Stereoelectronic effects in intramolecular S→N acyl migrations in diastereoisomeric 3-amino- and 3-methylamino-1,2,3-triphenylpropyl thiolacetates

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Abstract

The kinetics of the intramolecular S⟶N acyl transfer in diastereoisomeric 3-amino- and 3-methylamino-1,2,3-triphenylpropyl thiolacetates catalyzed by triethylamine could be conveniently studied by means of IR spectroscopy. The rates of migration depend strongly on the *N*-substitution as well as on the configuration. These rates clash with the steric effects expected in the cyclic tetrahedral intermediate, but are in full agreement with the requirements of Deslongchamps' stereoelectronic hypothesis of two lone pairs on adjacent heteroatoms to be antiperiplanar to the cleaving bond. The formation or breaking of the endocyclic C-S bond demands an equatorial lone pair on nitrogen forcing an *N*-methyl group into the axial position thus changing the order of steric hindrance in the diastereoisomers.

Keywords: Intramolecular S→N acyl migration, stereoelectronic effects, thiolacetates, acetamido thiols, triphenylpropane skeleton, diastereoisomers, IR monitoring

Introduction

Stereoelectronic effects are a subject of long-standing interest as it has been found that they play an important role in the cleavage of carbon-heteroatom bonds in many transformations, such as oxidation and hydrolysis of α- and β-glycosides, hydrolysis of ortho-esters, esters, lactones, lactams, amides, their sulfur analogues, and many others.[1-3] They are exhibited as the dependence of conformation and reactivity of molecules on the orientation of electron lone pairs in space. The stabilization of a molecule, which occurs when a lone pair on oxygen or other heteroatom is oriented antiperiplanar to a polar bond due to a shortening of the C-O and lengthening of the polar bond, is known as the anomeric effect. The effect on rates, which has been invoked at first in the acetal oxidation, is called a kinetic anomeric effect or antiperiplanar lone pair hypothesis (ALPH). The latter has been extended to the formation and cleavage of

tetrahedral intermediates by Deslongchamps,[4-8] who formulated the so-called "Stereoelectronic theory". It was founded on the observation that the preferred conformation of the tetrahedral intermediate in the hydrolysis of esters and amides, and hemi-orthoesters and hemi-orthoamides, respectively, is of decisive importance for the nature of hydrolysis products. The author has defined as, "stereoelectronically controlled cleavage of the tetrahedral intermediate" the specific breakdown of a C-O or a C-N bond, which occurs when two lone pair orbitals on adjacent heteroatoms (O or N) are oriented antiperiplanar to the cleaving C-N or C-O bond. Subsequently, considerable experimental evidence for stereoelectronic control has been accumulated [9–14] and supported by calculations.[15,16] Alternate explanations for the phenomena have been put forward.[17,18] In a recent critique to objections concerning the ALPH Chandrasekhar has shown that it is a viable theory despite certain limitations.[19]

Lyapova *et al*.[20] have studied the intramolecular acid catalyzed N⟶O and base catalyzed O⟶N acyl transfer in diastereoisomeric aminoalcohols with a 1,2,3-triphenylpropane skeleton. The authors observed inversion of the ratio of migration rates of the *EE*/*ET* isomers[21] upon *N*-substitution which could only be explained by a stereoelectronic requirement for equatorial orientation of the nitrogen lone pair in the making or breaking of the tetrahedral intermediates. This forces the *N*-substituent to be axial, causing significant changes to the steric hindrances in the two isomeric cyclic intermediates of practically single allowed conformations.

Recently it has been elaborated that the stereoelectronic effects are of importance at an N⟶O acyl transfer into serine proteinases,[22] *i.e*., they matter for the determination of the geometry of the active center in these proteinases. Thus, it may be assumed that in the plant proteinases, *i.e.*, the cysteine ones, whereby an N⟶S transfer of acyl groups occurs during the catalytic act, the stereoelectronic effects will be of importance too.

Stereoelectronic effects in the synthesis and equilibration of conformationally rigid tricyclic mono- and di-thioacetals have been studied by Deslongchamps *et al*.[23] and the anomeric effect for sulfur has evaluated to be of the same order as that for oxygen.

