A Triple Newman-Kwart Rearrangement at a Fully Substituted Benzene Ring

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 75th birthday

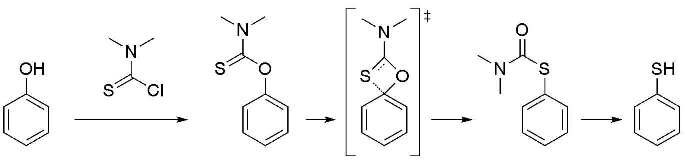
The Newman-Kwart rearrangement of *O*-thiocarbamates to *S*-thiocarbamates is a versatile method for the conversion of phenols into thiophenols. The triple rearrangement of the *O*-trithiocarbamate 2,4,6-triacetyl-1,3,5-tri-(dimethylthiocarbamoyloxy)benzene (**2**) to the *S*-trithiocarbamate 2,4,6-triacetyl-1,3,5-tri-(dimethylthiocarbamoylthio)benzene (**3**) is performed, which is unprecendented for fully substituted benzene rings. The synthesis and characterization of the *O*-trithiocarbamate **2** and the *S*-trithiocarbamate **3** including the single-crystal X-ray structure analysis of compound **3** are presented.

Key words: Newman-Kwart Rearrangement, Thiocarbamates, Thiols

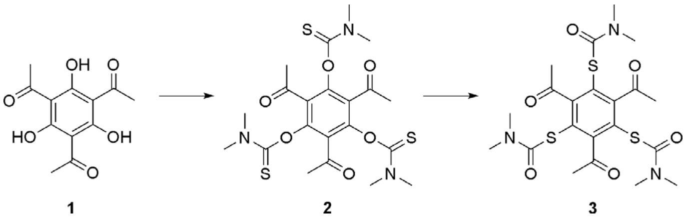
Introduction

The synthesis of thiols has broad applications in chemistry ranging from biochemistry to coordination chemistry [1 – 5]. A convenient synthetic route to thiophenols is the Newman-Kwart rearrangement of phenols (Scheme 1) [6, 7].

In the first step, the phenol is converted to a *O*-thiocarbamate. A typical procedure is the reaction of the phenol with dimethylthiocarbamoyl chloride under basic conditions. This *O*-thiocarbamate is converted into the *S*-thiocarbamate by a thermal rearrangement. A four-membered cyclic transition state is proposed, which results from the nucleophilic attack of the sulfur atom to the *ipso*-carbon atom of the benzene ring. The thermodynamic driving force is the conversion of the formal C=S double bond into the energetically more favorable C=O double bond. While this Newman-Kwart rearrangement has been applied to many different substrates, there are only few examples for a double rearrangement at one aromatic ring [8 – 13]. To the best of our knowledge, only one triple rearrangement at one benzene ring has been reported, which is the conversion of the triple *O*-thiocarbamate of 1,3,5-trihydroxybenzene into its triple *S*-thiocarbamate [9]. The rearrangement conditions vary tremendously in dependence of the other substituents of the aromatic ring. Some synthetic protocols are without a solvent at high temperatures (170 °C to 335 °C) with different reaction times (2 min to 20 h) [7 – 10, 12, 14 – 21]. Other routines use high-boiling solvents like diphenyl ether (b. p. 259 °C) or *o*-dichlorobenzene (b. p. 180 °C) [8, 14, 18]. It is well accepted that electron-withdrawing substituents at the aromatic ring reduce the temperature needed for the rearrangement. For example, formyl or nitro substituents allow successful rearrangement in toluene (b. p. 110 °C) [22, 23]. Lewis acids like $BF_3 \cdot Et_2O$ reduce the rearrangement temperatures strongly [7, 24]. Newman-Kwart rearrangements with several substituents in the *ortho*



Scheme 1.



Scheme 2.

position to the thiocarbamate have been described in the literature [6, 7, 16, 22, 23, 25]. The above-mentioned multiple Newman-Kwart rearrangements at one aromatic ring were performed on little-substituted benzene rings with at least one hydrogen atom in *ortho*-position to the thiocarbamate.

Herein, we describe the synthesis of *O*-trithiocarbamate **2** starting from the triketone **1** which has been frequently used in our group for the synthesis of trinucleating ligands (Scheme 2) [26–31]. The triple Newman-Kwart rearrangement of the *O*-trithiocarbamate **2** to the *S*-trithiocarbamate **3** at a fully substituted benzene ring is unprecedented.

