Study of the Reactivity of Ketone Enolates with 3-Halo-2-amino Derivatives of Benzo[*b*]thiophene under Photostimulated $S_{RN}1$ Reaction Conditions.

Lluís Beltran, Carmen Gálvez, Montserrat Prats* and Juan Salgado

Departament de Química Orgànica, Universitat de Barcelona, Martí i Franquès 1-11, 08028 Barcelona, Spain

Received January 2, 1992

Reactivity of the 3-halo-2-amino derivatives of benzo[*b*]thiophene **1a-c** and **2** with several ketone enolates **3-5** have been studied under photostimulated $S_{RN}1$ reaction conditions. The normal substitution product **6** only was obtained in low yields using potassioacetophenone **3** as the enolate ion and 2-(*tert*-butoxycarbonylamino)-3-chlorobenzo[*b*]thiophene (**1a**) and 2-(*tert*-butoxycarbonylamino)-3-iodobenzo[*b*]thiophene (**1c**) as substrates. In all reactions the main product was the corresponding dehalogenated substrate **7a-b**, thus indicating that reduction of the substrate strongly competes with the desired substitution reaction.

J. Heterocyclic Chem., **29**, 905 (1992).

Introduction.

In connection with a research program directed toward the development of methodologies suitable for the preparation of policyclic heteroaromatic compounds [1] of potential therapeutic interest, we required a procedure to perform the preparation of α-benzo[*b*]thenyl ketones. Thus, we focused our attention on a new synthetic route to thenyl ketones that has been provided by Bunnett and Gloor [2], who found that acetone enolate ion undergoes photostimulated reaction with chloro- and bromothiophenes in liquid ammonia to give α-thenyl ketones. These substitutions which are believed to occur by the $S_{RN}1$ mechanism (Scheme 1), turn out to be particularly useful for the preparation of 3-substituted thiophenes.

Aromatic nucleophilic substitutions *via* the $S_{RN}1$ mechanism were discovered by Kim and Bunnett in 1970 [3] and are believed to proceed by the chain mechanism shown in Scheme 1, in which ArX represents an aromatic substrate with nucleofugal group X and Nu^- is an appropriate nucleophile. Initiation (equation 1) involves an electron transfer to the substrate. The radical anion thus formed expels the nucleofuge (equation 2) and the resulting aryl radical combines with the nucleophile to form a product radical anion (equation 3). The propagating cycle is completed by transfer of an electron from the product radical anion to another substrate molecule (equation 4). Initiation has been shown to be effected by near uv light [4], by dissolved alkali metals [3] [5], and by electrochemical means [6].

Scheme 1

• Photochemical initiation step

$$ArX + Nu^- \longrightarrow ArX^{\cdot-} + Nu^{\cdot} \quad (1)$$

• Chain propagation

$$ArX^{\cdot-} \longrightarrow Ar^{\cdot} + X^- \quad (2)$$

$$Ar^{\cdot} + Nu^- \longrightarrow ArNu^{\cdot-} \quad (3)$$

$$ArNu^{\cdot-} + ArX \longrightarrow ArNu + ArX^{\cdot-} \quad (4)$$

This new type of reaction enabled the substitution of appropriate nucleofuges or leaving groups on unactivated carboaromatic systems with suitable nucleophiles and is now understood as a mechanism of rather wide scope, both as to nucleophiles (carbanions, sulfanions, phosphanions) and the substrates (aliphatic, carboaromatic, heteroaromatic) that participate [7].

One of the most important synthetic applications of these $S_{RN}1$ reactions is the α-arylation and α-hetarylation of ketones [7b,d]. These reactions are the key step of a new methodology for the synthesis of heterocyclic compounds *via* intramolecular cyclization of the substitution product. A good example of this is the preparation of indoles, azaindoles, benzo[*b*]furans, isoquinolines, isoquinolones, and isocoumarins [8a,b,d].

Most of heteroaromatic $S_{RN}1$ reactions that have been reported are on six membered azaheterocyclic compounds as pyridine, quinoline, pyrimidine, pyrazine, and pyridazine [8], but there are few examples implicating this mechanism in the area of five membered heterocyclic compounds and their benzo fused systems as it is the case of haloderivatives of thiophene [2] [9] [10] and benzo[*b*]thiophene. To the best of our knowledge nothing is described for halosubstituted benzo[*b*]thiophenes.

