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REACTIVITY OF CYCLOOCTENE DERIVED EPISULFONIUM IONS TOWARD NUCLEOPHILES AND THE COURSE OF SULFENYL HALIDE ADDITION TO CYCLOOCTENE

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Abstract—The reactions of the stable S-methylepisulfonium ions derived from *cis*-cyclooctene with various nucleophiles were found to proceed mainly as the attack at a C atom of episulfonium ring in contrast to the previous data of Helmkamp *et al.*[4] The course of the RSCl Ad_E-reaction with cyclooctene under the conditions of increased polarity corresponded to the formation of intermediates closely related to episulfonium ions. Transannular 1,5-hydride shift was observed for the reaction of 2,4-dinitrobensenesulfenyl derivatives with *cis*-cyclooctene.

The electrophilic addition of RSHal to alkenes is often regarded as a reliable model of two-step Ad_E-reaction involving the initial formation of the bridged cationoid intermediates-episulfonium ions (ESI).[1] In view of this concept it is surprising that this reaction usually proceeds without noticeable formation of mixed and/or solvoaddition products while the latter are formed in the vast majority of other Ad_E-reactions.[2] To account for this, it has been suggested,[2,3] that strongly bridged ESI's are weak electrophiles and hence are rather unreactive toward external nucleophiles.

The chemistry of stable ESI's provided by Helmkamp *et al.*[4] seemed to substantiate this view. It has been claimed that stable cyclooctene-S-methylepisulfonium 2,4,6-trinitrobenzene-sulfonate (**1a**, $Y = 2,4,6\text{-}(O_2N)_3C_6H_2SO_3^-$, TNBS) is either inert toward nucleophiles or undergoes preferential nucleophile attack at a S atom leading to the regeneration of cyclooctene, **2**. Thus **2** is formed as a single product in the reactions of **1a** with NaI, n-Bu_4NBr, Ph_4AsCl, NH_2CSNH_2, $(CH)_2S$, n-Bu_3N, n-Bu_3P; for KF the yield of **2** is about 44% while the interaction of **1a** with MeCOONa produced 52% of **2** together with 16% of 1,2-acetoxyadduct,**3**.[4] Among all the reagents used[4] only pyridine yielded the respective 1,2-adduct as the major product resulting from the nucleophile attack on the C atom of episulfonium ion **1a**.

Later studies disclosed a different reactivity pattern for other ESI's derived from alkenes such as cyclohexene,[5] 2-butenes,[6] t-butylethylene,[7] isobutylene[8] or styrene.[9] Thus it was reported[10] that all these ESI's reacted with nucleophiles such as MeCOOH, MeCN, Et_2NH, H_2O, MeOH, F^-, Cl^-, $H^-(NaBH_4)$, $\bar{C}H(COOMe)_2$ with the exclusive or at least predominant formation of 1,2-adducts which must have arisen from an attack on the C atoms of the ESI's. Moreover the classical RSHal Ad_E-reaction[11-14] produced solvoadducts (with the participation of MeCOOH or MeCN) provided the process was carried out under the conditions favourable for the intermediate formation of ESI's.

In view of these contradictory conclusions regarding the reactivity of ESI **1a**,[4,10] we considered it necessary to reinvestigate more closely the reactivity of cyclooctene derived ESI's.

We prepared several ESI's **1** differing by the nature of counterion to evaluate the possible influence of the latter on the course of the nucleophilic attack. Salt **1a** was prepared[15] and salts **1b** ($Y^- = BF_4^-$) and **1c** ($Y^- = SbF_6^-$) were prepared similarly. All these salts are stable as solids; **1a,c** are non-hydroscopic but **1b** is moderately hydroscopic.

