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GUAIAZULENOPENTATHIEPIN AND RELATED COMPOUNDS: REACTIONS OF GUAIAZULENE WITH REACTIVE SULFURATION REAGENTS

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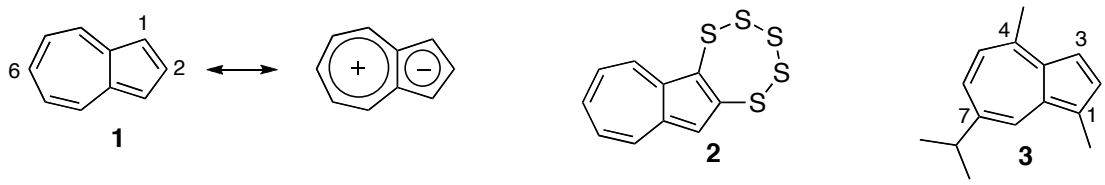
Abstract – Guaiazulene reacted with reactive sulfuration reagents to give guaiazulenopentathiepin together with a 1,2-dithiin compound and a mixture of bis(guaiazulyl)sulfides. The yield of the pentathiepin was improved by the reaction with the reagent prepared from sulfur chloride and imidazole in a molar ratio of one to two. Reduction of the pentathiepin and the successive reaction with *N,N'*-(thio)carbonyldiimidazoles afforded 2-(thi)oxo-1,3-dithioles.

INTRODUCTION

Azulene (**1**) and its derivatives, which have polarized structures, are familiar class in non-benzenoid aromatics, and their chemical, physical and biological properties have attracted much attention.[1] Even among them, azulenes with sulfur groups should be expected to the key compounds for the construction of azulene-based electron donors, whereas synthetic methods for them have not been much investigated.[2] Recently we have reported the reaction of **1** with S_8/pyridine[3] to produce azulenopentathiepin (**2**).[4] It is well known the low reactivity at a 2-position of azulenes in electrophilic substitutions.[5] Therefore, the investigation has been the only method for direct introduction of sulfur groups at the 2-position, so far.[6] Pentathiepins[7] are stable seven-membered ring compounds with five sulfur atoms, and the fusion with azulenes is of interest. Thus we next focused on guaiazulene (**3**).[8] It is a low cost azulene derivative, and the alkyl substituents will cause good solubility to organic solvents and restriction of reaction points. In this manuscript, we report the preparation of guaiazulenopentathiepin (**4**) and related compounds by the reactions with reactive sulfuration reagents.

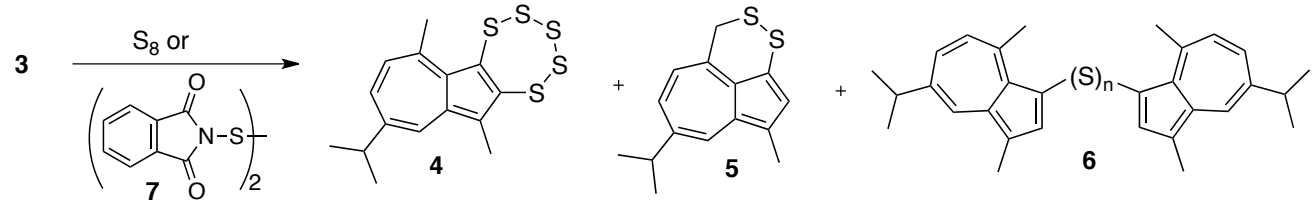
This paper is dedicated to Professor Dr. Lutz F. Tietze on the occasion of the 75th birthday



RESULTS AND DISCUSSION

We first applied the synthetic method for azulenopentathiepin (**2**)[4] to guaiazulene (**3**). That is, **3** reacted with elemental sulfur in pyridine under thermal conditions (Table 1, Entry 1). Unfortunately, the product was not guaiazulenopentathiepin (**4**) but a small amount of bis(guaiazulyl)sulfides (**6**) and recovery of **3** even though the long reaction time. The results suggested that the reactivity of the 3-position of **3** is very low due to the existence of the 4-methyl group. *N,N*'-Dithiobisphthalimide (**7**),[9] a more reactive sulfuration reagent than elemental sulfur, reacted in the same solvent at 80 °C to afford **4** and an unexpected dithin compound (**5**) in low yields, respectively. The reaction in DMF with pyridine as an additive slightly increased the yields of **4** and **5** (Entry 3).

