Palladium-Catalyzed Hetero-Cope Rearrangement of Alkyl Allyl *N*-Aryldithiocarbonimidates

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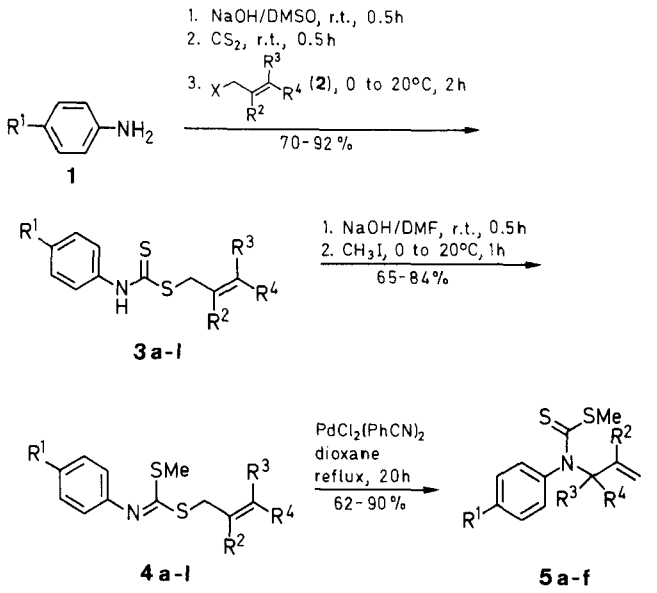
Palladium-catalyzed [3,3] sigmatropic rearrangement of allyl methyl *N*-aryldithiocarbonimidates affords methyl *N*-allyl-*N*-aryldithiocarbamates. Very high yields of rearranged products can be obtained depending on the substitution pattern of the allyl group.

[3,3] Sigmatropic rearrangements are very versatile reactions for the formation of either C–C or C-heteroatom bonds. Thus, the classical thermal Cope and Claisen rearrangements show a high degree of regio- and stereochemical control and have been widely used in organic synthesis.[1,2] Both, the introduction of heteroatoms in the 1,5-diene system and the development of catalytic methods have greatly increased the synthetic applications of these reactions, since a very large number of structures can, in theory, undergo the rearrangement and, moreover, under mild conditions.[3–5]

Due to our experience in the field of dithiocarbamic and dithiocarbonimidic acid derivatives,[6] we thought that certain allylic esters could be easily prepared and used to determine whether they undergo hetero-Cope rearrangement which, to the best of our knowledge, is still unknown in the series of *S*-allyl dithiocarbonimidates, though related reactions have been described with *S*-allyl thioimidates,[7] *O*-alkyl-*S*-allyl iminothiocarbonates[5] and allyl thiocarbamates.[8]

This is in fact the case and in this paper we report that allyl methyl *N*-aryldithiocarbonimidates **4** smoothly rearrange to methyl *N*-allyl-*N*-aryldithiocarbamates **5** in the presence of dichlorobis(benzonitrile)palladium(II) (Scheme).



3–5	R^1	R^2	R^3	R^4	3–5	R^1	R^2	R^3	R^4
a	H	H	H	H	**g**	H	Me	H	H
b	Cl	H	H	H	**h**	Cl	Me	H	H
c	MeO	H	H	H	**i**	MeO	Me	H	H
d	H	H	H	Me	**j**	H	H	Me	Me
e	Cl	H	H	Me	**k**	Cl	H	Me	Me
f	MeO	H	H	Me	**l**	MeO	H	Me	Me

Scheme

The preparation of starting materials **4** involves a two-step procedure: (a) synthesis of the corresponding allyl *N*-aryldithiocarbamates **3** (Table 1) using the method previously reported by us,[9] with minor modifications, and (b) alkylation of **3**, in a separate step, with methyl iodide. Some properties of compounds **4** are summarized in Table 2. This method proved to be more convenient than the alternative (introduction of the allyl group on methyl *N*-aryldithiocarbamates) due to purification drawbacks.

