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One pot synthesis of 1,2,3-benzodithiazol-6-ones

Cecilia Polo, Vicente Ramos, Tomás Torroba*

Departamento de Química Orgánica, Facultad de Veterinaria, Universidad de Extremadura, 10071 Cáceres, Spain

Oleg A. Rakitin

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky Prospect, 47, 117913 Moscow, Russia

Charles W. Rees*

Department of Chemistry, Imperial College of Science, Technology and Medicine, London, SW7 2AY, UK

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Abstract: The reaction of *p*-benzoquinone-4-oximes with disulfur dichloride affords the red 6*H*-1,2,3-benzodithiazol-6-ones. Some ring chlorination occurs, but 2,6-substituents are retained in the products except for a *tert*-butyl group, which is, exceptionally, replaced by chlorine. 1,4-Naphthoquinone 4-oxime and 1,2-naphthoquinone 2-oxime similarly give the red 4-chloro-5*H*-naphtho[1,2-*d*][1,2,3]dithiazol-5-one and the blue 9-chloro-4*H*-naphtho[2,3-*d*][1,2,3]dithiazol-4-one respectively. A unified set of mechanisms is proposed for all of the reactions.

INTRODUCTION

The conversion of 2-unsubstituted aromatic amines into 1,2,3-benzodithiazolium chlorides by disulfur dichloride (Herz reaction) is employed in the dye industry for the synthesis of various heterocycles such as thioindoxyls and thioindigos, benzothiazoles, phenothiazines, benzothiadiazoles, and thiazolobenzo-2,1,3-thiadiazoles.[1] Formation of the benzodithiazolium system is accompanied by chlorination of the carbocyclic ring.[2] Electron withdrawing groups are often displaced by chlorine but electron donating groups are unchanged.[3] Some heterocyclic amines also react with disulfur dichloride, S_2Cl_2, affording 1,2,3-dithiazolium chlorides without further chlorination.[4] In this way, fused thiopheno- and pyrazolo-1,2,3-dithiazoles have been prepared. 1,2,3-Benzodithiazolium salts have been the subject of much research because of their pharmaceutical applications,[5] but neutral 1,2,3-benzodithiazoles are scarcely known, with the exception of a few benzodithiazole-2-oxides.[6] Although formed in very low yield, a benzodithiazole fused to a dithiatriazepine ring has been fully described,[7] showing that quinonoid 1,2,3-benzodithiazoles may be obtained as stable compounds. We have previously synthesised cyclopenta- and cyclohepta-1,2,3-dithiazoles[8] as well as dithioles[9] by reaction of cyclic oximes or diisopropylamines with S_2Cl_2. A related reaction applied to quinone monoximes could provide a rational synthesis of quinonoid benzodithiazoles and in this paper we describe such an easy one-pot method to yield 6*H*-1,2,3-benzodithiazol-6-ones, together with the scope and limitations of the method.

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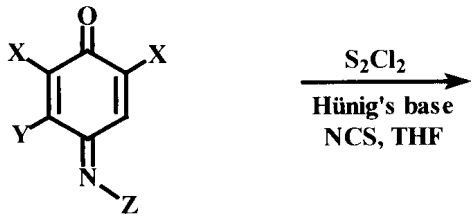
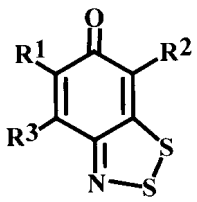
RESULTS AND DISCUSSION

A mixture of *p*-benzoquinone monoxime **1** with S_2Cl_2 (10 mol) in the presence of *N*-ethyldiisopropylamine (Hünig's base) (10 mol) and *N*-chlorosuccinimide (NCS) (10 mol) was kept in dry THF for 3 days at 4°C, and then refluxed for 30 min. In these conditions some unstable intermediates, detected by TLC, were trapped by *in situ* chlorination with the NCS and two compounds **7** (10%) and **8** (3%) were obtained in low yields (see Scheme 1). It is remarkable that in the absence of NCS the reaction afforded a complex mixture from which no stable compounds were isolated after repeated chromatography. We considered that both positions α to the oxo group may have to be protected in order to obtain stable compounds. The same compounds **7** (10%) and **8** (7%) were also obtained from Gibbs reagent **2** and S_2Cl_2 in the presence of Hünig's base, but without addition of NCS. Di-, tri- and tetrachloro-*p*-benzoquinones were also obtained.



S_2Cl_2
Hünig's base
NCS, THF



	1	2	3	4	5	6
X	H	Cl	^{t}Bu	Me	^{i}Pr	Me
Y	H	H	H	H	H	Me
Z	OH	Cl	OH	OH	OH	OH

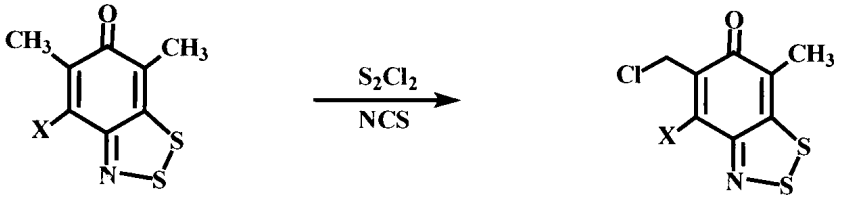
	7	8	9	10	11	12	13	14	15	16
R^1	Cl	Cl	^{t}Bu	Me	Me	^{i}Pr	^{i}Pr	Me	$ClCH_2$	$ClCH_2$
R^2	Cl	Cl	Cl	Me	Me	^{i}Pr	^{i}Pr	Me	Me	Me
R^3	H	Cl	H	H	Cl	H	Cl	Me	Me	Cl
%	10	7	45	20	14	40	15	30	8	9