Table 1. The reaction of guaiazulene (**3**) with elemental sulfur or *N,N*'-dithiobisphthalimide (**7**)



Entry	S_8 or **7** (atoms as S)	Solvent (mol·L^{-1})	Additive (molar *eq.*)	Temperature	Time	Yield **4**	**5**	**6**	**3**
1	S_8 (14)	Pyridine (6.0×10^{-2})	-	reflux	3 d	-	-	4wt.%[a]	56%
2	**7** (5)	Pyridine (1.0×10^{-2})	-	80 °C	3 d	2%	2%	38wt.%[a]	5%
3	**7** (5)	DMF (1.0×10^{-2})	Pyridine (3.5)	80 °C	1 d	5%	11%	51wt.%[a]	5%

[a] Percent by weight

Sulfur chloride is a highly reactive sulfuration reagent and has been used to produce pentathiepins fused with pyrroles and thiophenes by the reaction with/without diazabicyclo[2.2.2]octane (DABCO).[10] We next applied these methods to **3** (Table 2, Entries 1 and 2). Sulfur chloride was added to **3** (Addition Method A) to give hardly complicated products within a small amount of **5** and **6** even though the reaction at low temperature (-40 °C). The reaction in the presence of DABCO gave **6** as a main product. In the case with imidazole instead of DABCO, the similar results were shown (Entry3). Whereas, the reaction in the high diluted concentration (Entry 4, 2.0×10^{-4} mol·L), which preferred an intramolecular cyclization, improved the yields of **4** (17%) and **5** (14%). The reverse addition (Method B), that is, **3** was added by drop to sulfuration reagents, was carried out as expected the similar effect in Entry 4. A

somewhat effective result was shown not in Entry 5 (**4**: 5%) but in Entry 6 (**4**: 12%). The difference is arising from sulfur chloride to imidazole ratio in sulfuration reagents (Entries 5 and 6, sulfur chloride/imidazole = 1/4 and 1/2). As shown in Scheme 1, the former might form a reagent (**I**) and the latter form a more reactive one (**II**). The reagents reacted with **3** to generate the intermediates (**III**) and the successive sulfuration formed the intermediate (**IV**), which cyclized intramolecularly to produce the pentathiepin (**4**). An increased reagent of **II** improved the yield of **4** (27%, Entry 7). Although the yield of **4** was still not enough, these results suggested that the imidazolium salt moieties of **II** and **IV** are reasonably good leaving groups to react at the 3-postion of **3** and at the 2-position of **IV**. The reactions of azulene (**1**) with sulfur chloride/imidazole gave hardly complicated products in any case.

Table 2. The reaction of guaiazulene (**3**) with sulfuration reagents derived from sulfur chloride in CH_2Cl_2

Entry	S_2Cl_2 (molar *eq.*)	Concentration ($mol \cdot L^{-1}$)	Additive (molar *eq.*)	Temperature / Time	Addition Method	Yield **4**	**5**	**6**	**3**
1	2.5	1.0×10^{-2}	-	-40 °C / 2 h	A[a]	trace	5%	10wt.%[c]	-
2	2.5	1.0×10^{-2}	DABCO (5)	-40 °C / 2 h	A[a]	-	-	66wt.%[c]	39%
3	2.5	1.0×10^{-2}	Imidazole (10)	-40 °C / 2 h	A[a]	trace	trace	76wt.%[c]	3%
4	2.5	2.0×10^{-4}	Imidazole (10)	-78 °C / 1 h	A[a]	17%	14%	14wt.%[c]	trace
5	5	1.0×10^{-2}	Imidazole (20)	-40 °C / 6 h	B[b]	5%	1%	81wt.%[c]	3%
6	5	1.0×10^{-2}	Imidazole (10)	-40 °C / 6 h	B[b]	12%	5%	27wt.%[c]	trace
7	7.5	1.0×10^{-2}	Imidazole (15)	-40 °C / 6 h	B[b]	27%	trace	11wt.%[c]	trace

