Rhodium(II)-mediated reactions of thiobenzoylketene *S*,*N*-acetals with α-diazo carbonyl compounds: synthesis of 2-substituted 3-alkylamino-5-phenylthiophenes †

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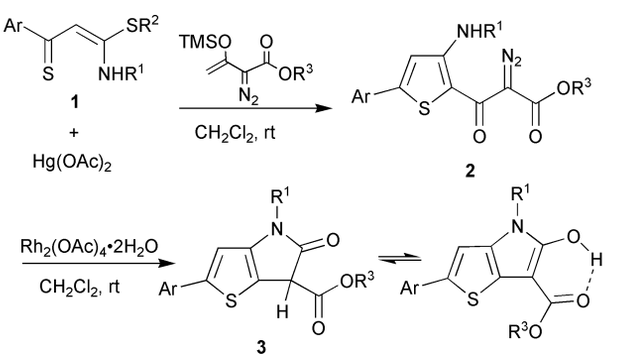
Treatment of 3-methylamino-3-methylsulfanyl-1-phenylpropenethione **1** with excess (2.5 equiv.) α-diazo carbonyl compounds such as α-diazoketones and α-diazoesters in the presence of a catalytic amount of Rh(II) acetate in CH_2Cl_2 at rt gave 2-acyl- or 2-aroyl-3-methylamino-5-phenylthiophenes and alkyl 3-methylamino-5-phenylthiophene-2-carboxylates, respectively, as major products along with 1-phenyl-2-methylsulfanylethanones. The formation of the major products indicates that the carbenes or carbenoids generated interact initially with the thione sulfur of **1**.

Introduction

The reaction of keto carbenoids with thiocarbonyl compounds is rapidly gaining prominence as an efficient method for synthesizing sulfur-containing compounds, especially three- and five-membered heterocycles. A survey of the literature shows that diverse classes of thiocarbonyl compounds such as thioketones,[1] thioketenes,[2] alkyl and aryl isothiocyanates,[3] *O*-alkyl thioesters,[4] dithioesters,[5] thioamides,[6] thioureas,[7] and 1,3-thiazole-5(4*H*)-thiones,[8] have been employed in the absence or presence of a catalyst for synthetic and mechanistic studies.

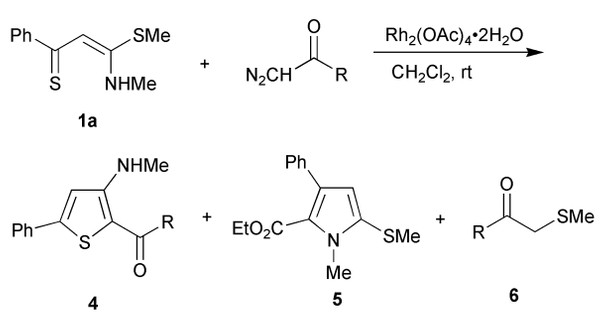
It has been shown that the reactions of carbenes or carbenoids generated from α-diazo carbonyl compounds with the C=S bonds of thiocarbonyl compounds initially proceeds with the formation of thiocarbonyl ylides, which subsequently undergo 1,3-dipolar cycloaddition or electrocyclic ring closure to give thiiranes followed by extrusion of sulfur leading to α,β-unsaturated carbonyl compounds. Nevertheless, it may be difficult to predict the chemo- and regioselectivities from the same reactions of thiocarbonyl compounds with multifunctionalities. Very recently, we reported the synthesis of 5,6-dihydro-4*H*-thieno[3,2-*b*]pyrrolid-5-ones **3** by treatment of alkyl 3-(thien-2-yl)-3-oxo-2-diazopropanoates **2**, prepared from thioaroylketene *S*,*N*-acetals **1**, $Hg(OAc)_2$, and 2-diazo-3-trimethylsilyloxybut-3-enoic acid alkyl esters,[9] with $Rh_2(OAc)_4 \cdot 2H_2O$[10] (Scheme 1). The result spurred us towards an examination of the reactivity of the C=S bond of **1** toward carbenes because compound **1** has two other heteroatoms, *i.e.*, a sulfur atom of the R^2S group and a nitrogen atom of the R^1NH group, which might act as electron donors to the electron-deficient carbenes.[11] Therefore, we have studied the reactions of **1** with α-diazo carbonyl compounds. The results are described herein.



