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STABLE CYCLIC SULFENOCARBOXYLIC ACID ANHYDRIDES DERIVATIVES OF 1,2-OXATHIOLE-5-ONE

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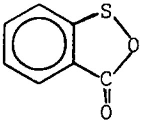
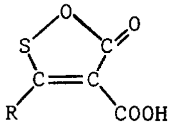
Previously Field and collaborators[1] have given evidence for the unstable cyclic o-sulfenobenzoic acid anhydride (I), which also has been proposed as an intermediate by D'Silva[2] and Danehy[3].

We now wish to report two stable 3-substituted 4-carboxy-1,2-oxathiole-5-ones (IIa,b), whose structures have been determined by spectroscopic data, elemental analysis and by means of chemical reactions.



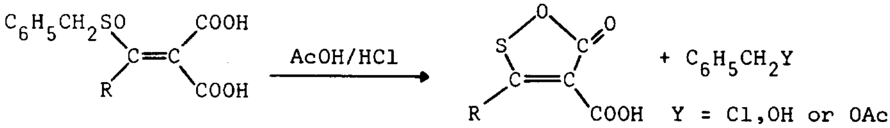
I



II

IIa R = Ph
IIb R = Me

The compounds (II) have been prepared by treatment of the corresponding benzylsulfinylmalonic acids (III)[4] in a mixture of acetic and hydrochloric acid at 45° C. Under these conditions the compounds (III) underwent a benzylic carbon-sulfur bond cleavage according to Scheme 1.



III II

Scheme 1

The benzylic part was isolated and identified as benzyl chloride, benzyl alcohol and benzyl acetate.

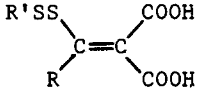
The other part (II) was isolated as white crystalline solids. The product derived from IIIa was shown to be the most stable one and could be kept at room temperature for several months. The proposed structures (II) are supported by the following data.

The mass spectrum of IIa gave a M^+-peak at m/e (rel int) 222(96), M^++1 (11.4) M^++2 (5.5) and for IIb m/e: M^+ 160(82), M^++1 (5.3), M^++2 (4.5). IR-spectrum of the crude product IIa shows two strong bands in the carbonyl region at 1786 and 1675

cm^{-1} (in KBr). An identical spectrum was obtained after recrystallization from chloroform. The absorption at 1786 cm^{-1} is in accordance with that found by Field[1] for compound I and also with that found by Putnam and Sharkey[5] for the acyclic carboxylates. For IIb the absorption bands within the same region are at 1757, 1730 and 1661 cm^{-1} (in KBr). The NMR-spectra, recorded in deuterochloroform with internal TMS, gave for IIa the phenyl shift at $\delta=7.78$ (5H) with the carboxylic proton (1H) approximately the same. The integral relation was obtained after adding small amounts of deuterated methanol. The shift for IIb was $\delta=2.92$ (3H) and $\delta=9.60$ (1H). The elemental analysis is also in good agreement with the proposed structure. Anal. Found for IIa C; 54.17 H: 2.75 S: 14.31. Calcd. for $C_{10}H_6O_4S$ C: 54.05 H: 2.72 S: 14.43 and for IIb Anal. Found C: 37.59 H: 2.57 S: 19.98 Calcd. for $C_5H_4O_4S$ C: 37.50 H: 2.52 S: 20.02.

The chemical behaviour of II also confirmed the proposed structure. The "anhydrides" (II) rapidly oxidized iodide to iodine (IIa: 93 % of expectation). This technique has earlier been demonstrated by Kharash and Wald[6] for the assay of sulfenyl carboxylates and also been used by Field[1] for compound I.

The sulfenyl character was further established by II:s reactivity towards mercaptans. Thus, II gave, when treated in chloroform solution with p-thiocresol or thiophenol at room temperature for five minutes, a crystalline product. The product, recrystallized from ethanol-water, was identified as expected as the disulfide IV on the basis of elemental analysis and spectroscopic data.



IV

IVa: R = Ph, R' = p-tolyl
IVb: R = Ph, R' = Ph
IVc: R = Me, R' = Ph

Further support for the disulfide structure is the immediate precipitation of di-(p-tolyl)-, and diphenyldisulfide respectively, when IV is treated with 1M NaOH. This rapid disproportionation of the disulfides could be accounted for as anchimerically assisted by the carboxylate group. This has also been found by Field[1] for the disproportionation of 2-(phenyldithio)benzoic acid.

On the other hand if IIa is treated with oxygen nucleophiles such as methanol or phenols, which are not as thiophilic as mercaptans, no reaction occurs within 24 hours.

Further work on this subject is now underway in these laboratories.

References

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