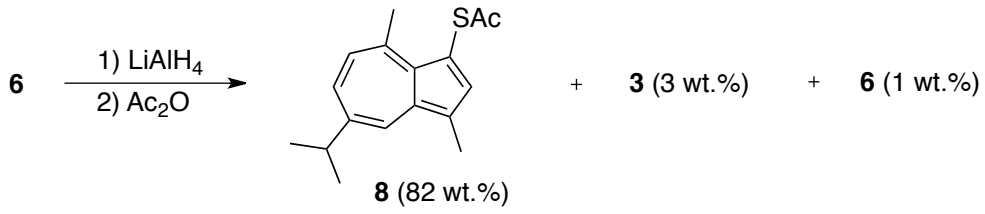
[a] Method A: The sulfuration reagent was added to **3**. [b] Method B: Reverse addition [c] Percent by weight

Guaiazulenopentathiepin (**4**) was bluish green plates (mp 110.5-111 °C). The ^{1}H NMR spectrum showed seven membered ring's protons at δ 7.18, 7.47 and 8.14 and alkyl groups' protons at δ 1.35 (6H), 2.72 (3H), 3.07 (1H) and 3.24 (3H). The ^{13}C NMR spectrum showed fourteen kinds of carbons arising from an azulene skeleton and alkyl side chains. The longest wave-maximum of UV-VIS spectrum appeared at 615 nm (log ε 2.78) as a characteristic peak of azulene derivatives. The MS spectra (FAB and MALDI-TOF) gave molecular ion and fragment ion peaks [*m/z* 356 (M^+), 292 (M^+-2S)]. Together with the result of elemental analysis, those spectral data supported the proposed structure. Cyclic voltammogram of **4** showed an irreversible wave and the first reduction potential was nearly equal to that of azulenopentathiepin (**2**) [$(E_1^{red})_{pc}$: **4**; -1.43 V, **2**; -1.48 V]. On the other hand, the electron donation ability was slight smaller than that of **2** [$(E_1^{ox})_{pa}$: **4**; +0.88 V, **2**; +0.75 V].

A 1,2-dithin compound (**5**) was green crystals (mp 56.0-57.0 °C), and might be formed by an intramolecular cyclization of the intermediate (**III**, Scheme 1). It is reported that the 4-Me proton of guaiazulene (**3**) is rather acidic.[11] The ^{1}H NMR spectrum showed seven membered ring's protons at δ

6.75, 7.36, 7.52 and 8.14 and alkyl groups' protons at δ 1.35 (6H), 2.61 (3H), and 3.05 (1H). The NOE correlation appeared between the protons at δ 4.37 (s, 2H, CH_2S) and δ 6.75 (d, J = 10.2 Hz, 1H, H-5). The ^{13}C NMR spectrum showed thirteen kinds of carbons (two carbons were overlapped at δ 135.0). The longest wave-maximum of UV-VIS spectrum appeared at 680 nm (log ε 2.34), which was a longer one than that of pentathiepin (**4**). The MS spectrum [MALDI-TOF: m/z 260 (M^+)] and elemental analysis data also supported the proposed structure.

