Available online at www.sciencedirect.com

Tetrahedron Letters 45 (2004) 8859–8861

Tetrahedron Letters

9*H*-Fluorene-9-carbodithioic acids and dithioates. First isolation and characterization of a *gem*-enedithiol

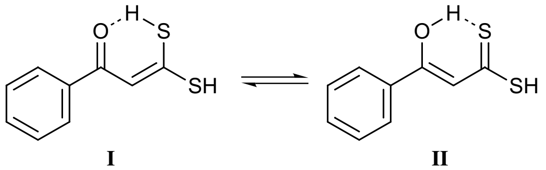
José Vicente, Pablo González-Herrero,* Yolanda García-Sánchez and María Pérez-Cadenas

Grupo de Química Organometálica, Departamento de Química Inorgánica, Facultad de Química, Universidad de Murcia, Apdo. 4021, 30071 Murcia, Spain

Received 15 September 2004; accepted 29 September 2004

Abstract—[2,7-Bis(octyloxy)fluoren-9-yliden]methanedithiol (**1a**) and its tautomer 2,7-bis(octyloxy)-9*H*-fluorene-9-carbodithioic acid (**2a**) can be isolated in pure form from the reaction of monolithiated 2,7-bis(octyloxy)-9*H*-fluorene with CS_2 followed by protonolysis with aqueous HCl. Compound **1a** is the first isolated and unambiguously characterized *gem*-enedithiol. When 9*H*-fluorene, 2,7-di-*tert*-butyl-9*H*-fluorene or 2,7-dimethoxy-9*H*-fluorene are used, the same synthetic procedure yields the unstable dithioic acids, which can be converted to the piperidinium salts.

The reactions of methylene active compounds $XYCH_2$ (X and/or Y = CN, CO_2R, C(O)R, $C(O)NH_2$, NO_2, etc.) with CS_2 in the presence of bases have been studied extensively.[1,2] In a first stage, dithioates of the type $XYCHCS_2^-$ are obtained, which, if the acidity of the remaining hydrogen is high enough, may be further deprotonated to give the 1,1-ethylenedithiolates $XYC{=}CS_2^{2-}$. The protonation of these species gives the unstable dithioic acids $XYCHCS_2H$, which are assumed to be in tautomeric equilibrium with the 1,1-ethylenedithiols $XYC{=}C(SH)_2$ in solution. However, as far as we know, there is no report of isolated 1,1-ethylenedithiols, or more generally *gem*-enedithiols, in the literature. Usually, 1,1-ethylenedithiolates are either generated and used in situ for the synthesis of other compounds,[3] most commonly ketene dithioacetals,[2,4] or isolated as alkali salts.[1,5,6] In fact, the results of literature searches using the $C{=}C(SH)_2$ structure query refer in most cases to alkali or transition metal 1,1-ethylenedithiolates, while in one case the product was detected by mass spectrometry[7] and some examples were model compounds used in theoretical calculations.[8] Additionally, β-hydroxydithiocinnamic acid $PhC(OH){=}CHCS_2H$ and its substituted derivatives, which are obtained from aryl methyl ketones,[9,10] are often represented or referred to as their dithiol tautomers $PhCOCH{=}C(SH)_2$ and frequently used for the preparation of heterocycles of pharmacological interest[11] or the synthetically versatile α-oxo ketene dithioacetals.[12] However, these compounds have not been isolated as such dithiols and are likely to exist in solution as equilibrium mixtures of the rapidly interconverting tautomers **I** (enethiol) and **II** (enol) (Scheme 1). The reported spectroscopic data, including those of other derivatives of the type $RC(OH){=}CHCS_2H$,[10,13] are consistent with the dithioic acid structure. Moreover, the predominant tautomer of the structurally related β-thioxoketones in solution is usually the enol form, which in certain cases is the only tautomer found in the solid state.[14] The dithioic acid is also the preferred tautomeric structure of related compounds with an amino group in the β position, such as 2-amino-1-cyclopentenecarbodithioic acid and its *N*-monoalkylated derivatives.[15]



Scheme 1.

