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Reactions of acylsulfonium salts with unsaturated hydrocarbons

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Abstract—The reactions of acylsulfonium salts, obtained from β-(ethylsulfanyl)propionyl fluoride and (ethylsulfanyl)acetyl fluoride, with various unsaturated hydrocarbons proceed through the formation of six- and five-membered cyclic sulfonium salts, respectively. Succeeding cleavage of sulfonium salts by bases affords the corresponding sulfur containing unsaturated ketones.

1. Introduction

The complexes of acylium salts with different nucleophiles are in most cases milder reagents than the parent acylium salts which tend to polymerize olefins.[1,2] Earlier we have found that dimethylacylsulfonium salts, obtained from acylium salts and dimethyl sulfide, are useful for the functionalization of multiple carbon–carbon bonds.[3–8] Their reactions with olefins and dienes proceed as conjugate addition of the acyl group and dimethyl sulfide and give rise to the corresponding sulfonium salts. Subsequent elimination of dimethyl sulfide results in unsaturated ketones (Scheme 1).

(β-Alkylsulfanyl)propionyl and (alkylsulfanyl)acetyl tetrafluoroborates may be considered as an intramolecular model of acylsulfonium salts mentioned above. Recently, we have shown that β-alkylthiopropionyl tetrafluoroborates react with alkenes and alkynes through the formation of six-membered sulfonium salts, which upon subsequent cleavage with base gives rise to the corresponding alkylsulfanyl substituted unsaturated ketones.[9,10] Also acylsulfonium salts react with various aromatic and heteroaromatic compounds.[11,12]

Below we describe our investigations of complexes β-(ethylsulfanyl)propionyl fluoride (**1**), (ethylsulfanyl)-acetyl fluoride (**2**) and their reactions with a number of alkenes and 1,3-dienes.

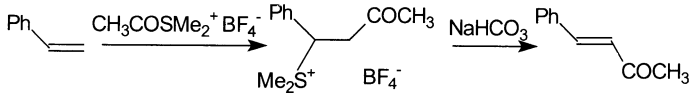
2. Results and discussion

2.1. Reactions of $EtSCH_2CH_2COF/BF_3$ with alkenes

The reactions of complex $EtSCH_2CH_2COF/BF_3$ (**1**) with various alkenes were performed at the temperature range −50 to 0°C in dry dichloromethane. The reaction products isolated after cleavage with base ($KHCO_3$ aq) were the products of substitution of hydrogen atom at double bond of alkene by (3-ethylsulfanyl)propionyl moiety and (or) the products of conjugated addition of ethylsulfanyl and acrylic groups to the double bond. Use of another Lewis acid ($TiCl_4$) led to the analogous results, but the yields were lower.

An investigation of the products structure allows us to propose the following reaction scheme. In the first step the C═C bond attacks carbonyl atom of the acylsulfonium salt resulting in the formation of a carbocation which is stabilized by intramolecular reaction with the sulfide moiety giving a six-membered sulfonium salt **A** (Scheme 2).

However, in most cases we failed to isolate salts **A** in pure form, (in the cases of *trans*-stilbene and methylenecyclobutane the signals of the intermediate sulfonium salt were observed in the NMR spectra). The stabilization of the carbocation by formation of the sulfonium salt seems to proceed both intramoleculary and intermoleculary. The last path yields non-cyclic oligomeric sulfonium salts



Scheme 1.

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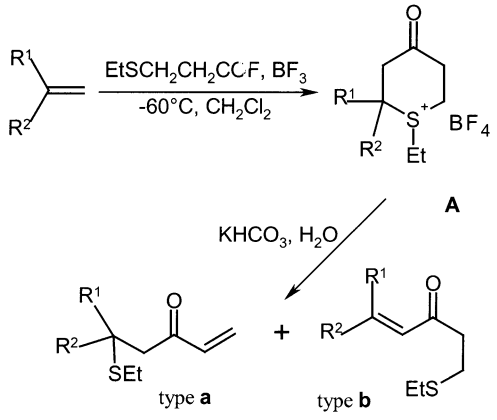


Scheme 2.

and makes the cyclic monomer hard to isolate in pure form.

The reaction of sulfonium salt **A** with aqueous $KHCO_3$ leads to elimination of protons α to the carbonyl group. The ring cleavage proceeds with cleavage of the C–S bond and gives rise to α,β-unsaturated ketones. We investigated the reactions of complex $EtSCH_2CH_2COF/BF_3$ with a number of alkenes posessing mono, 1,1-di, 1,2-disubstituted double bonds, and also alkenes with *exo*- and *endo*cyclic double bonds. Depending on the structure of the starting alkene the formation of two types of unsaturated ketones (**a** and **b**) is possible. Type **a** is the product of conjugate addition of ethylsulfanyl and acryloyl groups to the C=C bond; type **b** is the product of substitution of hydrogen atom at the double bond of the alkene by the (3-ethylsulfanyl)propionyl moiety.

The only product in the reaction of styrene with complex $EtSCH_2CH_2COF/BF_3$ is the unsaturated ketone of type **b** (**3b**) (Scheme 3).

The formation of the double bond conjugated with the aromatic ring in the reaction with styrene leads to only one product—ketone of type **b**—(*E*)-1-phenyl-5-ethylsulfanylpent-1-en-3-one (**3b**) (^3J=16.2 Hz). The stereoselectivity of this reaction can be explained by the fact that the initially formed sulfonium salt exists in the conformation with equatorial phenyl ring, and anti-elimination of the sulfonium moiety leads to *trans* phenyl and carbonyl groups in the reaction product.

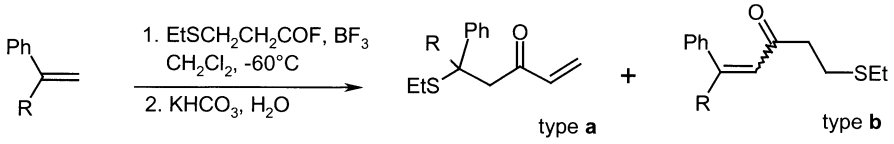
The reactions of α-methylstyrene and 1,1-diphenylethylene with complex **1** yield a mixture of products: in the case of α-methylstyrene the ratio of ketone type **a**/type **b** was 1:1, in the case of 1,1-diphenylethylene—type **a**/type **b** was 2:1 (Scheme 3). It seems that in these reactions the ratio of products depends on both the steric size of substituents at C-2 in the sulfonium salt **A** and the formation of the double bond conjugated with aromatic ring. Actually, the presence of methyl and phenyl or two phenyls at C-2 in the sulfonium salt **A** sterically hinders the 3-position and makes the formation of ketones type **a** preferable.

The reactions of complex **1** with *trans*-1-phenyl-2-methylethylene and *trans*-stilbene proceed chemo- and stereoselectively and yields the products of conjugate addition of acryloyl and ethylsulfanyl groups to double bond of alkenes (ketone type **a**). Only one diastereomer of the corresponding ketone is formed (Scheme 4).

To determine the relative configuration of these ketones we tried to determine the structure of the initially formed sulfonium salts, since during base cleavage the chiral centers at C-2 and C-3 are not affected. However, we failed to isolate those sulfonium salts in pure form from the reaction mixture. At the same time, it was found that treatment of ketones **6a** and **7a** with perchloric acids led to six-membered sulfonium salts **8** and **9** (Scheme 5). Since cleavage of the latter with base give rise to starting ketones **6a** and **7a**, the perchlorates **8** and **9** seems to be of the same structure as the sulfonium salts **A** formed in the acylation reaction. In other words the reaction of sulfonium ring cleavage is reversible.

