveal a slow decay of Bu^tOH, $BrSiEt_3$, Et_3SiH, $CH_3OCH(Br)CO_2CH_3$, and (8) in conjunction with the formation of Bu^tBr, $(CH_3O)_2CHCO_2CH_3$, hexaethyldisiloxane, and product (9). These compounds were isolated in pure form. The most important result of this product study is the occurrence of (8), indicating an additional process for the disappearance of radical (3). This side-reaction destroys 30—40% of radical (3). Therefore, the deviation of the kinetic parameters from the expected values is not surprising.

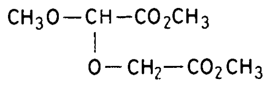
G.l.c. analysis of the photolysed methyl methoxyacetate–DTBP–chlorobenzene solution shows the formation of three


$$\begin{array}{l} CH_3O-CH-CO_2CH_3 \\ \quad\;\; | \\ CH_3O-CH-CO_2CH_3 \end{array}$$

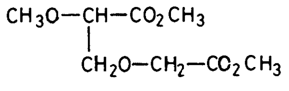
(7)



(8)


$$\begin{array}{l} CH_3O-CH-CO_2CH_3 \\ \quad\;\; | \\ \quad\;\; O-CH_2-CO_2CH_3 \end{array}$$

(9)


$$\begin{array}{l} CH_3O-CH-CO_2CH_3 \\ \quad\;\; | \\ \quad\;\; CH_2O-CH_2-CO_2CH_3 \end{array}$$

(10)

main products in the ratio 1.3 : 1.2 : 1. After separation by preparative g.l.c., the n.m.r. and mass spectra reveal these products to be the *meso*- and DL-dimers (7) of radical (3) and the cross-coupling product (10), formed by recombination of radicals (3) and (6).*

Discussion

As mentioned in the introduction, the presence of radical-stabilizing substituents, *e.g.* CN, $CH{:}CH_2$, OR, CO_2R, C_6H_5, *etc.*, will not necessarily change the termination rate of a particular radical. This has clearly been demonstrated in the case of delocalized radicals, such as allyl,[6,7b] benzyl,[7a] cyanoallyl,[11] and a multitude of other carbon-centred and hetero-atom-centred radicals bearing radical-stabilizing substituents.[7c] Because the introduction of a radical-stabilizing substituent relatively lowers the ground-state energy of the radical, some reaction paths for radical decay (*e.g.* disproportionation, atom abstraction) may no longer be accessible. Nevertheless, radical termination still can occur with a diffusion-controlled rate *via* dimerization. The latter situation holds for the cd-radicals (1)—(3). As shown by product analysis, recombination of the radicals is the almost exclusive way of termination.

At ambient temperatures, bimolecular rate constants in the range 10^9—10^{10} l mol^{-1} s^{-1} and activation energies close to the activation energies for translational diffusion are arguments for the diffusion control of radical self-termination in solutions of low viscosity.[5, 9] Theoretical rate constants of diffusion-controlled bimolecular radical reactions are often calculated by the Smoluchowski equation (9). In many cases, a

$$2k_t^D = 8\pi D\rho\sigma N_L 1000^{-1} \qquad (9)$$

fairly good agreement between experimental and calculated rate constants is found[7-9] ($2k_t^{exp} : 2k_t^D \simeq 1$). If the diffusion coefficient D is unknown, it can be approximated by the dynamic viscosity η of the solvent, using the Stokes–Einstein equation (10) or related equations.[8] Combination of (9) and

$$D = kT/6\pi r\eta \qquad (10)$$

$$2k_t^D = RT/1500\eta \qquad (11)$$

(10) leads to equation (11) from which estimates of diffusion-controlled rate constants can be calculated in a simple manner. Sometimes corrections are introduced[8] in equation (11) to achieve complete correspondence between experimental and calculated rate constants. However, in our study corrections do not seem to be practicable because of the high concentration of the radical precursors and DTBP in the radical-generating solutions. Thus, we calculated the theoretical rate constants by using equation (11) in order to get some indications of rate-influencing effects. Calculated rate constants $2k_t^D$ and $2k_t^{exp} : 2k_t^D$ ratios are collected in the last two columns of Tables 2—4.

In the case of the t-butoxy(cyano)methyl radical (1) the agreement between $2k_t^{exp}$ and $2k_t^D$ † is surprisingly good at low temperatures but diverges with increasing temperature (Table 2). The almost continuous lowering of the ratio $2k_t^{exp} : 2k_t^D$ can be interpreted in such a way, that there is no longer a *complete* diffusion control of the recombination at temperatures above 0 °C. Possibly, a more rapid rotation about the C–OBu^t bond leads to a higher steric repulsion in the encounter radical pair at elevated temperatures, slightly reducing the recombination rates. Nevertheless, because the corresponding Arrhenius activation energy E_a is in good agreement with the viscosity activation energy E_η, the dimerization of (1) still can be safely regarded as diffusion-controlled.

