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Supporting Information Placeholder

- ✓ Room temperature
- ✓ Ambient atmosphere
- ✓ Inexpensive Ce(IV) catalyst
- ✓ Electron donating groups
- ✓ Up to 99% yield
- ✓ 15 examples
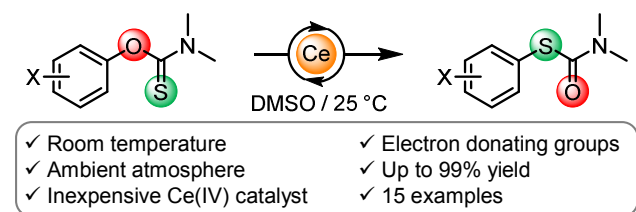
ABSTRACT: *Yes we CAN!* The discovery that the Newman-Kwart rearrangement can be performed at room temperature by action of a simple and readily available oxidant, cerium ammonium nitrate (CAN) is described. The conditions give clean conversion when using electron rich aromatic substrates and the reactions are often quantitative. Computational studies support a reaction mechanism where the *O*-thiocarbamate is first oxidized to the radical cation, followed by nucleophilic attack by the *ipso* carbon of the aromatic system.

Introduction

The Newman-Kwart rearrangement (NKR) is the thermal $O_{Ar} \rightarrow S_{Ar}$ rearrangement of aromatic thiocarbamates (Figure 1) and remains one of the most reliable ways of preparing thiophenols from the corresponding phenol (3 steps).[1-2] It has found use across such diverse fields as molecular electronics,[3] ligand synthesis,[4] medicinal chemistry,[5] dynamic combinatorial chemistry,[6-7] along with the chemical industry.[8-9] The generally accepted mechanism for the NKR involves nucleophilic attack of the sulfur atom of the thiocarbamate functionality to the *ipso*-position of the aromatic ring, which gives a cyclic four-membered ring transition state (Figure 1**A**).[10-11] The rearrangement proceeds relatively smoothly, but at very high temperatures (usually > 200 °C), making it unpractical for substrates with thermally sensitive functional groups. Also electron rich substrates, where even higher temperatures are often needed, often prove unsuccessful due to significant decomposition of the substrate.

Lately a series of developments have attracted renewed attention to the NKR.[12-14] A Pd catalyzed NKR was described where the rearrangement proceeds at 100 °C using catalytic Pd(*t*-Bu₃P)₂ (Figure 1**B**).[15] Here, substrates with electron withdrawing groups react faster than substrates with electron donating groups, nonetheless high yields were obtained for both classes. Recently Nicewicz and co-workers showed that the NKR can proceed at room temperature using a photo-redox catalyst (2,4,6-tri(*p*-tolyl)pyrylium tetrafluoroborate) combined with irradiation by blue light (Figure 1**C**).[16] The concept of using transient generated radical cations to mediate the NKR had previously been suggested by Lloyd-Jones *et. al.*[17]

Interestingly, a qualitative reversal of reactivity trend was observed: electron rich aromatic substrates readily underwent NKR while electron deficient substrates were unreactive. This is an important addition to the NKR.
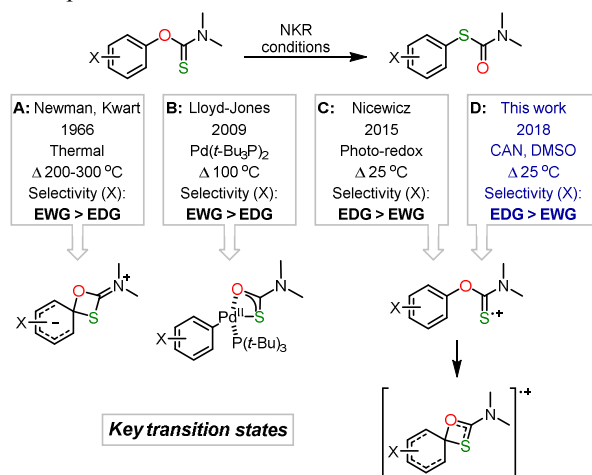
Figure 1. Highlights in the development of new conditions for the Newman-Kwart rearrangement (NKR) and structures of the corresponding transition states.

Photo-redox catalysis has gained increased popularity in the last years,[18-19] but it does come with certain drawbacks, i.e. photolabile substrates are not compatible. Also, the exclusion of oxygen is occasionally needed to avoid unwanted side reactions, associated with the photocatalyst generating reactive oxygen species.[20] Finally, specialized equipment is needed for the scale up of the reaction.

Results and discussion

We were intrigued by the observations described by Nicewicz and co-workers and wondered if it would be possible to choose a more commonplace chemical oxidant of sufficient potency to match the oxidation strength of the photo-redox catalyst, and thereby mediate the rearrangement. This would potentially give a convenient and simple protocol for the NKR without the use of a photo-redox catalyst or light (Figure 1**D**).