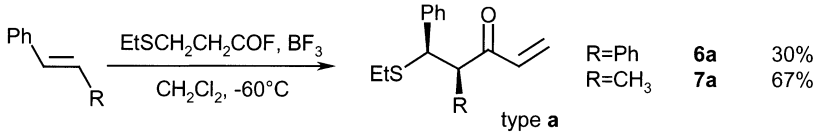
The coupling constants H-2 and H-3 in the salts **8** and **9** correspond to axial–axial protons in the six membered ring (**8**—J=12.8 Hz, **9**—J=12.5 Hz). That is in agreement with formation of *threo*-isomers of ketones **6a** and **7a**.

In the reactions of complex **1** with hydrocarbons with



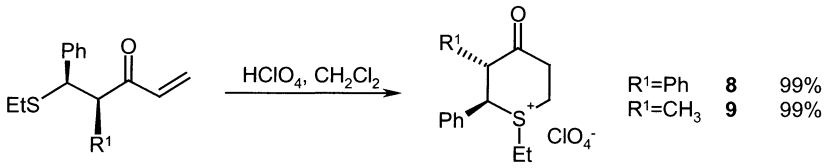
R=H	**3b**(*E*)		34%
$R=CH_3$	**4a** / **4b**(*E*) / **4b**(*Z*)	2 / 1 / 1	68%
R=Ph	**5a** / **5b**	2 / 1	87%

Scheme 3.

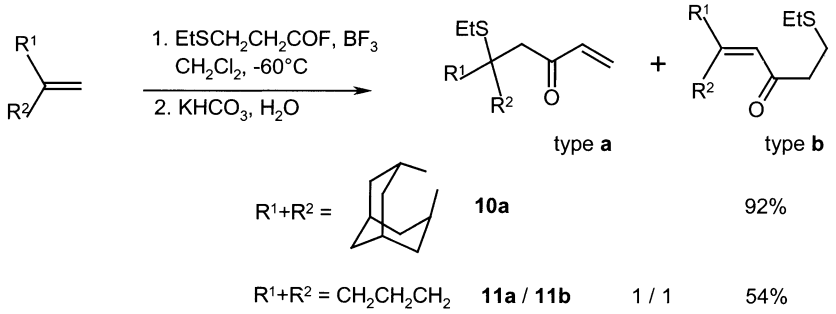


R=Ph	**6a**	30%
$R=CH_3$	**7a**	67%

Scheme 4.



Scheme 5.



Scheme 6.

*exo*cyclic double bonds the ratio of products type **a**/type **b** seems to depend mostly on steric factors. In the case of 2,2-disubstituted adamantane **10a** (Scheme 6) was obtained. In the reaction with methylenecyclobutane, protons at C-2 in the intermediate salt **A** are not so sterically hindered as in the previous case and after cleavage both possible types of unsaturated ketones are formed **11a/11b** 1:1.

The interaction of complex **1** and cyclic alkenes was studied using cyclopentene and cyclohexene (Scheme 7). It was found that in the case of cyclopentene only one product, ketone of type **b** (**12b**), was isolated. In contrast, with cyclohexene the ratio of ketones type a/type b was found to be 1:1 (**13a/13b**). Only one diastereomer of ketone **13a** was formed, but the determination of its configuration from coupling constants was not successful due to overlapping of signals in the ^{1}H NMR spectrum.

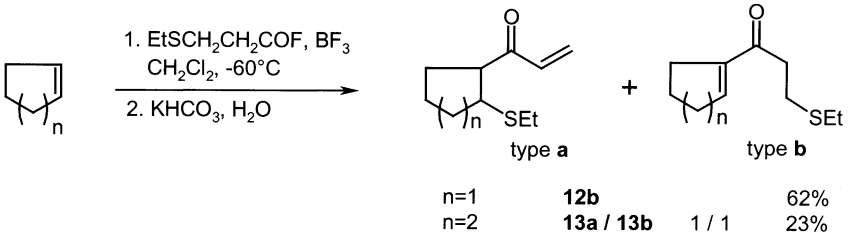
We suppose that predominant formation of ketone of type **b** in the case of cyclopentene is due to the reduction of vicinal straine in the cyclopentane ring on introducing a double bond. This facilitates cleavage of intermediate **A** (Scheme 1) to ketone of type **b** (Scheme 7).

2.2. Reactions of $EtSCH_2CH_2COF/BF_3$ with 1,3-dienes

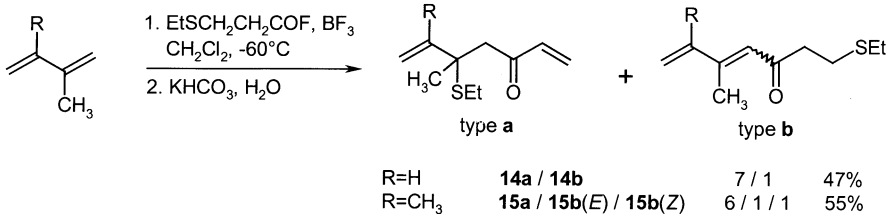
Reactions with 1,3-dienes proceed in mild conditions and almost without polymerization of substrates. The products in these reaction are ketones of type **a** and (or) **b** (Scheme 8). The 1,4-addition of acryloyl and ethylsulfanyl groups to the 1,3-diene system was not observed.

We have studied the reactions of complex **1** with isoprene and 2,3-dimethylbutadiene. In both cases we isolated the mixtures of ketones. The formation of ketones of type **b** proceeded non-stereoselectively.

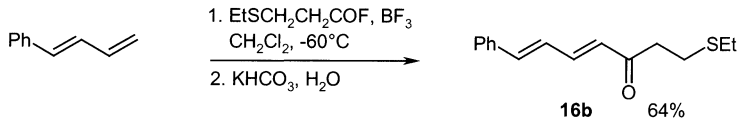
In the reaction of complex **1** with (*E*)-1-phenyl-1,3-butadiene only ketone type **b** (**16b**) was isolated. This can be



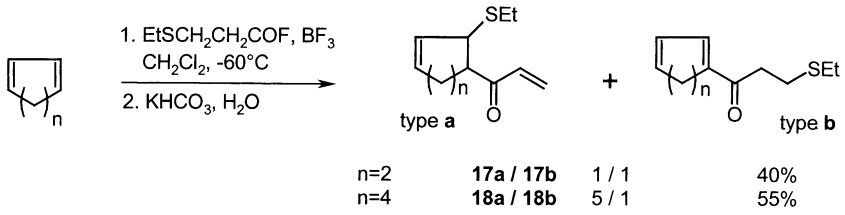
Scheme 7.



Scheme 8.



Scheme 9.



Scheme 10.

explained by the formation of the conjugated phenyl-1,3-diene-carbonyl group (Scheme 9).

The reaction with 1,3-cyclohexadiene leads to the mixture of ketones type **a**/type **b** of 1:1. 1,3-Cyclooctadiene also gives rise to a mixture of products, but in the last case the ratio type **a**/type **b** is 5:1 (Scheme 10).