According to NMR spectra, ESI's **1a–c** have similar structures (Table 1) each with a plane of symmetry. Accordingly only five ^{13}C-resonance signals were observed in their CMR-spectra, with δ-values of bridged carbon-13 atoms being close to those reported for other ESI's.[9]

In order to compare the reactivity of **1a–c** under identical conditions, we studied the PMR-monitored reaction of these salts in CD_3NO_2 solution with a CD_3COOD–$Me_4NOCOMe$ mixture (1:1 molar ratio; 1,2 equiv was used per equiv of **1**) at −10°. It was found that the nature of the counterion in ESI **1a–c** did not effect the course or the rate of the reaction. The formation of 1-acetoxy-2-methylthio-cyclooctane, **3**, was essentially complete after 2–5 min (yields of **3** were almost quantitative as judged by glc data with the use of an internal standard; no cyclooctene could be detected†). These results were in

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†It has also been found that **1d** ($Y = SbCl_6^-$) prepared according to the procedure[16] revealed a similar behaviour toward acetate-anion.

Table 1. Spectral data for ESI's **1***

ESI	δ (p.p.m.) / Y^-	^1H - NMR***		^{13}C - NMR				
		CH_3	CH	^{13}CH***		$^{13}CH_2$ and $^{13}CH_3$		
1a	$TNBS^-$	2.62,s	4.36,m	66.05	28.51	26.56	26.08	23.65
1b	BF_4^-	2.64,s	4.32,m	65.68	28.53	26.47	25.98	23.56
1c	SbF_6^-	2.63,s	4.30,m	66.18	28.53	26.47	26.05	23.56

*PMR spectra were recorded at 100 MHz in CD_3CN solution (+20°); CMR spectra- at 15.08 MHz in CD_3NO_2 solution (+20°). TMS was used as internal standard in both series.

**The signals of CH_2-protons appeared as the broad multiplets in the region 2.6–2.7(2H) and 1.4–1.9(10H).

***Signals were identified from the "off-resonance" spectra.

contrast with those reported previously[4] which pointed to the predominant regeneration of **2** in the reaction of **1a** with MeCOONa.

According to the data,[4] **1a** was completely inert toward MeCOOH (this reaction had been carried out in the solvent mixture MeCN-MeCOOH-CH_2Cl_2, 2:1:1).[4] We observed only a slow interaction between **1a–c** and MeCOOH in organic solvents. Thus when the solutions of **1b** in $MeNO_2$-MeCOOH (5:1) were kept at +20° for several hours only small amounts of **3** ($\leq 5\%$) could be detected (PMR). However the rate of this process could be increased if the reaction was carried out in neat MeCOOH. Under these conditions the transformation **1b**→**3** proceeded to half-completion after 30 min at +20° (again the formation of **2** could not be detected).

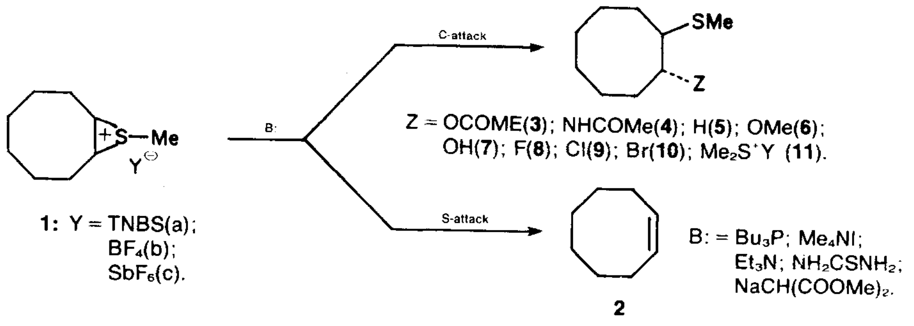
All the experiments described[4] were carried out with MeCN as a cosolvent on the assumption that the latter was inert toward ESI's. Not unexpectedly (compare the data given)[5,7] we found that such an assumption is only partially correct. Thus the PMR spectra of the freshly prepared MeCN solutions of **1a–c** revealed the presence of typical ¹H-signals of unchanged ESI's (Table 1). Upon standing overnight at ambient temperature, these signals completely disappeared and subsequent quenching of the reaction mixture with $NaHCO_3$-H_2O produced 1-acetamido-2-methylthiocyclooctane; **4** (isolated yield 81% from **1b**).