Scheme 1

In an attempt to obtain better yields of products, by protecting C-2 and C-6 of the starting materials, we performed the reaction of 2,6-di-*tert*-butyl-*p*-benzoquinone-4-oxime **3** with S_2Cl_2 and Hünig's base in THF, in the same conditions. Compound **9** (45%) was obtained as the only reaction product. This compound showed, by mass spectrometry, the presence of a chlorine atom and only one *tert*-butyl group; the 6*H*-1,2,3-benzodithiazol-6-one structure was confirmed by ^1H and ^{13}C-NMR spectroscopy. The NOE difference spectrum of **9** showed an increase in signal strength (1.3%) of the C-4 proton when the *tert*-butyl group is irradiated, proving the structure of **9** as the 5-*tert*-butyl-7-chloro-6*H*-1,2,3-benzodithiazol-6-one. Although the displacement of a *tert*-butyl group from 2,4,6-tri-*tert*-butyl-*N*-thiosulfinylaniline by a sulfur atom was reported in the synthesis of 1,2,3-benzodithiazole-2-oxide,[10] the displacement of a *tert*-butyl group by chlorine from S_2Cl_2 has not been reported. Indeed the 2- and 4-*tert*-butyl groups used for the stabilisation of cyclopentadienone oxime survived its reaction with S_2Cl_2.[11]

To test the scope of the new synthesis and the possible substitution by chlorine of other alkyl groups, we performed the reaction of 2,6-dimethyl- and 2,6-diisopropyl-1,4-benzoquinone-4-oximes **4** and **5** with S_2Cl_2 in the presence of Hünig's base. These reactions afforded the corresponding 5,7-dialkyl-6*H*-1,2,3-benzodithiazole-6-ones **10** (20%) and **12** (40%), together with their corresponding 4-chloro derivatives **11** (14%) and **13** (15%), whose structures were proved by spectroscopy. No displacement of methyl or isopropyl groups by chlorine was detected in these reactions. However, the reaction of 2,3,6-trimethyl-1,4-benzoquinone-4-oxime **6** and S_2Cl_2 in the same conditions afforded the corresponding 4,5,7-trimethyl-6*H*-1,2,3-benzodithiazole-6-one **14** (30%) and a by-product **15** (8%) in which mass spectrometry showed the presence of one chlorine atom, also confirmed by

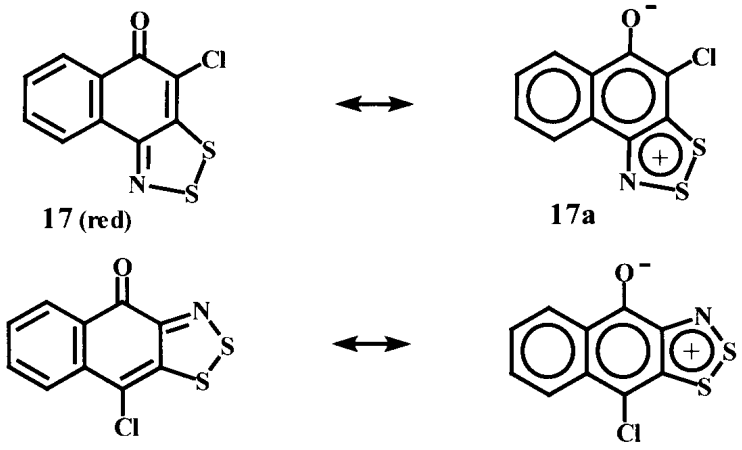
microanalysis. Careful examination of ^{1}H and ^{13}C NMR spectra and NOE difference spectra by irradiation of each methyl group (see Experimental) proved the structure 5-chloromethyl-4,7-dimethyl-6*H*-1,2,3-benzodithiazol-6-one for **15**, probably formed by chlorination of **14**. In order to test the possible chlorination of other alkyl groups we performed all the above reactions in the presence of NCS (10 mol). Unexpectedly, oximes **3**, **5** and **6** afforded only the above reported products in much lower yields, indicating that chlorination of the oximes may be favoured over the ring closure reaction. On the other hand, oxime **4** afforded products **10** (17%) and **11** (35%) in acceptable yields, and a by-product **16** (9%) in which mass spectrometry showed the presence of two chlorine atoms, also confirmed by microanalysis. The ^{1}H NMR spectrum of **16** showed a signal at δ 4.74 assigned to the 5-methylene group and a signal at δ 2.21 assigned to the 7-methyl group, by comparison with the ^{1}H NMR spectra of **10** and **11**, and confirmed by ^{13}C NMR spectroscopy.



11, X = Cl
14, X = CH_3

16, X = Cl
15, X = CH_3

We then reasoned that the extension of conjugation might also give rise to stable products, with additional stabilisation of the intermediates, so we performed the reaction of two naphthoquinone monoximes and S_2Cl_2 in the presence of Hünig's base. 1,4-Naphthoquinone-4-oxime gave 4-chloro-5*H*-naphtho[1,2-*d*][1,2,3]dithiazol-5-one **17** in relatively high yield (50%) as red needles and 1,2-naphthoquinone-2-oxime gave 9-chloro-4*H*-naphtho[2,3-*d*][1,2,3]dithiazol-4-one **18** (20%) as blue prisms (Scheme 2).



17 (red) **17a**

18 (blue) **18a**

Scheme 2

These structurally similar compounds are both formally 14π heteroaromatic systems with analogous opportunities for electronic delocalisation (**17a**, **18a**). The striking difference in their colour and electronic spectra (figure 1) is presumably associated the angular tricyclic structure of **17** compared with the higher energy linear structure of **18**, as found in similar carbocyclic systems like phenanthrene and anthracene and their aza derivatives.

