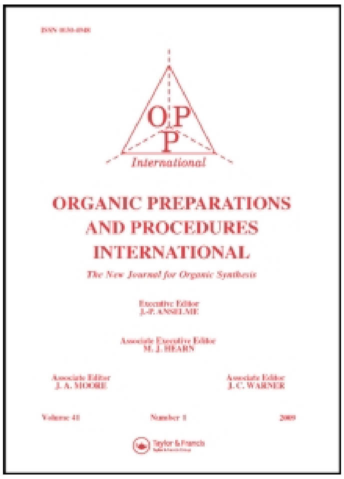

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SYNTHESIS OF UNSYMMETRICAL α-(N-ARYLCARBONYL)AMINO DIORGANYL SELENIDES *via* BENZOTRIAZOLE INTERMEDIATES PROMOTED BY SmI_2

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SYNTHESIS OF UNSYMMETRICAL α-(N-ARYLCARBONYL)AMINO DIORGANYL SELENIDES *via* BENZOTRIAZOLE INTERMEDIATES PROMOTED BY SmI_2

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Various selenium-containing compounds are widely used as reagents and intermediates in organic synthesis.[1] Benzotriazole has taken its place as one of the most useful synthetic auxiliary groups available in the last decade.[2] Because the benzotriazole anion is a good leaving group, it may be used in place of a halogen in many reactions. The benzotriazolyl group has the advantage, however, that the derivatives are frequently much more stable than their chloro or bromo anologues. For example, α-benzotriazolylalkyl amines are stable, easily prepared compounds, whereas the corresponding α-chloroalkyl analogues are highly reactive. Many types of compounds have been synthesized *via* benzotriazole auxiliary, they include amines,[3] enamines,[4] esters,[5] ethers,[6] sulfides,[7] sulfones[8] and phosphorus-containing compounds.[9] To the best of our knowledge, no selenium-containing compounds have been synthesized with benzotriazole.

It has recently been found that selenolate anion (RSe^-) and tellurolate anion (RTe^-) obtained from reductive cleavage of diorganyl diselenides and ditellurides with samarium diiodide are powerful nucleophilic reagents. Some interesting reactions were described with the use of RSe^- or RTe^- such as aromatic nucleophilic substitution and ring opening of isopropylidene malonate derivatives[10].

TABLE. Yield, mp. and Spectra Data of **6a-h**

Entry	Yield (%)	mp. (°C)	Elem. Anal. Calcd (Found) C	H	^{1}H NMR (δ)	IR (cm^{-1})
6a	82	52	49.50 (49.32)	5.41 (4.49)	7. 87-7.72 (m, 2H), 7.38-7.26 (m, 3H), 4.65 (d, 2H, *J* = 6.2Hz), 2.70 (q, 2H, *J* = 7.8Hz), 1.40 (t, 3H, *J* = 7.8Hz)	3310, 3090, 3050, 2970, 2945, 2880, 1740, 1645, 1612, 1590, 1550, 1500, 1455, 1410, 1382, 1335, 1325, 1260, 1230, 1185, 1150, 1080, 1040, 922, 810, 780, 718, 695
6b	87	44	53.34 (53.26)	6.34 (6.38)	7.88-7.73 (m, 3H, ArH, NH) 7.37-7.25 (m, 3H) 4.62 (d, 2H, *J* = 6.2Hz) 2.71 (t, 2H, *J* = 6.8Hz) 1.77-0.82 (m, 7H)	3340, 3080, 3050, 2975, 2945, 2885, 1735, 1655, 1612, 1590, 1540, 1495, 1470, 1410, 1385, 1315, 1245, 1205, 1185, 1150, 1075, 1035, 1000, 925, 780, 760, 705, 687
6c	78	Oil	53.34 (53.26)	6.34 (6.38)	7.94-7.78 (m, 214), 7.65-7.17 (m, 3H), 4.63 (d, 2H, *J* = 6.2Hz), 2.68 (t, 2H, *J* = 7Hz), 1.74-1.16 (m, 8H), 0.81 (t, 3H, *J* = 4.2Hz)	3340, 3090, 3055, 2980,2950, 2890, 2880, 1655,1617, 1592, 1550, 1500,1415, 1386, 1320, 1250, 1190, 1150, 1080, 1040, 925, 785, 760, 708, 690
6d	87	25	53.34 (53.26)	6.34 (6.38)	8.5 1 (t, 1H, *J* = 6.6Hz) 7.90-7.75 (m, 2H), 7.33-7.21 (m, 3H), 4.61 (d, 2H, *J* = 6.6Hz), 2.59 (d, 2H, *J* = 6.4Hz), 2.02-1.50 (m, 1H), 0.91 (d, 6H, *J* = 6.6Hz)	3330, 3085, 3050, 2978, 2945, 2885, 1740, 1655, 1615, 1590, 1546, 1479, 1470, 1410, 1388, 1370, 1320, 1250, 1220, 1190, 1150, 1080, 1040, 1000, 925, 785, 760, 710, 690
6e	80	48	54.93 (54.69)	6.74 (6.85)	7.86-7.71 (m, 2H), 7.51-7.22 (m, 4H, ArH, NH), 5.83-5.43 (m, 1H), 2.90-2.33 (m, 2H), 1.95-1.22 (m, 7H), 0.88 (t, 3H, *J* = 6.5Hz)	3320, 3085, 3055, 2980, 2985, 2890, 1650, 1615, 1590, 1540, 1500, 1475, 1460, 1385, 1340, 1315, 1300, 1238, 1190, 1150, 1125, 1080, 1030, 975, 785, 760, 710, 680
6f	75	Oil	59.99 (59.65)	7.99 (7.85)	7.88-7.72 (m, 2H), 7.35-7.13 (m, 4H, ArH, NH), 5.83-5.43 (m, 1H), 2.84-2.40 (m, 2H), 1.97-0.87 (m, 18H)	3320, 3080, 3050, 2980, 2950, 2890, 2875, 1740, 1650, 1615, 1590, 1540, 1500, 1475, 1385, 1340, 1300, 1190, 1150, 1125, 1080, 1030, 975, 710, 690
6g	75	22	57.69 (57.84)	7.42 (7.51)	7. 83-7.67 (m, 2H), 7.37-7.22 (m, 3H), 6.66 (d, 1H, *J* = 10.8), 5.78-5.28	3320, 3080, 3055, 2980, 2950, 2890, 1655, 1615, 1590, 1540, 1500, 1470, 1385, 1340, 1300,