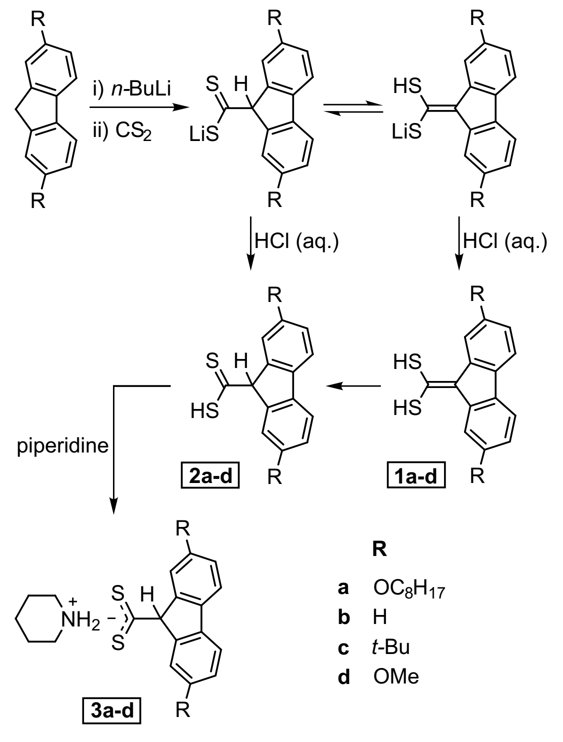
Keywords: Dithiols; Dithioic acids; Methylene active compounds; Tautomerism; Fluorene.

* Corresponding author. Tel.: +34 968367097; fax: +34 968364143; e-mail: pgh@um.es

0040-4039/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2004.09.180

In the present paper, we describe the first isolation and characterization of a *gem*-enedithiol, obtained by using a synthetic procedure initially designed to prepare its tautomer 2,7-bis(octyloxy)-9*H*-fluorene-9-carbodithioic acid, which is also isolable. We also describe the synthesis of dithioic acids from 9*H*-fluorene and its 2,7-di-*tert*-butyl- and 2,7-dimethoxy-substituted derivatives, which were converted to the corresponding piperidinium salts. The compounds here described are suitable precursors for the synthesis of transition metal complexes containing the (fluoren-9-ylidene)methanedithiolato ligand or its substituted analogues.[16]

Monolithiated 9*H*-fluorene and its 2,7-di-*tert*-butyl-, 2,7-dimethoxy- or 2,7-bis(octyloxy)-substituted derivatives, which can be generated in THF solution through reaction with *n*-butyllithium at −15 °C,[17] reacted with CS_2 to give the corresponding lithium dithioates (Scheme 2). The protonolysis of these intermediates with aqueous HCl led to the formation of the dithioic acids, which, according to the literature,[1,2] must be in tautomeric equilibrium with the enedithiols in solution. In the case of the bis(octyloxy)-substituted derivative, evaporation of the organic layer and treatment of the residue with diethyl ether led to the formation of a bright yellow precipitate of [2,7-bis(octyloxy)fluoren-9-yliden]methanedithiol (**1a**). By storing the mother solution at −20 °C for several days a yellow-orange precipitate of the highly soluble 2,7-bis(octyloxy)-9*H*-fluorene-9-carbodithioic acid (**2a**) was obtained along with a small amount of its tautomer **1a**. To isolate pure **2a** it is sufficient to warm this mixture in undistilled chloroform for several hours, because in this way **1a** completely converts to **2a**. Both **1a** and **2a** are remarkably air-stable compounds, which can be stored at room temperature for several months. In the other cases (R = H, *t*-Bu, OMe), the evaporation of the organic layer led to the precipitation of orange solids, which were mainly composed of the dithioic acids **2b–d** and only contained trace amounts of the dithiols **1b–d**. Satisfactory elemental analyses could be obtained for **2d**, but **2b** and **2c** are quite unstable and soon become contaminated with decomposition products. For this reason, in order to use them as ligand precursors, it is better to isolate the piperidinium salts **3b–d**, which precipitate upon addition of piperidine to diethyl ether solutions of the acids. The piperidinium salt **3a** can be obtained from **2a** in the same way, but it is a sticky and difficult to manipulate solid, which could not be purified. Compounds **3b–d** are relatively stable and can be stored at room temperature under a nitrogen atmosphere for several weeks.



Scheme 2.

The tautomerization of the dithiol **1a** to the dithioic acid **2a** in undistilled chloroform occurs irreversibly and completely after ca. 6 h at 35 °C. The presence of water in the solvent is necessary for this process to take place and, in fact, it is drastically slowed down in deuterated chloroform, which has been previously dried over Al_2O_3 (basic, activity grade I). Moreover, the tautomerization in undistilled deuterated chloroform (usually containing a small amount of water) is inhibited if triflic acid is added, thus revealing that the process is base catalyzed. To further support this, the complete conversion takes place within a few minutes when a catalytic amount of piperidine (less than 2 mol%) is added to chloroform suspensions of **1a**. The reverse process, that is, the tautomerization of dithioic acid **2a** to dithiol **1a**, does not take place under acidic conditions in diethyl ether, THF or chloroform. In spite of this, **1a** is obtained in a higher yield (56%) than the more stable tautomer **2a** (36%), which could be due to the existence of a tautomeric equilibrium between their lithium salts[2] displaced to the right (Scheme 2) and to the fact that the tautomerization of **1a** to give **2a** is slow under the acidic conditions of the protonolysis.