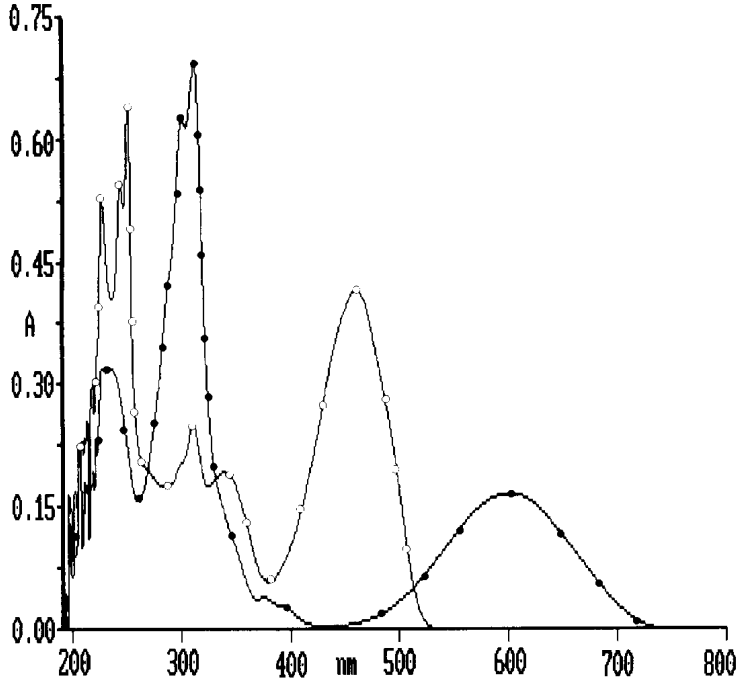


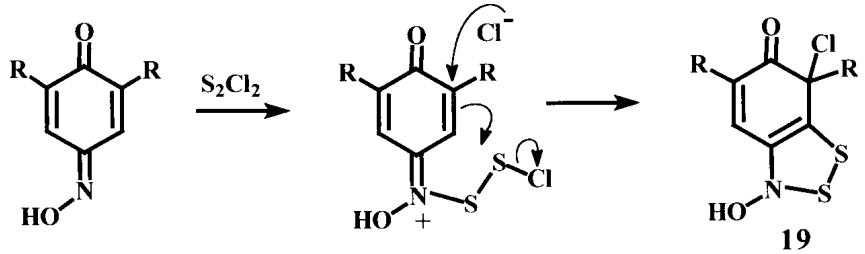
Figure 1. Electronic spectra (absorbance vs wavelength (nm)) of **17** (○) and **18** (●) both in dichloromethane at 4.2×10^{-5} mol L^{-1}.

Although the yields in the simplest quinone-monoxime-S_2Cl_2 reactions are very poor to modest, they are much improved with polysubstituted quinones, and the reactions provide a very simple one pot route to fused 1,2,3-dithiazoloquinones from readily available compounds.

REACTION MECHANISMS

Whilst not yet investigated in detail, it is possible to propose a reasonably simple and consistent set of reaction mechanisms for these quinone oxime - S_2Cl_2 reactions, based upon the nature of the products described above. We have proposed earlier a detailed pathway for the reaction of S_2Cl_2 and base with saturated cyclic oximes.[8] Although formally similar, the present reactions differ from the earlier ones since the starting oximes do not have adjacent saturated carbon atoms bearing hydrogen which allowed ready loss of the oxime oxygen as water. In the present work, as before, we never isolated *N*-oxide products in which this oxygen has been retained. This is in contrast with Hafner's observation of the conversion of 2,4-di-*tert*-butylcyclopentadienone oxime with S_2Cl_2 in THF into the corresponding bicyclic dithiazole *N*-oxide in good yield.[11] It is possible that, under our conditions, the excess of S_2Cl_2 could have deoxygenated an intermediate *N*-oxide, but this seems unlikely in view of Hafner's result.[11] Hence in our scheme we propose that the oxime oxygen is lost by an acid catalysed cleavage of an oxygen to saturated nitrogen bond in a reaction intermediate; indeed this is a key step in the following reaction sequences.

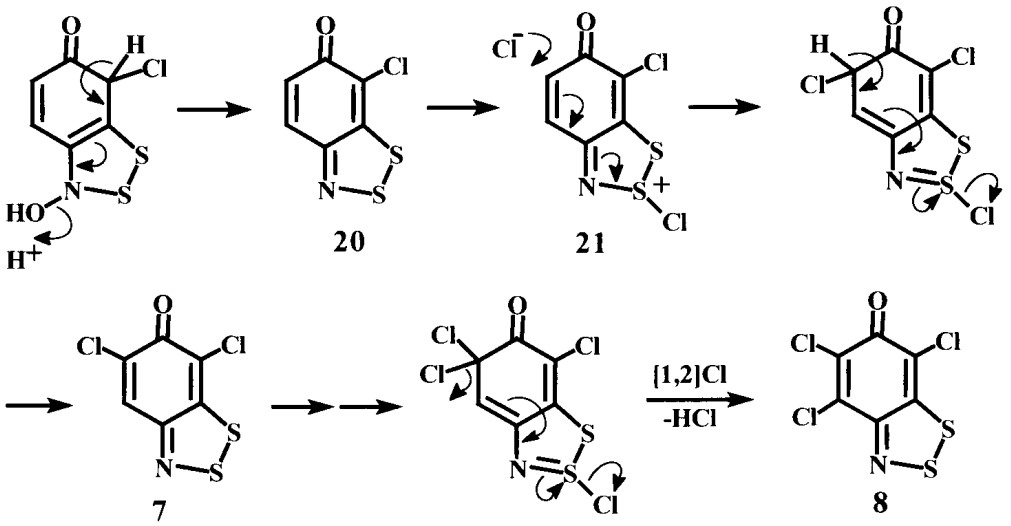
All the reactions are thought to start, as before,[8] by nucleophilic substitution of S_2Cl_2 by the oxime nitrogen atom, followed by conjugate addition of chlorine ion to the iminium ion and cyclisation to the fused dithiazole **19** (Scheme 3). The fate of **19** then depends upon the nature of the R groups, as follows.