Initially a range of single electron transfer (SET) oxidants and their applicability in mediating the NKR of *p*-methoxy-*O*-aryl thiocarbamate **1** at room temperature were tested. No formation of the corresponding *S*-aryl thiocarbamate **2** was observed when treating **1** with readily available SET oxidants such as 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), (diacetoxyiodo)benzene (PIDA), and [bis(trifluoroacetoxy)iodo]benzene (PIFA) in acetonitrile (Table 1, entry 1-3). Instead formation of the oxygenated product, carbamate **3**, was solely observed. Interestingly, with cerium ammonium nitrate (CAN) in acetonitrile, full conversion of **1** to a mixture of products was observed. Thorough investigation of the ^{1}H-NMR spectrum of the reaction mixture revealed trace formation of the rearranged product **2** (Table 1, entry 4). Motivated by this observation, CAN was investigated in a series of alternate polar solvents. Using DMF, as the solvent, 17% conversion to the rearranged product **2** was observed with no formation of **3** or any other byproducts (Table 1, entry 5). Satisfactorily, using DMSO as the solvent led to quantitative formation of **2** (Table 1, entry 6). Having established DMSO as an ideal solvent for the rearrangement DDQ, PIDA and PIFA where reinvestigated. Nonetheless, no formation of **2** was observed (Table 1, entry 7-9).

Table 1. Optimization of the single electron transfer (SET) oxidant and solvent for the oxidative NKR.[a]
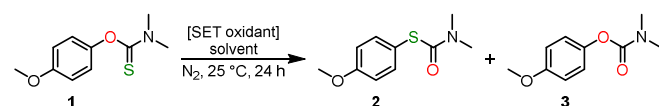
| Entry	Solvent	[SET oxidant]	Conversion to 2[b]	Conversion to 3[b]
1	MeCN	DDQ	0	52
2	MeCN	PIDA	0	84
3	MeCN	PIFA	0	84
4	MeCN	CAN	Trace	0
5	DMF	CAN	17	0
6	DMSO	CAN	>99 (97)	0
7	DMSO	DDQ	0	0
8	DMSO	PIDA	0	22
9	DMSO	PIFA	0	27

[a]All reactions were conducted on a 0.1 mmol scale with 0.05 M substrate concentration and 1.0 equiv. of oxidant. [b]Determined by ^{1}H-NMR analysis of the reaction mixture. Yield of isolated product given within parentheses.

The rearrangement was found to be sensitive to substrate concentration. At high concentrations (< 0.5 M) no conversion was observed while more diluted conditions (> 0.05 M) gave quantitative conversion (Supporting Information). These dependencies are consistent with the results by Nicewizc and co-workers.[16] It has previously been discussed whether the reaction kinetics of the thermal NKR changes from first to second order upon increasing concentration of substrate, but it has been proven that the mechanism of the thermal reaction is indeed intramolecular.[10, 21] We observe no conversion at the higher concentrations, even with excess of the oxidant added, and even when conducting the reaction under an atmosphere of O_2. We do not have experimental evidence explaining this phenomenon, but aggregation of the thiocarbamate-based reactants could contribute to the explanation, either as a neutral specie or as a mixed-valence aggregate.