2.3. Synthesis of polyconjugated unsaturated ketones

We have found that ketones, obtained in the reactions of **1** with alkenes and 1,3-dienes, after elimination of ethylsulfanyl group, give rise to the corresponding polyenones **19**–**23** (Scheme 11). Noteworthy, the mixture of ketones type **a** and type **b** can be converted into only one polyenone.

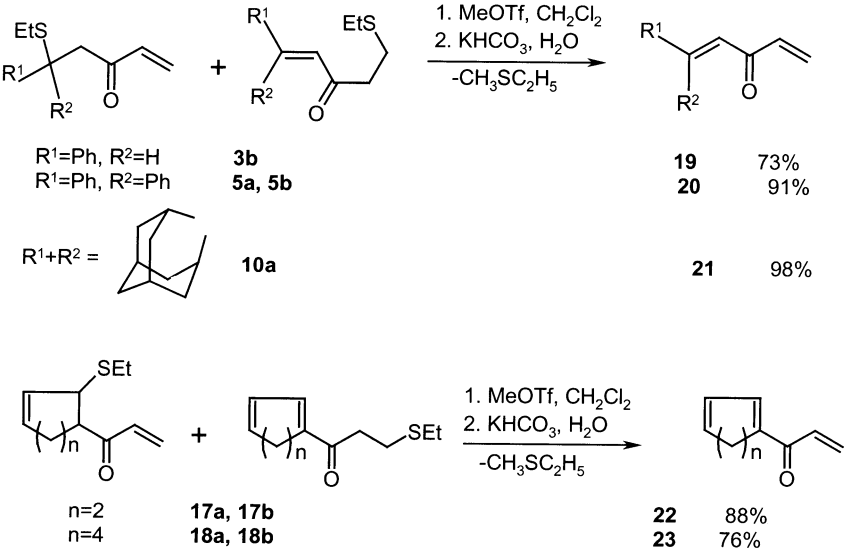
Such transformations have been achieved by S-methylation and elimination of methyl ethyl sulfide by treatment with base. Yields for these two steps are almost quantitative and the work up is very simple.

We studied S-methylation using several methylating agents, such as methyl iodide and methyl sulfate. However, in those cases reactions proceeded very slowly (2–4 days) and sometimes the starting materials were not fully converted. When methyl triflate was used as alkylating reagent the reactions usually were complete in 1–2 h and no side products were observed.

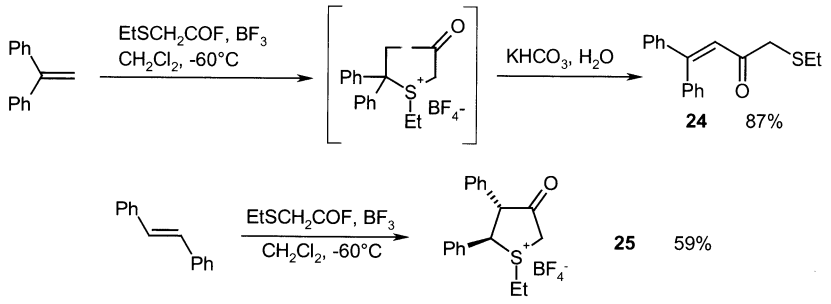
This type of polyenones is synthetically very useful, for example in Nazarov cyclisations.[13] The polyenones might be obtained by direct acylation of corresponding unsaturated hydrocarbons with acrylic acid derivatives. But, as was shown, the reactions of methacryloyl tetrafluoroborate with alkenes give rise to α,β-β′,γ′-unsaturated ketones.[14] Complex $EtSCH_2CH_2COF/BF_3$ **1** could be considered in the reactions with alkenes and 1,3-dienes as a synthetic equivalent of acryloyl cation, and could be used for introducing the acryloyl moiety.

2.4. Reactions of complex $EtSCH_2COF/BF_3$ with alkenes

In the reactions of complex **2** with alkenes the formation of cyclic sulfonium salts also takes place. In this case the opening of five-membered sulfonium ring proceeds unambiguously and furnishes substituted (4-ethylsulfanyl)but-1-en-3-ones: the reaction of 1,1-diphenylethylene yields the corresponding unsaturated ketone **24** (Scheme 12).



Scheme 11.



Scheme 12.

In the reaction of **2** with *trans*-stilbene the intermediate sulfonium salt **25** was isolated as one diastereomer. We assume pseudo-equatorial–equatorial phenyl groups in this salt, since the coupling constant between H-2 and H-3 is 13.8 Hz.

3. Conclusion

Thus, the reaction of alkenes and dienes with (β-ethylsulfanyl)propionyl fluoride/BF_3 and (ethylsulfanyl)acetyl fluoride/BF_3 complexes proceeds as addition of acyl moiety to a double bond followed by the intramolecular conjugate addition of sulfide which results in six- or five-membered sulfonium salts, respectively. Subsequent cleavage of these salts by base gives rise to ethylsulfanyl substituted unsaturated ketones, which can be converted into synthetically useful polyenones by S-methylation and elimination of methyl ethyl sulfide.

4. Experimental

4.1. General

Reagents and solvents were handled by using standard techniques. NMR spectra were recorded on Bruker AMX 400 and Varian VXR-300 spectrometers with TMS as an internal standard. IR spectra were obtained with UR-20 spectrometer as films. Silica gel Merck 60 and Merck $60F_{254}$ plates were used for conventional and analytical (TLC) chromatography, respectively.

4.2. General procedure for ethylsulfanyl substituted unsaturated ketones 3–7, 10–18, 24

A well-stirred solution of ethylsulfanyl substituted acyl fluoride (0.02 mole) in dichloromethane (40 mL) was saturated by gaseous BF_3 at −60°C. A solution of alkene (0.02 mole) dichloromethane (in 10 mL) was added. The reaction mixture was stirred for 15 min at −40°C and the temperature was raised to 0°C. The reaction mixture was stirred for 1 h and then was added to a mixture of ether and aqueous $KHCO_3$ and stirred for an additional 1 h. The organic layer was separated, the aqueous layer was extracted with ether (2×50 mL). The organic solvents were removed in vacuo. The products were purified by column chromatography (silica gel, hexane/EtOAc 9/1).

4.2.1. (*E*)-1-Phenyl-5-ethylsulfanylpent-1-en-3-one (3b). Oil, yield 34%, n_D^{21}=1.5520. IR (ν, cm^{-1}): 1670 (CO), 1620 (C=C). NMR ^1H (400 MHz, $CDCl_3$, δ, ppm): 7.59–7.31 (m, 6H, C_6H_5, H-1), 6.87 (d, 1H, H-2, ^3J=16.2 Hz), 3.11–2.97 (m, 4H, $2CH_2$), 2.71 (q, 2H, S-CH_2, ^3J=7.5 Hz), 1.39 (t, 3H, CH_3, ^3J=7.5 Hz). NMR ^{13}C (100 MHz, $CDCl_3$, δ, ppm): 198.2 (CO), 142.8 (C-2), 134.3, 130.5, 128.9, 128.3 (6C-arom.), 125.7 (C-1), 40.9, 26.2, 25.8 ($3CH_2$), 14.8 (CH_3). Found, %: C 70.56, H 7.44. $C_{13}H_{16}SO$. Calcd, %: C 70.87, H 7.32.