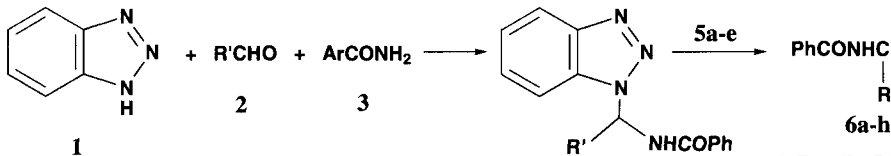
					(m, 1H), 2.97-2.50 (m, 2H), 1.93-0.87 (m, 14H)	1190, 1150, 1125, 1075, 1020, 970, 710, 690
6h	78	76-77	57.94 (58.26)	4.51 (4.57)	7.67-7.08 (m, 11H, ArH, NH), 4.79 (d, 2H, $J = 7.2$Hz)	3490, 3340, 3100, 3080, 3040, 2978, 1645, 1590, 1540, 1500, 1485, 1420, 1330, 1320, 1308, 1235, 1145, 1080, 1040, 1020, 925, 740, 715, 690

Recently, we obtained α-amino unsymmetrical diorganyl selenides by displacement of benzotriazole with RSe⁻. Here we report that unsymmetrical α-(N-arylcarbonyl)amino diorganyl selenides can be synthesized through nucleophilic substitution of the benzotriazole anion by selenolates RSe⁻.

$$\mathrm{RSeSeR} + 2\mathrm{SmI_2} \longrightarrow 2\ \mathrm{RSe^-}\ \mathrm{SmI_2^+}$$

5a-e

a) R = Et b) R = Bu c) R = *n*-Hexyl d) R = *i*-Bu e) R = Ph



1 2 3

4a,b

a) R' = H; b) R' = Pr

6a-h

a) R = Et, R' = H
b) R = *n*-Bu, R' = H
c) R = *n*-Hex, R' = H
d) R = *i*-Bu, R' = H
e) R = Et, R' = *n*-Pr
f) R = *n*-Hex, R' = *n*-Pr
g) R = *n*-Bu, R' = *n*-Pr
h) R = Ph, R' = H

It has now been shown that the seleno group can been introduced into organic molecules *via* the benzoltriazole methodology (Scheme). The yields of selenides **6a-h** thus obtained are good. These compounds apparently are difficult to synthesize by other methods since we did not find any reports on this type of compounds. The starting materials containing benzotriazolyl group **4a**, **4b** are readily available.[11] We also carried out the same transformations with tellurolate anions, but the corresponding reaction products are unstable and decomposed during separation.

EXPERIMENTAL SECTION

^{1}H NMR spectra were recorded in CCl_4 on JEOL PMX 60si spectrometer using TMS as internal standard. IR spectra were obtained on a PE 683 spectrometer. Elemental analyses were conducted on a Carlo Erba 1106 instrument. SmI_2 was prepared from samarium and iodine in dry THF under nitrogen. Caution should be used.

General Procedure.- To a solution of SmI_2 (2.1mmol) in 20mL THF, were added the diselenide (1 mmol) and HMPA (0.5mL). After stirring for 3 hrs at room temperature, N-[1-(benzotriazol-1-yl)alkyl]amide (2mmol) were added, and the mixture was heated at 70° for 4 hrs. The reaction mixture were treated with dilute hydrochloric acid (0. 1M, 1mL) and extracted with ether (2 x 30mL). Organic phase were washed with brine and dried with $MgSO_4$. The product were seperated by preparative TLC (silica gel) with cyclohexane and ethyl acetate (2:1) as eluent.

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