The results of previous studies[10] demonstrated that various ESI's reacted with typical quenchers for cationoid species such as hydride donors (e.g. Et_3SiH, $NaBH_4$). It was found that the interaction of **1a–c** with n-Bu_4N BH_4 proceeded similarly. The preferential formation of methylthiocyclooctane **5** (yield ~70%) evidenced that the nucleophilic attack of the hydride ion was directed mainly on the C atoms of ESI, the competitive attack on a S atom being of minor importance (glc analyses revealed the formation of small amounts of cyclooctene, yield 3 ÷ 7%).

Several other representative nucleophiles were studied as quenchers for **1b**† and a summary of the results are given in Scheme 1 and Table 2. For such necleophiles as CH_3O^- or OH^- the exclusive formation of 1,2-adducts (**6** or **7**) was observed. This is in full accord with the data reported for the reactions of these nucleophiles with other ESI's.[5–10] For several other nucleophiles the results corroborated the data published.[4] Thus complete recovery of **2** was observed for the reactions of **1b** with Me_4NI, NH_2CSNH_2, Bu_3P and Et_3N (Bu_3N was used[4]), showing that these reagents certainly prefer to attack the S atom of ESI **1**. In addition it was found that the reaction of **1b** with sodium malonate produced mainly **2** and methylthiomalonic ester (isolated yields 78 and 45% respectively).‡

However contrary to the claim[4] that such nucleophiles as F^-, Cl^-, Br^- and Me_2S did not reveal any tendency to attack the C atom of **1**, the PMR monitored reactions of **1b** in CD_3NO_2 with such bases as CsF, Me_4NCl, Me_4NBr and Me_2S indicated the exclusive formation of β-substituted methylthiocyclooctanes **8–11**.

These results demonstrated that in the majority of the reactions studied salts **1a–c** revealed the ability to undergo the preferential attack on the C atoms in a way typical for other ESI's.[5–10] Thus the general conclusion,[4] that "the reactions of **1a** with a variety of nucleophilic reagents occurs more often by attack at sulfur to give a sulfenyl compound and cyclooctene then on carbon to



Scheme 1.

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†The majority of the experiments have been done with **1b** as the most soluble in such organic solvents as $MeNO_2$ or CH_2Cl_2.

‡As we have shown earlier, sodium malonate yields "normal" C-adducts in the reactions with ESI's derived from cyclohexene[5] or t-butylethylene.[7]

Table 2. Summary of the data for the adducts **3–8**

Adduct	Base used for quenching	Reaction conditions		Yield	B.P.*	Analytical data calculated/found			PMR – data**			
		Time	T°C	%	°C/Torr	C	H	S	CHS	CHZ	Z	MeS
3	$Me_4NOAc+MeCOOH$	5min	-10;+20	95	108-11/2	60.78 61.11	9.36 9.26	14.29 14.81	2.68,m	4.76,m	1.92,s (MeOOC)	1.98,s
4	MeCN/HOH	12 h	+20	81	200/4 m.p.76-78	61.22 61.40	9.77 9.77	14.31 14.88	2.65,m	3.80,m	7.19,d (NH) 1.87,s (MeCO)	1.96,s
5	$(n\text{-}C_4H_9)_4NBH_4$	1 h	+40	70***	100/4	68.85 68.35	11.40 11.39	19.95 20.25	2.62,m	-	-	1.96,s
6	$MeOH/K_2CO_3$	1 h	+20	85	130/4	62.92 63.83	10.54 10.54	17.09 17.04	1.54,m	3.15,m	3.12,m (MeO)	1.97,s
7	$HOH/NaHCO_3$	1 h	+20	98	100/2	62.23 62.07	10.59 10.35	18.46 18.39	2.56,m	3.45,m	2.95,s (OH)	2.00,c
8	CsF	6 h	+20	45****	80/2	61.36 61.64	9.66 9.70	18.18 18.11	2.80,m	4.65,m J_{HF}= 47Hz	-	2.16,s

*Bath temperature is given (short-path distillation).

Spectra were recorded at 60 MHZ with HMDS as the internal standard; chemical shifts (δ) are given in P.P.M.; for multiplets δ-values refer to the center of the signals; CH_2-ring protons appeared as the unresolved broad signals at 1.7. Vicinal position of MeS and Z groups was substantiated by the appropriate ^1H–^1H decoupling experiments for all the adducts except **5.

