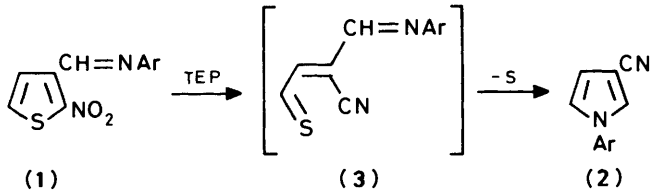
Thermal Fragmentation of 2-Azidobenzo[*b*]thiophene in the Presence of Alkenes: A New Synthetic route to 1-(2-Benzo[*b*]thienyl)aziridines and/or Thiochroman-4-carbonitriles

Piero Spagnolo
Istituto di Chimica, Università della Basilicata, Via N. Sauro 85, 85100 Potenza, Italy
Paolo Zanirato
Dipartimento di Chimica Organica, Università di Bologna, Viale Risorgimento 4, 40136 Bologna, Italy

Mild thermal fragmentation of 2-azidobenzo[*b*]thiophene in the presence of olefins results in the formation of 1-(2-benzo[*b*]thienyl)aziridines and/or 4-cyanothiochromans in fairly good yields. The formation of aziridines, at the expense of thiochromans, is favoured by electron-poor olefins and by a decrease in the reaction temperature. Evidence is presented in favour of a singlet nitrene intermediate which adds to the olefin double bonds or undergoes a ring-opening reaction to give an *ortho*-quinoidal enethione which is trapped by the alkene present. These findings provide the first example of ready ring-opening by a 2-nitreno substituted thiophene.

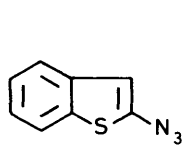
Five-membered heteroatomic compounds undergo ring-opening when a suitable anionic substituent is generated at C-2[1] and useful intermediates so generated can be conveniently employed in the structural elaboration of various heterocyclic rings by inter- or intra-molecular trapping reactions. In principle, analogous ring-opening reactions can be exhibited by singlet carbenes or nitrenes generated as 2-substituents of five-membered heterocycles and/or by precursors of these intermediates, such as diazo compounds and azides, since there is a lone pair available on these substituents which can interact with the 1,2-bond of the ring.[1] In fact, several five-membered heteroatomic diazo compounds and azides have been previously shown to undergo thermal ring-opening fragmentation.[1,2] As for 2-azido (or -nitreno) thiophenes definitive evidence is lacking. In the course of our previous study of the chemistry of azidothiophenes we have obtained some proof that the rather unstable 2-azidothiophenes may suffer ring-cleavage fragmentation.[3] Moreover, the reported conversion of the Schiff's bases (**1**) of 2-nitrothiophene-3-carbaldehyde into pyrroles (**2**) in the presence of hot triethyl phosphite (TEP) possibly involves ring-opening of a nitrene intermediate followed by ring closure of the resulting enethione (**3**)[4] (Scheme 1).



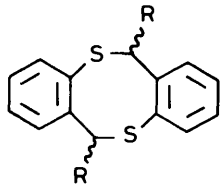
(1) (3) (2)

Scheme 1.

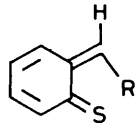
A similar mechanism apparently occurs also in related reactions of the Schiff's bases of 2-nitrobenzo[*b*]thiophene-3-carbaldehyde with TEP.[5] However, intermediacy of phosphorus intermediates rather than nitrenes is plausible in these reactions. Here we report our findings from a study of the mild thermal decomposition of 2-azidobenzo[*b*]thiophene (**4**) in the presence of various alkenes. This study provides the first definite example of smooth ring-opening by a 2-nitreno substituted thiophene ring.[6]



(4)



(5) **a**; R = CN
b; R = H

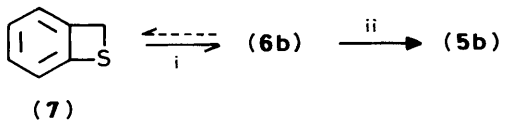


(6) **a**; R = CN
b; R = H

Results and Discussion

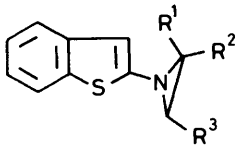
Thermal decomposition of 2-azidobenzo[*b*]thiophene (**4**) in benzene at 60 °C for *ca.* 10 h [until t.l.c. showed the disappearance of the starting material (**4**)] gave mainly an unresolved mixture of two isomeric compounds (I) and (**II**), which were thought to be the *E*- and *Z*-isomers of the dibenzo[*bf*][1,5]dithiocine-6,12-dicarbonitrile (**5a**). The i.r. spectrum showed CN stretching absorption bands at *ca.* 2 260 and 2 250 cm^{-1} and the mass spectrum showed predominant fragmentation ions at *m/z* 294 ($C_{16}H_{10}N_2S_2$), 261, and 229. The ^1H n.m.r. spectrum showed a complex pattern at δ 7.7—7.5 (8 ArH), two 1:1 singlets at δ 6.68 and 6.65, and two 1:1 singlets at δ 6.25 and 6.15, in the ratio of *ca.* 40:60 respectively, corresponding to two aliphatic protons.