4.2.2. 2-Phenyl-2-ethylsulfanylhex-5-en-4-one (4a), (*E*)-2-phenyl-6-ethylsulfanyl-hex-2-en-4-one (4b(*E*)), (*Z*)-2-phenyl-6-ethylsulfanylhex-2-en-4-one (4b(*Z*)). 2:1:1, oil, yield 68%. IR (ν, cm^{-1}): 1695 (CO), 1610 (C=C). NMR ^1H (400 MHz, $CDCl_3$, δ, ppm): **4b** (*E*+*Z*): 7.46–7.15 (m, 5H, C_6H_5), 6.43 (m, 1H, =CHCO (*Z*)), 6.09 (m, 1H, =CHCO (*E*)), 2.52–2.05 (m, 12H, $6CH_2$), 2.45 (br.s, 3H, CH_3C=, (*E*) or (*Z*)), 2.09 (br.s, 3H, CH_3C=, (*E*) or (*Z*)), 1.19 (t, 3H, CH_3, (*E*) or (*Z*), ^3J=7.4 Hz), 1.08 (t, 3H, CH_3, (*E*) or (*Z*), ^3J=7.4 Hz), **4a**: 7.46–7.15 (m, 5H, C_6H_5), 6.12 (dd, 1H, H-5, ^3J=17.4, 10.1 Hz), 6.01 (dd, 1H, H-6, ^3J=17.4 Hz, ^2J=1.6 Hz), 5.53 (dd, 1H, H-6, ^3J=10.1 Hz, ^2J=1.6 Hz), 3.32 (d, 1H, H-3, ^2J=5.3 Hz), 3.02 (d, 1H, H-3, ^2J=5.3 Hz), 2.22 (q, 2H, S-CH_2, ^3J=7.6 Hz), 1.84 (s, 3H, CH_3), 0.96 (t, 3H, CH_3, ^3J=7.6 Hz). NMR ^{13}C (100 MHz, $CDCl_3$, δ, ppm): **4b** (*E*+*Z*): 198.4 and 198.4 (CO), 153.6 and 152.1 (C-2), 141.9 and 140.3 (C-q arom.), 128.8, 127.9, 127.6, 126.7, 126.2, 126.0, 123.3 (5C-arom., C-3), 44.4, 42.5, 26.7, 25.9, 25.4, 25.4, 25.3, 18.0 ($3CH_3$, C-1), 14.4 and 14.3 (CH_3). **4a** 196.4 (CO), 143.5 (C-q arom.), 136.4 (C-5), 128.1, 127.6, 126.3 (5C arom.), 127.3 (C-6), 51.4, 48.9, 25.8, 22.4 ($2CH_2$, C-1, C-2), 13.4 (CH_3). Found, %: C 71.57, H 7.79. $C_{14}H_{18}SO$. Calcd, %: C 71.75, H 7.74.

4.2.3. 1,1-Diphenyl-1-ethylsulfanylpent-4-en-3-one (5a), 1,1-diphenyl-5-ethylsulfanylpent-1-en-3-one (5b). 2:1, oil, yield 87%. IR (ν, cm^{-1}): 1700, 1680 (CO), 1610 (C=C). NMR ^1H (200 MHz, $CDCl_3$, δ, ppm): **5a**: 7.51–7.16 (m, 10H, $2C_6H_5$), 5.95 (m, 2H, H-5, H-4), 5.36 (m, 1H, H-4), 3.61 (s, 2H, CH_2CO), 2.11 (q, 2H, S-CH_2, ^3J=7.5 Hz), 0.98 (t, 3H, CH_3, ^3J=7.5 Hz), **5b**: 7.51–7.16 (m, 10H, $2C_6H_5$), 6.54 (s, 1H, H-2), 2.67–2.40 (m, 4H, CH_2–CH_2), 2.32 (q, 2H, S-CH_2, ^3J=7.5 Hz), 1.12 (t, 3H, CH_3, ^3J=7.5 Hz). NMR ^{13}C (50 MHz, $CDCl_3$, δ, ppm): **5a**: 196.5 (CO), 143.7 (C-4), 136.0–125.6 (C_6H_5, C-5), 114.0 (C-l), 51.3 (C-2), 23.7 (S-CH_2), 13.1 (CH_3). **5b**: 199.8 (CO), 136.0–125.6 (C_6H_5, C-l, C-2), 57.5, 44.4 (C-4, C-5), 25.7 (S-CH_2), 14.5 (CH_3). Found, %: C 77.24, H 7.21. $C_{19}H_{20}SO$. Calcd, %: C 76.99, H 6.80.

4.2.4. 1,2-Diphenyl-1-ethylsulfanylpent-4-en-3-one (6a). Yield 30%, pale yellow crystals, mp 72–74°C. IR (ν, cm^{-1}): 1680 (CO), 1610 (C=C). NMR ^1H (200 MHz, $CDCl_3$, δ, ppm): 7.12–6.90 (m, 10H, $2C_6H_5$), 6.41 (dd, 1H, H-4, ^3J=17.5, 9.3 Hz), 6.14 (dd, 1H, H-5, ^3J=17.5 Hz, ^2J=2.1 Hz), 5.65 (dd, 1H, H-5, ^3J=9.3 Hz, ^2J=2.1 Hz), 4.60 (d, 1H, H-1 or H-2, ^3J=11.2 Hz), 4.39 (d, 1H, H-1 or H-2, ^3J=11.2 Hz), 2.32 (q, 2H, SCH_2, ^3J=7.4 Hz), 1.11 (t, 3H, CH_3, ^3J=7.4 Hz). NMR ^{13}C (50 MHz, $CDCl_3$, δ, ppm): 197.5 (CO), 140.1, 135.9 (C-4), 135.5, 129.5, 129.3, 128.6, 128.2, 127.8, 126.9, 126.6 (10C-arom., C-5), 61.1, 50.7 (C-l, C-2), 25.9 (SCH_2), 14.1 (CH_3). Found, %: C 77.46, H 6.89. $C_{19}H_{20}SO$. Calcd, %: C 76.99, H 6.80.

4.2.5. 4-Methyl-5-phenyl-5-ethylsulfanylpent-1-en-3-one (7a). Yield 67%, oil. IR (ν, cm^{-1}): 1680 (CO), 1620 (C=C). NMR ^1H (400 MHz, $CDCl_3$, δ, ppm): 7.40–7.15 (m, 5H, C_6H_5), 6.49 (dd, 1H, H-2, ^3J=18.8, 11.2 Hz), 6.32 (d, 1H, H-1, ^3J=18.8 Hz), 5.85 (d, 1H, H-1, ^3J=11.2 Hz), 3.96 (d, 1H, H-5, ^3J=10.8 Hz), 3.27 (m, 1H, H-2), 2.3–2.1 (m, 2H, SCH_2), 1.06 (t, 3H, CH_3, ^3J=7.6 Hz). NMR ^{13}C (100 MHz, $CDCl_3$, δ, ppm): 202.3 (CO), 148.6, 136.1 (C-2), 128.6, 128.4, 128.4, 127.2 (5C-arom., C-1), 51.4, 48.0 (C-4, C-5), 25.7 (SCH_2), 16.6, 14.1 ($2CH_3$). Found, %: C 71.46, H 7.87. $C_{14}H_{18}SO$. Calcd, %: C 71.75, H 7.74.