***The reaction mixture contained also *ca.* 3–7% of **2** (glc data with the use of calibrated standard).

****The low yield is due to the slow rate of the quenching; PMR data of the reaction mixture (prior to any treatment) did not reveal the presence of any other compounds than **1b** and **8**.

give a 1,2-di-substituted cyclooctanes"—is actually misleading.

The discrepancy between the data of this study and those of Helmkamp *et al.*[4] can be explained. All the experiments described[4] were carried out in the presence of excess cyclohexene which was added as a trap for the sulfenyl compound, CH_3SZ, presumably formed due to the attack of nucleophile, Z, on the S atom of **1a**.

Later studies[17] revealed that in the presence of excess alkene equilibration between this compound and various β-chloroalkylaryl sulfides could take place. Therefore for the cases reported,[4] the recovery of **2** could be ascribed to the equilibration between **1a** and cyclohexene or between 1,2-cyclooctane adducts (e.g. **8–11**) and cyclohexene.

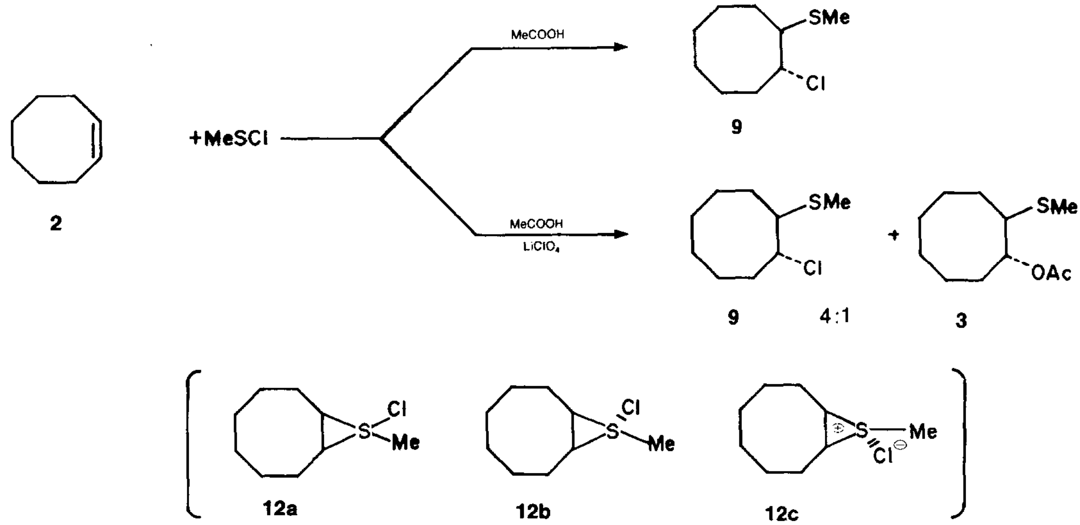
This argument is valid for the reactions of **1a** with Me_2S and Cl^- since according to the data,[18,19] these reactions while performed in the absence of added cyclohexene clearly produced the 1,2-adducts: 2-(methylthio-1-cyclooctyldimethylsulfonio-TNBS (**11**, Y = TNBS) or 2-methylthio-1-chlorcyclooctane **9**. A second possible source of error could be due to the use of MeCN as solvent while in this paper (*vide supra*) we show that MeCN can participate as a nucleophile in the reactions of **1**.

The ability of **1** to react with nucleophilic solvents, suggested that solvoadduct formation in the course of RSHal Ad_E-reaction under the conditions of increased polarity[11–14] could also be observed for the reaction of **2** with MeSCl. To check this assumption, the PMR monitored addition of MeSCl to **2** was carried out in (i) neat CD_3COOD and (ii) in the same solvent containing $LiClO_4$. In the first case the reaction proceeded with the exclusive formation of 1-chloro-2-(methylthio)cyclooctane **9**, while in the second case the formation of 20% of acetate **3** was detected. In the preparative runs the acetate **3** was isolated in 15% yield. Blank experiments showed that under the conditions used the acetolysis of **9** did not take place to any noticeable extent.