For the t-butylthio(cyano)methyl radical (2) the values of $2k_t^{exp} : 2k_t^D$ are constantly lower than 1 (0.72 ± 0.12) thus indicating slightly lower than complete diffusion-controlled recombination rates. This view is supported by the 5.4 kJ mol^{-1} higher value of the activation energy compared to the viscosity activation energy. Near at hand are small steric effects of the SBu^t group but electronic repulsion due to the lone pairs of the sulphur atoms or radical–solvent interactions may also be possible.

The assumption of small steric interactions in the dimerization of radicals (1) and (2) is supported by the $2k_t^{exp} : 2k_t^D$ values calculated for the methoxy(methoxycarbonyl)methyl radical (3), generated from methyl methoxyacetate by hydrogen abstraction (see lower part of Table 4). Here, as generally found,[8,9] the ratios $2k_t^{exp} : 2k_t^D$ are >1 and the specified activation energies E_a and E_η are comparable, indicating complete diffusion control of dimerization of radical (3). The exceedingly high activation energy in the case of the silane-generated radical (3) is easily explained by the above mentioned side-reaction. In this case, the displayed values of $2k_t^{exp}$, E_a, and log A are of little significance. They are presented here only for demonstration purposes.

According to equation (11) diffusion-controlled rate constants should be linearly dependent on $T\eta^{-1}$. Such a correlation is customarily regarded as evidence for the diffusion control of the reaction rate.[7-9] Figure 4 displays the plot of the experimental rate constants $2k_t^{exp}$ of radicals (1)—(3) *versus* $T\eta^{-1}$ together with the theoretically expected $2k_t^D$, calculated by equation (11). The linear behaviour is fulfilled in all cases for values of $T\eta^{-1}$ lower than 3×10^4 KP^{-1} but for t-butoxy(cyano)methyl radical (1) an increasing deviation from linearity occurs at higher values. Figure 4 illustrated the conclusions drawn from the ratio $2k_t^{exp} : 2k_t^D$: the recombination rate of methoxy(methoxycarbonyl)methyl radical (3) can be regarded as completely diffusion-controlled because the values of the rate constants are always higher than those predicted by equation (11), in good agreement with the results found for other sterically unhindered carbon-centred radicals, *e.g.* t-butyl[8] and allyl.[6] The lower than predicted rate constants of radicals (1) and (2) may indicate a factor which decreases the rate of recombination. As the effect is very small we hesitate to interpret this as consequence of capto-dative substitution.

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* In contrast to this result, no significant formation of the cross-coupling product (10) was found in the thermolysis of methyl methoxyacetate in DTBP at 140 °C.[4d] This may be due to rapid intermolecular hydrogen transfer between methyl methoxyacetate and radical (6) at higher temperatures.

† $2k_t^D$ was calculated with the actual values of η taking into consideration the curvature of the plot log η *versus* $1/T$.

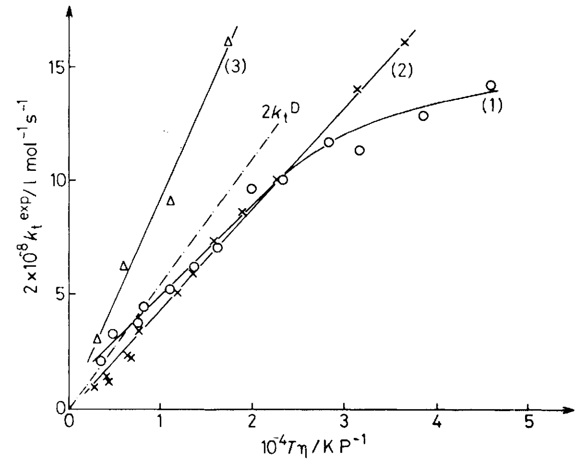

Figure 4. Plot of the experimental second-order rate constants of radicals (1)—(3) *versus* $T\eta^{-1}$

From the comparison with the rate of recombination of methoxy(methoxycarbonyl)methyl radical only a small steric effect might be invoked. As a general conclusion, however, we can state that the results do not indicate noticeable intrinsic kinetic stabilization of the radicals due to electronic effects of the capto-dative substituents.

Experimental

E.s.r. Measurements.—Radicals were generated from the solutions by u.v. photolysis (1 kW Hg–Xe lamp, Hanovia 977B-1) while slowly flowing (0.2 ml min^{-1}) through a flat quartz cell (0.7 mm optical path length) inside the cavity of a X-band e.s.r. spectrometer (Bruker ER-420). Most of the experimental arrangement has been described elsewhere.[6] In this study the light was filtered by a combination of uranium-glass filters (UG-5 and UG-11; 0.3, 0.5 mm; Schott).