With the optimal reaction conditions in hand the scope of the CAN mediated NKR was established (Figure 2). As already stated, the *p*-methoxy-*S*-aryl thiocarbamate **2** was obtained quantitative under the given conditions. Using the corresponding ethyl analogue **4** also gave full conversion. Moving to the more labile benzyl ether substituted **5** and allyl ether **6**, clean conversions were observed for both substrates. The allyl ether **6** serves as an excellent example of the applicability of the presented methodology, as this compound would be prone to Claisen rearrangement if subjected to the thermal NKR conditions. Investigations of more electron deficient systems, through addition of electron withdrawing groups in the *ortho*-position, as for nitro substituted **7** or formyl substituted **8**, showed that these substrates also successfully underwent rearrangement. Interestingly, the methylester substituted substrate **13** lead to only 52% conversion. Changing the methoxy group from the *para*- to the *ortho*-position high yield was retained affording **9** while the *meta*-position (**16**) hampered the rearrangement. Moving onto amino analogues, we found that with a BOC protecting group as substituent (**10**), which is thermally labile, high yield was obtained.[22] With the *N*-acetyl group as substituent (**11**) full conversion to product was also observed. Finally, we found that *S*-(naphthalene-1-yl) dimethylcarbamothioate (**12**) could be obtained in high yields while the 2-napthalene derivative **17** was not prone to the rearrangement. The difference between the two naphthol substrates is attributed to the increased electron density on the 1 position compared to the 2 position, allowing for only **12** to rearrange under the presented conditions.[23]
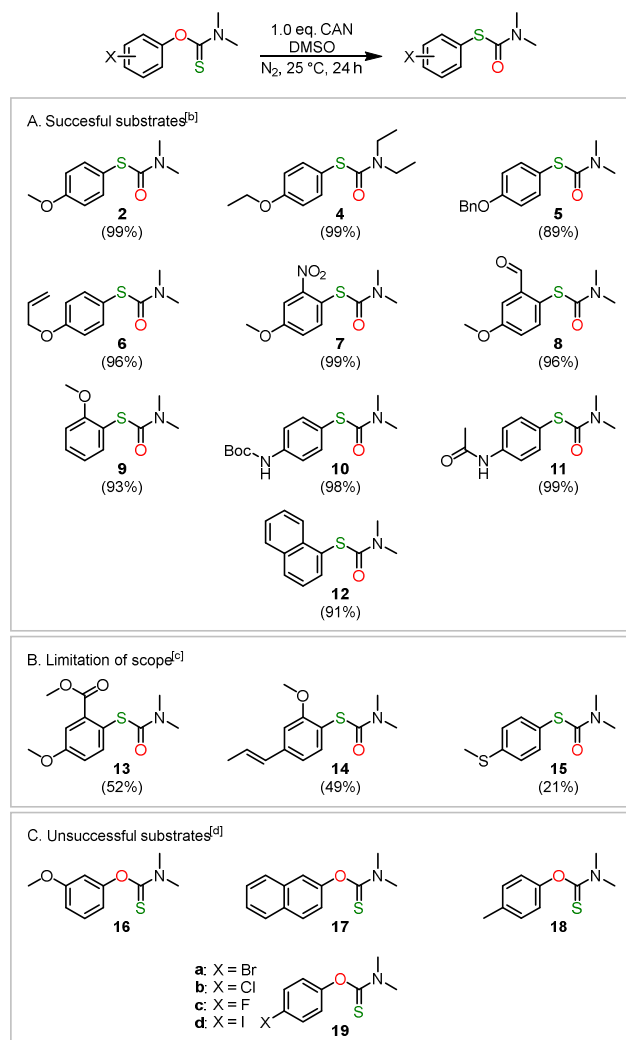
Figure 2. Substrate scope of the oxidative NKR.[a]

[a]All reactions were done on a 0.25 mmol scale with 0.05 M substrate concentration. [b]Yield of isolated product. [c]Conversion is determined by ^{1}H-NMR analysis of the reaction mixture. [d]No product is detectable by ^{1}H-NMR analysis.

The natural product derivative, *O*-aryl thiocarbamate of isoeugenol, undergoes oxidative NKR in a decent 49% conversion to yield substrate **14**. Replacing the *p*-methoxy substituent with a thioether functionality was also feasible and *p*-methylthio-*S*-aryl thiocarbamate (**15**) could be obtained, albeit only in a 21% yield. Having an inductively electron donating group in the *para*-position, as in the *p*-methyl derivative **18**, no conversion was observed. This substrate rearranged successfully by Nicewicz and co-workers method, thus highlighting a case where that protocol is advisable to use.[16] For the *para*-substituted arylhalides (**19**) neither our nor the photoredox catalyzed protocol provided the rearranged product. Doing the reaction at elevated temperature, none of the arylhalides showed formation of the target NKR product. This indicates the essentiality that the substrate should feature a resonance electron donating substituent, either in the *ortho*- or *para* position increasing the nucleophilicity of the *ipso* carbon on the aromatic ring.

The rearrangement also proved successful at a larger scale. For example, 5 grams of *p*-methoxy-*O*-aryl thiocarbamate **1** gave analytically pure **2** in 95 % isolated yield.

Previous reports show that single electron oxidations, mediated by CAN, can be catalytic if done in the presence of molecular oxygen, which oxidizes cerium(III) back to the active cerium(IV).[24-25] As a proof of principle we tested these conditions on the NKR of **1**, using 50 mol% CAN under an atmosphere of oxygen, and it was indeed found that the reaction went to completion (Table 2, entry 1). The equivalents of CAN could be lowered to 5 mol%, while still maintaining full conversion (Table 2, entry 2-4). It was even found that the rearrangement proceeded smoothly when simply run in an open reaction flask showing how atmospheric oxygen is sufficient to reform the active cerium(IV) species (Table 2, entry 5). The reaction was also tested under a pure nitrogen atmosphere with 10 mol% of CAN (Table 2, entry 6). Only 14% conversion to product was observed. This rules out the terminal reductant of the oxidative NKR is Ce(IV) being reduced to the active Ce(III) species. The fact that the conversion is higher than the expected 10 % is attributed to leakage of oxygen in to the system, either during the reaction or in the work up.