In the agreement with the interpretation[11–14] (see also Ref. 20) the effect of $LiClO_4$ on the course of MeSCl addition to cyclooctene should be ascribed to the shift of the polarity of the intermediate in this process from **12a** or **b** toward ESI-like species **12c** (Scheme 2), the ability of the latter to produce **3** having been demonstrated by direct experiments (*vide supra*).

It is well-documented that the RSHal Ad_E-reaction in the presence of $LiClO_4$ afforded not only solvoadducts but rearranged products as well.[14,20–22] In particular,[14] under these conditions the reaction of cyclooctene with 2,4-$(O_2N)_2$ C_6H_2SCl(2,4-DNBSC) produced 1-chloro-2-arylthiocyclooctane **13** and two acetoxy adducts **14** and **15** in the ratio 6:1:2 (total yield 83%) while in the absence of $LiClO_4$ the exclusive formation of **13** took place.[14] The preliminary spectral data[14] did not reveal the structures for **14** and **15**. The results provided by {^1H–^1H}-PMR data showed that **14** is a 1,2-acetoxy adduct while in **15** the substituents are certainly not in a vicinal position. The presence of eight signals of the cyclooctene residue in the CMR spectra of **15** ruled out a symmetrical 1,5-structure. The observed ^{13}C chemical shift pattern in the CMR of **15** together with the data on $Eu(fod)_3$ shifted CMR-spectra (Experimental) pointed to the 1,4-structure of **15** as the most probable one as compared to the alternative with a 1,3-position of the substituents.

The formation of acetate **15** was of special interest since it involved a transannular hydride shift—most probably 1,5-shift—a process which was not observed in the reactions of medium-size ring compounds with "weak" electrophiles. This result prompted us to attempt



Scheme 2.

the preparation of the respective Ar-ESI **16**($Y^- = BF_4^-$ or SbF_6^-) in order to study its stability and reactivity toward various nucleophiles. But it was found that **16** is unstable even in solutions at −60°. Thus by analogy with previous data[6,8] interaction of **2** with 2,4-$(O_2N)_2C_6H_3$ S^+ BF_4^-(or SbF_6^-) (prepared *in situ*) in CH_2Cl_2–CH_3NO_2–$C_2H_4Cl_2$ at −60° gave a mixture containing **16**. However the immediate quenching of this mixture with acetate-anion did not lead to the exclusive formation of unrearranged acetate **14**—the expected product of the "normal" nucleophile opening of **16**. Instead, a mixture containing **14**, **15** and unsaturated sulfide **18** was formed (ratio 10:1:8; total yield 76%).

The ratio of these products changed if the solution presumably containing **16** was kept for several hours at −60° or warmed up to −20° (prior to the quenching). The subsequent quenching with acetate-anion produced mixture **14**:**15**:**18** in the ratio 13:25 (total yield 60%).

According to PMR data (Experimental) sulfide **18** has the structure of Δ^3-cyclooctenyl-arylsulfide† and hence its formation could be envisaged via a pathway similar to that suggested for the formation of **15** (Scheme 3) and must involve as a necessary step a 1,5-hydride shift.

