A Simple Synthesis of Conjugated Imine–α-Thio- and α-Seleno-vinylamines

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The addition of ynamines to *N*-acyl-*S*-alkyl(or -aryl)thiobenzimidates and *N*-acyl-*Se*-arylselenobenzimidates gives the conjugated acylimine-α-thio- and α-seleno-vinylamines, respectively (together with small amounts of the corresponding amidines); the structure was confirmed by an *X*-ray structure determination of 1-benzenesulphonyl-4-diethylamino-3-methyl-2-phenyl-4-phenylthio-1-azabutadiene hydrochloride, and a 1,3-sulphur, selenium, or nitrogen shift is proposed to explain formation of these products.

α-Thiovinylamines[1a] and ketene dithioacetals[1b] have found many useful synthetic applications. More recently, conjugated ketene dithioacetals have been attracting much attention[2] and have been used in the synthesis of α-pyrones,[3] furans,[4] and in the so-called 1,3-carbonyl transpositions.[5] We now report a novel facile synthesis of conjugated imine–α-thio- and α-seleno-vinylamines, which should allow useful extensions of the above reactions.

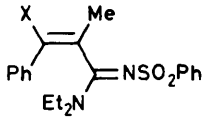
Addition of 1-diethylaminoprop-1-yne (**1a**) to the *N*-sulphonylimine (**2**) gave the *N*-sulphonylamidine (**3**) (98%), m.p. 98—99 °C, identical with an authentic sample prepared from *cis*-α-methylcinnamoyl chloride. On the other hand, addition of (**1a**) to *N*-benzenesulphonyl-*S*-phenylthiobenzimidate (**4**) (readily available from benzamide *via* the *N*-benzenesulphonyl derivative and the imidoyl chloride[6]) in Et_2O at room temperature followed by chromatography on a column of silica gel gave amidine (**5**) (16%), m.p. 121—122 °C as white needles,† whose geometry was assigned by analogy with that of (**3**), and 1-benzenesulphonyl-4-diethylamino-3-methyl-2-phenyl-4-phenylthio-1-azabutadiene (**6**) (76%) as an orange oil, b.p. 130—140 °C at 0.05 mmHg. The orange oil was initially assigned an azete structure (**7**) mainly on the basis of analogy with the brightly coloured cyclobutenes reported to be formed from the addition of indoles with dimethyl acetylenedicarboxylate,[7] but this structure was discounted since the compound formed crystalline salts with HCl, HBr, H_2SO_4, and BF_3 but no β-lactam[8] could be obtained under any of the hydrolytic conditions used. Hydrolysis of (**6**) under neutral or mild basic conditions (room temp., 10% aq. NaOH–diethyl ether, 10 h) gave an α,β-unsaturated amide (95%), m.p. 156—157 °C [i.r. (KBr) 3170 (NH), 1620 cm^{-1} (C=O)].

The structure of (**6**)‡ (excluding geometry) was established unambiguously by a single crystal *X*-ray structure analysis of its hydrochloride, m.p. 169—170 °C. The crystal data were as follows: $C_{26}H_{29}N_2O_2S_2^+Cl^-\cdot H_2O$; M = 519.1; orthorhombic; space group *Pbca*; a = 27.376(2), b = 9.782(1), c = 19.661(2) Å; Z = 8; D_c = 1.31 g cm^{-3}. Single crystal *X*-ray diffraction data were measured with a Philips PW1100 diffractometer using the ω–2θ scan technique with graphite

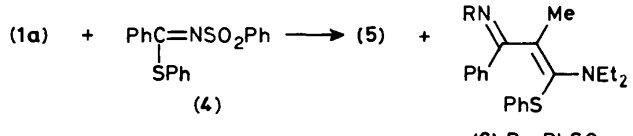
$R-C\equiv CNR^1R^2$ (**1**)

a; R = Me; R^1 = R^2 = Et
b; R = H; R^1 = Me; R^2 = Ph

$PhCH=NSO_2Ph$ (**2**)