**Table 2.** Screening of catalytic conditions for the oxidative NKR.[a]

Entry	Atmosphere	Amount CAN [mol%]	Conversion[b]
1	O$_2$	50	>99
2	O$_2$	10	>99 (99)
3	O$_2$	5	98
4	O$_2$	2	22
5	ambient	10	>99
6	N$_2$[c]	10	14

[a]All reactions were done on a 0.1 mmol scale with 0.05 M substrate concentration. [b]Determined by ^{1}H-NMR analysis of the reaction mixture. [c] Additionally the solvent was sparged with N$_2$. Yield of isolated product given within parentheses.

To gain further insight to the mechanism, some mechanistic studies were performed. A kinetic study of the rearrangement of *p*-methoxy-*O*-aryl thiocarbamate (**1**) showed how the oxidative NKR proceeds with first order kinetics, as the thermal NKR,[21] with a reaction rate constant, k_{obs}, of $2.9 \cdot 10^{-4}$ s^{-1} (25 °C, DMSO; Supporting Information). This is slightly faster than the thermal NKR of *p*-nitro-*O*-arylthiocarbamate (k_{obs} = $2.1 \cdot 10^{-4}$ s^{-1}, 160 °C, DMA).[10]

A cross-over experiment between *p*-methoxy-*O*-aryl thiocarbamate (**1**) and its ethyl analogue **20** was conducted to investigate whether the rearrangement is inter- or intramolecular. The two non-crossover rearranged products **2** and **4** formed with comparable rates and in addition, to our satisfaction, we found that none of the crossover products were observed (Figure 3, Supporting Information). Thus, under the presented conditions, the rearrangement can be considered as being solely intramolecular.
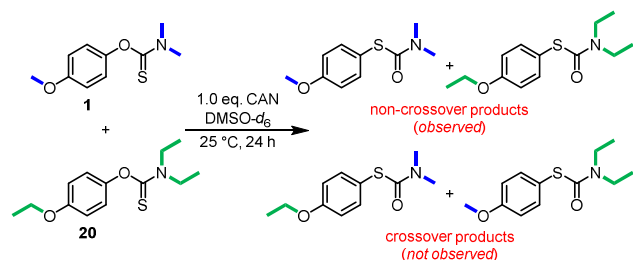
Figure 3. Cross-over experiment between **1** and **20** indicating the oxidative NKR is intramolecular.

To further understand the underlying cause of reactivity observed we turned to computational chemistry. The study was performed on five *O*-aryl thiocarbamates (**2**, **16**, **19b**, **21**, and **22**) and the results show a cyclic four-membered ring transition state in both the oxidative and thermal NKR (Figure 4). A charge analysis shows that the electron is removed from the (non-bonding) sulfur lone pair upon oxidation and the ionization potential values are similar for all substrates (Supporting Information). This is supported experimentally by Nicewicz and co-workers,[16] thus indicating that the oxidation indeed takes place on sulfur.
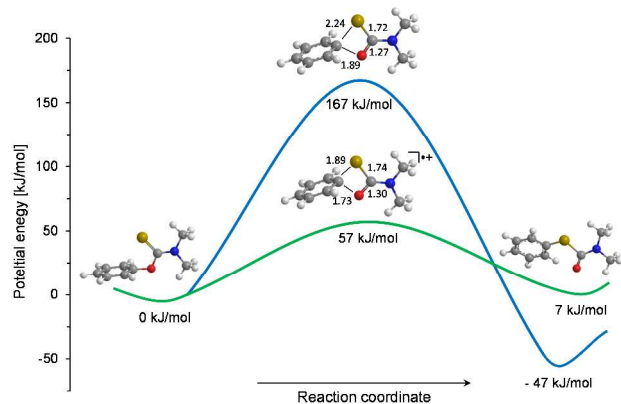
Figure 4. Schematic potential energy profile comparing the G4MP2 calculated reaction coordinates for the thermal NKR (blue) and the oxidative NKR (green). The reactant is set at 0 kJ/mol for each reaction, the energetic separation between the two should in reality be the ionization energy of ~ 750 kJ/mol.

The reaction barrier is significantly reduced when comparing the thermal and oxidative NKR (Table 3, Supporting Information). The lower reaction barrier is a result of the fact that sulfur is more easily accommodated by the aromatic ring when the sulfur lone pair is ionized, *i.e.* a reversal takes place compared to the neutral system where sulfur is more likely to act as the nucleophile. These considerations are in agreement with the experimental observations that the thermal NKR is facilitated by electron withdrawing substituents, making the ring more electrophilic whereas the oxidative NKR only proceeds when electron donating substituents are present to stabilize the positive charge that is introduced on the ring when the ionized sulfur lone pair attacks. The thermochemical data in Table 3 corroborates that the thermal rearrangement is facilitated by electron withdrawing groups. This is shown using the 4-nitro substrate **22** as an example.