Chlorobenzene (Merck) was purified by distillation over P_2O_5 and filtered over basic alumina (Woelm) prior to use. Di-t-butyl peroxide (DTBP) (Peroxid Chemie) was passed over neutral alumina.

The solutions were deoxygenated by purging with dry argon for 1 h.

Spectra simulations were carried out on a Digital Equipment PDP-41/34 minicomputer (128 kB) using an extended version of a QCPE program.[12]

Time-resolved E.s.r. Measurements.—Details of the rotating-sector arrangement were described elsewhere.[6] The equipment was improved by using a signal-averager (Tracor-Northern NS-570A-2; 2048 addresses) connected to a PDP-11/34 computer, equipped with a graphic display (Tektronix 4010) and a digital plotter (Tewidata 281). The decay data, stored on magnetic disk, were fitted to equation (4) using a nonlinear least-squares fit program.[13] Data handling, transfer, and plotting was performed using self-written routines. For details of the temperature measurement and determination of the absolute radical concentration see ref. 6.

Viscosity Measurements.—Dynamic viscosities of the solutions used in the kinetic experiments were determined with the aid of an Ubbelohde microviscosimeter (Schott).

Materials.—t-Butoxyacetonitrile was synthesized[14] from glycolonitrile and isobutene in 57% yield, b.p. 69—70 °C at 15 mbar. t-Butylthioacetonitrile was synthesized from sodium t-butylmercaptan and chloroacetonitrile,[15] b.p. 68 °C at 9.5 mbar. Methyl methoxyacetate was prepared from chloroacetic acid by the method of Moffet[16] in 50% yield, b.p. 131 °C at 763 mmHg. Methyl (α-bromo-α-methoxyacetate) was prepared by bromination of methyl methoxyacetate[17] in 85% yield, b.p. 72—74 °C at 5 mmHg.

Product Analyses.—^{1}H and ^{13}C n.m.r. spectra were recorded on a Varian XL-200 spectrometer at ambient temperature for C_6D_6 as solvent and Me_4Si as internal standard. Mass spectra (70 eV) were obtained with a Varian MAT 312/188 spectrometer coupled to a Varian 3700 g.l.c. instrument equipped with a 70 m OV-101 glass capillary column. G.l.c. analyses were carried out on a Varian 3700 instrument with a 70 m SE-30 glass capillary column. The percentages given in the text refer to integrated peak areas. I.r. spectra were recorded on a Perkin-Elmer 397 spectrometer.

Samples (2.0 ml) of the deoxygenated solutions were irradiated in sealed quartz tubes (5 mm i.d.) under the conditions of the e.s.r. experiments at different temperatures (u.v. source Hanovia 977B-1 instrument with UG-5 and UG-11 filters). Identification of products occurred by g.l.c. comparison with authentic samples and/or g.l.c.–m.s. Major reaction products were isolated either by preparative g.l.c. (column A: 2 m glass column, 0.5 in, packed with 10% SE-30 on Chromosorb G; column B: 3 m aluminium column, 0.5 in, packed with 10% DEGS on Chromosorb G) or by preparative column and thin layer chromatography on silica gel.

meso-2,3-Di-t-butoxysuccinonitrile (4) was isolated by g.l.c. (column B) at 175 °C, m.p. 115 °C (sublimation), δ_H 1.07 (9 H, s) and 4.10 (1 H, s); δ_C 27.0 (q), 63.5 (d), 78.3 (s), and 118.1 p.p.m. (s). $\nu_{max.}$ 2 165vw, 1 390, 1 370s, and 1 095vs cm^{-1}; *m*/*e* 209 (0.3%, $M^+ - CH_3$), 113 (3.3), 57 (100), 43 (16), and 41 (17.7).

DL-2,3-Di-t-butoxysuccinonitrile (4) was isolated by g.l.c. at 175 °C, m.p. 131 °C. δ_H 1.04 (9 H, s), and 3.9 (1 H, s); δ_C 27.1 (q), 63.7 (d), 77.8 (s), and 117.3 p.p.m. (s); $\nu_{max.}$ 2 155vw, 1 390m, and 1 085vs cm^{-1}; m.s. identical with that of *meso*-isomer.

meso-2,3-Bis-t-butylthiosuccinonitrile (5) was isolated by preparative t.l.c. (ether–light petroleum 1 : 3) forming light brown hexagons, m.p. 138—140 °C, δ_H 1.00 (9 H, s) and 3.40 (1 H, s); δ_C 30.2(q), 34.2(d), 46.3(s), and 117.8 p.p.m. (s); $\nu_{max.}$ 2 245m, 1 360, 1 370s, and 1 160s,br cm^{-1}; *m*/*e* 256 (2.7%, M^+), 129 (16.2, $M^+/2$), and 57 [100, $(CH_3)_3C^+$].