The dithiols **1b–d** analogous to **1a** were detected only in trace amounts when starting from 9*H*-fluorene or its 2,7-di-*tert*-butyl- or 2,7-dimethoxy-substituted derivatives, which could be due to their fast tautomerization to the corresponding dithioic acids **2b–d** under the protonolysis conditions. Therefore, the surprising stability of **1a** is most probably an effect of the long aliphatic chain of the octyloxy substituents, which may hinder the tautomerization process by preventing the water molecules from approaching the SH groups.

The tautomers **1a** and **2a** display remarkably different physical and spectroscopic properties. Thus, while the dithioacid **2a** is highly soluble in all common organic solvents, the dithiol **1a** is only sparingly soluble in diethyl ether and dissolves with difficulty in chloroform and dichloromethane. The most remarkable feature of the ^1H NMR spectra of **1a** and **2a** is the resonance of the SH protons, which appears as a sharp singlet at δ 4.14 for **1a**, while for **2a** it is observed as a somewhat broadened singlet at δ 5.71, indicating that an exchange process takes place to some extent. The ^{1}H NMR spectra of the analogous acids **2b–d** show the broad SH resonance at similar chemical shifts (around δ 5.70). The chemical shifts of the signals corresponding to the aromatic protons of **1a** and **2a** are very similar except for H1 and H8, which are shifted downfield by 0.86 ppm for **1a** with respect to **2a**; this fact might be attributable to the magnetic anisotropy of the C(9)=CS$_2$ double bond, which produces a considerable deshielding of the H1 and H8 atoms situated at its nodal plane. The trace amounts of the dithiols **1b–d** were identified by the resonances of the SH protons at ca. 4.14 and the H1 and H8 protons in the range δ 7.8–8.4. The ^{13}C{^{1}H} NMR spectrum of **1a** shows the resonance of the *C*S$_2$ carbon atom considerably highfield-shifted (δ 134.4) with respect to the dithioic acids **2a–d** (around δ 237) and the dithioates **3b–d** (around δ 263).

The solid state IR spectrum of **1a** displays a weak and narrow band at 2560 cm^{-1} assignable to ν(SH) and one intense band at 1542 cm^{-1} assignable to the ν(C=CS$_2$) mode. For alkali and transition metal 1,1-ethylenedithiolates, as well as ketene dithioacetals, ν(C=CS$_2$) bands are usually observed in the region 1300–1530 cm^{-1}.[1,6] As expected, this band is absent in the spectrum of **2a**, which shows the characteristic bands of dithioic acids: one ν(SH) band at 2520 cm^{-1} and one ν(C=S) band at 1266 cm^{-1} (absent in the spectrum of **1a**). The most important feature observable in the IR spectra of the dithioates **3b–d** is the ν(CS$_2$) band in the range 986–996 cm^{-1}.

Additionally, the dithiol **1a** displays solid state luminescence at room temperature and, at low temperature (77 K), it is luminescent both in CH$_2$Cl$_2$ glass and in the solid state. Its emission spectrum at 77 K shows one maximum at 526 nm in CH$_2$Cl$_2$ glass, while in the solid state a maximum at 520 nm with a shoulder at 480 nm can be observed. The corresponding excitation spectra are complicated and show several maxima in the range 300–450 nm. The dithioic acid **2a** and the dithioates **3b–d** are not luminescent.

Acknowledgements

We thank Ministerio de Ciencia y Tecnología (Spain), FEDER (BQU2001-0133) for financial support. P.G.-H. thanks Fundación Séneca (Comunidad Autónoma de la Región de Murcia, Spain) for a grant and Ministerio de Ciencia y Tecnología and Universidad de Murcia for a contract under the *Ramón y Cajal* Program. Y.G.-C. and M.P.-C. thank Ministerio de Educación, Cultura y Deporte and Ministerio de Ciencia y Tecnología, respectively, for research grants. We are grateful to Dr. M. Bardají (Universidad de Valladolid, Spain) for the measurements of the excitation and emission spectra of **1a**.