The present paper describes the results obtained studying the reactivity of the 3-halo-2-amino derivatives of benzo[*b*]thiophene **1a-c** and **2** with several ketone enolates **3-5** under photostimulated $S_{RN}1$ reaction conditions. The desired substitution product **6** (Scheme 2) could be subsequently deprotected and cyclized under mild conditions to give polycyclic heteroaromatic compounds.

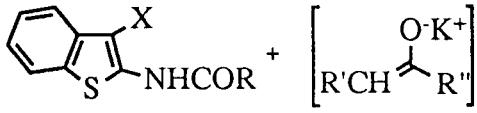
Results and Discussion.

It is apparent from reviews [7a-c] and several works [8a]

[9], that on heteroaromatic substrates the photostimulation is better than initiation by solvated electrons (dissolved alkali metals). The last initiation favours the reduction of radicals to provide the dehalogenated substrate. Also it has been proved that the potassium counter-ion is the best for ion enolates affording the substitution product in higher yield [11]. Finally, the solvent of choice for a majority of aromatic and heteroaromatic $S_{RN}1$ reactions has been liquid ammonia [12] although several solvents other than liquid ammonia (tetrahydrofurane, *N,N*-dimethylformamide, and dimethyl sulfoxide) have been tested as possible media for heteroaromatic $S_{RN}1$ reactions [12b].

Hence, we have studied the photostimulated $S_{RN}1$ reaction of the 3-halo-2-amino derivatives of benzo[*b*]thiophene **1a-c** and **2** with the potassium salts of acetophenone (**3**), pinacolone (**4**) and cyclohexanone (**5**) in, generally, liquid ammonia (Scheme 2). The amino group of compounds **1a-c** and **2** had been protected as an amide ($NHCOCF_3$) or as a carbamate (NHBoc) because of the known instability of the corresponding amines [13].

Scheme 2

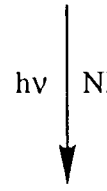


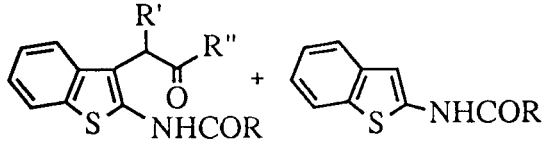
X = Cl, R = O^{t}Bu **1a** R' = H, R" = Ph **3**

X = Br, R = O^{t}Bu **1b** R' = H, R" = $CHMe_2$ **4**

X = I, R = O^{t}Bu **1c** R'-R" = $(CH_2)_4$ **5**

X = I, R = CF_3 **2**





6

R' = H, R" = Ph **6a**

R = O^{t}Bu **7a**

R = CF_3 **7b**

In all these experiments, the haloaminoderivative was added under inert atmosphere to a solution of the potassium enolate in liquid ammonia or in dimethyl sulfoxide. The resulting mixture was irradiated with a lamp Philips HPK 125 W using a Pyrex reaction flask. The results obtained are summarized in Table 1.

Table 1. Photoinduced $S_{RN}1$ Reactions of 3-Halo-2-amino Derivatives of Benzo[*b*]thiophene with Several Ketone Enolates [a].

expt.	substr.	ket. enol.	solvent	temp. (°C)	time (h)
1	**1a**	**3**	NH_3(l)	-78	5
2 [b]	**1b**	**3**	NH_3 (l)	-78	5
3	**1c**	**3**	NH_3 (l)	-78	5
4	**2**	**3**	NH_3 (l)	-78	4
5	**2**	**4**	NH_3 (l)	-78	7
6	**1c**	**5**	NH_3 (l)	-78	1.5
7	**1c**	**5**	DMSO	25-30	2
8	**2**	**5**	DMSO	25-30	2

expt.	product composition (%)		
	start. mat.	dehl.substr.	subst.prod.
1	**1a** (10)	**7a** (38)	**6a** (8)
2 [b]	**1b** (6)	**7a** (37)	---
3	**1c** (2)	**7a** (58)	**6a** (17)
4	**2** (41) [c]	**7b** (19) [c]	---
5	---	**7b** (78) [c]	---
6	---	**7a** (100) [c]	---
7	**1c** (4) [c]	**7a** (92) [c]	---
8	**2** (7) [c]	**7b** (45) [c]	---