Scheme 3

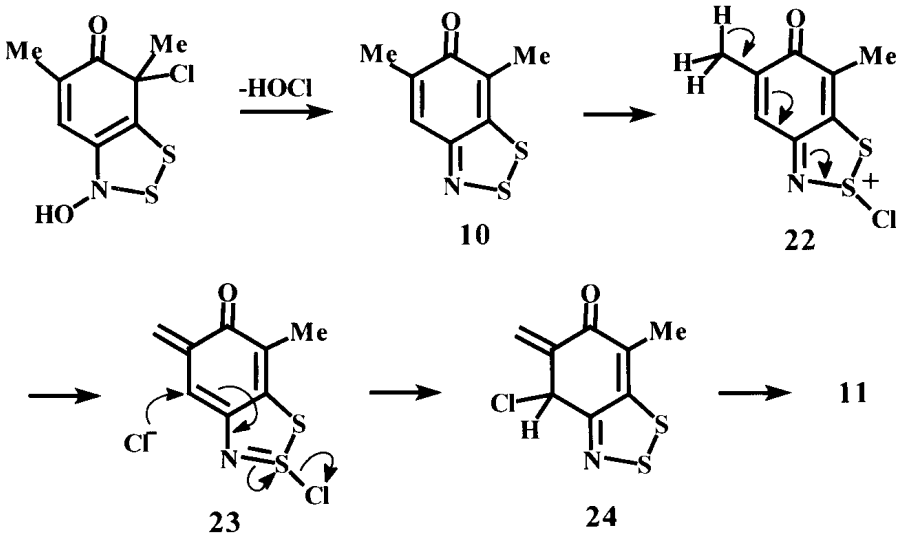
When R = H, **19** undergoes acid catalysed dehydration to give the monochloro compound **20**, which is chlorinated further to give the observed dichloro **7** and trichloro compound **8** (Scheme 4). Introduction of the

second chlorine into position 5 of **20** could be by electrophilic chlorine, from S_2Cl_2 or NCS, activated by electron release from the conjugated S-2 atom of the dithiazole ring. However the carbocyclic ring is quite strongly deactivated to electrophilic attack and a possible alternative is that chlorine collapses onto the more nucleophilic S-2 atom to give a sulfonium ion **21**, now strongly activated to nucleophilic addition of chloride at C-5 (**21**). The third chlorine atom becomes attached to C-4, which is not activated, and it is possible that the same sequence involves Cl^- attack at C-5 again, followed by a 1,2-shift of chloride, as shown in Scheme 4.



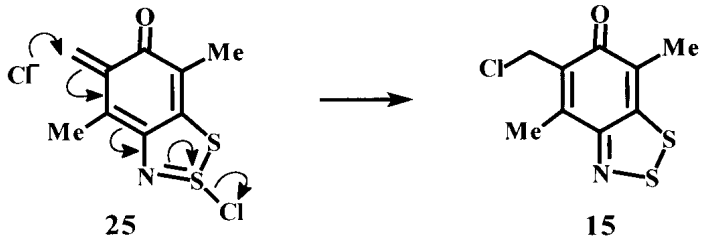
Scheme 4

When R = Me or Pr^i, the observed dialkyl products **10** and **12** can be formed directly from **19** by acid catalysed elimination of HOCl (or Cl_2 and H_2O). The sulfonium ion **22**, analogous to **21** (Scheme 4), can now lose a proton from the activated 5-alkyl group (shown in Scheme 5 for R = Me) to give **23** which readily rearranges from *S*-chloro **23** to *C*-chloro **24** and hence to the 4-chloro derivative **11**.

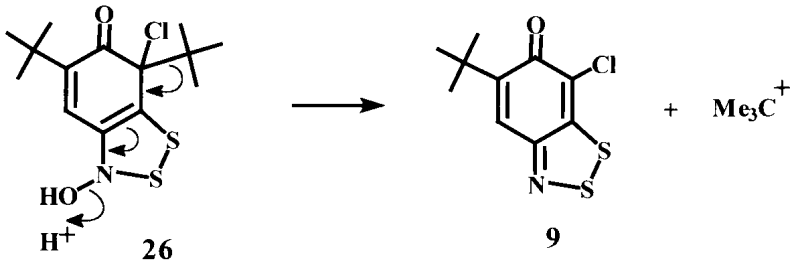


Scheme 5

When the 4-position is already substituted, as with the trimethyl compound **6**, the analogous intermediate **25** suffers attack by Cl^- at the exocyclic double bond, rather than at C-4, thus explaining the formation of the chloromethyl derivative **15**.



Finally, when R = Bu^t in **19**, the special stability of the *tert*-butyl cation leads to its loss, as is often observed in acid-catalysed de-*tert*-butylation of *tert*-butyl aromatics.[12] Although the displacement of *tert*-butyl by Cl^+, as opposed to H^+, is relatively rare, loss of the butyl group here will be favoured by the crowded nature



of the intermediate **26** and the absence of sites to which the carbonium ion can migrate intramolecularly. We note that this mechanism explains why only one of the *tert*-butyl groups (that adjacent to sulfur) is lost, and why the reaction stops at product **9**, in relatively high yield (45%), since there is not the possibility of further chlorination at the 4-position via an exocyclic methylene intermediate like **23** and **25**. The dithiazolonaphthalenes **17** and **18** are the expected products of entirely analogous reaction pathways.