For the oxidative NKR the lowest barrier is obtained when an oxygen atom is present in the *para*-position (**2**). Moreover, the substituent has to be in direct electronic contact with the *ipso* position, i.e. the *meta*-substituted **16** does not decrease

the reaction barrier. The high electronegativity of chlorine in **19b** counterbalances the electron releasing effect of the chlorine lone pairs and thus the barrier is found to be too high to make the oxidative NKR feasible, this being in agreement with the experimental results.

Table 3. Comparison of G4MP2 calculated values of the reaction barriers ($\Delta E^{\ddagger}$) and energies ($\Delta_r E$) for selected substrates undergoing either the thermal or the oxidative NKR.[a]

		Thermal NKR		Oxidative NKR	
		$\Delta E^{\ddagger}$	$\Delta_r E$	$\Delta E^{\ddagger}$	$\Delta_r E$
Entry	Substrate	[kJ/mol]	[kJ/mol]	[kJ/mol]	[kJ/mol]
1	**2**	176.3	-52.1	37.0	-60.3
2	**16**	168.4	-46.1	51.3	-24.8
3	**19b**	162.4	-50.9	53.4	-17.3
4	**21**	166.8	-46.5	56.5	6.6
5	**22**	149.6	-48.0	63.0	2.5

[a]For further information, see Supporting Information.

To conclude, we have developed a room temperature NKR for electron rich substrates. The use of CAN as the oxidant and DMSO as the solvent provides a simple and convenient approach that proved scalable and simple to reproduce using standard equipment and chemicals. The mechanism is an intramolecular rearrangement of a radical cation species, which initially forms on the sulfur atom of the thiocarbamate. As the thermal NKR can be understood as an intramolecular nucleophilic aromatic substitution, the oxidative NKR is more similar to that of an electrophilic aromatic substitution. This satisfactorily explains the trend that thermal NKR proceeds smoothly for electron-poor aromatic systems, and why an inversion of reactivity is observed for the oxidative NKR.

Current studies are ongoing to expand on the catalytic conditions as they would be an appealing alternative to the conditions that have been reported for the NKR thus far in the literature.

Experimental Section

Computational methods

The calculations were carried out with a fourth generation composite method referred to as G4MP2 with the GAUSSIAN09 suite of programs.[26-27] G4MP2 theory is approximating a large basis set CCSD(T) single point calculation on a B3LYP/6-31G(2df,p) geometry and is incorporating a so-called higher level correction that is derived by a fit to the experimental values in the G3/05 test set with 454 experimental values.[28] The average absolute derivation from the

experimental test set values is 1.04 kcal mol^{-1}, which places the G4MP2 results well within chemical accuracy of 10 kJ mol^{-1}. The transition structures for the reactions reported in this work have been confirmed in each case by the calculation of vibrational frequencies (one imaginary frequency) and an intrinsic reaction coordinate analysis. Relative free energies stated within the text correspond to G4MP2 values at 298.15 K.[27]

General methods

All chemicals, unless otherwise stated, were purchased from commercial suppliers and used as received. All solvents were high-performance liquid chromatography (HPLC) grade, except solvents used for dry column vacuum chromatography, which were technical grade. Solvents were degassed by bubbling N$_2$ through the solvent, while ultrasonicated for 20 minutes. All reactions were carried out under an anhydrous nitrogen atmosphere unless otherwise stated.

Analytical thin layer chromatography (TLC) was performed on SiO$_2$ 60 F$_{254}$ 0.2 mm thick precoated TLC plates. Dry column vacuum chromatography was performed using SiO$_2$ (SI 1722, 60 Å, 15–40 μm respectively). Melting points (m.p.) are uncorrected.

^{1}H NMR and ^{13}C NMR spectra were recorded at 500 MHz and 125 MHz, respectively, using residual non-deuterated solvent as the internal standard. All chemical shifts (δ) are quoted in ppm and all coupling constants (J) are expressed in Hertz (Hz). The following abbreviations are used for convenience in reporting the multiplicity for NMR resonances: s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Samples were prepared using CDCl$_3$ or DMSO-d_6. Assignment of all ^{1}H and ^{13}C resonances was achieved using standard 2D NMR techniques as ^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC, and ^{1}H-^{13}C HMBC.