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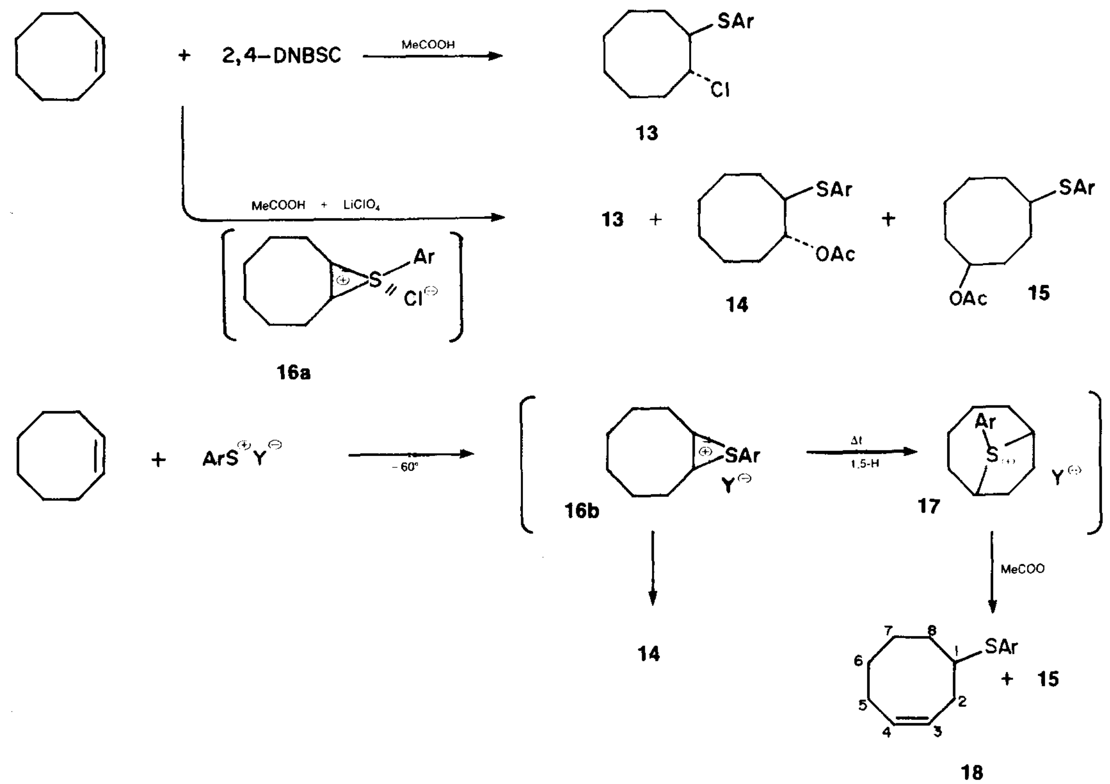
†This is certainly the major isomer; however the PMR-data revealed also the presence of minor admixture, presumably, of Δ^4-isomer.



Scheme 3.

Hence the Ad_E-reactions of **2** with covalent 2,4-DNBSC in MeCOOH in the presence of $LiClO_4$[14] and with 2,4-$DNBS^+Y^-$ suggested similar reaction pathways for these processes involving the intermediate formation of ESI-like species **16a**, **b**. These intermediates could either be directly trapped by the nucleophiles (the formation of **13** and **14**) or alternatively undergo a 1,5-hydride shift thus yielding adducts **15** and/or **18**. The formation of the latter products could be envisaged as proceeding via the bicyclic sulfonium intermediate **17** the course of its stabilization being dependent on the reaction conditions and—especially—on the presence of nucleophiles in the media.

Thus, for both MeSCl and 2,4-DNBSC, we have shown that the data on the course of their Ad_E-reactions under various conditions could be rationally correlated with the direct experimental data on the reactivity of the respective ESI's and such a comparison allows one to identify the possible involvement of the latter species in Ad_E-reactions of sulfenyl halides.

EXPERIMENTAL

NMR spectra were taken with BS-497 Tesla 100 MHz and Bruker-WP-60 (15.08 MHz for ^{13}C) spectrometers. PMR-monitored reactions were carried out with a Tesla spectrometer.

ESI **1a–c** were prepared according to the procedure described for **1a**[15] in yields of 80% (**1a**, m.p. 118–120; lit.[15] m.p. 122–124°), 75% (**1b**, m.p. 104°, lit.[23] m.p. 106°), 84% (**1c**, m.p. 152–154°), (Found: C, 27.0; H, 4.23. Calc for $C_9H_{17}SSbF_6$: C, 27.5; H, 4.36).

(a) *Reactions of salt* **1a–c** *with nucleophiles*

The preparation of the adducts **3–8** was carried out according to the following general procedure: 1.0 mmol of **1b** in CH_2Cl_2(5 ml) was treated with 2–5 molar excess of the respective base under the conditions specified in Table 2. The mixture was then treated with $NaHCO_3$aq and extracted with ether. After the removal of ether the residue was purified by tlc (SiO_2) and/or short path distillation. Analytical and spectral date for **3–8** are given in Table 2; yields refer to the purified products.