Experimental Section

Dimethylformamide (DMF), 1,4-diazabicyclooctane (DABCO), dimethylthiocarbamoyl chloride, chloroform, *n*-hexane, ethyl acetate, and ethanol have been received from commercial sources and were used without further purification. Triketone **1** was synthesized as described in the literature [32]. IR spectra were recorded on a Bruker Vektor 22 spectrometer, NMR spectra on a Bruker AC200 spectrometer, and MS-MALDI-ToF spectra on a Bruker Reflex 4 instrument with the use of 2,5-dihydroxybenzoic acid (DHB) as matrix. Elemental analysis were performed on an Elementar Vario EL III instrument.

*Synthesis of 2,4,6-triacetyl-1,3,5-tris(dimethylthiocarbamoyloxy)benzene (**2**)*

A suspension of triketone **1** (2.504 g, 9.93 mmol) in DMF (25 mL) was purged with argon for 30 min. DABCO (6.683 g, 59.58 mmol) was added, and the resulting yellow solution was stirred for 30 min. Dimethylthiocarbamoyl chloride (7.366 g, 59.59 mmol) was added, and the reaction mixture was heated to 80 °C for 4 h. The suspension was filtered and the filter cake washed with a small amount of DMF. The filtrate was slowly poured into 500 mL of water, and the resulting solid was collected and dried *in vacuo*. *O*-Trithiocarbamate **2** was obtained as a pale-brown solid and used without further purification. Yield: 4.415 g (8.60 mmol, 86.6 %). A small amount was purified *via* column chromatography to get satisfying analytical data (silica gel, *n*-hexane/ethyl acetate 1 : 1). – IR (KBr): ν = 2934, 1699, 1546, 1395, 1276, 1194, 1109 cm^{-1}. – ^{1}H NMR (500.05 MHz, CDCl$_3$): δ = 3.39, 3.30 (2 × s, 18H, N*Me*$_2$), 2.47 (s, 9H, CO*Me*). – ^{13}C NMR (125.75 MHz, CDCl$_3$): δ = 196.2 (*C*OMe), 184.4 (O*C*S), 148.8 (C^{ar}-O), 128.5 (C^{ar}-COMe), 43.4, 39.2 (2 × N*Me*^{2}), 31.6 (CO*Me*). – MS (MALDI, matrix: DHB): *m/z* = 514 [M+H]$^+$, 536 [M+Na]$^+$. – $C_{21}H_{29}N_3O_7S_3$ (531.68): calcd. C 47.44, H 5.50, N 7.90; found C 47.75, H 5.26, N 7.92.

*Synthesis of 2,4,6-triacetyl-1,3,5-tris(dimethylthiocarbamoylthio)benzene (**3**)*

O-Trithiocarbamate **2** (3.053 g, 5.94 mmol) was dissolved in *o*-dichlorobenzene (150 mL) and purged with argon for 30 min. The solution was heated at reflux for 8 h. The solvent was removed under reduced pressure. The raw material was dissolved in CHCl$_3$ and purified *via* column chromatography (silica gel, 1. *n*-hexane/ethyl acetate 1 : 1, 2. EtOH). The solvents were removed under reduced pressure. *S*-Trithiocarbamate **3** was obtained as a pale-yellow solid. Yield: 1.767 g (3.44 mmol, 57.9 %). – IR (KBr) ν = 2931, 1713, 1673, 1370, 1256, 1177, 1098, 903, 676 cm^{-1}. – ^{1}H NMR (200.13 MHz, CDCl$_3$): δ = 2.98 (s, 18H, N*Me*$_2$), 2.47 (s, 9H, CO*Me*). – ^{13}C NMR (50.33 MHz, CDCl$_3$): δ = 201.4 (*C*OMe), 163.2 (S*C*O), 157.1 (C^{ar}-S), 120.8 (C^{ar}-COMe), 37.2 (N*Me*$_2$), 31.5 (CO*Me*). – MS (MALDI, matrix: DHB): *m/z* = 514 [M+H]$^+$, 536 [M+Na]$^+$. – $C_{21}H_{29}N_3O_7S_3$ (531.68): calcd. C 47.44, H 5.50, N 7.90, S 18.09; found C 47.69, H 5.25, N 8.02, S 17.87.