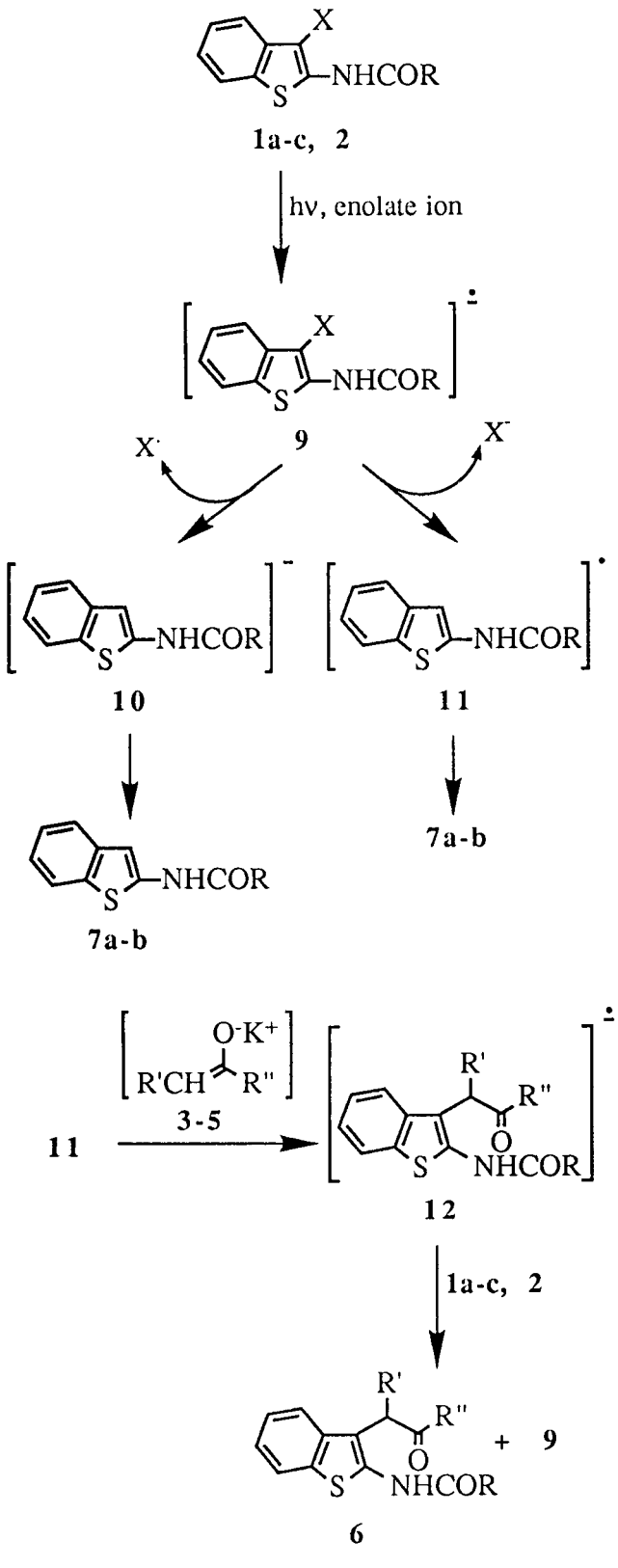
[a] The molar ratio substrate:potassium enolate ion was 1:2.5 in liquid ammonia and 1:3.75 in dimethyl sulfoxide. The potassium enolates were generated using potassium *tert*-butoxide as a base.

[b] 2-(*Tert*-butoxycarbonylamino)-3-nitrosobenzo[*b*]-thiophene (**8**) was isolated in 13% yield.

[c] Determined by hplc analysis.