EXPERIMENTAL

Melting points were determined using a Kofler hot-stage apparatus and are uncorrected. IR spectra were measured with Perkin-Elmer 399 and 1310 spectrophotometers. ^1H and ^{13}C NMR spectra were recorded with Bruker AC200-E, DRX400 and AM500 spectrometers; chemical shifts are reported in ppm relative to tetramethylsilane as internal standard; coupling constants are in Hz. Methyl, methylene and methine groups, as well as quaternary carbon atoms, were discriminated in the ^{13}C-NMR spectra by DEPT experiments. Mass spectral data were taken with VG7070E and VG-Autospec mass spectrometers. UV spectra were taken with a Perkin Elmer Lambda 9 spectrophotometer. Elemental analyses were performed with a Perkin Elmer 240-B apparatus. Column chromatography was carried out in a medium pressure Gilson liquid chromatography apparatus on silica gel C60 (Merck). Light petroleum refers to the fraction bp 40-60°C. 2,6-Dialkyl-1,4-benzoquinone-4-oximes **3-5** and 2,3,6-trimethyl-1,4-benzoquinone-4-oxime **6** were obtained by nitrosation of the corresponding 2,6-dialkylphenols using standard methods.[13] 1,4-Naphthoquinone-4-oxime[14] and 1,2-naphthoquinone-2-oxime[15] were obtained by nitrosation of 1-methoxynaphthalene or 1-naphthol, respectively.

General procedures for the reaction of quinone monoximes and disulfur dichloride

Method A. The quinone monoxime (5 mmol) and *N,N*-diisopropylethylamine (Hünig's base, 6.45 g, 50 mmol) were dissolved in THF (40 ml) and cooled to –50 °C. To the resulting stirred solution was added consecutively, disulfur dichloride (4.0 ml, 50 mmol) and a solution of NCS (6.65 g, 50 mmol) in THF (30 ml), and the mixture was stirred at 4 °C for 72 h. Then the mixture was heated under reflux for 1.5 h, monitoring the reaction by TLC every 30 min. Then the solvent was removed under reduced pressure and the products were separated by column chromatography (light petroleum, then light petroleum-dichloromethane mixtures).

Method B. Disulfur dichloride (4.0 ml, 50 mmol) was added to a stirred, cold (-50 °C) solution of the quinone monoxime (5 mmol) and *N,N*-diisopropylethylamine (6.45 g, 50 mmol) dissolved in THF (40 ml) and the mixture was stirred at 4 °C for 72 h. Then, a solution of NCS (6.65 g, 50 mmol) in THF (30 ml), was added, and the resulting mixture was heated under reflux for 1.5 h, monitoring the reaction by TLC each 30 min. Then the solvent was removed under reduced pressure and the products were separated by column chromatography as above.

5,7-Dichloro-6*H*-1,2,3-benzodithiazol-6-one (**7**): Red needles from light petroleum-dichloromethane (0.12g, 10% from **2**), mp 257-258°C; IR ν_{max} (CCl_4) 1608 (s, C=O), 1506 (s, C=N), 1458 (s) and 1226 cm^{-1} (m); UV λ_{max} (CH_2Cl_2) 482 (logε 3.88), 350 (3.75), 275 (3.58) and 225 nm (3.94); ^1H NMR δ (200 MHz, $CDCl_3$) 8.39 (s, 1H, *aromatic*H); ^{13}C NMR δ (50 MHz, $CDCl_3$) 167.53 (C=O), 152.57 and 152.39 (2xC-Cl), 137.80 (C=N), 127.07 (intense, C-H), 115.73 (C-S); MS (EI, 70 eV) *m/z* (%) 241 (16, $M^{+\cdot}$+4), 239 (73, $M^{+\cdot}$+2), 237 (100, $M^{+\cdot}$), 213 (16, M-CO+4), 211 (67, M-CO+2), 209 (86, M-CO), 202 (14, M-Cl), 174 (33, M-CO-Cl); HRMS found 236.8872; $C_6HCl_2NOS_2$ requires 236.8877; Anal. Calcd for $C_6HCl_2NOS_2$: C, 30.27; H, 0.42; N, 5.88. Found: C, 29.92; H, 0.54; N, 5.89.

4,5,7-Trichloro-6*H*-1,2,3-benzodithiazol-6-one (**8**): Red amorphous solid from light petroleum-dichloromethane (0.10g, 7% from **2**), mp 216-217°C; IR ν_{max} (CCl_4) 1592 (s, C=O), 1554 (s, C=N), 1503 (s), 1461 (m), 1261 (s) and 1013 cm^{-1} (m); UV λ_{max} (CH_2Cl_2) 496 (logε 3.91), 361 (3.81), 281 (3.65) and 227 nm (4.01); ^1H NMR δ (200 MHz, $CDCl_3$) *no signals*; ^{13}C NMR δ (50 MHz, $CDCl_3$) 166.96 (C=O), 152.08 and 150.40 (2xC-Cl), 136.22 (C=N), 131.68 (C(4)-Cl), 114.43 (C-S); MS (EI, 70 eV) *m/z* (%) 275 (14, $M^{+\cdot}$+4), 273 (37, $M^{+\cdot}$+2), 271 (35, $M^{+\cdot}$), 247 (16, M-CO+4), 245 (42, M-CO+2), 243 (39, M-CO), 236 (5, M-Cl), 208 (10, M-CO-Cl); HRMS found 270.8483; $C_6Cl_3NOS_2$ requires 270.8487; Anal. Calcd for $C_6Cl_3NOS_2$: C, 26.44; N, 5.14. Found: C, 27.12; N, 4.71.