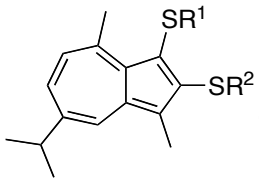
Bis(guaiazulyl)sulfides (**6**), an inseparable mixture of sulfides, would be produced by the condensation of guaiazulene (**3**) with intermediates (**III**, **IV** and the other ones with different numbers of sulfur atoms, Scheme 1). As part of the structure determination of **6**, reductive acetylation was carried out (Scheme 2). Treatment of **6** with $LiAlH_4$ in THF generated the corresponding thiolate, which was acetylated by acetic anhydride to afford acetylthioguaiazulene (**8**, purple needles, mp 69.5-70.5 °C, 82wt.%). A small amount of **3** was also obtained, therefore, not only cleavage of S-S bonds of **6** but also C-S ones would be occurred in this reaction conditions. Physical data of **8** were consistent with the proposed structure. These results suggested that the structure of **6** could be accepted as described above.



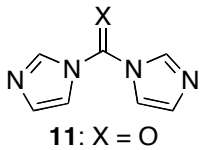
Scheme 2

It is expected that guaiazulenopentathiepin (**4**) is a useful precursor for the conversion into 1,2-*S*-substituted guaiazulenes as with azulenopentathiepin (**2**). Reduction of **4** with $NaBH_4$ in benzene/EtOH generated a bis(thiolate), which was methylated by iodomethane to give not bis(methylthio)guaiazulene (**10**) but methylthioguaiazulenethiol (**9**, blue viscous oil). The result was different from the case of **2**, forming a bis(methylthio) derivative.[4] The ^1H NMR spectrum of **9** showed three kinds of methyl groups (δ 2.51, 2.68 and 2.80 as two methyl and one methylthio moieties) and a thiol proton (δ 7.01). The MS spectrum showed a molecular ion peak [FAB: m/z 276 (M^+)]. Further instrumental data could not be measured due to rather instability of **9**. Although the position of a methylthio group is undecided as far, the 2-substitute (**9**: R^1 = H, R^2 = Me) is plausible considering the steric hindrance at the 4-methyl group.

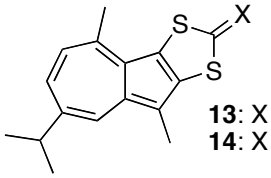
A bis(thiolate), generated from **4** with $LiAlH_4$ in THF, was treated with *N,N'*-carbonyldiimidazole (**11**) or *N,N'*-thiocarbonyldiimidazole (**12**) to afford a 2-oxo-1,3-dithiole (**13**, green solid, mp 125-126 °C, 72%) or a 2-thioxo-1,3-dithiole (**14**, dark green needles, mp 186-187 °C, 78%), respectively. Corresponding physical data of **13** and **14** were consistent with their proposed structures.



9 (observed): R^1 = H, R^2 = Me
or R^1 =Me, R^2 = H
10 (not observed): R^1 = R^2 = Me



11: X = O
12: X = S



13: X = O (72%)
14: X = S (78%)

In conclusion, we have carried out the reactions of guaiazulene (**3**) with reactive sulfulation reagents such as sulfur chloride/imidazole to produce guaiazulenopentathiepin (**4**), which is a precursor for the conversion into 1,2-*S*-substituted guaiazulenes, together with a 1,2-dithiin (**5**) and bis(guaiazulyl)sulfides (**6**). Further work, aimed at the construction of novel azulene-based electron donors derived from **4** and its azulene derivative (**2**), is now under investigation and will appear elsewhere.

EXPERIMENTAL

Mps were determined with a Laboratory Devices MEL-TEMP apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra ($SiMe_4$ as the internal standard) were obtained with Bruker AV500, AM400, AV300, AC300 and/or AC200 spectrometers. IR spectra were obtained with a Perkin Elmer System 2000 FT instrument and electronic spectra (UV-VIS) with a JASCO V-560 spectrophotometer. MS spectra were obtained with a JEOL JMS700AM and/or a Bruker AutoflexIII spectrometers. CV was obtained with an ALS-600 electrochemical measuring apparatus. Unless otherwise stated the spectra were taken in the following solvents/media: IR, KBr; UV-VIS, CH_2Cl_2; ^{1}H and ^{13}C NMR, $CDCl_3$; MS spectra were taken at fast atom bombardment (FAB) and/or MALDI-TOF method; CV, V *vs*. Ag/Ag^+, GC, Pt wire, 0.1 M TBAP in DMF. The progress of reactions was followed by TLC method using Merck Silica gel $60F_{254}$.