4.3. Preparation of sulfonium salts 8 and 9

To corresponding unsaturated ketone (0.005 mole) dissolved in dichloromethane (10 mL) was added 70% aqueous solution of perchloric acid (4.5 mL). After 0.5 h of stirring sulfonium salt was precipitated by addition of ether (20 mL). The crude product was purified by reprecipitation from methanol.

4.3.1. Rel-(2*R*,3*R*)-4-oxo-2,3-diphenyl-1-ethyltetrahydro-2*H*-thiopyranium perchlorate (8). Yield 99%, oil. IR (ν, cm^{-1}): 1700 (CO). NMR ^1H (400 MHz, CD_3CN, δ, ppm): 7.49–7.02 (m, 10H, $2C_6H_5$), 5.39 (d, 1H, H-2, ^3J=12.8 Hz), 4.80 (d, 1H, H-3, ^3J=12.8 Hz), 4.11–3.76 (m, 2H, CH_2), 3.49–3.12 (m, 4H, $2CH_2$), 1.19 (t, 3H, CH_3, ^3J=7.5 Hz). ^{13}C NMR (100 MHz, CD_3CN, δ, ppm): 199.8 (CO), 132.5, 130.6, (2C-q), 129.8, 129.5, 129.2, 128.7, 127.9, 127.4 (10CH-arom.), 60.1, 58.7 (2CH), 36.6, 36.0, 34.6 ($3CH_2$), 8.1 (CH_3).

4.3.2. Rel-(2*R*,3*R*)-3-Methyl-4-oxo-2-phenyl-1-ethyltetrahydro-2*H*-thiopyranium perchlorate (9). Yield 99%, oil. IR (ν, cm^{-1}): 1700 (CO). NMR ^1H (400 MHz, CD_3CN, δ, ppm): 7.55 (m, 5H, C_6H_5), 4.85 (d, 1H, H-2, ^3J=12.5 Hz), 3.99–3.03 (m, 7H, CH, $3CH_2$) 1.17 (t, 3H, CH_3, ^3J=7.4 Hz), 0.87 (d, 3H, CH_3, ^3J=7.2 Hz). ^{13}C NMR (100 MHz, CD_3CN, δ, ppm): 203.8 (CO), 130.8, 129.9, 129.3, 128.2 (6C-arom.), 61.9, 53.9 (2CH), 35.7, 35.4, 34.3 ($3CH_2$), 11.2, 8.8 ($2CH_3$).

4.3.3. 1-(2-Ethylsulfanyladamant-2-yl)but-3-en-2-one (10a). Yield 92%, pale yellow crystals, mp 51–52°C. IR (ν, cm^{-1}): 1700 (CO), 1620 (C=C). NMR ^1H (200 MHz, $CDCl_3$, δ, ppm): 6.46 (dd, 1H, H-3, ^3J=17.4, 10.4 Hz), 6.15 (dd, 1H, H-4, ^3J=17.4 Hz, ^2J=1.4 Hz), 5.68 (dd, 1H, H-4, ^3J=10.4 Hz, ^2J=1.4 Hz), 3.19 (s, 2H, CH_2-1), 2.65–2.51 (m, 2H, CH adamantyl), 2.41 (q, 2H, SCH_2, ^3J=7.5 Hz), 2.24–1.40 (m, 12H, adamantyl), 1.15 (t, 3H, CH_3, ^3J=7.5 Hz). NMR ^{13}C (50 MHz, $CDCl_3$, δ, ppm): 199.1 (CO), 137.7 (CH=), 126.4 (CH_2=), 54.5 (S-C-q), 45.6, 42.0, 39.0, 34.5, 33.0, 32.6, 27.4, 27.3, 20.5 (adamantyl, SCH_2), 13.6 (CH_3). Found, %: C 72.35, H 9.20, S 12.20. $C_{16}H_{24}SO$. Calcd, %: C 72.68, H 9.15, S 12.12.

4.3.4. 1-(1-Ethylsulfanylcyclobut-1-yl)but-3-en-2-one (11a), 1-cyclobutyliden-4-ethylsulfanylbutan-2-one (11b). 1:1, oil, yield 54%. IR (ν, cm^{-1}): 1700 (CO), 1640 (C=C). NMR ^1H (200 MHz, $CDCl_3$, δ, ppm): **11a**: 6.50–6.10 (m, 2H, H-4, H-5), 5.85–5.65 (m, 1H, H-5), 3.80–1.80 (m, 12H, $6CH_2$), 1.40–1.11 (m, 3H, CH_3); **11b**: 6.00–5.86 (m, 1H, H-2), 3.80–1.80 (m, 12H, $6CH_2$), 1.40–1.11 (m, 3H, CH_3). NMR ^{13}C (50 MHz, $CDCl_3$, δ, ppm): 198.0, 197.5 (CO, **11a** and **11b**), 166.5 (C q **11b**), 136.7 (=CH **11a**), 127.5 (=CH **11b**), 120.4 (=CH_2 **11a**), 49.0, 42.5 (CH_2CO **11a** and **11b**), 47.7 (C q **11a**), 33.7 (C-2 and C-4 cyclobut. **11a**), 34.2, 32.4 (C-2 and C-4 cyclobut. **11b**), 25.8, 25.2, 22.7 ($3CH_2$ **11a** and **11b**) 17.6, 16.1 (C-3 cyclobut. **11a** and **11b**), 14.3, 14.1 ($2CH_3$, **11a** and **11b**). Found, %: C 65.35, H 8.70. $C_{10}H_{16}SO$. Calcd, %: C 65.17, H 8.75.

4.3.5. 1-(1-Cyclopentenyl)-3-(ethylsulfanyl)-1-propanone (12b). Oil, yield 62%. IR (ν, cm^{-1}): 1680 (CO), 1620 (C=C). NMR ^1H (200 MHz, $CDCl_3$, δ, ppm): 6.79–6.77 (m, 1H, =CH), 2.98–2.70 (m, 4H, $COCH_2CH_2$), 2.61–2.45 (m, 6H, $2CH_2$-allyl., CH_2-ethyl.), 1.98–1.86 (m, 2H, CH_2-cyclopent.), 1.25 (t, 3H, CH_3, ^3J=7.6 Hz). NMR ^{13}C (50 MHz, $CDCl_3$, δ, ppm): 196.1 (CO), 144.8 (C-1 cyclopent.), 143.1 (C-2 cyclopent.), 38.6, 33.4, 30.0, 25.5, 25.3, 22.1 ($6CH_2$), 14.1 (CH_3). Found, %: C 64.84, H 9.32. $C_{10}H_{16}SO$. Calcd, %: C 65.17, H 8.75.