Uncatalyzed and catalyzed versions of the [3,3] sigmatropic rearrangement of products **4** were attempted. When no catalyst was used, prolonged heating in solvents such as toluene or diglyme either caused no reaction or led to complete decomposition. On the other hand, when dichlorobis(benzonitrile)palladium(II)[10] was used as a catalyst (10 mol%) compounds **4a–f** underwent the expected rearrangement in medium to very good yields (Table 3) using refluxing dioxane as a solvent. Nevertheless, no reaction could be observed for compounds **4g–l**, even when greater quantities of catalyst or longer reaction times were used. In the case of products **4j–l** (3,3-dimethylallyl derivatives) steric hindrance seems to account for the reaction not taking place, a phenomenon which has also been described for substituted allyl vinyl ethers.[11] The lack of reactivity observed for the 2-methylallyl derivatives **4g–i** is consistent with the mechanism proposed by Overman[4,8] (cyclization-induced rearrangement) since, for those compounds, bonding of the metal ion to the tertiary carbon atom bearing the methyl group is disfavoured, this should not be the case if a charge-induced rearrangement were operative.

From the synthetic point of view it is worth mentioning that the separation of compounds **4** and **5** is extremely simple, taking advantage of the fact that the former is far more soluble in concentrated hydrochloric acid, which makes chromatographic methods unnecessary.

On the other hand, the corresponding allyl methyl *N*-alkyldithiocarbonimidates did not undergo the expected rearrangement when treated with dichlorobis(benzonitrile)palladium(II) and, under a variety of conditions, only complex mixtures resulted.

Table 1. Allyl *N*-Aryldithiocarbamates **3** Prepared

Product	Yield (%)	mp (°C)	Molecular Formula[a]	^{1}H-NMR ($CDCl_3$/TMS) δ, J (Hz)	MS (70 eV) m/z (%)
3a	88	40–42	$C_{10}H_{11}NS_2$ (209.3)	3.9 (d, 2H, J = 8), 5.1–5.4 (m, 2H), 5.7–6.1 (m, 1H), 7.2–7.5 (m, 5H), 9.1 (br s, 1H)	209 (M^+, 19), 135 (96)
3b	70	58–60	$C_{10}H_{10}ClNS_2$ (243.8)	4.0 (d, 2H, J = 8), 5.1–5.4 (m, 2H), 5.7–6.1 (m, 1H), 7.4 (s, 4H), 9.0 (br s, 1H)	243 (M^+, 4), 169 (100)
3c	86	42–44	$C_{11}H_{13}NOS$ (239.3)	3.8–4.0 (m, 5H), 5.0–5.3 (m, 2H), 5.6–6.0 (m, 1H), 6.8–7.3 (m, 4H), 9.0 (br s, 1H)	239 (M^+, 11), 165 (100)
3d	78	70–72	$C_{11}H_{13}NS_2$ (223.3)	1.8 (d, 3H, J = 8), 3.9 (d, 2H, J = 8), 5.6–5.9 (m, 2H), 7.3–7.5 (m, 5H), 9.1 (br s, 1H)	223 (M^+, 5), 135 (87)
3e	76	88–90	$C_{11}H_{12}ClNS_2$ (257.8)	1.8 (d, 3H, J = 8), 4.0 (d, 2H, J = 7), 5.7–6.0 (m, 2H), 7.3 (s, 4H), 9.1 (br s, 1H)	257 (M^+, 4), 169 (100)
3f	86	36–38	$C_{12}H_{15}NOS_2$ (253.4)	1.8 (d, 3H, J = 8), 3.7–3.9 (m, 5H), 5.6–5.9 (m, 2H), 7.0–7.5 (m, 4H), 9.1 (br s, 1H)	253 (M^+, 15), 165 (98)
3g	92	72–74	$C_{11}H_{13}NS_2$ (223.3)	1.7 (s, 3H), 3.9 (s, 2H), 4.9 (d, 2H, J = 8), 7.3–7.5 (m, 5H), 9.1 (br s, 1H)	223 (M^+, 5), 135 (100)
3h	88	54–56	$C_{11}H_{12}ClNS_2$ (257.8)	1.8 (s, 3H), 3.9 (s, 2H), 5.0 (d, 2H, J = 8), 7.3 (s, 4H), 9.0 (br s, 1H)	257 (M^+, 5), 169 (100)
3i	84	54–56	$C_{12}H_{15}NOS_2$ (253.4)	1.8 (s, 3H), 3.8 (s, 3H), 4.0 (s, 2H), 4.9 (d, 2H, J = 8), 6.8–7.4 (m, 4H), 9.0 (br s, 1H)	253 (M^+, 7), 165 (100)
3j	83	88–90	$C_{12}H_{15}NS_2$ (237.4)	1.7 (s, 6H), 3.9 (d, 2H, J = 8), 5.2–5.4 (m, 1H), 7.3–7.5 (m, 5H), 9.1 (br s, 1H)	237 (M^+, 12), 135 (42)
3k	80	78–80	$C_{12}H_{14}ClNS_2$ (271.8)	1.8 (s, 6H), 3.9 (d, 2H, J = 8), 5.1–5.3 (m, 1H), 7.3 (s, 4H), 9.1 (br s, 1H)	271 (M^+, 5), 169 (68)
3l	82	72–74	$C_{13}H_{17}NOS_2$ (267.4)	1.7 (s, 6H), 3.7–4.0 (m, 5H), 5.2–5.4 (m, 1H), 6.9–7.4 (m, 4H), 9.1 (br s, 1H)	267 (M^+, 13), 165 (65)