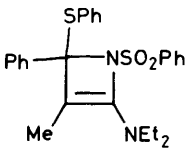
(**3**) X = H
(**5**) X = SPh
(**13**) X = OMe



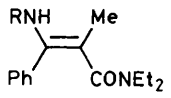
(**6**) R = $PhSO_2$
(**11**) R = PhCO

† (**5**): I.r. (KBr) 1535 (C=N), 1260, 1135 cm^{-1} (SO_2); u.v. (MeCN) $\lambda_{max.}$ 260 nm; n.m.r. ($CDCl_3$) δ 8.2—6.8 (m, 15H), 4.0—3.3 (m, 2H), 3.1—2.6 (m, 2H), 2.5 (s, 3H), 1.1—0.8 (tt, 3H, *J* 7 Hz), 0.7—0.4 (tt, 3H, *J* 7 Hz); mass spectrum *m/z* (rel. intensity) 464($M^{\cdot+}$, 17), 355(60), 323(49), 252(51), 213(24), 210(29), 115(58), 109(18), 77(100), 72(58).

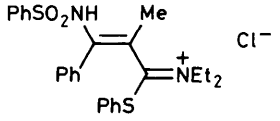
‡ (**6**): I.r. (film) 1600 (C=N), 1310, 1150 cm^{-1} (SO_2); n.m.r. ($CDCl_3$) δ 8.3—7.3 (m, 15H), 3.2 (q, 4H, *J* 6 Hz), 2.2 (s, 3H), 0.95 (tt, 6H, *J* 7 Hz); mass spectrum *m/z*(rel. intensity) 464($M^{\cdot+}$, 4.7), 355(18), 323(25), 212(49), 141(28), 110(36), 109(69), 77(100), 72(6).



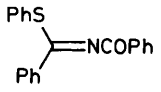
(7)



(8) R = $PhSO_2$
(12) R = PhCO



(9)



(10)

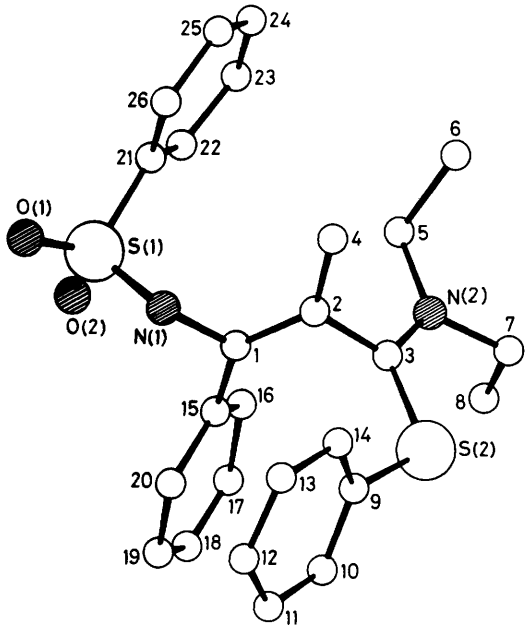
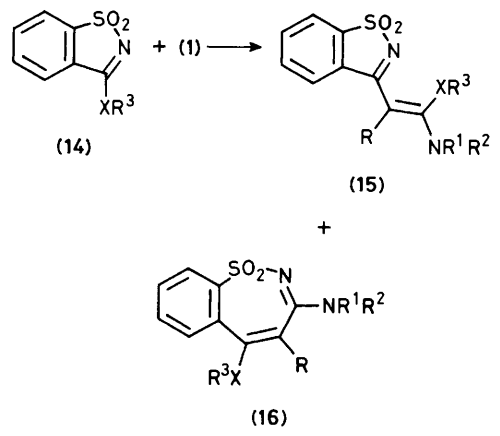
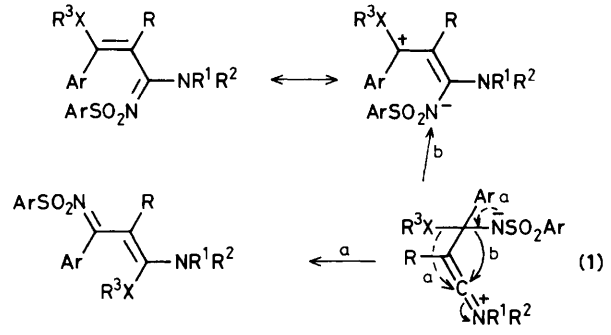