Kaloustian *et al.* have examined the role of the stereoelectronic effects at the cleavage of hemi-orthothiol,[24, 25] hemi-orthothiolate,[26] and thio-hemi-orthoamide [27–29] intermediates. The authors have observed that the C-S cleavage is the preferred route for the breakdown of hemi-ortho-thioamide tetrahedral intermediate at room temperature, while the kinetically favored route in aprotic media at –78 ^{o}C and in the presence of an "acetyl sink" involves the cleavage of the C-N bond. As the latter is in agreement with the requirements of Deslongchamps' hypothesis, they claim that, "to the extent that this preference is dictated by stereoelectronic factors, it is likely that the specificity and reaction rates of cysteine proteinases may also be governed by similar stereoelectronic restraints." However the question of whether the relevance of the stereoelectronic effect at low temperatures is only due to competitive acyl migration is left open. In addition, it is not clear whether the barriers for conformational changes at room temperature become commensurate with those for breakdown of the intermediate, and thus provide a thermodynamically preferable reaction route for C-S bond cleaving.

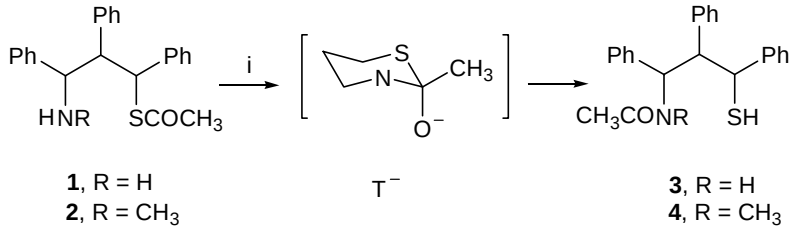
The limited number of sterically allowed conformations in triphenylpropane derivatives, practically single ones in saturated six-membered heterocycles, can cause large differences in the reactivity of the various diastereoisomers, which can be reliably interpreted. Thus, in contrast to the mobile systems, studied by Kaloustian, the presence of a stereoelectronic effect in these highly hindered systems, it is expected to be more unambiguously detected in the fashion indicated above [20] because the antiperiplanar lone-pair disposition cannot be reached readily by rotations around single bonds or nitrogen inversions.

A study on the rates of intramolecular S→N acyl transfer in diastereoisomeric 3-amino- and 3-methylamino-1,2,3-triphenylpropyl thiolacetates, aimed at elucidating the role of stereoelectronic effects in the reaction, is presented herein.

Results and Discussion

The diastereoisomeric 3-amino- and 3-methylamino-1,2,3-triphenylpropyl thiolacetates **1** and **2** were obtained in our laboratory [30] from the corresponding chlorides and potassium thiolacetate. An intramolecular S→N acyl transfer converts an amino thiolacetate into an acetamido thiol *via* a tetrahedral intermediate as shown on Scheme 1.

When the migrations were performed in NMR tubes, the proton resonances of the products indicated the desired acetamido thiols **3** and **4**. However, the latter were found to be highly unstable and could not be isolated and characterized. It is known that benzyl thiols undergo spontaneously a broad variety of transformations.[31]



Scheme 1. Intramolecular S⟶N acyl transfer in diastereoisomeric thiolacetates **1** and **2**. (i) 0.02 *M* solution in 0.2 *M* solution of Et_3N in CH_3CN, 25±0.5°C.

The rates of migration were determined by IR, monitoring the decrease in the thioester absorbance or increase of that of the thioamide with time. The presence of an isosbestic point, which is illustrated for *ET*-3-amino-1,2,3-triphenylpropyl thiolacetate in Fig. 1, is observed in all cases studied, and indicates that the acetamides are obtained in a clean reaction. The IR frequencies of acetamido thiols **3** and **4** (Table 1), compared with those of the corresponding acetamido propanols,[32] (1671 cm^{-1} for *ET*-amino, 1632 cm^{-1} for *ET*-methylamino and 1630 cm^{-1} for *EE*-methylamino), represent an additional proof for the structure of the former, because the amide frequencies should be practically unchanged upon replacing OH for SH.