General procedure for the reaction of guaiazulene (3) with elemental sulfur or *N,N'*-dithiobisphthalimide (7). To a solution of **3** in the solvent with/without an additive, elemental sulfur or *N.N'*-dithiobisphthalimide (**7**) was added and stirred for the time at the temperature under Ar. After removal of the solvent *in vacuo*, the residue was dissolved in hexane. The soluble component was purified by SiO_2 column chromatography to give guaiazulenopentathiepin (**4**), a 1,2-dithiin compound (**5**) and/or bis(guaiazulyl)sulfides (**6**, an inseparable mixture of sulfides). Atoms as S of sulfuration reagents, solvents, concentrations, (an additive), temperatures, times and yields were indicated in Table 1.

Guaiazulenopentathiepin (4): bluish green plates; mp 110.5-111 °C; ^{1}H NMR δ 1.35 (d, J = 6.9 Hz, 6H), 2.72 (s, 3H), 3.07 (sep, J = 6.9 Hz, 1H), 3.24 (s, 3H), 7.18 (d, J = 10.5 Hz, 1H), 7.47 (dd, J = 10.5, 1.8 Hz, 1H), 8.14 (d, J = 1.8 Hz, 1H); ^{13}C NMR δ 12.6 (2C), 24.5, 29.6, 37.8, 124.1, 130.8, 132.5, 137.4, 137.7, 138.5, 139.7, 145.7, 149.5, 151.8; UV-VIS (log ε) λ_{max} 615 (2.78), 302 (4.28), 280 (4.28); CV (V *vs*. Ag/Ag^+) $(E^{red})_{pc}$ -1.92, -1.43, $(E^{ox})_{pa}$ +0.88; MS (FAB, NBA) *m/z* 356 (M^+), 292 (M^+-2S); MS (MALDI,

Dithranol) *m/z* 356 (M^+), 292 (M^+-2S). Anal. Calcd for $C_{15}H_{16}S_5$: C, 50.52; H, 4.52. Found: C, 50.52; H, 4.44.

1,2-Dithiin (5): green crystals; mp 56.0-57.0 °C; ^{1}H NMR δ 1.35 (d, J = 6.9 Hz, 6H), 2.61 (s, 3H), 3.05 (sep, J = 6.9 Hz, 1H), 4.37 (s, 2H), 6.75 (d, J = 10.2 Hz, 1H), 7.36 (dd, J = 10.2, 1.8 Hz, 1H), 7.52 (s, 1H), 8.14 (d, J = 1.8 Hz, 1H); ^{13}C NMR δ 12.6 (2C), 24.5, 38.2, 42.0, 114.8, 122.8, 124.0, 128.9, 133.7, 135.0 (2C), 139.8, 140.8, 141.7; UV-VIS (log ε) λ_{max} 680 (2.34), 410 (3.67), 294 (4.30), 251 (4.35), 233 (4.26), 225 (4.27); MS (MALDI, Dithranol) *m/z* 260 (M^+). Anal. Calcd for $C_{15}H_{16}S_2$: C, 69.18; H, 6.19. Found: C, 69.17; H, 6.16.