[a] Satisfactory microanalyses obtained: C ±0.25, H ±0.18, N ±0.20.

Table 2. Allyl Methyl *N*-Aryldithiocarbonimidates **4** Prepared

Product	Yield (%)	Molecular Formula[a]	^{1}H-NMR ($CDCl_3$/TMS) δ, J (Hz)	MS (70 eV) m/z (%)
4a	72	$C_{11}H_{13}NS_2$ (223.3)	2.5 (s, 3H),3.7 (d, 2H, J = 6), 5.0–5.3 (m, 2H), 5.6–6.0 (m, 1H), 6.7–7.2 (m, 5H)	223 (M^+, 11), 150 (100)
4b	80	$C_{11}H_{12}ClNS_2$ (257.8)	2.5 (s, 3H), 3.7 (d, 2H, J = 6), 5.0–5.4 (m, 2H), 5.6–6.1 (m, 1H), 6.7–7.3 (m, 4H)	257 (M^+, 21), 184 (100)
4c	77	$C_{12}H_{15}NOS_2$ (253.4)	2.5 (s, 3H), 3.6–3.8 (m, 5H), 5.0–5.4 (m, 2H),5.6–6.1 (m, 1H), 6.8 (s, 4H)	253 (M^+, 8), 180 (49)
4d	70	$C_{12}H_{15}NS_2$ (237.4)	1.7 (d, 3H, J = 5), 2.5 (s, 3H),3.7 (d, 2H, J = 6), 5.4–5.6 (m, 2H), 6.7–7.4 (m, 5H)	237(M^+, 8), 150 (100)
4e	67	$C_{12}H_{14}ClNS_2$ (271.8)	1.7 (d, 3H, J = 7), 2.5 (s, 3H), 3.6 (d, 2H, J = 6), 5.5–5.7 (m, 2H), 6.7–7.3 (m, 4H)	271 (M^+, 5), 184 (41)
4f	65	$C_{13}H_{17}NOS_2$ (267.4)	1.7 (d, 3H, J = 6), 2.5 (s, 3H), 3.6–3.8 (m, 5H), 5.4–5.7 (m, 2H), 6.8 (s, 4H)	267 (M^+, 8), 165 (49)
4g	75	$C_{12}H_{15}NS_2$ (237.4)	1.8 (s, 3H),2.5 (s, 3H), 3.6 (s, 2H), 4.7–5.1 (m, 2H), 6.7–7.4 (m, 5H)	237 (M^+, 6), 150 (100)
4h	84	$C_{12}H_{14}ClNS_2$ (271.8)	1.7 (s, 3H), 2.5 (s, 3H), 3.8 (s, 2H), 4.7–5.1 (m, 2H), 6.7–7.3 (m, 4H)	271 (M^+, 3), 184 (65)
4i	72	$C_{13}H_{17}NOS_2$ (267.4)	1.9 (s, 3H), 2.5 (s, 3H), 3.6–3.8 (m, 5H), 4.7–5.1 (m, 2H), 6.8 (s, 4H)	267 (M^+, 11), 180 (100)
4j	70	$C_{13}H_{17}NS_2$ (251.4)	1.6 (s, 6H), 2.5 (s, 3H), 3.7 (d, 2H, J = 7), 5.2–5.3 (m, 1H), 6.7–7.4 (m, 5H)	251 (M^+, 18), 150 (73)
4k	74	$C_{13}H_{16}ClNS_2$ (285.8)	1.7 (s, 6H), 2.5 (s, 3H), 3.8 (d,2H, J = 7), 5.1–5.3 (m, 1H), 6.7–7.3 (m, 4H)	285 (M^+, 7), 184 (39)
4l	68	$C_{14}H_{19}NOS_2$ (281.4)	1.7 (s, 6H), 2.5 (s, 3H), 3.5–3.8 (m, 5H), 5.1–5.3 (m, 1H), 6.8 (s, 4H)	281 (M^+, 24), 180 (98)