Crystal structure determination

X-Ray crystal structure analysis of **3**: $C_{21}H_{27}N_3O_6S_3$, M_r = 513.64, colorless crystals, 0.15 × 0.15 × 0.10 mm^3, a = 17.915(1), b = 11.680(1), c = 11.717(1) Å, β = 91.76(1)°, V = 2450.6(3) Å^3, ρ_{calc} = 1.39 g cm^{-3}, μ = 3.1 mm^{-1}, empirical absorption correction ($0.651 \leq T \leq 0.745$), monoclinic, space group $P2_1/c$ (no. 14), Z = 4, λ = 1.54178 Å, T = 223(2) K; ω and φ scans, 27402 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.58 Å^{-1}, 3949 independent (R_{int} = 0.042) and 3710 observed reflections [$I \geq 2\ \sigma(I)$], 298 refined parameters, R = 0.051, $wR2$ = 0.137, max. / min. residual electron density: 0.74 / –0.36 e Å^{-3}; hydrogen atoms calculated and refined as riding atoms. The data set was collected with a Nonius KappaCCD diffractometer. Programs used: data collection COLLECT [33], data reduction DENZO-SMN [34], absorption correction DENZO [35], structure solution SHELXS-97 [36], structure refinement SHELXL-97 [37].

CCDC 745611 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

The reaction of triketone **1** with dimethylthiocarbamoyl chloride is the first step of the synthesis described in Scheme 2. The reaction using NaH as a base, which is frequently used for the synthesis of *O*-thiocarbamates [7, 8], in DMF does not provide a homogeneous sample, as evidenced by FTIR, NMR, and MS analyses. A possible explanation is a deprotonation of the acetyl group and the reaction of the resulting carbanion with dimethylthiocarbamoyl chloride, with another molecule of **1**, or even with the solvent DMF. Using the weaker base DABCO in DMF results in good yields of the triple *O*-trithiocarbamate **2**. A band at 1699 cm^{-1} in the FT-IR spectrum can be assigned to the C=O stretching mode of the acetyl function which is shifted to higher energy in comparison to the triketone **1** due to the absence of hydrogen bonding with the neighboring phenol function [38]. Another characteristic vibration at 1546 cm^{-1} may be assigned to the C=S stretching vibration [6, 8], although also other assignments have been given for this vibration [7, 17]. The ^{1}H NMR spectrum shows the methyl group of the acetyl function at δ = 2.47 ppm in comparison to 2.71 ppm in **1**. The two methyl groups of the three *O*-thiocarbamate functions give two signals at 3.39 ppm and 3.30 ppm. This behavior is due to a reduced rotation along the C–N bond by partial double-bond character [9, 14–17, 20, 21, 24, 39, 40].

The second step, the Newman-Kwart rearrangement of the *O*-trithiocarbamate **2** into the *S*-trithiocarbamate **3**, has been thought to be the problematic step. Brooker *et al.* described the attempted Newman-Kwart rearrangement of 2,6-diacetyl-4-methylphenyl-*O*-thiocarbamate. This reaction was not successful in boiling toluene even on addition of $BF_3{\cdot}Et_2O$ [24], which is surprising due to the presence of the electron-withdrawing acetyl substituents. Already the parent report of Newman and Karnes mentioned problems for the rearrangement of *O*-thiocarbamates that carry acetyl functions in *ortho* positions [7].

Table 1. Selected interatomic distances (Å) and angles (deg) in **3**.

C(1)–S(1)	1.781(3)	C(23)–N(21)	1.332(4)
C(3)–S(2)	1.780(3)	C(23)–S(2)	1.834(3)
C(5)–S(3)	1.778(3)	C(33)–O(31)	1.217(4)
C(1)–C(2)	1.390(4)	C(33)–N(31)	1.340(4)
C(1)–C(6)	1.399(4)	C(33)–S(3)	1.816(4)
C(2)–C(3)	1.396(4)		
C(2)–C(11)	1.519(4)	O(11)–C(13)–N(11)	124.8(4)
C(3)–C(4)	1.392(4)	O(11)–C(13)–S(1)	121.7(3)
C(4)–C(5)	1.399(4)	O(21)–C(23)–N(21)	125.7(3)
C(4)–C(21)	1.519(4)	O(21)–C(23)–S(2)	119.8(3)
C(5)–C(6)	1.398(4)	O(31)–C(33)–S(3)	121.3(3)
C(6)–C(31)	1.516(4)	N(31)–C(33)–S(3)	113.3(3)
C(13)–O(11)	1.210(5)	C(1)–S(1)–C(13)	101.1(2)
C(13)–N(11)	1.352(5)	C(3)–S(2)–C(23)	96.1(2)
C(13)–S(1)	1.805(4)	C(5)–S(3)–C(33)	101.2(2)
C(23)–O(21)	1.202(4)		