4.3.6. 1-[2-(Ethylsulfanyl)cyclohexyl]-2-propen-1-one (13a), 1-(1-cyclohexenyl)-3-(ethylsulfanyl)-1-propanone (13b). Oil, 1:1, yield 23%. IR (ν, cm^{-1}): 1695 (CO), 1630 (C=C). NMR ^1H (200 MHz, $CDCl_3$, δ, ppm): **13a**: 6.44 (dd, 1H, CH acryl., ^3J=15.3, 10.4 Hz,), 6.26 (dd, 1H, CH_2 acryl., ^3J=15.3 Hz, ^2J=1.3 Hz), 5.82 (dd, 1H, CH_2 acryl., ^3J=10.4 Hz, ^2J=1.3 Hz), **13b**: 6.58 (m, 1H, CH vinyl.), **13a** and **13b**: 2.95–1.30 (m, 26H, $5CH_2$, 2CH **13a**; $7CH_2$ **13b**), 1.30–1.18 (m, 6H, $2CH_3$ **13a** and **13b**). NMR ^{13}C (50 MHz, $CDCl_3$, δ, ppm): 202.6, 199.3 (CO, **13a** and **13b**), 140.1, 138.0, 136.2, 128.2 (C=, **13a** and **13b**), 52.1, 43.8, 37.2, 34.1, 30.5, 26.2, 26.2, 25.7, 25.3, 25.0, 23.6, 23.2, 21.8, 21.4 ($5CH_2$, 2CH **13a**; $7CH_2$ **13b**), 14.8, 14.6 (CH_3 **13a** and **13b**). Found, %: C 66.85, H 8.98. $C_{11}H_{18}SO$. Calcd, %: C 66.62, H 9.15.

4.3.7. 5-Ethylsulfanyl-5-methyl-1,6 heptadien-3-one (14a) (4(*E*+*Z*))-1-ethylsulfanyl-5-methyl-4,6-heptadien-3-one (14b). 7:1, yield 47%, oil. IR (ν, cm^{-1}): 1680, 1640 (CO, C=C). **14a**. NMR ^1H (400 MHz, $CDCl_3$, δ, ppm): 6.37 (dd, 1H, H-2, ^3J=17.5, 10.5 Hz), 6.19 (d, 1H, H-1, ^3J=17.5 Hz), 5.86 (dd, 1H, H-6, ^3J=17.3, 10.5 Hz), 5.78 (d, 1H, H-1, ^3J=10.5 Hz), 5.07 (d, 1H, H-7, ^3J=10.5 Hz), 4.95 (d, 1H, H-7, ^3J=17.3 Hz), 2.87 (s, 2H, CH_2CO), 2.42–2.35 (m, 2H, SCH_2), 1.55 (br.s, 3H, CH_3), 1.17 (t, 3H, CH_3, ^3J=7.4 Hz). NMR ^{13}C (100 MHz, $CDCl_3$, δ, ppm): 197.2 (CO), 142.1, 137.2, 128.1, 112.4 (2CH=, $2CH_2$=), 51.1 (C-q), 49.3 ($COCH_2$), 25.0 (SCH_2), 20.6 (CH_3), 14.0

(CH_3). **14b**. NMR ^1H (400 MHz, $CDCl_3$, δ, ppm): 5.3–5.2 (m, 1H, H-4(*E*+*Z*)), 3.12–2.65 (m, 4H, SCH_2CH_2(*E*+*Z*)), 1.99 (br.s, 3H, CH_3(*E*)), 1.69 (br.s, 3H, CH_3(*Z*)), 1.28–1.19 (m, 3H, CH_3(*E*+*Z*)). NMR ^{13}C (100 MHz, $CDCl_3$, δ, ppm): 198.7, 198.6 (CO(*E*+*Z*)), 140.3, 135.4, 129.2, 120.6 (C=(*E*+*Z*)), 26.4, 25.9, 25.3, 24.8 (SCH_2CH_2(*E*+*Z*)), 14.5, 14.5 (CH_3(*E*+*Z*)). Other signals of **14b** are overlapped with those of **14a**. Found, %: C 65.63, H 8.77. $C_{10}H_{16}OS$. Calcd, %: C 65.17, H 8.75.

4.3.8. 5-Ethylsulfanyl-5,6-dimethyl-1,6-heptadien-3-one (15a), (4(*E*+*Z*))-1-ethylsulfanyl-5,6-dimethyl-4,6-heptadien-3-one (15b). 3:1, yield 55%, oil. IR (ν, cm^{-1}): 1690, 1640 (CO, C=C). **15a**. NMR ^1H (400 MHz, $CDCl_3$, δ, ppm): 6.36 (dd, 1H, H-2, ^3J=17.5, 10.4 Hz), 6.21 (dd, 1H, H-1, ^3J=17.5 Hz, ^2J=1.2 Hz), 5.76 (dd, 1H, H-1, ^3J=10.4 Hz, ^2J=1.2 Hz), 4.95 (br.s, 1H, H-7), 4.79 (br.s, 1H, H-7), 3.06 (d, 1H, H-4, ^2J=15.8 Hz), 2.87 (d, 1H, H-4, ^2J=15.8 Hz), 2.38–2.27 (m, 2H, SCH_2), 1.92 (br.s, 3H, CH_3), 1.58 (s, 3H, CH_3), 1.18 (t, 3H, CH_3, ^3J=7.4 Hz). NMR ^{13}C (100 MHz, $CDCl_3$, δ, ppm): 197.0 (CO), 145.5, 136.8, 127.8, 112.3 (4C=), 51.0 (C-q), 48.3 ($COCH_2$), 25.0 (SCH_2), 22.4, 19.4 ($2CH_3$), 13.9 (CH_3). **15b**. NMR ^1H (400 MHz, $CDCl_3$, δ, ppm): 6.23 (br.s, 2H, H-4(*E*+*Z*)), 5.17–5.12 (m, 4H, H-7(*E*+*Z*)), 3.02–2.45 (m, 12H, $CH_2SCH_2CH_2$(*E*+*Z*)), 1.94 (br.s, 3H, CH_3(*E* or *Z*)), 1.90 (br.s, 3H, CH_3(*E* or *Z*)), 1.89 (br.s, 3H, CH_3(*E* or *Z*)), 1.71 (br.s, 3H, CH_3(*E* or *Z*)), 1.25–1.15 (m, 6H, CH_3(*E*+*Z*)). NMR ^{13}C (100 MHz, $CDCl_3$, δ, ppm): 198.6 (CO(*E*+*Z*)), 147.6, 141.2, 140.2, 123.5, 117.8, 115.9 (8C=(*E*+*Z*)), 40.5, 28.9, 28.9 (SCH_2CH_2(*E*+*Z*)), 23.1, 22.7, 22.6, 19.3, (4CH_3(*E*+*Z*)), 15.0, 14.8 (CH_3(*E*+*Z*)). Found, %: C 66.64, H 9.47. $C_{11}H_{18}OS$. Calcd, %: C 66.62, H 9.15.

4.3.9. (4*E*,6*E*)-1-(Ethylsulfanyl)-7-phenyl-4,6-heptadien-3-one (16). Yield 64%, oil. IR (ν, cm^{-1}): 1660, 1640 (CO, C=C). NMR ^1H (400 MHz, $CDCl_3$, δ, ppm): 7.50–7.26 (m, 6H, C_6H_5, H-6), 6.95 (d, 1H, H-7, ^3J=15.6 Hz), 6.88 (dd, 1H, H-5, ^3J=15.6, 10.2 Hz), 6.29 (d, 1H, H-4, ^3J=15.6 Hz), 2.95–2.81 (m, 4H, $2CH_2$), 2.55 (q, 2H, S-CH_2, ^3J=7.4 Hz), 1.25 (t, 3H, CH_3, ^3J=7.4 Hz). NMR ^{13}C (100 MHz, $CDCl_3$, δ, ppm): 198.3 (CO), 143.8, 142.9, (2CH=), 135.8 (C-q), 129.2, 129.1, 128.8, 127.2, 126.5 (5CH-arom., 2CH=), 40.7, 26.2, 25.8 ($3CH_2$), 14.7 (CH_3). Found, %: C 73.55, H 7.36. $C_{15}H_{18}SO$. Calcd, %: C 73.13, H 7.36.

