

UNUSUAL CARBON-CARBON DOUBLE BOND CLEAVAGE IN THIOPHENOHOMOTROPONE  
SYSTEM PROMOTED BY ETHANEDITHIOL

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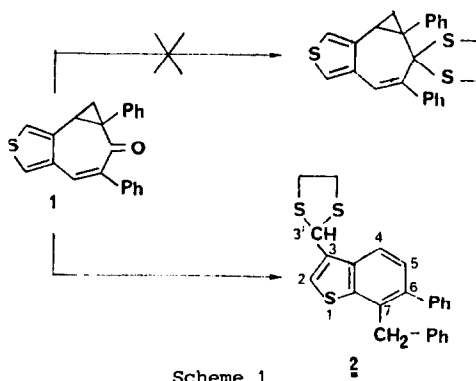
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Summary : Non classical carbon-carbon double bond cleavage in a homoaromatic system is initiated by ethanedithiol and *p*-toluenesulfonic acid. The structure of the unexpected product is proved by X-ray analysis. The proposed mechanism is supported by deuterium labelling experiments and common reactivity considerations.

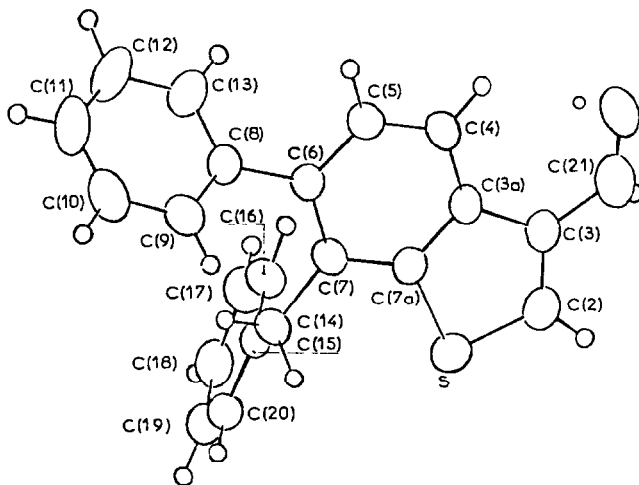
In previous publications, we reported the synthesis and structural data of thiopheno- $[a]$ tropones<sup>1</sup> and homotropones<sup>2</sup>. Numerous attempts to protect the carbonyl group of thiophenotropones lead only to recovered materials, while some acetal and dithioacetal compounds had been formed in other troponoid systems<sup>3-5</sup>. *A priori*, the protection of the less conjugated thiopheno $[a]$ homotropone 1 could be expected to succeed. In our case, a dithioacetal 2<sup>††</sup> was obtained (Scheme 1), rather than the anticipated carbonyl regeneration. In this paper we describe the reaction, the structural data of the obtained product, and we propose a possible mechanism for this transformation.



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<sup>††</sup>Satisfactory analytical data were obtained for all new compounds.