5-*tert*-Butyl-7-chloro-6*H*-1,2,3-benzodithiazol-6-one (**9**): Orange-red needles from light petroleum-dichloromethane (0.59g, 45%), mp 202-203°C; IR ν_{max} (CCl_4) 3005 (w), 2964 (m), 1587 (s) and 1556 (s) (C=O), 1522 (s, C=N), 1453 (s), 1385 (w), 1227(m) and 1096 cm^{-1} (s); UV λ_{max} (CH_2Cl_2) 472 (logε 4.11), 341 (3.89), 272 (3.62) and 226 nm (3.81); ^1H NMR δ (400 MHz, $CDCl_3$) 7.67 (s, 1H, *aromatic*H), 1.39 (s, 9H, 3xCH_3); NOEDS δ (%) (400 MHz, $CDCl_3$) 7.67 (1.3), 1.39 (-100); ^{13}C NMR δ (100 MHz, $CDCl_3$) 175.08 (C=O), 155.01, 151.98, 150.34, 123.87 (C-H, from DEPT), 121.35 (C-S), 36.25 (*quaternary*C, from DEPT), 28.93 (3xCH$_3$, from DEPT); MS (EI, 70 eV) *m/z* (%) 261 (15, $M^{+\cdot}$+2), 259 (36, $M^{+\cdot}$), 246 (41, M-CH_3+2), 244 (100, M-CH_3), 230 (10, M-HCO), 224 (7, M-Cl), 217 (42, M-42), 204(20, M-55); HRMS found 258.9889; $C_{10}H_{10}ClNOS_2$ requires 258.9892; Anal. Calcd for $C_{10}H_{10}ClNOS_2$: C, 46.24; H, 3.88; N, 5.39. Found: C, 46.39; H, 3.91; N, 5.18.

5,7-Dimethyl-6*H*-1,2,3-benzodithiazol-6-one (**10**): Bright red needles from light petroleum-dichloromethane (0.20g, 20%), mp 147-148°C; IR ν_{max} (CCl_4) 2963 (w), 1603 (s, C=O), 1558 (s, C=N), 1275 (m), 1260 (m) and 1008 cm^{-1} (m); UV λ_{max} (CH_2Cl_2) 470 (logε 4.53), 337 (4.34) and 227 nm (4.23); ^1H NMR δ (400 MHz, $CDCl_3$) 7.58 (s, 1H, *aromatic*H), 2.20 (s, 3H, CH_3), 2.19 (s, 3H, CH_3); ^{13}C NMR δ (100 MHz, $CDCl_3$) 181.58

(C=O), 155.60, 150.97 ($^2J_{C-H}$ = 6 Hz), 140.85 ($^2J_{C-H}$ = 6 Hz), 125.47 (C-H, from DEPT, $^1J_{C-H}$ = 174 Hz, $^3J_{C-H}$ = 6 Hz), 123.30 (C-S, $^3J_{C-H}$ = 6 Hz), 17.45 and 17.40 (2xCH$_3$, from DEPT, $^1J_{C-H}$ = 128 Hz); MS (EI, 70 eV) *m/z* (%) 197 (100, M^+), 169 (17, M-CO), 168 (35, M-HCO), 154 (68, M-CO-CH$_3$); HRMS found 196.9980; $C_8H_7NOS_2$ requires 196.9970; Anal. Calcd for $C_8H_7NOS_2$: C, 48.71; H, 3.58; N, 7.10. Found: C, 48.66; H, 3.31; N, 6.89.

4-Chloro-5,7-dimethyl-6*H*-1,2,3-benzodithiazol-6-one (**11**): Red needles from light petroleum-dichloromethane (0.16g, 14%), mp 161-162°C; IR ν_{max} (CCl_4) 2928 (m), 1599 (m) and 1565 (s, C=O), 1548 (s, C=N), 1464 (m), 1226 (m) and 1010 cm^{-1} (m); UV λ_{max} (CH_2Cl_2) 484 (logε 3.97), 348 (3.86), 262 (3.61) and 226 nm (3.82); ^{1}H NMR δ (400 MHz, $CDCl_3$) 2.31 (s, 3H, CH$_3$(5)), 2.19 (s, 3H, CH$_3$(7)); ^{13}C NMR δ (100 MHz, $CDCl_3$) 180.00 (C=O), 153.11, 149.92, 138.45, 132.03, 122.13, 17.54 and 14.59 (2xCH$_3$); MS (EI, 70 eV) *m/z* (%) 233 (38, $M^{+\cdot}$+2), 231 (100, $M^{+\cdot}$), 205 (10, M-CO+2), 203 (28, M-CO), 196 (15, M-Cl), 188 (8, M-CO-CH$_3$), 168 (83, M-CO-Cl); HRMS found 230.9585; $C_8H_6ClNOS_2$ requires 230.9579; Anal. Calcd for $C_8H_6ClNOS_2$: C, 41.47; H, 2.61; N, 6.04. Found: C, 41.38; H, 2.53; N, 5.79.