Scheme 1

Results and discussion

Treatment of a mixture of **1a** (Ar = Ph, $R^1 = R^2 = Me$) and a catalytic amount of $Rh_2(OAc)_4 \cdot 2H_2O$ (8 mg) in CH_2Cl_2 with ethyl diazoacetate (R = OEt, 1.5 equiv.) in CH_2Cl_2 for 72 h at rt gave 3-methylamino-5-phenyl-2-thiophenecarboxylate (**4a**, R = OEt) and 1-methylpyrrole derivative **5** in 53% and 16% yields, respectively (Scheme 2). Similar reactions with other



Scheme 2

α-diazoesters and α-diazoketones under the same conditions gave the corresponding 2-thiophenecarboxylates **4b**,**c** and acyl-**4d**,**e** and aroylthiophene derivatives **4f**,**j** in moderate yields. Interestingly, the reactions with the foregoing α-diazo carbonyl compounds we tried (entries 2–10) did not give pyrrole derivatives analogous to **5** other than for ethyl diazoacetate. Instead, 1-phenyl-2-methylsulfanylethanone **6f** and 1-(4-tolyl)-2-methylsulfanylethanone **6g** were isolated in the reactions with benzoyl- and 4-methylbenzoyldiazomethanes, respectively. Reaction time and yields of compounds **4**, **5**, and **6** are summarized in Table 1.

When excess (2.5 equiv.) diazo compounds were used under the same conditions, yields of **4** increased significantly except for that of **4h** (entry 8). Nevertheless unreacted **1a** albeit in

† Electronic supplementary information (ESI) available: spectral and analytical data. See http://www.rsc.org/suppdata/p1/b2/b203931a/

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Table 1 Reactions of **1** with α-diazo carbonyl compounds in the presence of $Rh_2(OAc)_4 \cdot 2H_2O$

Entry	RN_2CHCOR	Time[a] (*t*/h) A	B		Yield[b] (%) **4**	**5**	**6**	**1**
1	EtO	72	72	**a**	53 (61)	16 (21)		
2	*t*-BuO	72	72	**b**	58[c] (64)[d]			
3	$NCCH_2O$	72	72	**c**	55 (74)[e]			
4	Cl_2CH	72	20	**d**	54 (69)			
5	$ClCH_2CH_2$	72	25	**e**	48 (74)			
6	Ph	72	35	**f**	63 (85)		16 (87)	12 (7)
7	*p*-MeC_6H_4	72	45	**g**	64 (86)		15 (90)	17 (17)
8	*p*-$MeOC_6H_4$	72	40	**h**	67 (67)		(0)	19 (10)
9	*m*-BrC_6H_4	72	43	**i**	64 (76)		(80)	14 (14)
10	*p*-ClC_6H_4	72	41	**j**	61 (79)[f]		(56)	19 (10)

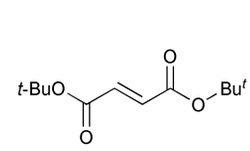
[a] Reaction times A and B represent stirred time when 1.5 and 2.5 equivalents of diazo compounds were employed, respectively. [b] Isolated yields. Numbers in parentheses represent yields when 2.5 equiv. of diazo compounds were used. [c] In addition, *t*-butyl fumarate **7** was isolated in 9% and 12% yields, respectively. [d] In addition, *t*-butyl fumarate **7** was isolated in 9% and 12% yields, respectively. [e] In addition, compound **8** (16%) was isolated. [f] In addition, 1,4-bis(4-chlorophenyl)-2-methylsulfanylbutane-1,4-dione **9** was isolated in 7% yield.

lower percentage (7–17%) compared with those involving 1.5 equiv. of diazo carbonyl compounds (12–19%), was recovered. Compounds **4** are all new except for **4a**,[9b,12] and **4f**.[9a,12] Synthesis of alkyl 3-amino-5-phenylthiophene-2-carboxylates has been mainly achieved by treatment of either β-chlorocinnamonitriles with thioglycolic acid esters in the presence of a base or a base-catalyzed cyclization of β-alkylsulfanyl-α-cyanocinnamonitriles.[14] However, synthesis of 2-acyl- and 2-aroyl-3-aminothiophenes has received little attention. Recently, compound **4a** was prepared in high yield by treating a mixture of **1a** and $Hg(OAc)_2$ in CH_2Cl_2 at rt with active methylene compounds such as diethyl 1,3-acetonedicarboxylate (83%),[9b] ethyl 3-nitrobenzoylacetate (89%),[9b] ethyl methylsulfonylacetate (74%),[9b] methylphenylsulfinylacetate (89%),[9b] and triethylphosphonoacetate (82%).[9b] Similarly **4f** was prepared using pentane-2,4-dione (91%),[9a] 1-phenylbutane-1,3-dione (90%)[9a] or 1-phenyl-4,4,4-trifluorobutane-1,3-dione (47%)[9a] by the same methodology. The reported method involving $Hg(OAc)_2$ appears to be superior to the present method involving α-diazo carbonyl compounds from various standpoints such as yield, reaction time, and reaction temperature, providing the corresponding active methylene compounds are readily available.