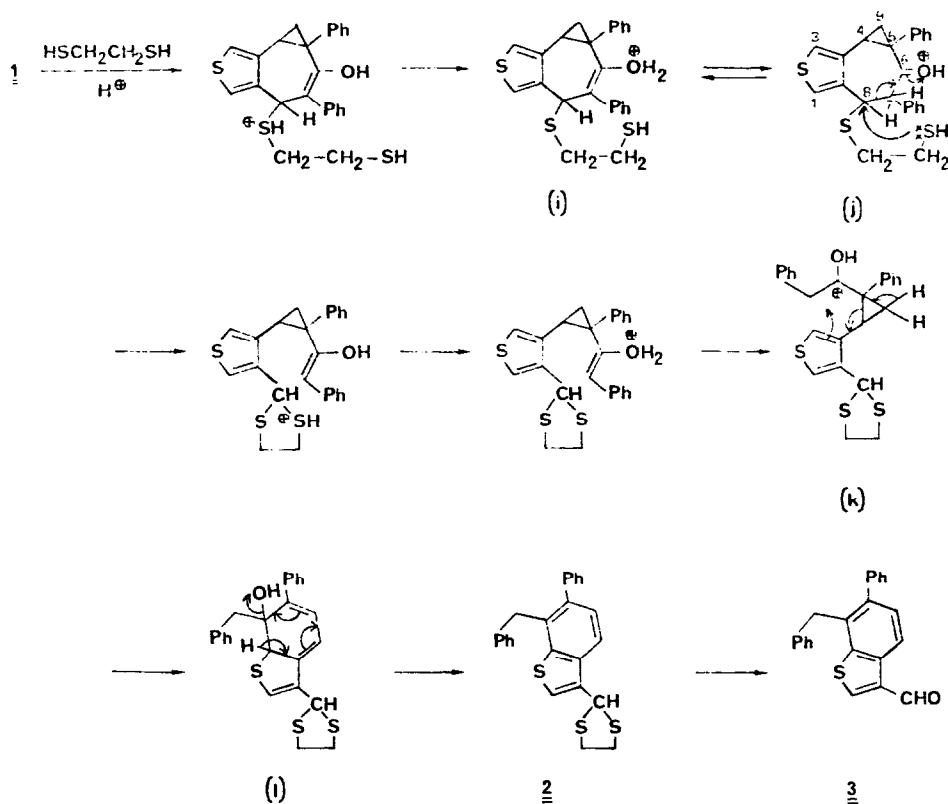
A mixture of 3.93 g (12 mM) of 5,7-diphenylthiopheno[*a*]homotropone 1, 5.0 cm<sup>3</sup> (60 mM) ethanedithiol and 2.28 g (12 mM) of *p*-toluenesulfonic acid in 100 cm<sup>3</sup> dry toluene was refluxed for twelve hours. The resulting brown solution was cooled and quenched with 50 cm<sup>3</sup> of 2N potassium hydroxide. Extraction with ether, purification by silica column chromatography eluting with a mixture of methylene chloride-hexane (1-1) gave a residue, which was recrystallized from the same mixture. 2 (1.94 g) mp 155°C in 40 % yield ; C<sub>24</sub>H<sub>20</sub>S<sub>3</sub> ; IR : no carbonyl absorption ; MS : m/e = 404 (M<sup>+</sup>), 376, 285, 253, 234, 221 ; <sup>1</sup>H NMR (100 MHz, δ ppm in CDCl<sub>3</sub> from TMS), 3.40 (m, 4H, -SCH<sub>2</sub>CH<sub>2</sub>S-) ; 4.24 (s, 2H, -CH<sub>2</sub>-) ; 5.98 (d, J = 1.0 Hz, 1H, -H<sub>3</sub>,) ; 7.0-7.3 (m, 5H, -C<sub>6</sub>H<sub>5</sub>) ; 7.32 (br.s, 5H, benzylic-C<sub>6</sub>H<sub>5</sub>) ; 7.39 (d, J = 8.3 Hz, 1H, -H<sub>5</sub>) ; 7.57 (d, J = 1.0 Hz, 1H, -H<sub>2</sub>) ; 7.86 (d, J = 8.3 Hz, 1H, -H<sub>4</sub>). Acid hydrolysis according to HOJO's procedure<sup>6</sup> gave an aldehydic compound (3, mp 136°C in 62 % yield ; C<sub>22</sub>H<sub>16</sub>OS ; IR : ν<sub>C=O</sub> = 1675 cm<sup>-1</sup> ; MS : m/e = 328 (M<sup>+</sup>), 221, 189 ; <sup>1</sup>H NMR (100 MHz, δ ppm in CDCl<sub>3</sub> from TMS), 4.30 (s, 2H, -CH<sub>2</sub>-) ; 7.0 - 7.3 (m, 5H, -C<sub>6</sub>H<sub>5</sub>) ; 7.34 (br.s, 5H, benzylic -C<sub>6</sub>H<sub>5</sub>) ; 7.49 (d, J = 8.4 Hz, 1H, -H<sub>5</sub>) ; 8.23 (s, 1H, -H<sub>2</sub>) ; 8.61 (d, J = 8.4 Hz, 1H, -H<sub>4</sub>) ; 10.11 (s, 1H, -CHO).

The molecular structure was proved by X-ray measurements. The compound crystallized in the triclinic system space group P $\bar{1}$  with a = 7.067 (2), b = 9.266 (2), c = 13.396 (2), α = 102.95 (2), β = 99.56 (2), γ = 101.06 (2) ; 2940 reflexions (σ(I)/I > 1) were used to refine the structure. The structure was solved by direct methods using the MULTAN program<sup>7</sup>. The final R was 0.053. The aldehydic group is attached to the C<sub>3</sub> of the thiophene ring and the oxygen atom is found 0.11 Å from the benzothiophene plane. The dihedral angle between the phenyl and benzyl groups is 92°. The angle formed between these two groups are 126° and 98° respectively with the benzothiophene plane.



Perspective view of the aldehyde 3.

A possible mechanism involving a carbon-carbon double bond cleavage<sup>8</sup> is shown in Scheme 2.

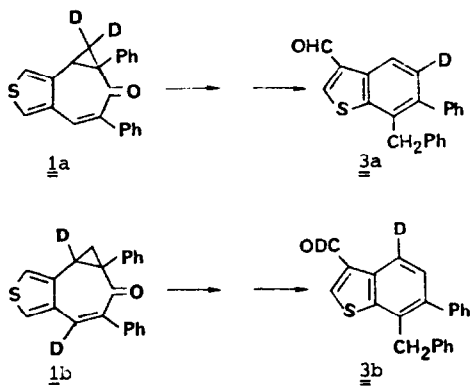


Scheme 2

The first step of the reaction involves 1,4 addition of ethanedithiol in the strongly acidic medium. After a proton migration, the Michael adduct is tautomerized to a protonated ketone (j) which undergoes a non-classical rearrangement : the nucleophilic sulfur attack at C<sub>8</sub> and the electrophilic character of the oxonium function induce the carbon-carbon bond cleavage. Two subsequent tautomeric displacements generate the substituted benzylic carbocation (k). This electrophilic species attacks the thiophene ring at the  $\alpha$ -carbon atom. Loss of the cyclopropyl hydrogen with concomitant ring opening allow the formation of the bicyclic system (l). A dehydration finally leads to the benzo[*b*]thiophene dithioacetal **3**.

Several steps have been proved by deuterium labelling (Scheme 3). The didetero-

pound 1a gives the monodeuterated product 3a. In the case of 1b, the dideuterated aldehyde 3b is isolated.



Scheme 3

Some studies concerning other systems and different thiols are in progress.

#### References

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