[a] Satisfactory microanalyses obtained: C ±0.25, H ±0.18, N ±0.20.

The main spectroscopic difference between compounds **4** and their rearranged counterparts **5** is found in the chemical shifts of the methylene (or methine) protons on C-1 of the corresponding allyl group. Thus, a difference of more than 1 ppm is observed for those protons when products **4a–c** are compared with **5a–c**. This effect is even more marked in the case of **5d–f**, where the NCH(CH$_3$) protons appear around δ = 6.5, that is, even

Table 3. Methyl *N*-Allyl-*N*-Aryldithiocarbamates **5** Prepared

Product	Yield (%)	mp (°C) (solvent)	Molecular Formula[a]	^{1}H-NMR ($CDCl_3$/TMS) δ, J (Hz)	MS (70 eV) m/z (%)
5a	82	oil	$C_{11}H_{13}NS_2$ (223.3)	2.5 (s, 3H), 4.8–5.2(m, 4H), 5.7–6.2 (m, 1H), 7.1–7.5 (m, 5H)[b]	223 (M^+, 49), 150 (83)
5b	90	oil	$C_{11}H_{12}ClNS_2$ (257.8)	2.5 (s, 3H), 4.8–5.3 (m, 4H), 5.7–6.2 (m, 1H), 7.0–7.5 (m, 4H)	257 (M^+, 46), 184 (100)
5c	80	60–61 (hexane)	$C_{12}H_{15}NOS_2$ (253.4)	2.5(s, 3H), 3.7 (s, 3H), 4.7–5.2 (m, 4H), 5.6–6.1 (m, 1H), 6.7–7.2 (m, 4H)	253 (M^+, 49), 180 (66)
5d	62	oil	$C_{12}H_{15}NS_2$ (237.4)	1.2 (d, 3H, J = 7), 2.5 (s, 3H), 4.9–5.2 (m, 2H), 5.5–6.0 (m, 1H), 6.3–6.6 (m, 1H), 7.0–7.5 (m, 5H)[c]	237 (M^+, 49), 150 (100)
5e	65	oil	$C_{12}H_{14}ClNS_2$ (271.8)	1.2 (d, 3H, J = 7), 2.5 (s, 3H), 5.0–5.2 (m, 2H), 5.6–6.1 (m, 1H), 6.4–6.6 (m, 1H), 6.9–7.4 (m, 4H)	271 (M^+, 18), 184 (33)
5f	63	oil	$C_{13}H_{17}NOS_2$ (267.4)	1.2 (d, 3H, J = 7), 2.5 (s, 3H), 3.8 (s, 3H), 5.0–5.3 (m, 2H), 5.5–6.0 (m, 1H), 6.4–6.6 (m, 1H), 6.7–7.1 (m, 4H)	267 (M^+, 32), 180 (80)