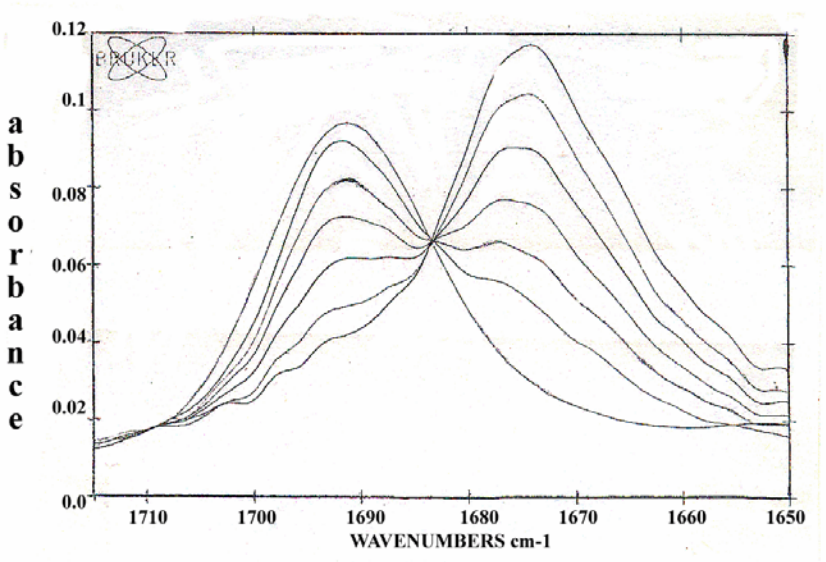


Figure 1. Intramolecular S⟶N acyl migration in *ET*-3-amino-1,2,3-triphenylpropyl thiolacetate, monitored by IR spectroscopy.

The rate constants were obtained by non-linear curve fitting by means of the GRAFIT 4 program using a first order rate equation as demonstrated on Fig. 2 for the case of *ET*-**1**.

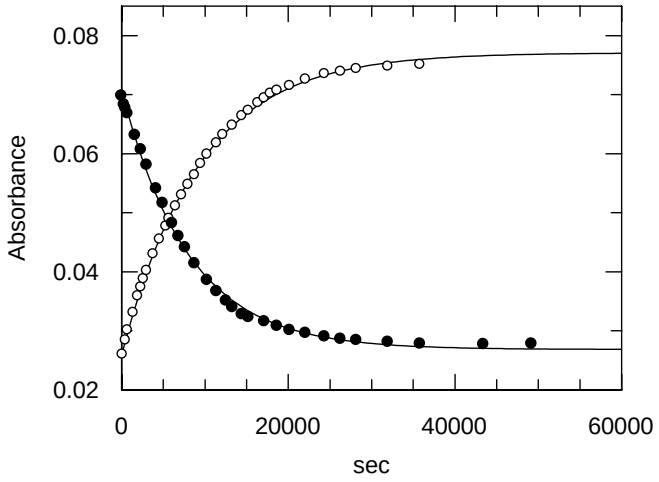


Figure 2. Change of absorbance with time for *ET*-**1** shown by full circles, decay of ester; shown by open circles – formation of amide (see text)**.**

The rate data are summarized in Table 1. As can be seen, the rates of the intramolecular S⟶N acyl transfer depend strongly on *N*-substitution as well as on the configuration. These dependences can be understood in terms of stereoelectronic effects governing the formation or breakdown of the cyclic tetrahedral intermediate $\mathbf{T}^{\pm}$ formed in the migration reaction. It is

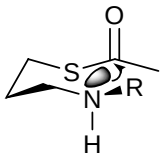
presumed to be negatively charged as a result of the base catalysis. In the previous study of the oxygen analogues [20] the crucial observation was that the migration rates, determined qualitatively, were *EE* > *ET* when R = H, while *EE* < *ET* when R = Me, the differences being strongly expressed.

Table 1. IR data and rate constants of intramolecular S→N acyl transfer in diastereoisomeric 3-amino- and 3-methylamino-1,2,3-triphenylpropyl thiolacetates **1** and **2**.

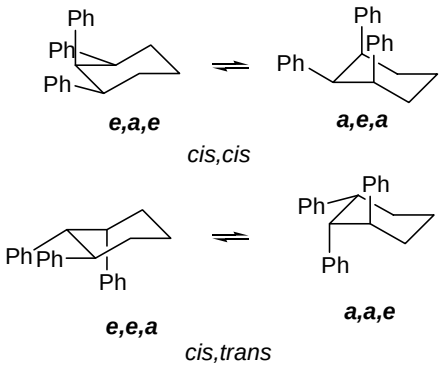
Compound	IR frequency, cm^{-1}		Rate constant, sec^{-1}
	$SCOCH_3$	$NCOCH_3$	
ET-**1** *(1R*,2S*,3R*)*	1691	1674	$(1.2 \pm 0.1) \times 10^{-4}$
ET-**2** *(1R*,2S*,3R*)*	1685	1630	7×10^{-6} [a]
TE-**2** *(1R*,2R*,3R*)*	1691	1638	$(3.7 \pm 0.6) \times 10^{-6}$
EE-**2** *(1R*,2S*,3S*)*	1691	1632	$(6.7 \pm 0.2) \times 10^{-7}$

[a] Approximate estimate from a single conversion for 13 h.