4.3.10. 1-[2-(Ethylsulfanyl)-3-cyclohexenyl]-2-propen-1-one (17a), 1-(1,3-cyclohexadienyl)-3-(ethylsulfanyl)-1-propanone (17b). 1:1, oil, yield 40%. IR (ν, cm^{-1}): 1690, 1630 (CO, C=C). NMR ^1H (400 MHz, $CDCl_3$, δ, ppm): **17a**: 6.56 (dd, 1H, CH-acryl., ^3J=17.5, 10.6 Hz), 6.26 (dd, 1H, CH_2-acryl., ^3J=17.5 Hz, ^2J=1.4 Hz), 5.90–5.68 (m, 2H, 2=CH-cyclohexen.), 5.76 (dd, 1H, CH_2-acryl., ^3J=10.6 Hz, ^2J=1.4 Hz), 3.72 (br.s, 1H, SCH), 3.17–3.10 (m, 1H, COCH), 2.55 (q, 2H, SCH_2-ethyl., ^3J=7.2 Hz), 2.15–1.80 (m, 4H, $2CH_2$-cyclohexen.), 1.24 (t, 3H, CH_3, ^3J=7.2 Hz), **17b**: 6.93 (d, 1H, =CH-2-cyclohexen., ^3J=5.6 Hz), 6.30–6.10 (m, 2H, CH=CH), 2.95 (t, 2H, $COCH_2$, ^3J=7.8 Hz), 2.80 (t, 2H, SCH_2CH_2, ^3J=7.8 Hz), 2.55 (q, 2H, SCH_2-ethyl., ^3J=7.2 Hz), 2.41 (t, 2H, CH_2-6-cyclohexen., ^3J=9.6 Hz), 2.29–2.18 (m, 2H, CH_2-5-cyclohexen.), 1.24 (t, 3H, CH_3, ^3J=7.2 Hz). NMR ^{13}C (100 MHz, $CDCl_3$, δ, ppm): **17a** and **17b**: 199.3, 198.1 (CO), 135.2, 134.8, 134.5, 133.0, 127.8, 127.3, 127.3, 123.8 (8C=), 49.2 (*CH*CO), 41.9 (CHS), 37.1 (CH_2CO), 26.1, 25.9, 24.9, 23.7, 19.4, 19.3 ($7CH_2$), 14.8, 14.6 ($2CH_3$). Found, %: C 67.29, H 8.37. $C_{11}H_{16}SO$. Calcd, %: C 67.30, H 8.21.

4.3.11. 1-[2-(Ethylsulfanyl)-3-cyclooctenyl]-2-propen-1-one (18a), 1-(1,3-cyclooctadienyl)-3-(ethylsulfanyl)-1-propanone (18b). 5:1, yield 55%. IR (ν, cm^{-1}): 1690, 1630 (CO, C=C). NMR ^1H (400 MHz, $CDCl_3$, δ, ppm): **18a**: 6.32 (dd, 1H, CH-acryl., ^3J=17.6, 10.4 Hz), 6.15 (dd, 1H, CH_2-acryl., ^3J=17.6 Hz, ^2J=1.2 Hz), 5.82–5.74 (m, 1H, =CH-cyclocten.), 5.66 (dd, 1H, CH_2-acryl., ^3J=10.4 Hz, ^2J=1.2 Hz), 5.58 (d.t, 1H, =CH, ^3J=9.8 Hz), 3.93 (dd, 1H, SCH, ^3J=9.8, 4.8 Hz), 3.93 (dd, 1H, COCH, ^3J=11.2 Hz, ^3J=4.8 Hz), 2.50–1.20 (m, 10H, $5CH_2$), 1.13 (t, 3H, CH_3, ^3J=7.2 Hz), **18b**: 6.95 (br.s, 1H, =CH-2-cyclocten.), 5.82–5.74 (m, 2H, CH=CH), 2.90 (t, 2H, $COCH_2$, ^3J=7.2 Hz), 2.72 (t, 2H, SCH_2CH_2, ^3J=7.2 Hz), 2.50–1.20 (m, 10H, $5CH_2$), 1.15 (t, 3H, CH_3, ^3J=7.2 Hz). NMR ^{13}C (100 MHz, $CDCl_3$, δ, ppm): **18a**: 200.7 (CO), 136.1, 131.5, 131.1, 127.8 (4C=), 54.8 (*CH*CO), 41.1 (CHS), 30.2, 29.3, 27.1, 26.3 ($5CH_2$), 14.6 (CH_3), **18b**: 198.9 (CO), 140.2 (C-q), 136.8, 136.6, 123.8 (3CH=), 37.5 (CH_2CO), 29.9, 26.0, 25.8, 24.6, 23.9, 21.5 ($6CH_2$), 14.6 (CH_3). Found, %: C 69.29, H 8.77. $C_{13}H_{20}SO$. Calcd, %: C 69.59, H 8.98.

4.4. General procedure for polyeneones preparation 19–23

To a solution of ethylsulfanyl substituted ketone (or to a mixture of ketones) in dichloromethane at 0°C solution of methyltrifluoromethanesulfonate in dichloromethane (1 equiv.) was added dropwise. The reaction mixture was stirred at rt until the starting material disappears (controlled by TLC). Then an excess of saturated aqueous $KHCO_3$ was added and the reaction mixture was stirred 2 h. The organic layer was separated, the aqueous layer was extracted with ether (2×20 mL). The combined organic phases were dried (Na_2SO_4) and concentrated at reduced pressure. The crude product was purified by colomn chromatography.

4.4.1. (1*E*)-1-Phenyl-1,4-pentadien-3-one (19). Yield 73%, oil. IR (ν, cm^{-1}): 1670, 1640 (CO, C=C). NMR ^1H (400 MHz, $CDCl_3$, δ, ppm): 7.67 (d, 1H, H-2, ^3J=15.8 Hz), 7.60–7.30 (m, 5H, C_6H_5), 7.01 (d, 1H, H-1, ^3J=15.8 Hz), 6.73 (dd, 1H, H-4, ^3J=17.4, 10.6 Hz), 6.39 (dd, 1H, H-4, ^3J=17.4 Hz, ^2J=1.2 Hz), 5.87 (dd, 1H, H-4, ^3J=10.6 Hz, ^2J=1.2 Hz). NMR ^{13}C (100 MHz, $CDCl_3$, δ, ppm): 189.4 (CO), 143.9, 135.4 (2CH), 134.5 (C-q), 130.6, 128.9 (2CH), 128.5 (CH_2), 128.4, 124.1 (2CH). Found, %: C 83.08; H 9.99; $C_{11}H_{10}O$. Calcd, %: C 83.51; H 10.11.