5,7-Di-*iso*-propyl-6*H*-1,2,3-benzodithiazol-6-one (**12**): Red solid from light petroleum-dichloromethane (0.51g, 40%), mp 70-71°C; IR ν_{max} (CCl_4) 3057 (w), 2964 (s), 1611 (s) and 1596 (s, C=O), 1539 (s, C=N), 1480 (s), 1462 (s), 1379 (m), 1265 (m), 1231 (m), 1056 (m) and 886 cm^{-1} (m); UV λ_{max} (CH_2Cl_2) 470 (logε 4.09), 337 (3.88) and 227 nm (3.79); ^{1}H NMR δ (400 MHz, $CDCl_3$) 7.53 (s, 1H, *aromatic*H), 3.38 (sept., 1H, CH(CH$_3$)$_2$, J = 3.5 Hz), 3.27 (sept., 1H, J = 3.3 Hz, CH(CH$_3$)$_2$), 1.33 (d, 6H, J = 3.5 Hz, 2xCH$_3$), 1.19 (d, 6H, J = 3.3 Hz, 2xCH$_3$) ; ^{13}C NMR δ (100 MHz, $CDCl_3$) 180.27 (C=O), 157.25, 150.26, 148.10 and 133.75 (*quaternary*C, from DEPT), 122.54 (C-H, from DEPT), 31.56 (CH, from DEPT), 27.38 (CH, from DEPT), 21.90 (CH$_3$, from DEPT), 18.37 (CH$_3$, from DEPT); MS (EI, 70 eV) *m/z* (%) 253 (60, M^+), 238 (100, M-CH$_3$), 225 (13, M-CO), 220 (29, M-SH), 210 [43, M-CH(CH$_3$)$_2$]; HRMS found 253.0619; $C_{12}H_{15}NOS_2$ requires 253.0595; Anal. Calcd for $C_{12}H_{15}NOS_2$: C, 56.88; H, 5.97; N, 5.53. Found: C, 56.75; H, 5.75; N, 5.32.

4-Chloro-5,7-di-*iso*-propyl-6*H*-1,2,3-benzodithiazol-6-one (**13**): Red solid from light petroleum-dichloromethane (0.22g, 15%), mp 93-94°C; IR ν_{max} (CCl_4) 2964 (s), 1669 (m), 1606 (s) and 1582 (s, C=O), 1543 (m, C=N), 1480 (m), 1457 (m), 1380 (w) and 1070 cm^{-1} (m); UV λ_{max} (CH_2Cl_2) 484 (logε 3.67), 348 (3.60), 278 (3.56) and 227 nm (3.75); ^{1}H NMR δ (400 MHz, $CDCl_3$), 3.66 (sept., 1H, J = 7.0 Hz, CH(CH$_3$)$_2$), 3.30 (sept., 1H, J = 7.0 Hz, CH(CH$_3$)$_2$), 1.37 (d, 6H, J = 7.0 Hz, 2xCH$_3$), 1.30 (d, 6H, J = 7.0 Hz, 2xCH$_3$); ^{13}C NMR δ (50 MHz, $CDCl_3$) 179.42 (C=O), 154.49, 147.12, 145.54, 132.78 and 131.60 (*quaternary*C, from DEPT), 31.44 (CH, from DEPT), 29.91 (CH, from DEPT), 19.47 (CH$_3$, from DEPT), 18.22 (CH$_3$, from DEPT); MS (EI, 70 eV) *m/z* (%) 289 (23, $M^{+\cdot}$+2), 287 (59, $M^{+\cdot}$), 274 (38, M-CH$_3$+2), 272 (100, M-CH$_3$), 259 (28, M-CO), 252 (48, M-Cl), 244 [16, M-CH(CH$_3$)$_2$]; HRMS found 287.0195; $C_{12}H_{14}ClNOS_2$ requires 287.0205; Anal. Calcd for $C_{12}H_{14}ClNOS_2$: C, 50.08; H, 4.90; N, 4.87. Found: C, 50.09; H, 4.94; N, 4.16.

4,5,7-Trimethyl-6*H*-1,2,3-benzodithiazol-6-one (**14**): Red needles from light petroleum-dichloromethane (0.32g, 30%), mp 91-92°C; IR ν_{max} (CCl_4) 2928 (w), 1572 (s, C=O), 1554 (s, C=N), 1460 (m) and 1242 cm^{-1} (m); UV λ_{max} (CH_2Cl_2) 469 (logε 3.75), 349 (3.70), 254 (3.66) and 226 nm (3.93); ^{1}H NMR δ (400 MHz, $CDCl_3$) 2.49 (s, 3H, CH$_3$(4)), 2.18 (s, 3H, CH$_3$(7)), 2.15 (s, 3H, CH$_3$(5)); NOEDS δ (%) (400 MHz, $CDCl_3$) 2.15 (-100), 2.18 (-17.5), 2.49 (0.2); NOEDS δ (%) (400 MHz, $CDCl_3$) 2.15 (-21.4), 2.18 (-100), 2.49 (0); ^{13}C NMR δ (100 MHz, $CDCl_3$) 181.86 (C=O), 157.09, 150.20, 136.85, 134.04 and 122.39 (*quaternary*C), 17.77, 16.08 and 13.07 (3xCH$_3$); MS (EI, 70 eV) *m/z* (%) 211 (100, M^+), 183 (15, M-CO), 182 (19, M-HCO), 168 (59, M-CH$_3$-CO); HRMS found 211.0130; $C_9H_9NOS_2$ requires 211.0126.

5-Chloromethyl-4,7-dimethyl-6*H*-1,2,3-benzodithiazol-6-one (**15**): Red solid from light petroleum-dichloromethane (0.10g, 8%), mp 84-85°C; IR ν_{max} (CCl_4) 2926 (w), 1602 (m, C=O), 1547 (s, C=N), 1433 (m), 1377 (w), 1256 (m), 1236 (m) and 1008 cm^{-1} (w); UV λ_{max} (CH_2Cl_2) 486 (logε 3.86), 342 (3.73), 281 (3.58) and 226 nm (3.83); ^{1}H NMR δ (400 MHz, $CDCl_3$) 4.67 (s, 2H, CH_2(5)), 2.64 (s, 3H, CH_3(4)), 2.20 (s, 3H, CH_3(7)); NOEDS δ (%) (400 MHz, $CDCl_3$) 4.67 (3), 2.64 (-100), 2.20 (0); NOEDS δ (%) (400 MHz, $CDCl_3$) 4.67 (0), 2.64 (0), 2.20 (-100); ^{13}C NMR δ (100 MHz, $CDCl_3$) 179.32 (C=O), 156.73, 151.00, 137.81, 135.22 and 122.71 (*quaternary*C, from DEPT), 36.87 (CH_2, from DEPT), 17.68 and 15.68 (2xCH_3, from DEPT); MS (EI, 70 eV) *m/z* (%) 247 (13, $M^{+\cdot}$+2), 245 (26, $M^{+\cdot}$), 210 (66, M-Cl), 182 (24, M-Cl-CO), 149 (25, M-HCl-CO-S), 36(100, HCl); HRMS found 244.9742; $C_9H_8ClNOS_2$ requires 244.9736; Anal. Calcd for $C_9H_8ClNOS_2$: C, 43.99; H, 3.28; N, 5.70. Found: C, 44.80; H, 3.38; N, 5.30.