Bis(guaiazulyl)sulfides (6, an inseparable mixture): green viscous oil; Selected ^{1}H NMR of the mixture (as a major component 1) δ 1.33 (d, J = 6.8 Hz, 6H), 2.48 (s, 3H), 3.06 (sep, J = 6.8 Hz, 1H), 3.19 (s, 3H), 6.81 (d, J = 10.7 Hz, 1H), 7.19 (s, 1H), 7.25 (dd, J = 10.7, 2.2 Hz, 1H), 7.98 (d, J = 2.2 Hz, 1H); Selected ^{1}H NMR of the mixture (as a major component 2) δ 1.33 (d, J = 6.8 Hz, 6H), 2.37 (s, 3H), 3.06 (sep, J = 6.8 Hz, 1H), 3.22 (s, 3H), 6.94 (d, J = 10.7 Hz, 1H), 7.32 (dd, J = 10.7, 2.2 Hz, 1H), 7.54 (s, 1H), 8.11 (d, J = 2.2 Hz, 1H); Selected MS (FAB, NBA) of the mixture *m/z* 459 [MH^+ (n = 2)], 458 [M^+ (n = 2)], 427 [MH^+ (n = 1)], 426 [M^+ (n = 1)].

General procedure for the reaction of guaiazulene (3) with sulfuration reagents prepared from sulfur chloride with/without an additive (method A). To a CH_2Cl_2 solution of **3**, a mixture of sulfur chloride with/without an additive in CH_2Cl_2 was added and stirred for the time at the temperature under Ar. The reaction mixture was quenched with water and the aqueous layer was extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by SiO_2 column chromatography to give guaiazulenopentathiepin (**4**), a 1,2-dithiin compound (**5**) and/or bis(guaiazulyl)sulfides (**6**, a mixture of sulfides). Molar *eq*. of sulfur chloride, concentrations, additives, temperatures, times, and yields were indicated in Table 2.

General procedure for the reaction of guaiazulene (3) with sulfuration reagents prepared from sulfur chloride with imidazole (method B). To a CH_2Cl_2 solution of a sulfuration reagent prepared from sulfur chloride with imidazole, a solution of **3** in CH_2Cl_2 was added by drop for 30 min and stirred for 6 h at -40 °C under Ar (concentration: 1.0 x 10^{-2} mol·L^{-1}). The reaction mixture was quenched with water and the aqueous layer was extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by SiO_2 column chromatography to give guaiazulenopentathiepin (**4**), a 1,2-dithiin compound (**5**) and bis(guaiazulyl)sulfides (**6**, a mixture of sulfides). Molar *eq*. of sulfur chloride, molar *eq*. of imidazole and yields were indicated in Table 2.

Reductive acetylation of bis(guaiazulyl)sulfides (6): To a solution of **6** (202 mg, a mixture of sulfides) in dry THF (10 mL), 105wt.% of $LiAlH_4$ (5.60 mmol) was added at 0 °C under Ar. The solution was stirred for 30 min at rt and then acetic anhydride (30.1 mmol) was added and stirred for 2 h. The reaction mixture was diluted with Et_2O and washed with sat. *aq*. $NaHCO_3$ and water. The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by SiO_2 column chromatography to give acetylthioguaiazulene (**8**, 165 mg, 82wt.%), guaiazulene (**3**, 6.1 mg, 3wt.%) and **6** (2.3 mg, 1wt.%).

Acetylthioguaiazulene (8): purple needles; mp 69.5-70.5 °C; ^{1}H NMR δ 1.33 (d, J = 6.9 Hz, 6H), 2.36 (s, 3H), 2.60 (s, 3H), 3.05 (sep, J = 6.9 Hz, 1H), 3.05 (s, 3H), 7.03 (d, J = 10.8 Hz, 1H), 7.39 (dd, J = 10.8, 2.1 Hz, 1H), 7.54 (s, 1H), 8.17 (d, J = 2.1 Hz, 1H); ^{13}C NMR δ 13.0 (2C), 24.7, 27.1, 29.6, 38.0, 107.0, 125.5, 129.7, 134.5, 136.0, 137.2, 140.1, 142.3, 144.8, 146.7, 197.5; IR ν 1682; MS (MALDI, Dithranol) *m/z* 273 (MH^+). Anal. Calcd for $C_{17}H_{20}OS$: C, 74.96; H, 7.40. Found: C, 74.78; H, 7.46.