Interestingly, the methanethiol liberated from **1** in the course of the reaction was trapped only by aroylcarbenes (entries 6–10) to give 1-aryl-2-methylsulfanylethanones **6** whose yields increased significantly in the presence of excess (2.5 equiv.) diazo compounds as expected.[15,16] However, no compounds analogous to **6** were isolated from the reactions with α-diazoesters and α-diazoketones. From the reaction with *tert*-butyl diazoacetate (entry 2) was isolated di-*tert*-butyl fumarate **7**, presumably formed by the reaction of *tert*-butoxycarbonylcarbene with its carbene precursor. The stereochemistry of **7** was assigned to be *trans* based on the chemical shift of the olefinic protons (6.66 ppm), which is in accord with the reported values (6.65 ppm).[17] The reaction with excess cyanomethyl diazoacetate (entry 3) afforded compound **8**

(16%) as a minor product, which was envisaged to be formed through the insertion reaction of excess carbene, generated from cyanomethyl diazoacetate into the methylamino group of **4c**.[15] The reaction with excess α-diazo-*p*-chloroacetophenone (entry 10) gave 1,4-bis(4-chlorophenyl)-2-methylsulfanylbutane-1,4-dione **9** in 7% yield. Compound **9** may be formed by dimerization of *p*-chlorobenzoylcarbene to give 1,4-bis(4-chlorophenyl)but-2-ene-1,4-dione, followed by addition of methanethiol.

The mechanism for the formation of **4** may be rationalized by an intramolecular nucleophilic attack of the carbanion **11**, produced by deprotonation from the resonance form of a thiocarbonyl ylide **10**, to the imino carbon to give dihydrothiophene



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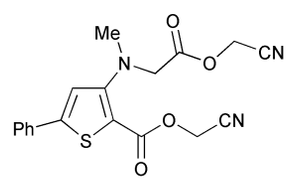

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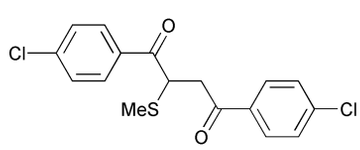

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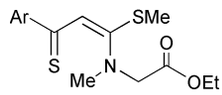
12 (Scheme 3). Loss of a methanethiolate ion, followed by aromatization would give **4**. On the other hand, either 1,3-dipolar cycloaddition of **10** or addition reaction of carbene into the C=S bond of **1** would give thiirane derivative **13**, whose C–S bond is cleaved by an intramolecular nucleophilic attack of the amino group to give a pyrroline intermediate **14**. A proton-transfer, followed by loss of a H_2S molecule would give **5**. Alternatively, one may envisage the formation of the intermediate **14** *via* an intramolecular cyclization of a nitrogen ylide **15**. However, the involvement of the intermediate **13** rather than **15** may be more plausible since no insertion product **16** was isolated.[11d]