HPLC analysis was performed on a UHPLC system coupled to an diode array UV/Vis detector. Separations were achieved using a C18 2.2 μm 120 Å 2.1 × 100 mm column maintained at 20 °C. The mobile phase solutions prepared with 0.1 % HCOOH in the solvents. The water used as eluent was purified by a Millipore system. LC/MS was carried out on a MicrO-TOF-QII-system with ESI-source with nebulizer 1.2 bar, dry gas 8.0 L min^{-1}, dry temperature 200 °C, capillary −4500 V, end plate offset −500 V, funnel 1 RF 200.0 Vpp, ISCID energy 0.0 eV, funnel 2 RF 200.0 Vpp, hexapole RF 100.0 Vpp, quadrupole ion energy 5.0 eV, low mass 100.00 m/z, collision energy 8.0 eV, collision RF 100.0 Vpp, transfer time 80.0 μs, and pre puls storage 1.0 μs. LC/HRMS samples were calibrated by an automated pre-run internal mass scale calibration of the individual samples by injecting a sodium formate solution, consisting of 10 mM NaOH$_{(aq)}$ in i-PrOH:H$_2$O 1:1 v/v (+ 1 % HCOOH).

Experimental procedures for the *O*-aryl thiocarbamates

Compounds **1**, **9-sm**, **16-sm**, **17-sm**, **18-sm**, **19a-sm**, **19b-sm** and **19c-sm** were synthesised according to the procedure published by Moseley *et al.*,[12] while the compounds **5-sm**, **8-sm**, **10-sm**, **11-sm**, **12-sm**, and **14-sm**, were synthesised following the protocol described by Perkowski *et al.*[16] Similarly, **7-sm**,[29] **13-sm**,[30] **15-sm**,[31] and **19d-sm**[32] were synthesised following previously reported literature procedures.

O-(4-ethoxyphenyl) *N,N*-diethylthiocarbamate (20)

4-Ethoxyphenol (1.75 g, 11.5 mmol) and DABCO (1.53 g, 13.6 mmol) were suspended in NMP (10 mL) and heated to 50 °C. To this clear reaction mixture *N,N*-ethylthiocarbamoyl chloride (1.45 g, 10.5 mmol), dissolved in NMP (5 mL), was added dropwise and the reaction mixture became turbid. The reaction mixture was hereafter left standing at 50 °C for 5 hours before it was cooled down to 25 °C. After this, H$_2$O (50 mL) and CH$_2$Cl$_2$ (50 mL) were added to the mixture and the phases were separated. The organic phase was washed with 2 M NaOH (50 mL), H$_2$O (2 × 50 mL), dried (Na$_2$SO$_4$) and concentrated *in vacuo* to yield **20** as a white solid (1.63 g, 6.45 mmol, 61 %), mp. 67 - 68 °C. ^{1}H NMR (500 MHz, CDCl$_3$, 298 K): δ = 6.96 (d, J = 9.1 Hz, 2H), 6.88 (d, J = 9.1 Hz, 2H), 4.02 (q, J = 7.0 Hz, 2H), 3.90 (q, J = 7.1 Hz, 2H), 3.68 (q, J = 7.1 Hz, 2H), 1.41 (t, J = 7.0 Hz, 3H), 1.33-1.31 (m, 6H). ^{13}C NMR (125 MHz, CDCl$_3$, 298 K): δ = 187.6, 156.8, 147.6, 123.6, 114.8, 63.9, 48.6, 44.3, 15.0, 13.7, 12.0. LC/HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd. for C13H20NO2S 254.1209; Found 254.1219.

O-(4-(Allyloxy)phenyl) *N,N*-dimethylthiocarbamate (6-sm)

4-(Allyloxy)phenol (1.00 g, 6.66 mmol) and DABCO (0.94 g, 8.38 mmol) were suspended in NMP (5 mL) and heated to 50 °C. To this clear reaction mixture *N,N*-dimethylthiocarbamoyl chloride (0.91 g, 7.32 mmol), dissolved in NMP (1 mL), was added dropwise and the reaction mixture became turbid. The reaction mixture was hereafter left standing at 50 °C for 3 hours before it was cooled down to 25 °C. After this, H$_2$O (15 mL) was added and the mixture was extracted with CH$_2$Cl$_2$ (3 × 15 mL), dried (MgSO$_4$) and concentrated *in vacuo*. The crude product was purified by dry column vacuum chromatography using a gradient of CH$_2$Cl$_2$ in heptane to yield **6-sm** as a pale yellow oil (63.2 mg, 2.66 mmol, 40 %). ^{1}H NMR (500 MHz, CDCl$_3$, 298 K): δ = 6.97 (d, J = 9.1 Hz, 2H), 6.91 (d, J = 9.1 Hz, 2H), 6.06 (ddt, J = 17.3, 10.6, 5.3 Hz, 1H), 5.42 (dd, J = 17.3, 1.5 Hz, 1H), 5.29 (dd, J = 10.6, 1.5 Hz, 1H), 4.53 (dt, J = 5.3, 1.5 Hz, 2H), 3.45 (s, 3H), 3.33 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$, 298 K): δ = 188.3, 156.4, 147.7, 133.2, 123.5, 117.7, 115.0, 69.2, 43.3, 38.7. LC/HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd. for C12H16NO2S 238.0896; Found 238.0903.