Reductive methylation of guaiazulenopentathiepin (4): To a solution of **4** in dry benzene and *abs*. EtOH (1 : 1), 10 molar *eq*. of $NaBH_4$ was added at rt under Ar. The solution was stirred for 15 min at rt and then 100 molar *eq*. of iodomethane was added and stirred for 30 min. The reaction mixture was quenched with sat. *aq*. NH_4Cl and the aqueous layer was extracted with hexane. The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The main product in the residue was rather unstable methylthioguaiazulenethiol (**9**), and further purification could not be carried out.

Methylthioguaiazulenethiol (9, an unstable material): blue viscous oil; ^{1}H NMR δ 1.35 (d, J = 6.9 Hz, 6H), 2.51 (s, 3H), 2.68 (s, 3H), 2.80 (s, 3H), 3.07 (sep, J = 6.9 Hz, 1H), 7.01 (s, 1H, SH), 7.04 (d, J = 10.6 Hz, 1H), 7.30 (dd, J = 10.6, 1.8 Hz, 1H), 8.01 (d, J = 1.8 Hz, 1H); MS (FAB, NBA) *m/z* 276 (M^+).

Preparation of 2-oxo-1,3-dithiole (13) or 2-thioxo-1,3-dithiole (14). To a solution of **4** in dry THF (concentration: 2.8 x 10^{-2} or 4.3 x 10^{-2} M), 10 or 5.0 molar *eq*. of $LiAlH_4$ was added at 0 °C under Ar. The solution was stirred for 30 min at rt and then 20 or 10 molar *eq*. of *N,N'*-carbonyldiimidazole (**11**) or *N,N'*-thiocarbonyldiimidazole (**12**) was added and stirred for 15 min or 1 h at rt. The reaction mixture was quenched with 2 N HCl and the aqueous layer was extracted with Et_2O. The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The resulting residue was purified by SiO_2 column chromatography to give **13** (72%) or **14** (78%), respectively.

2-Oxo-1,3-dithiole (13): green solid; mp 125-126 °C; ^{1}H NMR δ 1.36 (d, J = 6.9 Hz, 6H), 2.61 (s, 3H), 2.83 (s, 3H), 3.06 (sep, J = 6.9 Hz, 1H), 7.01 (d, J = 10.8 Hz, 1H), 7.38 (dd, J = 10.8, 1.8 Hz, 1H), 8.05 (d, J = 1.8 Hz, 1H); ^{13}C NMR δ 12.8 (2C), 24.7, 26.7, 38.3, 111.8, 117.6, 127.1, 130.5, 132.2, 135.9, 136.8, 139.6, 141.6, 142.6, 195.2; UV-VIS (log ε) λ_{max} 607 (2.75), 377 (3.94), 360 (3.90), 315 (4.76), 256 (4.30),

217 (4.22); IR ν 1651; MS (MALDI, Dithranol) *m/z* 288 (M^+). Anal. Calcd for $C_{16}H_{16}OS_2$: C, 66.63; H, 5.59. Found: C, 66.50; H, 5.44.

2-Thioxo-1,3-dithiole (14): dark green needles; mp 186-187 °C; ^{1}H NMR δ 1.37 (d, J = 6.9 Hz, 6H), 2.61 (s, 3H), 2.85 (s, 3H), 3.09 (sep, J = 6.9 Hz, 1H), 7.11 (d, J = 10.8 Hz, 1H), 7.47 (dd, J = 10.8, 1.8 Hz, 1H), 8.11 (d, J = 1.8 Hz, 1H); ^{13}C NMR δ 12.3 (2C), 24.6, 26.5, 38.3, 115.8, 122.2, 127.8, 128.7, 133.3, 136.7, 138.3, 142.3, 143.4, 149.0, 216.4; IR ν 1047; MS (MALDI, Dithranol) *m/z* 304 (M^+). Anal. Calcd for $C_{16}H_{16}S_3$: C, 63.11; H, 5.30. Found: C, 62.94; H, 5.00.

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