For the case when R=H an obvious explanation considers the steric interactions in the chair conformation of $\mathbf{T}^{\pm}$. The same kinds of interactions arise with the thiols reported here and will be exhibited with the latter. For simplicity, only the preferred conformers will be considered, with an equatorial orientation of the methyl group arising from the acetyl moiety. These are the expected products from attack on the thioester group in the *Z*-configurations, as shown on Scheme 2.



Scheme 2. Initial attack in thiolacetates **1** and **2**.



Scheme 3. Chair conformations of diastereoisomeric cyclohexanes with three neighboring phenyl groups.

Characteristically, six-membered rings with three neighboring phenyl groups give rise to two chair conformations differing strongly in stability. This is readily illustrated by the cyclohexanes shown in Scheme 3.

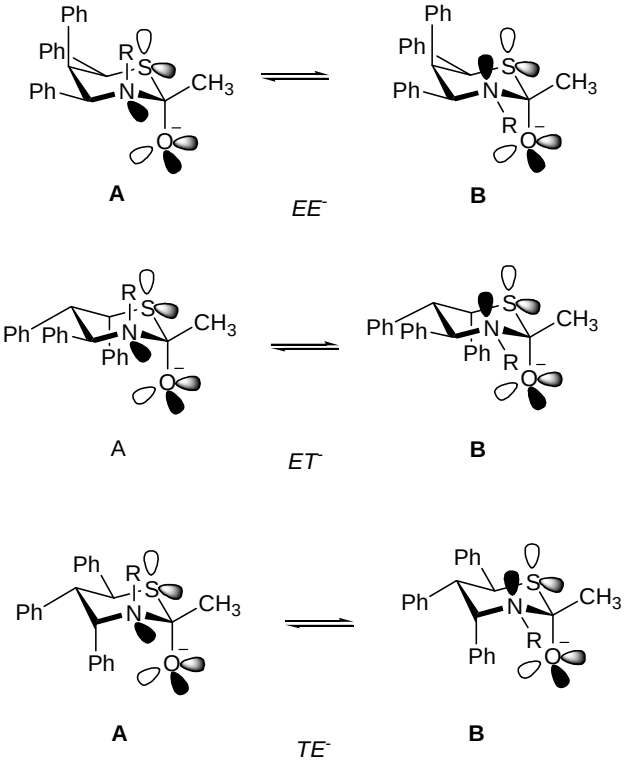
The two configurations depicted are relevant to the cyclic intermediates discussed below. The conformations with two axial phenyl groups will be strongly disfavored, more so in the *cis-, cis*- isomer because of the 1,3-parallel interaction of the axial phenyl groups.

Thus, the transition states should resemble the tetrahedral intermediates with two equatorial phenyl groups and the latter are shown on Scheme 4. **A** are the conformations demanded by APLH for cleaving of the C-S bond. The equilibria of Scheme 4 can take place *via* nitrogen inversion. When R = H, because the steric demands of H are small and not much different from that of a lone pair, it is readily seen that the tetrahedral intermediate in *EE* is less hindered than in *ET*, irrespective of the conformation of R – the axial Ph in *EE* opposes either two lone-pairs or H and a lone pair, while in *ET* there is a substantial 1,3- parallel Ph ↔ O^- interaction. This explains why with the oxygen analogues studied before [20] the *EE*- isomer reacts faster than *ET* when R = H. When R = Me, if the *N*-Me group is equatorial (forms **B**) there is no apparent reason why the reactivity ratio should not to be retained. The observation with *N*-Me of an inversed ratio, *i.e.*, *ET* migrating faster than *EE***,** is readily explained by an axial Me (forms **A**) enforced by the demand for an antiperiplanar nitrogen lone pair to the breaking C-O. Now the difference in strain is 1,3 parallel Ph ↔ Me in *EE*-A *versus* Ph ↔ O^- in *ET*-A, and no doubt the former is stronger.