Experimental procedures for the *S*-aryl thiocarbamates

Standard conditions for oxidative Newman-Kwart Rearrangement

Conditions A (CAN stoichiometric, N$_2$ atmosphere)
The *O*-aryl *N,N*-dimethylthiocarbamate (1.0 equiv., 0.25 mmol) and CAN (1.0 equiv., 0.25 mmol) were dissolved in DMSO (5.0 mL) and stirred at room temperature for 24 hours under a nitrogen atmosphere. To the completed reaction mixture was added H$_2$O (40 mL) and the solution was extracted with Et$_2$O (4 × 40 mL). The combined organic phase was washed with H$_2$O (40 mL), dried (MgSO$_4$) and concentrated *in vacuo* to give the rearranged product.

Conditions B (CAN catalytic, O$_2$ atmosphere)
Identical to *Conditions A*, with the only alteration being the amount of CAN is reduced to the desired equivalents (0.5 or 0.1 equiv.), and the reaction is performed under an oxygen atmosphere.

Conditions C (CAN catalytic, ambient atmosphere)
Identical to *Conditions A*, with the only alteration being the amount of CAN is reduced to 0.1 equivalents, and the reaction

is performed under ambient atmosphere, i.e. the reaction mixture is simply stirred in an open reaction flask.

S-(4-Methoxyphenyl) *N,N*-dimethylcarbamothioate (2)

Yield: 0.052 g, 0.248 mmol, 99 % (*Conditions A*), 0.052 g, 0.248 mmol, 99 % (*Conditions B*), 0.052 g, 0.248 mmol, 99 % (*Conditions C*). ^{1}H NMR (500 MHz, CDCl$_3$, 298 K): δ = 7.40 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 3.82 (s, 3H), 3.07 (bs, 3H), 3.02 (bs, 3H).
The analytic data is in accordance with the literature.[12]

S-(4-Ethoxyphenyl) *N,N*-diethylcarbamothioate (4)

After the general work up described under *Conditions A*, the title compound is obtained as a yellow oil. Yield: 0.063 g, 0.248 mmol. 99 % (*Conditions A*), 0.063 g, 0.248 mmol, 99 % (*Conditions C*). ^{1}H NMR (500 MHz, CDCl$_3$, 298 K): δ = 7.39 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 4.03 (q, *J* = 7.0 Hz, 2H), 3.42 (q, *J* = 7.1 Hz, 4H), 1.41 (t, *J* = 7.0 Hz, 3H), 1.28 (bs, 3H), 1.16 (bs, 3H). ^{13}C NMR (125 MHz, CDCl$_3$, 298 K): δ = 166.5, 159.9, 137.4, 119.3, 115.1, 63.6, 42.3 (2×C), 14.8, 13.9, 13.3. LC/HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd. for C13H20NO2S254.1209; Found 254.1216.

S-(4-(Benzyloxy)phenyl) *N,N*-dimethylcarbamothioate (5)

Yield: 0.050 g, 0.223 mmol, 89 % (*Conditions A*). ^{1}H NMR (500 MHz, CDCl$_3$, 298 K): δ = 7.46 – 7.35 (m, 6H), 7.33 (t, *J* = 7.0 Hz, 1H), 6.98 (d, *J* = 8.7 Hz, 2H), 5.07 (s, 2H), 3.07 (bs, 3H), 3.03 (bs, 3H).

The analytic data is in accordance with the literature.[16]

S-(4-(allyloxy)phenyl) *N,N*-dimethylcarbamothioate (6)

After the general work up, the title compound is obtained as a pale yellow oil. Yield: 0.057 g, 0.240 mmol, 96 % (*Conditions A*), 0.054 g, 0.228 mmol, 91 % (*Conditions C*). ^{1}H NMR (500 MHz, CDCl$_3$, 298 K): δ = 7.42 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 6.07 (ddt, *J* = 17.3, 10.5, 5.3 Hz, 1H), 5.44 (dd, *J* = 17.3, 1.5 Hz, 1H), 5.32 (dd, *J* = 10.5, 1.5 Hz, 1H), 4.57 (dt, *J* = 5.3, 1.5 Hz, 2H), 3.08 (bs, 3H), 3.04 (bs, 3H). ^{13}C NMR (125 MHz, CDCl$_3$, 298 K): δ = 167.8, 159.7, 137.4, 133.1, 119.7, 118.0, 115.5, 69.0, 37.0 (2×C). LC/HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd. for C12H16NO2S 238.0896; Found 238.0898.