The expected substitution product 2-[2-(*tert*-butoxycarbonylamino)-3-benzo[*b*]thienyl]-1-phenylethanone (**6a**)

Scheme 3



only was obtained in the reaction of 2-(*tert*-butoxycarbonylamino)-3-chlorobenzo[*b*]thiophene (**1a**) and 2-(*tert*-butoxycarbonylamino)-3-iodobenzo[*b*]thiophene (**1c**) with the potassium enolate of acetophenone (**3**) (experiments 1 and 3) in a low yield (8-17%), the dehalogenated substrate 2-(*tert*-butoxycarbonylamino)benzo[*b*]thiophene (**7a**) being the main product. Thus, the reduction of the hetaryl radical **11** to anion **10** and subsequent protonation by the solvent [14] strongly competes with the desired combination of hetaryl radical **11** with potassium enolate **3**. The dehalogenated compound **7a** can also be formed by protonation of the anion **10** which proceeds from the radical anion **9** (Scheme 3) [15]. Surprisingly, when 3-bromo-2-(*tert*-butoxycarbonylamino)benzo[*b*]thiophene (**1b**) was used as the substrate, the unexpected 2-(*tert*-butoxycarbonylamino)-3-nitrosobenzo[*b*]thiophene (**8**) was obtained in 13% yield (experiment 2). This product could be formed by oxidation of the corresponding 3-amino compound.

On the other hand, the results obtained with 3-iodo-2-(trifluoroacetyl)aminobenzo[*b*]thiophene (**2**) and the acetophenone enolate (**3**) indicate that compound **2** reacts more slowly than 2-(*tert*-butoxycarbonylamino)-3-iodobenzo[*b*]-thiophene (**1c**) does, under practically the same reaction conditions (experiments 3 and 4), to produce only a 19% yield of 2-(trifluoroacetyl)aminobenzo[*b*]thiophene (**7b**). The desired substitution product was not detected. This substrate **2** also reacts slowly with pinacolone enolate (**4**) to give a 78% yield of the dehalogenated substrate **7b** (experiment 5) and the desired substitution product was not obtained.

In an attempt to improve the yield of the substitution product **6a**, we have treated the more reactive substrate **1c** with the potassium enolate of cyclohexanone (**5**) which is known to be reactive under photostimulated $S_{RN}1$ reaction conditions toward several heterocyclic substrates [7d] [16]. In fact, the reaction was very fast but unfortunately, the dehalogenated compound **7a** was produced quantitatively (experiment 6). Then, the compound **1c** showed a certain sensitivity to enolate ion structure, giving the substitution product **6a** only with acetophenone enolate in liquid ammonia (experiments 3 and 6). The results were not better changing the solvent and temperature. Thus, in dimethyl sulfoxide at room temperature (experiment 7), a 92% yield of 2-(*tert*-butoxycarbonylamino)benzo[*b*]thiophene (**7a**) was produced and the desired substitution product **6a** was not formed.

Finally, the compound **2** in dimethyl sulfoxide at room temperature reacts similarly to compound **1c** with potassiocyclohexanone enolate (**5**), but the material balance is lower (experiment 8). It seems that the trifluoroacetamide derivative **2** could be more labile under the reaction conditions used than the corresponding carbamate analog **1c**.

In summary, the reactions between the 3-halo-2-amino derivatives **1a-c** and **2** and the ketone enolates **3-5** under light-induced $S_{RN}1$ reaction conditions leads mainly to the corresponding reduction products **7a-b**. The desired substitution product **6** only was obtained in low yields using potassioacetophenone **3** as the enolate ion and the carbamates **1a** and **1c** as the substrates.

EXPERIMENTAL

All reactions were performed under a nitrogen atmosphere. Melting points were determined on a Köfler block and are uncorrected. The ^{1}H-nmr spectra were recorded on a Varian XL-200 spectrometer. Chemical shifts are reported in ppm relative to TMS and coupling constants are in hertz. The ir spectra were recorded on a Perkin-Elmer 681 Infrared spectrophotometer. The mass spectra were obtained on a Hewlett-Packard 5988-A spectrometer. Elemental analyses were performed by the C.S.I.C. (Barcelona) Micro-Analysis Laboratory. Flash column chromatography refers to the method of Still *et al.* [17]. Hplc analyses of crude materials were carried out on a Waters Associates (Milford, MA, USA) instrument equipped with high-pressure pumps (Model M-45 and M-6000A), a Model 450 variable-wavelength detector, a Model 660 solvent programmer and a integrator data module. The injector was a Rheodyne 7125.