In the case of the presently studied amino thiolacetates when R = H only the *ET*- isomer was available because the *EE* isomer of the amino thiolacetate **1** defied all attempts at synthesis, the product of elimination being formed exclusively.[30] When R = Me, however, we could compare the migration rates of two diastereoisomers *ET*-**2** and *TE*-**2** giving *cis, trans*- phenyls in the intermediates with that of the *EE*- isomer with *cis, cis*- phenyl groups. The results in Table 1 demonstrate that *EE*-**2** reacts 6 and 10 times more slowly than *TE*-**2** and *ET*-**2,** respectively. This is a clear indication that by introducing a 1,3-parallel Ph↔Me interaction in *EE*-**2** the stereoelectronic effect overrides the disadvantage of a 1,3-parallel Ph↔O^- in *ET*-**2** and *TE*-**2**. Although the rate for *ET*-**2** is only a rough estimate, its faster migration compared to that of *TE*-**2** is in line with the greater Ph↔O^- distance in *ET*-**2** because the C–S bonds are longer than the C–N bonds. Another argument on the faster migration of *ET*-**2** *versus TE*-**2**, is that in *ET*-**2** at the transition state level, the C-S bond will be much longer, as the sulfur is the leaving group. On the other hand, the Ph<O^- interaction in the TE-2 will remain the same or even shorter due to amide formation.

Further support for the operation of the stereoelectronic effect comes from comparison of the rates of *ET*-**1** with *ET*-**2.** The difference in rates is 20 fold – a value corresponding to a change in the free energy of activation of 1.8 kcal/mol, which happens to be the same as the conformational energy for a methyl in cyclohexane,[33] adding credence to the assumption that the retardation observed is due to the axial Me in the transition state for *ET*-**2**. It should be noted that

aminolysis of acyl derivatives can be slowed by *N*-methyl substitution[34] but such effects are relatively small.



Scheme 4. Conformations of the tetrahedral intermediates ($T^{\pm}$) of the intramolecular S→N acyl transfer in the 3-amino- and 3-methylamino-1,2,3-triphenylpropyl thiolacetates **1** and **2**.

When comparing these relationships with those in the corresponding O- analogues the parallelism in the results is quite obvious. This could be due to very similar anomeric effects for sulfur and for oxygen, as has been evaluated by Deslongchamps *et al*.[23]

Although the differences in reactivities of diastereoisomeric amino thiolacetates with a triphenylpropane skeleton are not extremely large, they are definitely in accord with Deslongchamps antiperiplanar lone pair hypothesis. In our case this tacitly assumes rate determining C-S bond breaking, agreeing with Kaloustian and Nader's results [28] on breakdown of hemi-orthothioamide intermediates at low temperatures, and could thus point to the role of stereoelectronic restrictions in the working of cysteine proteinases. It should be admitted, however, that in the base-catalyzed aminolysis of esters, deprotonation of amino groups is usually rate determining.[35] Since in our case the proton is removed by triethylamine it can be readily seen from the formulae on Scheme 4 that deprotonation of the nitrogen atom carrying an equatorial Me group will be more severely hampered in the *EE*- isomers. Recently, drastic decreases have been described [36] in the rates of acyl transfers involving amides, owing to steric hindrance of the rate-determining proton transfers. Irrespective of the exact mechanism, the

ALPH appears to be a useful tool in predicting reactivities in intramolecular S→N acyl transfer in amino thiolacetates.

Conclusions

The kinetics of base-catalyzed intramolecular S→N acyl transfer in diastereoisomeric 3-amino- and 3-methylamino-1,2,3-triphenylpropyl thiolacetates can be followed conveniently by means of IR spectroscopy. The single allowed conformations of the cyclic tetrahedral intermediates modeling the transition states allow definite predictions of the relative reactivity of the different diastereoisomers in the presence or absence of the stereoelectronic effect due to the requirement of an antiperiplanar lone pair. In the *N*-methyl derivatives this forces the *N*-methyl group into an axial position, causing strong additional hindrance only in the *EE*- isomer, thus changing the expected order of reactivities. The observed migration rates are in full agreement with the requirements of Deslongchamps' stereoelectronic hypothesis of two lone pairs on adjacent heteroatoms being antiperiplanar to the cleaving bond.

Experimental Section

General Procedures. Fluka acetonitrile for UV-spectroscopy was dried over P_2O_5 to give less than 0.2% water content, determined by a Fischer test. Triethylamine was dried over P_2O_5. The IR spectra were recorded on a Bruker IFS 113v in CaF_2 cells and are quoted in cm^{-1}. NMR spectra were recorded on a Bruker AVANCE DRX 250 spectrometer, with chemical shifts quoted in ppm as δ-values, against tetramethylsilane (TMS) as internal standard; the coupling constants are in Hz.