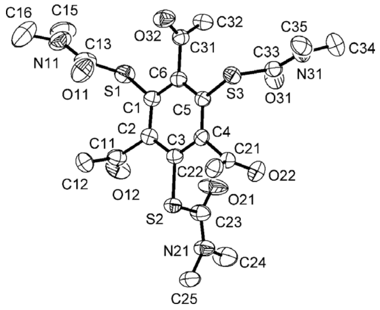


Fig. 1. Molecular structure of **3** and crystallographic labeling scheme used (displacement ellipsoids at the 50 % probability level, hydrogen atoms omitted for clarity).

Attempts to carry out the rearrangement of *O*-trithiocarbamate **2** without a solvent resulted in a mixture of products without showing spectral signatures of the expected *S*-trithiocarbamate **3**. The rearrangements at 180 °C and 250 °C resulted in a mass reduction of 9 % and 47 %, respectively.

The successful rearrangement of the *O*-trithiocarbamate **2** into the *S*-trithiocarbamate **3** has been performed in *ortho*-dichlorobenzene within 8 h at reflux. The FT-IR spectra showed two C=O double bond vibrations at 1713 cm^{-1} (acetyl) and 1673 cm^{-1} (*S*-thiocarbamate) [8, 14]. Additional evidence for the successful triple rearrangement is the appearance of two singlets in the ^{1}H NMR spectrum at 2.98 ppm (*S*-thiocarbamate) and 2.47 ppm (acetyl), with an intensity ratio of 2 : 1. While the acetyl methyl function exhibits only a minor shift, the two methyl group signals of the *O*-trithiocarbamate **2** merge to one signal in the *S*-trithiocarbamate **3**, bcause the C–N

Table 2. Structural parameters calculated for **3**. *d* (Å) is the shortest distance of the respective atom to the best plane formed by the six carbon atoms of the benzene ring. ψ (deg) is the angle between the best planes of the six carbon atoms of the benzene ring and the best plane of the atoms of the respective substituent.

	d	ψ		*d*	ψ
S1	−0.262	90.5	C11	0.241	92.8
S2	−0.049	83.7	C21	0.019	90.8
S3	0.292	95.5	C31	−0.032	87.2

bond of the *S*-thiocarbamate has less double-bond character and therefore a lower rotation barrier [9, 14–17, 20, 21, 24]. Slow evaporation of a solution of the *S*-trithiocarbamate **3** in $CHCl_3$ led to the formation of colorless crystals. Single-crystal X-ray diffraction analysis confirmed the formation of **3**. The molecular structure is shown in Fig. 1, and selected interatomic distances and angles are given in Table 1. The mean C–S distances of 1.78 Å are in the range expected for aromatic carbon-sulfur bonds [41]. All bond lengths and angles are in the typical ranges and in good agreement with related compounds reported in the literature [42].

The sterical demand of the six bulky substituents on the carbon ring results in a nearly perpendicular orientation of the planes of the substituents with respect to the central benzene ring plane (Fig. 2a and Table 2). Interestingly, the structure does not show an alternating up-and-down arrangement of the substituents with all thiocarbamates pointing to one side of the central benzene ring and the three $COCH_3$ carbonyl functions to the other side (Fig. 2b). The equivalence of the individual substituents in the NMR spectrum indicates a low barrier for the rotation along the C^{ar}–C and C^{ar}–S bonds in solution.

The cleavage of the *S*-thiocarbamate groups of **3** should result in 2,4,6-triacetyl-1,3,5 benzenetrithiol. *S*-Thiocarbamates are usually cleaved under basic conditions in protic solvents with at least two equivalents of base per thiocarbamate. Temperatures ranging from r. t. to reflux conditions and reaction times ranging from several minutes to one day have been applied [7–9, 20, 22, 23, 25].