The dimethyl sulfoxide was purified by drying for two days over molecular sieves followed by vacuum distillation through a Vigreux column (< 45°). After a second distillation from calcium hydride, the dimethyl sulfoxide was stored under nitrogen. Potassium *tert*-butoxide was freshly sublimed just prior to use. The ketones (analytical grade) were supplied by Fluka (Buchs, Switzerland) and used as recived. 2-(*Tert*-butoxycarbonylamino)-3-chlorobenzo[*b*]thiophene (**1a**) [13], 3-bromo-2-(*tert*-butoxycarbonylamino)benzo[*b*]thiophene (**1b**) [13], 2-(*tert*-butoxycarbonylamino)-3-iodobenzo[*b*]thiophene (**1c**) [18], and 3-iodo-2-(trifluoroacetyl)aminobenzo[*b*]thiophene (**2**) [18] were prepared by halogenation of the corresponding carbamate **7a** or amide **7b** according to the described methods.

General Procedure for the Photostimulated Reaction in Liquid Ammonia of the Ketone Enolates **3-5** with the 3-Halo-2-amino Derivatives of the Benzo[*b*]thiophene **1a-c** and **2**.

Liquid ammonia (350 ml) was condensed into a 500 ml, three-necked cylindrical Pyrex flask equipped with a mechanical stirrer, nitrogen inlet, and dry ice condenser. This reactor was constantly swept with dry nitrogen. Potassium *tert*-butoxide and the ketone were then added. The ammonia solution was stirred for 5 minutes before addition of the required 3-halo-2-aminocompound. The resulting mixture was then irradiated by using a 125-W Philips HPK lamp restricting the light to ≥ 350 nm. The temperature was kept at −78° by external cooling jacket refrigeration charged with solid dioxide of carbon and acetone. Samples were periodically taken, hydrolyzed (aqueous ammonium chloride solution), extracted (dichloromethane), and analyzed by using tlc on silica (dichloromethane). Irradiation was stopped when the starting material was consumed. An excess of ammonium chloride was introduced when irradiation was finished, and ammonia was allowed to evaporate. Hydrolysis, extraction (dichloromethane), drying over magnesium sulfate, and solvent removal under vacuum afforded a crude solid, which was further purified or analyzed by hplc.

Photostimulated Reaction of Acetophenone Enolate (**3**) with 2-(*Tert*-butoxycarbonylamino)-3-chlorobenzo[*b*]thiophene (**1a**). 2-[2-(*Tert*-butoxycarbonylamino)-3-benzo[*b*]thienyl]-1-phenylethanone (**6a**).

A mixture of substrate **1a** (0.76 g, 2.7 mmoles) and potassium enolate **3** (6.7 mmoles) was irradiated for 5 hours. Standard workup and purification of the obtained crude material by flash chromatography (silica gel, dichloromethane) yielded 74 mg (10%) of starting material **1a**, 255 mg (38%) of 2-(*tert*-butoxycarbonylamino)benzo[*b*]thiophene (**7a**), and 80 mg (8%) of the desired 2-[2-(*tert*-butoxycarbonylamino)-3-benzo[*b*]thienyl]-1-phenylethanone (**6a**) as a light yellow solid, mp 146-148°; ^{1}H nmr (deuteriochloroform): δ 8.49 (br s, 1 H, NH), 8.10 (m, 2 H, H arom), 7.77-7.18 (m, 7 H, H arom), 4.36 (s, 2 H, CH_2CO), 1.57 (s, 9 H, $C(CH_3)_3$); ir (potassium bromide): ν 3410 (NH), 3050 (CH), 2960 (CH_3), 1725 (carbamate CO), 1680 (ketone CO) cm^{-1}; ms: m/z (relative intensity) 367 (M^+, 8), 162 (100).

Anal. Calcd. for $C_{21}H_{21}NO_3S$: C, 68.64; H, 5.76; N, 3.81; S, 8.73. Found: C, 68.40; H, 5.86; N, 3.88; S, 8.58.

Photostimulated Reaction of Acetophenone Enolate (**3**) with 3-Bromo-2-(*tert*-butoxycarbonylamino)benzo[*b*]thiophene (**1b**). 2-(*Tert*-butoxycarbonylamino)-3-nitrosobenzo[*b*]thiophene (**8**).