Supplementary data

Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.tetlet.2004.09.180. General experimental procedures. Preparations and spectroscopic and analytical data for 2,7-bis(octyloxy)-9*H*-fluorene, **1a**, **2a**, **2d** and **3b–d**. NMR data for **2b** and **2c**. Excitation and emission spectra of **1a**.

References and notes

1. Jensen, K. A.; Henriksen, L. *Acta Chem. Scand.* **1968**, *22*, 1107–1128.
2. Gompper, R.; Töpfl, W. *Chem. Ber.* **1962**, *95*, 2861–2870.
3. (a) Lahlil, K.; Moradpour, A.; Merienne, C.; Bowlas, C. *J. Org. Chem.* **1994**, *59*, 8030–8033; (b) Curphey, T. J.; Libby, A. H. *Tetrahedron Lett.* **2000**, *41*, 6977–6980.
4. Kolb, M. *Synthesis* **1990**, 171–190.
5. (a) Coucouvanis, D. *Prog. Inorg. Chem.* **1970**, *11*, 233–371; (b) Kuhn, N.; Weyers, G.; Henkel, G. *Chem. Commun.* **1997**, 627–628.
6. Coucouvanis, D. *Prog. Inorg. Chem.* **1979**, *26*, 301.
7. Kappe, C. O.; Kvaskoff, D.; Moloney, D. W. J.; Flammang, R.; Wentrup, C. *J. Org. Chem.* **2001**, *66*, 1827–1831.
8. (a) Epiotis, N. D.; Larson, J. R.; Yates, R. L.; Cherry, W. R.; Shaik, S.; Bernardi, F. *J. Am. Chem. Soc.* **1977**, *99*, 7460–7464; (b) Adams, F.; Gompper, R.; Hohenester, A.; Wagner, H. U. *Tetrahedron Lett.* **1988**, *29*, 6921–6924; (c) Frenking, G. *J. Am. Chem. Soc.* **1991**, *113*, 2476–2481; (d) Ma, N. L.; Wong, M. W. *Eur. J. Org. Chem.* **2000**, 1411–1421.
9. (a) Thuillier, A.; Vialle, J. *Bull. Soc. Chim. Fr.* **1959**, 1398; (b) Larsson, F. C. V.; Lawesson, S.-O. *Tetrahedron* **1972**, *28*, 5341–5357; (c) Weigand, W.; Bosl, G.; Polborn, K. *Chem. Ber.* **1990**, *123*, 1339–1342; (d) Curphey, T. J.; Joyner, H. H. *Tetrahedron Lett.* **1993**, *34*, 7231–7234; (e) Schubert, K.; Saumweber, R.; Gorls, H.; Weigand, W. *Z. Anorg. Allg. Chem.* **2003**, *629*, 2091–2096.
10. Weigand, W.; Saumweber, R.; Schulz, P. *Z. Naturforsch.* **1993**, *48b*, 1080–1088.
11. (a) Cortés-Cortés, E.; Cortés-Romero, C. A.; García-Mellado, O. *J. Heterocycl. Chem.* **2002**, *39*, 1321–1324; (b) Cortés-Cortés, E.; García-Mellado, O.; Hernández-Cruz, E. *J. Heterocycl. Chem.* **1999**, *36*, 477–480; (c) Zayed, S. E. *Phosphorus Sulfur Silicon Relat. Elem.* **1996**, *116*, 29–37; (d) Zayed, S. E. *Phosphorus Sulfur Silicon Relat. Elem.* **1996**, *108*, 7–13; (e) Zayed, S. E.; Hussin, I. A. *Phosphorus Sulfur Silicon Relat. Elem.* **1993**, *84*, 191–196.
12. Dieter, R. K. *Tetrahedron* **1986**, *42*, 3029–3096.
13. Buchweitz, J.; Gompper, R.; Polborn, K.; Robl, C.; Sailer, M.-T.; Weigand, W. *Chem. Ber.* **1994**, *127*, 23–26.
14. Duus, F. In *Comprehensive Organic Chemistry. The Synthesis and Reactions of Organic Compounds*; Jones, D. N., Barton, D., Ollis, W. D., Eds.; Pergamon: Oxford, 1979; Vol. 3, p 385.
15. Bordás, B.; Sohár, P.; Matolcsy, G.; Berencsi, P. *J. Org. Chem.* **1972**, *37*, 1727–1730.
16. Vicente, J.; González-Herrero, P.; García-Sánchez, Y.; Jones, P. G.; Bardají, M., *Inorg. Chem.* in press.
17. Linti, G.; Rodig, A.; Pritzkow, H. *Angew. Chem., Int. Ed.* **2002**, *41*, 4503–4506.