The reaction of *S*-trithiocarbamate **3** with KOH in MeOH at reflux resulted in the quantitative isolation of the starting material. This indicates some sterical protection of the thiocarbamate so that more severe reaction conditions had to be chosen. Changing the solvent to ethanol or mixtures with chloroform and variation of the reaction times and of the metal hydroxide (LiOH, NaOH) did not lead to any measurable reactions. At even harsher reaction conditions using isopropanol, ethylene glycol, or 2-methoxyethanol reactions occured, but the expected trithiol could not be obtained. NMR spectroscopic inspection of the products showed the presence of a mixture of several as yet unidentified compounds.

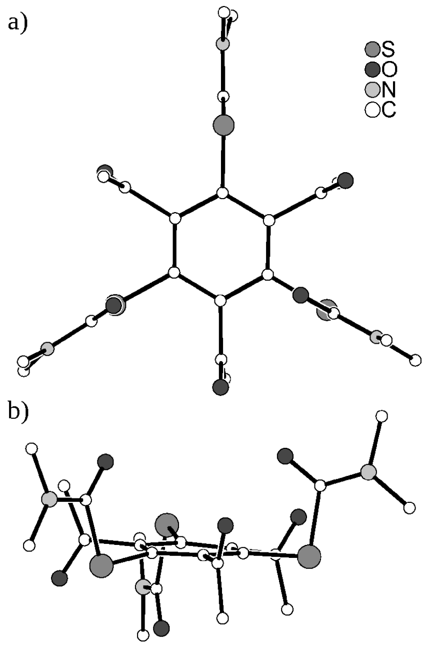


Fig. 2. Molecular structure of **3**: a) View perpendicular to the central benzene ring; b) view nearly parallel to the central benzene ring.

These results are consistent with a report by Lau *et al.* [18]. They showed that the treatment of an *ortho*-acetyl *S*-thiocarbamate unit with base under harsh conditions led to the deprotonation of the acetyl function which then attacks the neighboring *S*-thiocarbamate group, resulting in 5-membered and 6-membered heterocycles. The presence of three acetyl and three thiocarbamate functions in **3** may therefore result in a mixture of various heterocyclic compounds.

The acidic cleavage of *S*-thiocarbamates has also been reported [16], but treatment of the *S*-trithiocarbamate **3** in mixtures of concentrated HCl in methanol or isopropanol only resulted in the recovery of the starting material.

The third kind of cleavage reaction is the reductive cleavage of *S*-thiocarbamates with $LiAlH_4$ in THF at reflux [10, 15, 19, 21]. These conditions lead to the reduction of the acetyl functions, producing three stereocenters and thus to diastereomeric mixtures. Therefore, the reduction of the *S*-trithiocarbamate **3** has been performed by using only a minimum amount of $LiAlH_4$ at r. t. However, NMR spectroscopic analysis of the products showed the reduction of both the thiocarbamate and the acetyl functions. Performing the reaction at lower temperatures did not result in a kinetically controlled reduction of the thiocarbamates only, and the reduction with sodium or sodium/naphthaline did also not lead to the chemoselective reduction of the thiocarbamates.

Conclusions

The reaction of triketone **1** with dimethylthiocarbamoyl chloride in the presence of DABCO resulted in the formation of *O*-trithiocarbamate **2**. The Newman-Kwart rearrangement of **2** in boiling *ortho*-dichlorbenzene afforded the *S*-trithiocarbamate **3**. The latter reaction performed smoothly contrary to reports that Newman-Kwart rearrangements with acetyl functions in *ortho* position cause severe problems [7, 24]. The molecular structure of **3** obtained by single-crystal X-ray diffraction shows the bulkiness of the six substituents on the central benzene ring resulting in an almost perpendicular orientation of the planes of the six substituents relative to the central benzene plane. The basic cleavage of *S*-trithiocarbamate **3** provides complex mixtures of heterocyclic rings initiated by the deprotonation of the acetyl function. Attempts of acidic cleavage of *S*-trithiocarbamate **3** were unsuccessful. The reductive cleavage of **3** leads also to the reduction of the acetyl functions and therefore to diastereomeric mixtures.

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