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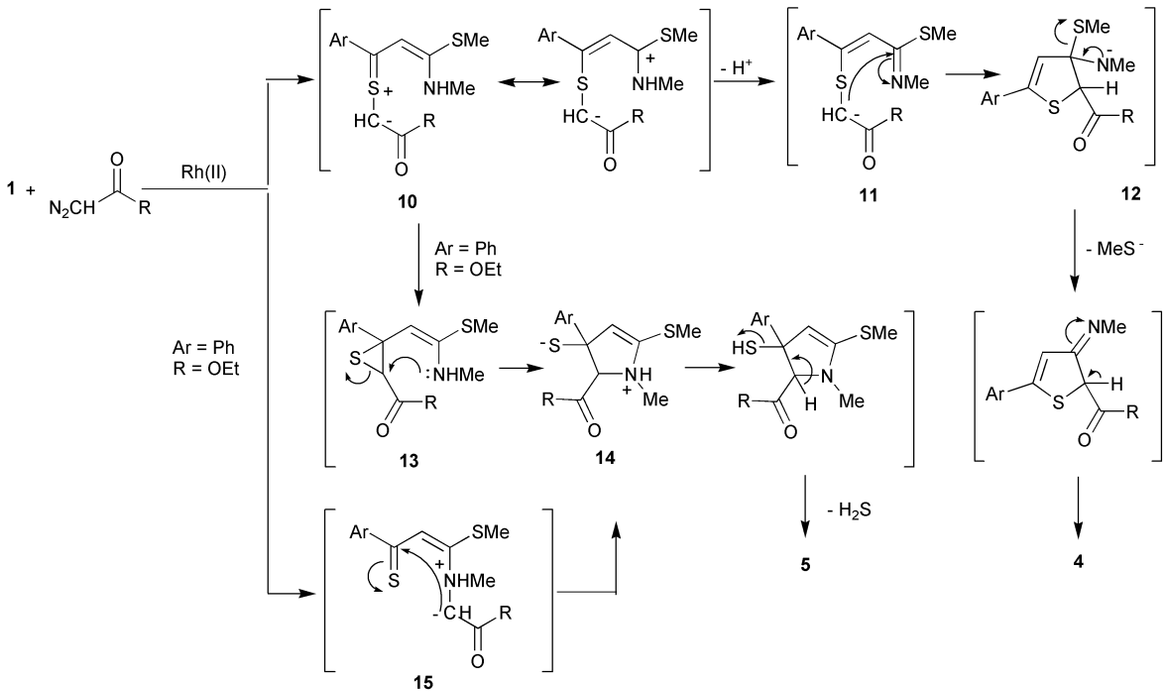
In summary, the reactions of thiobenzoylketene *S*,*N*-acetals **1** having C=S, alkylamino, and alkylsulfanyl functionalities with α-diazo carbonyl compounds in the presence of a Rh(II) catalyst gave thiophene derivatives as major products, which indicates that the carbene or carbenoid generated interacts preferentially with the thione sulfur of **1**.

Experimental

The ^1H and ^{13}C NMR spectra were recorded at 300 MHz in $CDCl_3$ solution containing tetramethylsilane as an internal standard; *J*-values are given in Hz. IR spectra were recorded in KBr or for thin-film samples on KBr plates. Mass spectra were obtained by electron impact at 70 eV. Elemental analyses were determined by the National Center for Inter-University Research Facilities, Seoul National University. Column



Scheme 3

chromatography was performed using silica gel (Merck, 70–230 mesh, ASTM). Mps were determined on a Fisher-Johns melting point apparatus and are uncorrected. 3-Methylamino-3-methylsulfanyl-1-phenylpropenethione **1a** was prepared according to the literature procedures.[9b] Ethyl,[18] *tert*-butyl,[19] and cyanomethyl diazoacetates[20] were prepared according to the literature procedures. α-Diazoacetophenone, and other α-diazoketones were prepared from the corresponding aroyl chloride and diazomethane.[21]

Reaction of 1a with ethyl diazoacetate

(i) To a solution of **1a** (75 mg, 0.336 mmol) in CH_2Cl_2 was added 1 mol% of $Rh_2(OAc)_4{\cdot}2H_2O$ (8 mg). The mixture was stirred for 5 min at rt, followed by dropwise addition of a solution of ethyl diazoacetate (57 mg, 0.504 mmol) in CH_2Cl_2 (6 ml). The mixture was stirred for 72 h at rt. Removal of the solvent *in vacuo* gave a deep reddish, and sticky residue, which was chromatographed on a silica gel (1.2 × 18 cm) using a mixture of *n*-hexane and EtOAc (4 : 1) to give ethyl 1-methyl-5-methylsulfanyl-3-phenylpyrrole-2-carboxylate **5** (15 mg, 16%): yellow liquid (Found: C, 65.3; H, 6.1; N, 5.2; S, 11.7. $C_{14}H_{17}NO_2S$ requires C, 65.4; H, 6.2; N, 5.1; S, 11.6%); ν_{max} (neat)/cm^{-1} 2960, 1689, 1408, 1260, 1180, 1097 and 732; δ_H 1.04 (3H, t, *J* 7.1, CH_3), 2.39 (3H, s, SCH_3), 3.97 (3H, s, NCH_3), 4.11 (2H, q, *J* 7.1, CH_2), 6.28 (1H, s, =CH), 7.28 (2H, m, ArH) and 7.33 (3H, m, ArH); *m*/*z* (EI) 275 (M^+, 100%), 260 (37), 232 (41), 203 (28), 147 (19) and 102 (11). Subsequent elution with the same solvent mixture (4 : 1) gave ethyl 3-methylamino-5-phenylthiophene-2-carboxylate **4a** (46 mg, 53%), mp 56–57 °C (from CH_2Cl_2–MeOH) (lit.[9b,12] 55–57 °C) (Found: C, 64.3; H, 5.7; N, 5.3; S, 12.2. $C_{14}H_{15}NO_2S$ requires C, 64.3; H, 5.8; N, 5.4; S, 12.3%); ν_{max} (neat)/cm^{-1} 3392, 1654, 1574, 1260, 1091 and 761; δ_H 1.29 (3H, t, *J* 7.1, CH_3), 2.96 (3H, d, *J* 5.2, NCH_3), 4.23 (2H, q, *J* 7.1, CH_2), 6.61 (1H, s, NH), 6.79 (1H, s, =CH), 7.35 (3H, m, ArH) and 7.57 (2H, m, ArH); *m*/*z* (EI) 261 (M^+, 100%), 215 (35), 187 (38), 160 (10) and 115 (14). (ii) From the reaction of **1a** (70 mg, 0.313 mmol), $Rh_2(OAc)_4{\cdot}2H_2O$ and ethyl diazoacetate (89 mg, 0.783 mmol) were isolated **5** (18 mg, 21%) and **4a** (51 mg, 61%).

