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بالرسالة صفحات

لم ترد بالأصل

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PREPARATIVE AND MECHANISTIC INVESTIGATIONS OF SELECTED SULFUR CUMULENES

A Thesis Submitted

by

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قَالُوا سُبْحَانَكَ لَا عِلْمَ لَنَا إِلَّا مَا
عَلَّمْتَنَا إِنَّكَ أَنْتَ الْعَلِيمُ الْحَكِيمُ .

سورة البقرة - ٣٢

جامعة المنوفية

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(أ.د. السيد أحمد حسن خلاف)

٩٨/٢/٢٢

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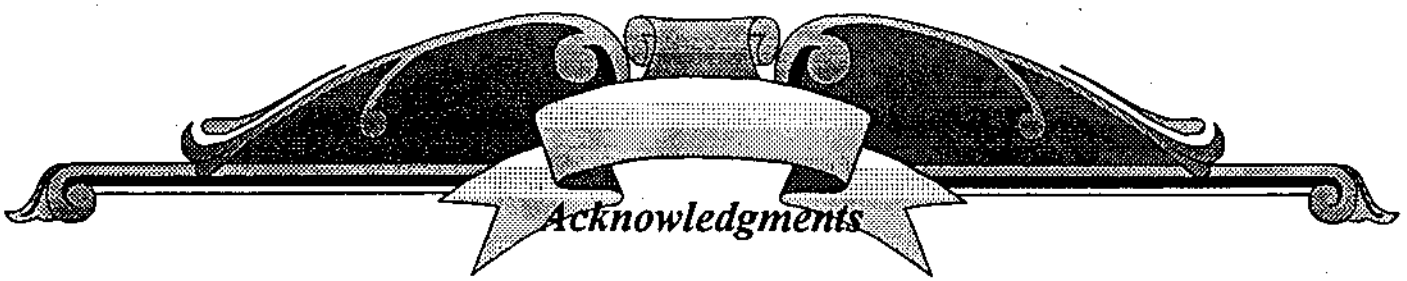

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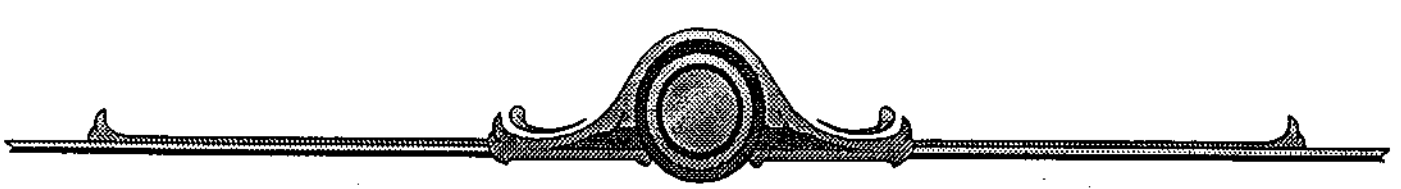

ENGLISH SUMMARY

Summary

The key intermediates for all subsequent work of this thesis were the 2,2-dialkylchroman-4-ones **190**. The methodology for their preparation is well documented,[22] i.e. the reaction of 2-hydroxyacetophenone with the appropriate ketone in the presence of base (pyrrolidine). Compounds **190a-d** were treated with thionyl chloride at room temperature overnight to give yellow crystals of α-chloro β-monooxo sulfenyl chlorides **191a-d**.[27]

Derivatization of sulfenyl chlorides with simple thiols such as thioacetic acid, thiobenzoic acid and thiophenol are uncomplicated to give the unsymmetrical disulfides **192a-j** and **193**.

The substitution of the sulfenyl chlorides **191** with cyanide ions takes a straightforward cause with formation of the thiocyanates **194a,c,d** which apparently are undisposed to rearrangement to the corresponding isothiocyanates **218**. The latter would have been interesting derivatives of the often elusive α-halo amines. As on ultimate proof an X-ray structure determination of **194a** was performed. When methoxide ions were employed as nucleophile vis-à-vis **191** we obtained the sulfenyl acid methyl esters **195a,c** corresponding to analogous observations. The alternative sulfoxide structure for **195a,c** (as a consequence of ionization-recombination rearrangement of **195**) could be excluded by spectroscopic arguments, i.e. the ^{1}H and ^{13}C NMR resonances of the *O*-methyl group of the ester are compared with those of, say, methanol and dimethyl sulfoxide.

Sulfinate when reacting with the sulfenyl chlorides **191a-d** gives concomitant substitution and reduction (with formation of the corresponding sulfonyl chloride as coproduct). This means that the treatment of **191a-d** with sulfinate ions revealed the operation of two competing reactions, straightforward nucleophilic substitution at sulfenyl sulfur, i.e. formation of **196**, and reduction to **197a-d** with subsequent dimerization to the Diels-Alder dimer **198a-d**.

Phosphine and iodide ions only effect reduction of our sulfenyl chlorides to give the Diels-Alder dimers **198** (with formation of iodine and triphenylphosphine oxide as coproduct, respectively). On the other hand, the reaction of sulfenyl chloride **33b**[16] with iodide ions stopped at the stage of the stable thiocarbonyl compound **1**.[10] This is the reverse of the ready chlorination of **1** to **33b**.