The reaction of **1** *with* $NaCH(COOMe)_2$ was carried out by the addition of the soln of **1b** (20 mmol, prepared *in situ* by the interaction of equivalent amounts of **10**[15] with $AgBF_4$ in CH_2Cl_2–$MeNO_2$ (40 ml, 3 : 1) at −60° to the soln of $NaCH(COOMe)_2$ in $CH_2(COOMe)_2$. The mixture was kept for 5 min at −20° and for 10 min at +20°, then quenched by $NaHCO_3$aq and extracted with ether. After ether removal, cyclooctene was distilled off, b.p. 148–150°, 1.44 gr, 78% of recovery. The distillation of the residue under reduced pressure afforded methylthiomalonic ester, 1.53 g (45%) b.p. 141–143° (12 mm), n_D^{20} 1.4622 (lit.[24] 154° (14 mm)). (Found: C, 46.93; H, 7.04; S, 15.39. Calc for $C_8H_{14}O_4S$: C, 46.60; H, 6.7; S, 15.34; M^+ 206).

PMR-monitored reactions of **1a–c** *with nucleophiles, Z*

Z = Acetate ion. A soln of 0.3 mmol of Me_4NOAc in 0.3 mmol of CD_3COOD was added to a solution of the respective salt **1a–c** (0.25 mmol) in CD_3NO_2 (0.5 ml) at −10° in a NMR tube. PMR spectra recorded immediately revealed the presence of acetate **3** as the single product and the complete disappearance of the PMR-spectra pattern of the starting salt **1**.

Z = Acetic acid. (a) Under the conditions described above the reaction of **1a–c** with CD_3COOD in CD_3NO_2 proceeded slowly even at +20°; thus after 6 hr at +20° the PMR spectra revealed the presence of the starting salt and no more than 5% of **3** was formed. No signals in the olefinic region could be observed. (b) For the reaction **1b**→**3** in neat CD_3COOD the PMR data registered the formation of 50% of **3** after 30 min at +20°, with an increase up to 75% in 3 hr.

Z = Acetonitrile. The immediately recorded PMR spectra of the soln of **1b** (0.25 mmol) in CD_3CN (0.5 ml, contained 0.15% of H_2O) revealed unchanged **1b** (Table 1). However these signals slowly disappeared and signals of **4** appeared instead (in 3 hr about a half of **1b** was transformed into **4**).

Z = Chloride ion. The reaction of 0.24 mmol of **1b** with the excess Me_4NCl in 0.5 ml CD_3NO_2 soln at +20° immediately produced **9** as the single product identified by comparison with the PMR of an authentic sample of **9** (see below).

Z = Bromide ion. Under similar conditions, the reaction of **1b** with Me_4NBr gave exclusively **10**. PMR: 4.34 (m, 1H, $\underline{CH}Br$, 3.05 m, 1H, $\underline{CH}$–S–2.07 s, 3H, CH_3S), identical with the PMR of a sample of **10**, prepared by the addition of MeSBr to **2**.[15]

Z = Dimethylsulfide. Under identical conditions, the interaction of **1b** with the excess of Me_2S immediately produced **11**, identified by its PMR spectra: 3.65, m, 1H, $C\underline{H}-\overset{+}{S}\langle$ 3.02, m, 1H, $C\underline{H}$–S, 2.86 and 2.74, pair of 3H-singlets, SMe_2, 2.16, s, 3H, SMe.[25]

Z = Tri-n-butylphosphine, triethylamine, thiourea or tetramethylammonia iodide. The addition of these reagents to a soln of **1b** in CD_3NO_2 immediately produced cyclooctene **2** as the single product. PMR: 5.52, m, 2H, CH=CH, 2.08 broad signal, 4H, $CH_2C{=}CCH_2$.

(b) *Reaction of* **2** *with* MeSCl

In neat MeCOOH. A soln of MeSCl (0.5 g, 6 mmol) in MeCOOH (3 ml) was added to a soln of **2** (0.5 g, 4.5 mmol) in MeCOOH (10 ml) at +20°. The mixture was kept for 3–5 min, then poured into water and extracted with $CHCl_3$. The residue after removal of solvent contained mainly **9**,† identified by glc and PMR comparison with a sample, prepared according the procedure given.[15]

In MeCOOH *containing* $LiClO_4$. Under identical conditions but in the presence of $LiClO_4$ (2.5 equiv per mole of alkene) the reaction afforded a mixture **9** and **3** in the ratio 4 : 1, (glc) from which **3** was isolated with the yield of about 15%.