[a] Satisfactory microanalyses obtained: C ±0.25, H ±0.18, N ±0.20.
[b] ^{13}C-NMR ($CDCl_3$/TMS): δ = 20.6(q), 59.9(t), 119.1(t), 127.9(d), 128.9(d), 129.4(d), 131.0(d), 143.1(s), 200.4(s).
[c] ^{13}C-NMR ($CDCl_3$/TMS): δ = 16.9(q), 20.4(q), 59.8(d), 117.1(t), 128.9(d), 129.2(d), 129.9(d), 136.7(d), 139.4(s), 200.9(s).

more deshielded than the vinylic hydrogen atoms. The ^{13}C-NMR spectra of **5a** and **5d**, chosen as model compounds, also confirm the proposed structures, the signals at δ = 59.9 and 59.8 (NCH) respectively, showing the expected multiplicity (triplet and doublet) in the off-resonance spectra.

To sum up, we report a new kind of hetero-Cope rearrangement which allows the synthesis of compounds **5** in medium to good yields, starting from commercially available anilines **1** and substituted allyl halides **2**.

All reagents were of commercial quality. Used allyl halides **2** were purchased from Merck (allyl bromide, 1-chloro-2-butene and 3-chloro-2-methyl-1-propene) and Fluka (3,3-dimethylallylbromide). Yields quoted are for purified materials. Melting points were determined using a Büchi 510 apparatus and are uncorrected. ^{1}H-NMR spectra were obtained on a Bruker WP 80 CW spectrometer using TMS as internal standard. ^{13}C-NMR spectra were recorded on a JEOL FX-90 Q spectrometer. Mass spectra were obtained using a Hewlett-Packard 5995-C spectrometer.

Allyl *N*-Aryldithiocarbamates 3; General Procedure:
To a well stirred solution of the corresponding amine **1** (0.1 mol) in DMSO (50 mL), 20 M aq NaOH (5 mL, 0.1 mol) is added. After 30 min, CS_2 (7.6 g, 0.1 mol) is added dropwise and the mixture is stirred for 0.5 h. The flask is immersed in an ice-water bath, the corresponding allyl halide **2** (0.13 mol) is added dropwise and the mixture is stirred for 2 h while allowed to reach r.t. The solution is slowly poured into ice-cooled H_2O (400 mL) with vigorous stirring. The resulting yellow solid is filtered off, washed with hexane, dried and recrystallized from EtOH/H_2O (Table 1). During recrystallization the temperature must not exceed 70 °C since, otherwise, products **3** decompose.

Allyl Methyl *N*-Aryldithiocarbonimidates 4; General Procedure:
To a well stirred solution of the corresponding compound **3** (0.1 mol) in DMF (50 mL), 20 M aq NaOH (10 mL, 0.2 mol) is added. After 0.5 h the mixture is cooled in an ice-water bath and MeI (18.5 g, 0.13 mol) is added dropwise. Stirring is continued for 0.5 h and then the solution is poured into ice-cooled H_2O (250 mL) with vigorous stirring. The mixture is extracted with hexane; the organic phase is then dried ($MgSO_4$) and evaporated to give crude compounds **4** which are purified by column chromatography on silica gel (eluent hexane/EtOAc, 5:1) to give pure products **4** as oils (Table 2).

Methyl *N*-Allyl-*N*-Aryldithiocarbamates 5; General Procedure:
A mixture of the corresponding compound **4** (1 mmol) and dichlorobis(benzonitrile)palladium(II) (40 mg, 0.1 mmol) in dioxane (5 mL) is refluxed for 20 h. The solvent is removed under vacuum and the residue is treated with hexane (10 mL) and then filtered. The filtrate is washed with 35% aq HCl (3 × 5 mL), H_2O (2 × 5 mL), dried ($MgSO_4$) and evaporated to yield pure compounds **5** as oils, except for **5c** which is a solid (Table 3).

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