General experimenmental procedures

*Intramolecular S→N acyl transfer in 3-amino- and 3-methylamino-1,2,3-triphenylpropyl thiolacetates **1** and **2***. The kinetic experiments were carried out in an IR cell in a thermostatted cell compartment of the instrument or kept in a thermostatted box for the slow reactions. Solutions of thiolacetate (0.02 *M*) were prepared in dry acetonitrile containing triethylamine as base in ten-fold molar excess to ensure pseudo-monomolecular conditions. To a suspension of hydrobromide of **1** or **2** in CH_3CN (equivalent to 0.02 *M* solution) triethylamine (equivalent to 0.2 *M*) was added at 25°C and the resulting solution was transferred to the IR cell. The IR spectra were recorded in suitable intervals at 25±0.5°C. The first point of the kinetic run was recorded before the addition of Et_3N only in the case of ET-**1**, as the rest of the hydrobromides are not soluble in CH_3CN. The rate constants (sec^{-1}) were obtained by means of a non-linear fitting of the variation of absorbance with time to the first order rate equation, by means of the Grafit 3 or 4 programs. Initial- and end- absorbance values were treated as adjustable parameters.

^1H- NMR experiments. A thiolacetate **1** or **2** was dissolved in the appropriate solvent and pyridine (10 equiv.) was added. The spectra were recorded immediately (a), and after 2-10 days

(b), to obtain the proton resonances of the amino thiolacetates **1** and **2** and acetamido thiols **3** and **4**, respectively.

From ET-3-amino-1,2,3-triphenylpropyl thiolacetate (ET-1) in deuteriochloroform

(a) ET-1. 2.089 (s, 3H, SCOC*H*$_3$), 4.844 (d, 1H, J 6.0, C*H*), 4.968 (dd, 1H, J 6.0, 9.8, C*H*-2), 5.236 (d, 1H, J 9.8, C*H*).

(b) ET-3-acetylamino-1,2,3-triphenylpropanethiol (ET-3) 1.850 (s, 3H, NCOC*H*$_3$), 3.943 (dd, 1H, J 8.3, 8.5, C*H*-2), 4.633 (d, 1H, J_{12} 8.5, C*H*-1), 5.617 (dd, 1H, J_{23} 8.3, $J_{NH,H-3}$ 8.5, C*HI*-3).

From TE-3-methylamino-1,2,3-triphenylpropyl thiolacetate (TE-2) in deuterioacetone

(a) TE-2. 2.214 (s, 3H, NC*H*$_3$), 2.300 (s, 3H, SCOC*H*$_3$), 4.647(dd, 1H, J 5.6, 9.8, C*H*-2), 4.830 (d, 1H, J 9.8, C*H*), 5.034 (d, 1H, J 5.6, C*H*).

(b) TE-3-acetylmethylamino-1,2,3-triphenylpropanethiol (TE-4). 2.076 (s, 3H, NCOC*H*$_3$), 2.958 (s, 3H, NC*H*$_3$), 5.217 (d, 1H, J 12.5, C*H*), 5.408 (dd, 1H, J 4.2, 12.5, C*H*-2), 5.571 (d, 1H, J 4.2, C*H*).

From EE-3-methylamino-1,2,3-triphenylpropyl thiolacetate (EE-2) in deuterioacetone

(a) EE-2. 2.191 (s, 3H, NC*H*$_3$), 2.288 (s, 3H, SCOC*H*$_3$), 4.558 (d, 1H, J 2.8, C*H*), 4.882 (dd, 1H, J 2.8, 10.8, C*H*-2), 5.270 (d, 1H, J 10.8, C*H*); The product, *EE*-3-acetylmethylamino-1,2,3-triphenylpropanethiol (*EE*-**4**), was not stable enough over the migration time scale and no explicit data were obtained.

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21. The relative configuration of the fragments C-1/C-2 and C-2/C-3 are denoted as *ET*, *TE* and *EE* for the sake of simplicity. *ET* means *erythro* at C-1/C-2*, threo* at C-2/C-3, *TE – threo* at C-1/C-2, *erythro* at C-2/C-3 and *EE – erythro* at C-1/C-2, *erythro* at C-2/C-3.
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