In the PMR monitored run (in CD_3COOH) the integration of CH–OAc and $\underline{CH}$–Cl peak area gave the ratio 9 : 3 = 4 : 1.

(c) *The reaction of cyclooctene with* $2,4\text{-}(O_2N)_2C_6H_5S^+\ BF_4^-$

1. *At* −65°. A soln of cyclooctene (0.3 g, 2.7 mmol) and $AgBF_4$ (0.65 g, 3.3 mmoles) in $MeNO_2$(1.8 ml) was added to a soln of $2,4\text{-}(O_2N)_2C_6H_3SBr$ (0.75 g, 2.7 mmoles) in CH_2Cl_2 (8 ml) at −65°. The mixture was kept for 30 min at this temp, treated with MeCOONa (1.2 g), stirred for 5 min at −30° and for 1 hr at +20° and then poured into $NaHCO_3$aq-ether mixture. The ethereal layer was washed with water and dried over Na_2SO_4. The removal of the solvent gave a semi-solid residue, 0.8 g. Preparative tlc (Al_2O_3, hexane-CH_3COOEt, 2 : 1) yielded **14** (0.39 gr, 40%); **15** (0.04 gr, 4%) and **17** (0.27 gr, 32%). **14**, m.p. 130°.[14] PMR: 1.88, s, OAe, 3.80, m, $\underline{CH}$, s, 5.11, m, $\underline{CH}$ OAc. The irradiation at $\underline{CH}$-OAc led to the simplification of $\underline{CH}$-S multiplate; the irradiation at δ 1.95 (region of protons at C_3 and C_8) transformed multiplets at $\underline{CH}$-S and CH-OAc into AB-doublets.

Compound **15**, m.p. 68°.[14] PMR: 2.0, s, OAc, 3.60, m, $\underline{CHS}$, 4.94, m. $\underline{CH}$ OAc. The irradiation at $\underline{CH}$–OAc did not change the $\underline{CH}$–S multiplet. CMR-data for **15** is given in Table 3.

Compound **18**, m.p. 84–86°. (Found: C, 55.12; H, 5.28; S, 10.69; N, 9.29. Calc for $C_{14}H_{16}O_4N_2S$: C, 54.55; H, 5.19; S, 10.39; N, 9.09%) PMR: 5.64, m, 2H, –CH=CH–, 3.54 m, 1H, CH–S, 2.44, m, 4H, CH_2–C=C–CH_2, 2.14 m, 2H, at C_8. Irradiation at $\underline{CH}$–S produced no changes in the olefinic region but simplified the multiplets centered at 2.44 and 2.14; the irradiation at the allylic region caused the collapse of the olefinic multiplet into a broadened singlet and simplified the CH–S signal.‡

2. *At* −25°. The preparation of a soln containing ESI **16** and its quenching with MeCOONa were carried out under conditions identical with those used in the preceeding experiment. However prior to quenching, the soln of **16** was warmed up to −25° and kept for 30 min at this temp. The products were isolated and purified in the manner described above and gave **14** (0.02 g, 2%), **15** (0.07 g, 7%) and **18** (0.42 g, 51%), identical with samples described.

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†Only trace amounts of **3** could be found by tlc and glc.

‡Spectral experiments for **18** were done with Bruker WP-200 spectrometer.

Table 3. CMR-spectra† of 15

		C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8
δ	^{13}C	45.47	29.75	31.62	73.46	30.78	25.38	22.70	27.63
$\Delta\delta_1$	^{13}C	0.18	0.36	0.55	0.85	0.55	0.12	0.12	0.18
$\Delta\delta_2$	^{13}C	0.30	0.72	0.87	1.7	0.84	0.24	0.30	0.36

†Spectra recorded for the $CDCl_3$ solutions with internal TMS standard. The ration $Eu(fod)_3$: substrate is 0.2:1.0 for $\Delta\delta_1$ and 0.4:1.0 for $\Delta\delta_2$.

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