Figure 1. Perspective view of *X*-ray model of 1-benzenesulphonyl-4-diethylamino-3-methyl-2-phenyl-4-phenylthio-1-azabutadiene hydrochloride, (**6**).

monochromated Cu-K_α radiation (λ = 1.5418 Å). The structure was solved by direct methods[9] and refined by the least-squares method.[10] A chloride ion and a water molecule§ were found on successive difference Fourier maps. Hydrogen atom positions were calculated and added as fixed contributions. The hydrogen atom on the nitrogen atom N(1) was located, the hydrogen atoms of the water molecule were not found. Refinement converged to the final R and R_w values of 0.048 and 0.052 for 2988 observed reflections. Temperature factors were anisotropic for non-hydrogen atoms. An overall isotropic temperature factor has been attributed to the H atoms and refined intensities were empirically corrected for absorption.[11] Figure 1 shows a perspective drawing of the molecule (less H-atoms). The two double bonds C(1)–C(2) and C(3)–N(2) are approximately perpendicular [torsional angle C(1)–C(2)–C(3)–N(2) = 111°]. The phenyl rings are approximately parallel. In the crystal the water molecule bridges two different symmetry related Cl^- ions

§ C, H microanalysis indicated the absence of this water molecule in the freshly dried sample.





($W \cdots Cl^-$ = 3.173 and 3.275 Å). The chloride ion is also hydrogen bonded to N(1)–H ($N \cdots Cl^-$ = 3.231 Å).¶ This establishes structure (**9**) for the hydrochloride and the conjugated imine–α-thiovinylamine structure (**6**) for the free base. The base hydrolysis product is acrylamide (**8**). Under more vigorous basic hydrolysis in ethanol the corresponding ethyl ester is obtained.

N-Benzoyl-*S*-phenylthiobenzimidate (**10**), m.p. 78—79 °C, reacted with (**1a**) in boiling CH_2Cl_2 to give (**11**) as a yellow oil (52%) together with the amide (**12**) (18%), m.p. 163—164 °C. On the other hand, no methoxy migration occurred with *N*-benzenesulphonyl-*O*-methylbenzimidate[6] and only the amidine (**13**) (84%), m.p. 92—93 °C, was formed with (**1a**) in $CHCl_3$.

The generality of the conjugated imine–α-thiovinylamine synthesis has been further examined by studying the reaction of (**1**) with 3-substituted 1,2-benzisothiazole 1,1-dioxides. Thus, reaction of (**14**) (R^3X = MeS, PhS, PhSe, prepared from saccharin pseudochloride) gave mainly the corresponding imine–vinylamine (**15**) as deep red oils, in good yields, together with small amounts of the colourless ring-expansion products (**16**). ‖ Separation could be readily effected by chromatography on silica gel. The imine–vinylamines are susceptible to hydrolysis to the corresponding propionamides.

A likely explanation is that the products are formed by a

¶ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‖ Compound (**16**) R^3X = MeS, R = Me, R^1 = R^2 = Et) has been reported[12] to be a red solid: m.p. 125 °C. It is actually a colourless solid: m.p. 116.5 °C which was clearly contaminated with the red oily (**15**) in the earlier work.

1,3-shift of S, Se (path a), or N (path b) in the initial dipolar adduct formed *e.g.* equation (1). When X = O, H, alkyl,[12] or aryl[12] only N migration occurs (path b). The alternative cyclization to give an azetine followed by ring opening to (**16**) seems less satisfying (Occam's Razor).

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