DL-2,3-Bis-t-butylthiosuccinonitrile (5) was isolated by preparative t.l.c. (ether–light petroleum 1 : 3), m.p. 118—120 °C, δ_H 1.11 (9 H, s) and 3.56 (1 H, s); δ_C 30.3 (q), 34.8 (d), 46.0 (s), and 118.0 p.p.m. (s), $\nu_{max.}$ 2 240m, 1 365, 1 370s, and 1 155s,br cm^{-1}; m.s. identical with that of *meso*-isomer.

Dimethyl 2,3-dimethoxysuccinate (7) was a mixture of *meso*- and DL-isomers isolated by preparative g.l.c. (column B) at 195 °C, crystals, m.p. 33—36 °C, δ_H 3.30 (3 H, s), 3.33 (3 H, s), 3.58 (6 H, s), 4.20 (2 H, s), and 4.27 (1 H, s); δ_C 51.7 (q), 59.0 (q), 58.6 (q), 81.5 (d), 81.7 (d), 169.4 (s), and 169.5 p.p.m. (s); *m*/*e* 206 (0.7% M^+), 119 (77.4), 103 (100, $M^+/2$), 75 (79.4), and 45 (55.7); identical spectra for *meso*- and DL-isomers found.

Methyldimethoxyacetate was isolated from the photolysed solution by distillation, b.p. 62 °C at 16 mbar (lit.,[18] 67 °C at 18 mmHg), and purified by preparative g.l.c. (column A), δ_H 3.28 (6 H, s), 3.53 (3 H, s), and 4.73 (1 H, s); δ_C 51.7 (q), 53.5 (q), 99.4 (d), and 167.6 p.p.m. (s); *m*/*e* 133 (0.2%, $M^+ - 1$), 103 (8.0, $M^+ - OCH_3$), 75 (100, $M^+ - CO_2CH_3$), 59 (3.9), and 47 (53.2).

Hexaethyldisiloxane was isolated by distillation from the photolysed solution, b.p. 115 °C at 22 mbar (lit.,[19] 231 °C at 760 mmHg); *m*/*e* 246 (0.6%, M^+), 217 (100, $M^+ - CH_3$), 189 (68.8, 217 $-$ C_2H_4), and 161 (41.8, 189 $-$ C_2H_4).

Dimethyl 2-methoxy-3-oxaglutarate (9) was isolated by g.l.c. (column A) at 120 °C, liquid, δ_H 3.30 (3 H, s), 3.45 (3 H, s), 3.47 (3 H, s), 4.23 (2 H, s), and 5.0 (1 H, s); δ_C 51.4 (q), 51.8 (q), 54.5 (q), 62.6 (t), 98.1 (d), 167.1 (s), and 170.0 p.p.m. (s); *m/e* 133 (62.6%, $M^+ - CO_2CH_3$), 161 (1.2, $M^+ - OCH_3$), 103 (30.1), 75 (100), and no M^+ peak.

1,2-Dimethoxy-1-triethylsiloxyethylene (8) had *m/e* no M^+ peak (218), 173 (4.0%), 161 (2.6), 159 (21.9, $M^+ - CO_2CH_3$), 115 (5.3, Et_3Si^+), 103 (100, $CH_3OCH^+CO_2CH_3$, $M^+ - Et_3Si$), and 75 (40.1); most of the m.s. peaks could be satisfactory interpreted in terms of compound (8).

Dimethyl 5-methoxy-3-oxa-adipate (10) was isolated by preparative g.l.c. (column A) at 196 °C, liquid, δ_H 3.21 (3 H, s), 3.29 (3 H, s), 3.38 (3 H, s), 3.9— 3.73 (3 H, m, ABC system), and 3.96 (2 H, s); δ_C 51.0 (q), 51.4 (q), 58.2 (q), 68.6 (t), 72.1 (t), 81.1 (d), 170.3 (s), and 170.4 p.p.m. (s); *m/e* no M^+ peak (206), 176 (0.9%), 147 (17.0, $M^+ - CO_2CH_3$), 119 (9.0), 103 (34.6), 87 (24.5), 75 (36.7), and 45 (100).

Acknowledgements

We thank Miss P. Lommes for valuable help in the synthetic work and the viscosity measurements. The development of the electronic equipment by Mr. W. Sicking is gratefully acknowledged. The Ministerium für Wissenschaft and Forschung and the Deutsche Forschungsgemeinschaft generously supported this work.

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Received 27*th April* 1982; *Paper* 2/690