S-(4-Methoxy-2-nitrophenyl) *N,N*-dimethylcarbamothioate (7)

Yield: 0.063g, 0.248 mmol, 99 % (*Conditions A*). ^{1}H NMR (500 MHz, CDCl$_3$, 298 K): δ = 7.56 (d, *J* = 8.7 Hz, 1H), 7.44 (d, *J* = 2.8 Hz, 1H), 7.11 (dd, *J* = 8.7, 2.8 Hz, 1H), 3.88 (s, 3H), 3.10 (bs, 3H), 3.01 (bs, 3H).
The analytic data is in accordance with the literature.[29]

S-(2-Formyl-4-methoxyphenyl) *N,N*-dimethylcarbamothioate (8)

Yield: 0.057 g, 0.240 mmol, 96 % (*Conditions A*). ^{1}H NMR (500 MHz, CDCl$_3$, 298 K): δ = 10.33 (s, 1H), 7.54 (d, *J* = 3.1 Hz, 1H), 7.46 (d, *J* = 8.5 Hz, 1H), 7.13 (dd, *J* = 8.5, 3.1 Hz, 1H), 3.88 (s, 3H), 3.16 (bs, 3H), 3.02 (bs, 3H).
The analytic data is in accordance with the literature.[16]

S-(2-Methoxyphenyl) *N,N*-dimethylcarbamothioate (9)

Yield: 0.049 g, 0.233 mmol, 93 % (*Conditions A*), 0.050 g, 0.238 mmol, 95 % (*Conditions C*). ^{1}H NMR (500 MHz, CDCl$_3$, 298 K): δ = 7.46 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.40 (ddd, *J* = 8.2, 7.5, 1.8 Hz, 1H), 7.00 – 6.94 (m, 2H), 3.87 (s, 3H), 3.13 (bs, 3H), 3.01 (bs, 3H).
The analytic data is in accordance with the literature.[12]

***tert*-Butyl (4-((*N,N*-dimethylcarbamoyl)thio)phenyl)carbamate (10)**

Yield: 0.073 g, 0.245 mmol, 98 % (*Conditions A*). ^{1}H NMR (500 MHz, CDCl$_3$, 298 K): δ = 7.39 (bs, 4H), 6.53 (bs, 1H), 3.05 (bs, 6H), 1.52 (s, 9H).
The analytic data is in accordance with the literature.[16]

S-(4-Acetamidophenyl) *N,N*-dimethylcarbamothioate (11)

Yield: 0.059 g, 0.248 mmol, 99 % (*Conditions A*). ^{1}H NMR (500 MHz, CDCl$_3$, 298 K): δ = 7.49 (d, *J* = 8.2 Hz, 2H), 7.41 – 7.39 (m, 3H), 3.09 (bs, 3H), 3.03 (bs, 3H), 2.15 (s, 3H).
The analytic data is in accordance with the literature.[16]

S-(Naphthalen-1-yl) *N,N*-dimethylcarbamothioate (12)

Yield: 0.053 g, 0.228 mmol, 91 % (*Conditions A*). ^{1}H NMR (500 MHz, CDCl$_3$, 298 K): δ = 8.32 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 7.1 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.52 – 7.47 (m, 2H), 3.24 (bs, 3H), 3.02 (bs, 3H).

The analytic data is in accordance with the literature.[16]

Methyl 2-((*N,N*-dimethylcarbamoyl)thio)-5-methoxybenzoate (13)

Conversion: 52 % (*Conditions A*).

The product is isolated as a mixture of starting material and product.

The analytic data is in accordance with the literature.[30]

(*E*)-S-(2-Methoxy-4-(prop-1-en-1-yl)phenyl) *N,N*-dimethylcarbamothioate (14)

Conversion: 49 % (*Conditions A*).

The product is isolated as a mixture of starting material and product.

The analytic data is in accordance with the literature.[16]

S-(4-(methylthio)phenyl) *N,N*-dimethylcarbamothioate (15)

Conversion: 21 % (*Conditions A*).

The product is isolated as a mixture of starting material and product.

The analytic data is in accordance with the literature.[31]

Analytical data for the rearrangement of **16**, **17**, **18**, **19a**, **19b**, **19c**, and **19d** were compared with the literature and it was concluded that no conversion had occurred.[12, 32]

ASSOCIATED CONTENT

Supporting Information

Spectral characterisation data, determination of the rate constant and crossover studies, as well as a description of the theoretical calculations. The Supporting Information is available free of charge on the ACS Publications website.

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