The thioketone *S*-imides **199a-c** were prepared from the corresponding α-chloro sulfenyl chlorides **191** and excess 1-adamantanamine. Interestingly, the more obvious procedure for the

preparation of **199**, i.e. treatment of **191** with an equivalent amount of 1-adamantanamine in the presence of excess triethylamine, failed and only led to recovery of unreacted sulfenyl chlorides. When the 1-adamantyl group of the thione *S*-imides **199** was replaced by a *tert*-butyl group the corresponding crude thioketone *S*-imides were liquids at room temperature which resisted our attempts at purification.

The treatment of sulfenyl chlorides **191b,c** with morpholine yielded the sulfenic acid morpholides **200b,c**. Also sulfenyl chloride **33b** yielded the sulfenic acid anilides **201a,b** when treated with aniline derivatives, in both cases the α-chlorine atom of the starting sulfenyl chlorides **33b** and **191** remaining unaffected.

Thiosulfines **176** and dithiiranes **181**, are compounds of high topical interest. The generation of thiosulfines/dithiiranes **176/181** from α-chloroalkanesulfenyl chlorides via acetyl α-chloroalkyl disulfides, is a convenient "unzipping" reaction under mild conditions.

In our present study we wished to examine the generation and reactive behavior of β-monooxo thiosulfines **176/181** derived from 4-chromanones **190**, i.e. 2,2-dialkyl-3-thioxochroman-4-one *S*-sulfides **202**.

The cycloaddition chemistry ensuing after the smooth formation of thiosulfine **202** is rich and, for so far obscure reasons, noticeably dependent upon the nature of the simple alkyl substituents R^1 and R^2. Thiosulfine **202** can disproportionate to the corresponding, highly reactive, 3-thioxochroman-4-one **197** and its *S*-disulfide **203**. The former **197a** can dimerize to the Diels-Alder dimers **198a**. The formation of Diels-Alder dimers such as **198a** from α-oxo thioketones has precedent in the work of Crossland. No straightforward evidence for the formation and subsequent fate of **203** can be derived from our present work.

The 1,2,4-trithiolanes **204a-d** must be formed in a manner reminiscent of the chemistry Huisgen *et al.* encountered in the thiation of thioketones. No 1,2,3-trithiolanes were found in our reactions.

The 1,2,4,5-tetrathianes **205a,d** isolated in our present study are most likely formed by a two-step dimerization of thiosulfine **202** since the concerted [3+3] dimerization of thiosulfine **202** is Woodward-Hoffmann forbidden.

However, in the three cases **202b**, **202c**, and **202d** we find, in competition with the previously mentioned reactions, the novel reaction mode of a [3+5] cycloadditive dimerization of thiosulfine to form 1,3,4,5,6-oxatetrathiocine **206b-d**.

In the case of thiosulfine **202d** also a monomeric product is formed, i.e. the spiro[chroman-2,7′-[1,2,3,4,5,6]hexathiepane] **207d**. The formation of sulfur-rich system like **207d** from relatively simple precursors and unspecified sources of active sulfur has been observed on several occasions.

The chlorination of thione *S*-imide (*E*)-**76t**[16] with chlorine (or sulfuryl chloride, as observed in the present investigation) leads to dichloro(phenylthio)methyl *p*-tolyl sulfone **174**[43] and, presumably, *tert*-butyliminosulfinyl dichloride.[123]

Not unexpectedly, dibromo(phenylthio)methyl *p*-tolyl sulfone **208** could be obtained smoothly from thione *S*-imide **76t** and bromine. Compound **199a** could likewise, by treatment with sulfuryl chloride, be converted to the corresponding *gem*-dichloro compound **93a**.[27]

Thionyl chloride converted **76t** to the coresponding α-chloro sulfenyl chloride **33b**. This novel metathesis should also yield the known *N*-sulfinyl-*tert*-butylamine[124] which was, however, not observed. Another unprecedented reaction was encountered when **76t** was treated with morpholine-*N*-sulfenyl chloride.[125] A net transfer of the *tert*-butylimino group from the thiocarbonyl *S*-imide to the sulfenyl chloride took place, yielding an (unobserved) chlorosulfinamidine and the known *C*-sulfonyldithioformate, the latter reacted with benzenesulfenyl chloride to give the known disulfide **82b**.[5]

The ozonolysis of **199a** failed to give any direct evidence of the formation of sulfur trioxide derivatives **219**, but only yielded 2,2-dimethylchroman-3,4-dione **209**. An authentic sample of **209** was prepared by selenium dioxide oxidation of 2,2-dimethylchroman-4-one **190a**.

We investigated the pyrolysis of **199a** and **199c**, respectively, in boiling chlorobezene with the expectation that extrusion of sulfur would lead to the corresponding imine **211**. Much to our surprise no **211** could be isolated and the only well defined pyrolysis product was the 1,2,4-trithiolane **204a** and **204c**.

Finally, all the new compounds mentioned here were elucidated by elemental analysis, spectroscopy (IR, MS, ^{1}H and ^{13}C NMR) and most of the key compounds also elucidated by X-ray crystallography.