4-Chloro-5-chloromethyl-7-methyl-6*H*-1,2,3-benzodithiazol-6-one (**16**): Red needles from light petroleum-dichloromethane (0.12g, 9%), mp 209-210°C; IR ν_{max} (CCl_4) 2971 (w), 1587 (m) and 1557 (s, C=O), 1537 (s, C=N), 1455 (m), 1421 (m), 1258 (m), 1236 (m) and 1009 cm^{-1} (m); UV λ_{max} (CH_2Cl_2) 502 (logε 4.04), 343 (3.90), 287 (3.75) and 227 nm (4.07); ^{1}H NMR δ (400 MHz, $CDCl_3$) 4.74 (s, 2H, CH_2(5)), 2.21 (s, 3H, CH_3(7)); ^{13}C NMR δ (100 MHz, $CDCl_3$) 177.66 (C=O), 153.00, 150.61, 147.33, 136.25, 122.65, 37.26 (CH_2), 17.48 (CH_3); MS (EI, 70 eV) *m/z* (%) 269 (12, $M^{+\cdot}$+4), 267 (54, $M^{+\cdot}$+2), 265 (73, $M^{+\cdot}$), 231 (33, M-HCl+2), 230 (26, M-Cl), 229 (100, M-HCl), 201 (17, M-HCl-CO), 195 (10, M-2Cl), 166 (11, M-2Cl-HCO); HRMS found 264.9186; $C_8H_5Cl_2NOS_2$ requires 264.9190; Anal. Calcd for $C_8H_5Cl_2NOS_2$: C, 36.10; H, 1.89; N, 5.26. Found: C, 35.99; H, 1.97; N, 5.07.

4-Chloro-5*H*-naphtho[1,2-*d*][1,2,3]dithiazol-5-one (**17**): Red needles from light petroleum-dichloromethane (0.63g, 50%), mp 234-235°C; IR ν_{max} (CCl_4) 1613 (s) and 1586 (s) (C=O), 1523 (s, C=N), 1286 (s) and 1157(s) cm^{-1} (s); UV λ_{max} (CH_2Cl_2) 461 (logε 4.03), 340 (3.69), 311 (3.81), 251 (4.22), 244 (4.14) and 226 nm (4.13); ^{1}H NMR δ (400 MHz, $CDCl_3$) 8.45 (m, 1H), 8.36 (m, 1H), 7.77 (m, 1H), 7.75 (m, 1H, J_{ortho} = 4.0 Hz, J_{meta} = 1.0 Hz); ^{13}C NMR δ (100 MHz, $CDCl_3$) 174.32 (C=O), 154.76, 153.37, 132.05 (C-H), 131.67 (C-H), 129.68, 128.58, 127.02 (C-H), 126.69 (C-H), 119.73 (C-S); MS (EI, 70 eV) *m/z* (%) 255 (46, $M^{+\cdot}$+2), 253 (100, $M^{+\cdot}$), 227 (9, M-CO+2), 225 (23, M-CO), 218 (6, M-Cl), 190 (9, M-CO-Cl); HRMS found 252.9436; $C_{10}H_4ClNOS_2$ requires 252.9423; Anal. Calcd for $C_{10}H_4NOS_2Cl$: C, 47.34; H, 1.58; N, 5.52. Found: C, 47.62; H, 1.35; N, 5.34.

9-Chloro-4*H*-naphtho[2,3-*d*][1,2,3]dithiazol-4-one (**18**): Blue prisms from light petroleum-dichloromethane (0.25g, 20%), mp 195-196°C; IR ν_{max} (CCl_4) 1591 (s) (C=O), 1565 (s), 1550 (s), 1537 (s), 1464 (m), 1256 (m) and 1011(m) cm^{-1} (s); UV λ_{max} (CH_2Cl_2) 602 (logε 3.63), 312 (4.25), 301 (4.20) and 228 nm (3.91); ^{1}H NMR δ (500 MHz, $CDCl_3$) 8.35 (m, 1H), 7.74 (m, 2H), 7.47 (m, 1H, J_{ortho} = 8.1 Hz, J_{meta} = 5.3 Hz, J_{para} = 3.0 Hz); ^{13}C NMR δ (125 MHz, $CDCl_3$) 175.81 (C=O), 154.21, 141.10, 135.11 (C-H), 134.44, 129.11 (C-H), 128.86, 127.41 (C-H), 123.38 (C-H), 116.43 (C-S); MS (EI, 70 eV) *m/z* (%) 255 (20, $M^{+\cdot}$+2), 253 (48, $M^{+\cdot}$), 191 (20, M-2S+2), 189 (57, M-2S), 154 (100, M-2S-Cl), 126 (39, M-2S-CO-Cl); HRMS found 252.9416; $C_{10}H_4ClNOS_2$ requires 252.9423; Anal. Calcd for $C_{10}H_4ClNOS_2$: C, 47.34; H, 1.59; N, 5.52. Found: C, 47.59; H, 1.30; N, 5.28.

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