4.4.2. 1,1-Diphenyl-1,4-pentadien-3-one (20). Yield 91%, oil. IR (ν, cm^{-1}): 1680, 1630 (CO, C=C). NMR ^1H (400 MHz, $CDCl_3$, δ, ppm): 7.45–7.13 (m, 10H, $2C_6H_5$), 6.68 (s, 1H, H-2), 6.12–6.07 (m, 2H, H-4, H-5), 5.50–5.40 (m, 1H, H-5). NMR ^{13}C (100 MHz, $CDCl_3$, δ, ppm): 191.7 (CO), 141.0, 138.9, 136.2, 130.0, 129.5, 128.9, 128.6, 128.4, 128.3, 127.4, 125.9 (12C-arom., 2C=C). Found, %: C 87.51; H 6.12; $C_{17}H_{14}O$. Calcd, %: C 87.15; H 6.02.

4.4.3. 1-(2-Adamantyliden)-3-buten-2-one (21). Yield

98%, oil. IR (ν, cm^{-1}): 1670, 1640 (CO, C=C). NMR ^1H (400 MHz, $CDCl_3$, δ, ppm): 6.38 (dd, 1H, H-4, ^3J=17.6, 10.4 Hz), 6.17 (d, 1H, H-5, ^3J=17.6), 6.10 (s, 1H, H-2), 5.67 (d, 1H, H-5, ^3J=10.4 Hz), 3.99 (br.s, 1H, CH-allyl.), 2.39 (br.s, 1H, CH-allyl.), 2.14–1.55 (m, 12H, adamantyl). NMR ^{13}C (100 MHz, $CDCl_3$, δ, ppm): 191.0 (CO), 172.5 (C-q), 138.3 (=CH_2), 126.7, 115.2 (2CH=), 41.6, 40.3, 39.2, 36.7, 33.3, 33.2, 27.8 (adamantyl). Found, %: C 83.44; H 9.14; $C_{14}H_{18}O$. Calcd, %: C 83.12; H 8.97.

4.4.4. 1-(1,3-Cyclohexadienyl)-2-propen-1-one (22). Yield 88%. IR (ν, cm^{-1}): 1680, 1640 (CO, C=C). NMR ^1H (400 MHz, $CDCl_3$, δ, ppm): 6.89 (dd, 1H, COCH=, ^3J=17.0, 10.5 Hz), 6.88 (d, 1H, H-2 cyclohexyl., ^3J= 4.5 Hz), 6.19 (dd, 1H, H-3 cyclohexyl., ^3J=4.5, 4.5 Hz), 6.19 (dd, 1H, =CH_2, ^3J=17.0 Hz, ^2J=2.0 Hz), 6.07–6.03 (m, 1H, H-4 cyclohexyl.), 5.62 (dd, 1H, =CH_2, ^3J= 10.5 Hz, ^2J=2.0 Hz), 2.44–2.40 (m, 2H, $COCCH_2$), 2.25–2.17 (m, 2H, CH_2-5 cyclohexyl.). NMR ^{13}C (100 MHz, $CDCl_3$, δ, ppm): 190.5 (CO), 136.3 (C-q), 135.4, 134.2, 131.1, 127.5, 124.0 (4CH=, CH_2=), 22.8, 19.8 (CH_2CH_2). Found, %: C 80.85; H 7.98; $C_9H_{10}O$. Calcd, %: C 80.56; H 7.51.

4.4.5. 1-(1,3-Cyclooctadienyl)-2-propen-1-one (23). Yield 76%. IR (ν, cm^{-1}): 1680, 1650 (CO, C=C). NMR ^1H (400 MHz, $CDCl_3$, δ, ppm): 7.00 (br.s, H-2 cyclooctyl.), 6.94 (dd, 1H, COCH=, ^3J=17.2, 10.8 Hz), 6.21 (dd, 1H, =CH_2, ^3J=17.2 Hz, ^2J=2.0 Hz), 5.90–5.87 (m, 2H, H-3, H-4 cyclooctyl.), 5.68 (dd, 1H, =CH_2, ^3J=10.8 Hz, ^2J= 2.0 Hz), 2.60–2.40 (m, 2H, CH_2-8 cyclooctyl), 2.25–2.10 (m, 2H, CH_2-5 cyclooctyl.), 1.60–1.40 (m, 4H, CH_2-6, CH_2-7 cyclooctyl.). NMR ^{13}C (100 MHz, $CDCl_3$, δ, ppm): 191.6 (CO), 140.8 (C-q), 137.9, 136.8, 131.9, 127.8, 124.0 (4CH=, CH_2=), 30.0, 25.1, 24.1, 21.7 (4CH_2-cyclooctyl.). Found, %: C 81.65, H 8.91. $C_{11}H_{14}O$. Calcd, %: C 81.44, H 8.70.

4.4.6. 1,1-Diphenyl-4-ethylsulfanylbut-1-en-3-one (24). Yield 87%, oil. IR (ν, cm^{-1}): 1690 (CO), 1620 (C=C). NMR ^1H (400 MHz, $CDCl_3$, δ, ppm): 7.42–7.20 (m, 10H, 2C_6H_5), 6.77 (s, 1H, =CH), 3.08 (s, 2H, CH_2), 2.32 (q, 2H, S-CH_2, ^3J=7.6 Hz), 1.20 (t, 3H, CH_3, ^3J=7.6 Hz). NMR ^{13}C (100 MHz, $CDCl_3$, δ, ppm): 195.3 (CO), 154.7 (C-1), 140.7, 138.7, 129.5, 129.3, 128.6, 128.4, 128.3, 128.2, 124.4 (2C_6H_5, C-2), 40.8 (C-4), 25.8 (S-CH_2-ethyl.), 14.1 (CH_3). Found, %: C 76.71, H 6.09. $C_{18}H_{18}SO$. Calcd, %: C 76.56, H 6.42.

4.4.7. Rel-(2*R*,3*R*)-4-oxo-2,3-diphenyl-1-ethyltetrahydrothiophenium tetrafluoroborate (25). A well stirred solution of ethylsulfanylacetyl fluoride (0.02 mole) in dichloromethane (50 mL) was saturated with BF_3 at −60°C. After stirring 10 min at −60°C *trans*-stylbene (0.02 mole) in dichloromethane (30 mL) was added. The reaction mixture was allowed to warm up to the rt and than poured into dry ether (100 mL). The precipitate was filtered off, washed with cold methanol, dry ether and dried in vacuo. Yield 59%, mp 109–111°C. IR (ν, cm^{-1}): 1760 (CO). NMR ^1H (400 MHz, CD_3CN, δ, ppm): 7.61–7.00 (m, 10H, 2C_6H_5), 6.05 (d, 1H, H-2, ^3J=13.8 Hz), 4.90 (d, 1H, H-3, ^3J=13.8 Hz), 4.42 (d, 1H, ^2J=18.1 Hz, CH_2CO), 4.25 (d, 1H, ^2J=18.1 Hz, CH_2CO), 3.40–2.78 (m, 2H, S^+-CH_2–CH_3), 0.91 (t, 3H, ^3J=7.2 Hz, S^+-CH_2–CH_3). ^{13}C NMR (100 MHz, CD_3CN, δ, ppm): 200.0 (CO), 132.7, 131.5, 130.4, 129.9, 129.6, 129.5, 129.0, 126.7 (12C arom.), 59.5, 53.0 (2CH), 43.7 (CH_2CO), 32.6 (CH_2CH_3), 10.0 (CH_2CH_3). Found, %: C 58.38, H 5.26. $C_{18}H_{19}BF_4OS$. Calcd, %: C 58.40, H 5.17.

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