Reaction of 1a with α-diazo-*m*-bromoacetophenone

(i) From the reaction of **1a** (65 mg, 0.291 mmol), $Rh_2(OAc)_4{\cdot}2H_2O$ and α-diazo-*m*-bromoacetophenone (98 mg, 0.437 mmol) was isolated a reaction mixture, which was chromatographed to give unreacted **1a** (9 mg, 14%) and 2-(*m*-bromobenzoyl)-3-methylamino-5-phenylthiophene **4i** (69 mg, 64%), mp 111–112 °C (from CH_2Cl_2–*n*-hexane) (Found: C, 58.0; H, 3.7; N, 3.8; S, 8.6. $C_{18}H_{14}BrNOS$ requires C, 58.1; H, 3.8; N, 3.8; S, 8.6 %); ν_{max} (neat)/cm^{-1} 3328, 1699, 1584, 1539, 1459, 1414, 1363, 1222, 1158 and 1017; δ_H 3.14 (3H, d, *J* 5.2, NCH_3), 6.95 (1H, s, =CH), 7.37 (1H, d, *J* 7.9, ArH), 7.42 (3H, m, ArH), 7.66 (3H, m, ArH), 7.76 (1H, d, *J* 7.9, ArH), 7.95 (1H, t, *J* 7.5, ArH) and 8.65 (1H, br d, *J* 4.4, NH); *m*/*z* (EI) 373 (100%), 372 (M^+, 91), 356 (38), 275 (18), 216 (32), 188 (20), 155 (16) and 115 (21). (ii) From the reaction of **1a** (80 mg, 0.385 mmol), $Rh_2(OAc)_4{\cdot}2H_2O$ and α-diazo-*m*-bromoacetophenone (201 mg, 0.895 mmol) was isolated 1-(*m*-bromophenyl)-2-methylsulfanylethanone **6i** (70 mg, 80%) by eluting the reaction mixture with a mixture *n*-hexane and EtOAc (8 : 1). Compound **6i** was purified by HPLC (μPorasil, 10 μm, 7.8 × 300 mm id) using acetonitrile, pale yellow liquid (Found: C, 44.0; H, 3.7; S, 13.2. C_9H_9BrOS requires C, 44.1; H, 3.7; S, 13.1%); ν_{max} (neat)/cm^{-1} 2928, 1670, 1558, 1414, 1254, 1190, 1132, 1062, 761 and 675; δ_H 2.15 (3H, s, SCH_3), 3.74 (2H, s, CH_2), 7.34 (1H, t, *J* 7.9, ArH), 7.71 (1H, m, ArH), 7.92 (1H, m, ArH) and 8.13 (1H, m, NH); *m*/*z* (EI) 246 (M^+ + 2, 28%), 244 (M^+, 21), 200 (16), 198 (16), 185 (100), 183 (100), 157 (31), 155 (30), 76 (15) and 74 (14). (ii) Unreacted **1a** (10 mg, 14%) and **4i** (82 mg, 76%) were isolated from the reaction of **1a** (65 mg, 0.291 mmol), $Rh_2(OAc)_4{\cdot}2H_2O$ and α-diazo-*m*-bromoacetophenone (169 mg, 0.756 mmol) after 43 h.

Acknowledgements

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