A mixture of substrate **1b** (0.88 g, 2.7 mmoles) and potassium enolate **3** (6.7 mmoles) was irradiated for 5 hours. Standard workup and purification of the obtained crude material by flash chromatography (silica gel, dichloromethane) yielded 55 mg (6%) of starting material **1b**, 250 mg (37%) of 2-(*tert*-butoxycarbonylamino)benzo[*b*]thiophene (**7a**), and 100 mg (13%) of 2-(*tert*-butoxycarbonylamino)-3-nitrosobenzo[*b*]thiophene (**8**) as a white solid, mp 127-129°; ^{1}H nmr (deuteriochloroform): δ 9.38 (br s, 1 H, NH), 8.98 (m, 1 H, H arom), 7.98 (m, 1 H, H arom), 7.58 (m, 2 H, H arom), 1.58 (s, 9 H, $C(CH_3)_3$); ir (potassium bromide): ν 3270 (NH), 3060 (CH), 2980 (CH_3), 1760 (CO), 1520 (NO) cm^{-1}; ms: m/z (relative intensity) 278 (M^+, 7), 57 (100).

Anal. Calcd. for $C_{13}H_{14}N_2O_3S$: C, 56.10; H, 5.07; N, 10.06; S, 11.52. Found: C, 55.90; H, 5.00; N, 10.16; S, 11.37.

Photostimulated Reaction of Acetophenone Enolate (**3**) with 2-(*Tert*-butoxycarbonylamino)-3-iodobenzo[*b*]thiophene (**1c**). 2-[2-(*Tert*-butoxycarbonylamino)-3-benzo[*b*]thienyl]-1-phenylethanone (**6a**).

A mixture of substrate **1c** (1.00 g, 2.7 mmoles) and potassium enolate **3** (6.7 mmoles) was irradiated for 5 hours. Standard workup and purification of the obtained crude material by flash chromatography (silica gel, dichloromethane) yielded 17 mg (2%) of starting materials **1c**, 387 mg (58%) of 2-(*tert*-butoxycarbonylamino)benzo[*b*]thiophene (**7a**), and 164 mg (17%) of the desired substitution product **6a**. The physical and spectral data are given above.

General Procedure for the Photostimulated Reaction of Cyclohexanone Enolate (**5**) with 2-(*Tert*-butoxycarbonylamino)-3-iodobenzo[*b*]thiophene (**1c**) and 3-Iodo-2-(trifluoroacetyl)aminobenzo-[*b*]thiophene (**2**) in DMSO.

A 500 ml, three-necked cylindrical Pyrex flask equipped with a mechanical stirrer and nitrogen inlet, was constantly swept with dry nitrogen. Potassium *tert*-butoxide (1.68 g, 15.0 mmoles) was placed in the flask and 150 ml of anhydrous dimethyl sulfoxide was added. After the solid had dissolved, cyclohexanone (1.47 g, 15.0 mmoles) was added and the mixture was stirred for 5 min-

utes. Then 2-(*tert*-butoxycarbonylamino)-3-iodobenzo[*b*]thiophene (**1c**) (1.50 g, 4.0 mmoles) was added and the resulting mixture was irradiated using a 125-W Philips HPK lamp restricting the light to ≥350 nm for 2 hours at 25-30° (the temperature was kept at 25-30° by external cooling jacket refrigeration). When irradiation was finished, the reaction mixture was neutralized with 3*M* sulfuric acid, diluted with water and extracted with dichloromethane. The organic extracts were washed with water, dried (magnesium sulfate) and concentrated. Analysis by hplc of the crude material showed a 92% of 2-(*tert*-butoxycarbonylamino)-benzo[*b*]thiophene (**7a**) and a 4% of starting material **1c**.

A mixture of substrate **2** (1.50 g, 4.0 mmoles) and potassium enolate **5** (15.0 mmoles) was irradiated for 2 hours and the usual workup gave a crude material that analysis by hplc indicated a 45% of 2-(trifluoroacetyl)aminobenzo[*b*]thiophene (**7b**) and a 7% of starting material **2**.

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