These results suggested that the azide (**4**) should undergo thermal ring-cleavage fragmentation to give the *ortho*-quinoidal enethione intermediate (**6a**), from which the cyclodimers (**I**) and (**II**) might have arisen. In fact, Meier and co-workers[7] had previously shown that the enethione (**6b**), resulting from thermal valence isomerisation of benzothiete (**7**), undergoes cyclodimerization to afford the parent dithiocine (**5b**) (Scheme 2). In the presence of alkene or alkyne dienophiles such cyclodimerization can be essentially suppressed in favour of cycloadditions, leading to the formation of thiochromans and

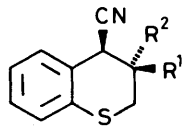


Scheme 2. *Reagents and conditions:* i, 110 °C, Toluene; ii, +(**6b**)

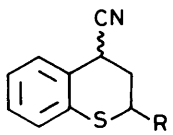
thiochromenes.[7] In the light of Meier's findings we were prompted to investigate the thermal decomposition of the azide (**4**) in the presence of a number of electron-rich and electron-poor alkenes. Thermolysis of the azide (**4**) in neat propene or hex-1-ene at 45 °C, after column chromatography, gave *trans*-3-methyl (**9a**) and *trans*-3-butylthiochroman-4-carbonitrile (**9b**)



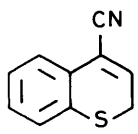
(**8**) **a**; $R^1 = R^2 = H$, $R^3 = Me$
b; $R^1 = R^2 = H$, $R^3 = Bu$
c; $R^1 = R^2 = Me$, $R^3 = H$
d; $R^1 = R^2 = H$, $R^3 = Cl$
e; $R^1 = R^2 = H$, $R^3 = CO_2Me$
f; $R^1 = R^2 = H$, $R^3 = CN$
g; $R^1 = R^2 = R^3 = H$
h; $R^1 = H$, $R^2 = R^3 = Me$ (*trans*)
i; $R^1 = H$, $R^2 = R^3 = Me$ (*cis*)
l; $R^1 = H$, $R^2, R^3 = -(CH_2)_4-$



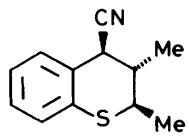
(**9**) **a**; $R^1 = H$, $R^2 = Me$
b; $R^1 = H$, $R^2 = Bu$
c; $R^1 = R^2 = Me$
d; $R^1 = H$, $R^2 = Cl$
e; $R^1 = H$, $R^2 = CO_2Me$
f; $R^1 = R^2 = CN$
g; $R^1 = R^2 = H$



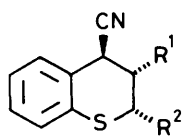
(**10**) **a**; R = Me
b; R = Bu



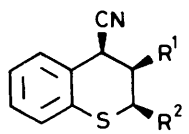
(**11**)



(**12**)



(**13**) **a**; $R^1 = R^2 = Me$
b; $R^1, R^2 = -(CH_2)_4-$



(**14**) **a**; $R^1 = R^2 = Me$
b; $R^1, R^2 = -(CH_2)_4-$

respectively in 63—68% yield in addition to minor amounts of the regioisomeric 2-methyl (**10a**) or 2-butylthiochroman-4-carbonitrile (**10b**) and the aziridines (**8a,b**) (Table 1). Under the same conditions the azide (**4**) in 2-methylpropene afforded 3,3-dimethylthiochroman-4-carbonitrile (**9c**) (65%) together with a mixture of the cyclodimers (**I**) and (**II**) (*ca.* 14%), whereas *trans*-3-chlorothiochroman-4-carbonitrile (**9d**) and the benzothiopyran-4-carbonitrile (**11**) (64 and 29% respectively) were the only identifiable products from the decomposition of (**4**) in chloroethylene (Table 1). Compound (**11**) probably resulted

Table 1. Product yields[a] (%) for the thermal reaction of the azide (**4**) with alkenes at 45 °C

Alkene	Aziridine	Thiochroman
Propene	(**8a**) (18)	(**9a**) (63) + (**10a**) (13)
Hex-1-ene	(**8b**) (13)	(**9b**) (68) + (**10b**) (7)
2-Methylpropene		(**9c**) (65)[b]
cis-But-2-ene	(**8i**) (9)	(**13a**) (38) + (**14a**) (39)
trans-But-2-ene	(**8h**) (7)	(**12**) (73)
Cyclohexene	(**8l**) (12)	(**13b**) (32) + (**14b**) (33)
Chloroethylene		(**9d**) (64)[c]
Acylonitrile[d]	(**8f**) (50)	(**9f**) (50)
Methyl acrylate[d]	(**8e**) (65)	(**9e**) (27)
Methyl acrylate[e]	(**8e**) (61)	(**9e**) (35)

[a] Isolated yields based on starting azide (**4**). [b] A mixture of the cyclodimers (**I**) and (**II**) was also obtained in 14% overall yield. [c] The benzothiopyran (**11**) (29%) was also obtained. [d] Reaction carried out at 60 °C. [e] Reaction carried out at 80 °C.

from facile *trans*-dehydrohalogenation of *cis*-3-chlorothiochroman-4-carbonitrile (**9**; $R^1 = Cl$, $R^2 = H$), initially produced in competition with the *trans*-isomer (**9d**). We could obtain no evidence of any formation of the *cis*-isomer (**9**; $R^1 = Cl$, $R^2 = H$) but a control experiment showed that the *trans*-isomer (**9d**) is quite stable under the reaction conditions.

No aziridine (**8c,d**) could be obtained with either 2-methylpropene or chloroethylene.

In the presence of *trans*-but-2-ene the azide (**4**) gave *t*-2,*t*-3-dimethylthiochroman-4-carbonitrile (**12**) in fairly good yield in addition to small amounts of the *trans*-dimethylaziridine (**8h**), whereas with *cis*-but-2-ene *c*-2,*t*-3-dimethyl (**13a**) and *c*-2,*c*-3-dimethylthiochroman-4-carbonitrile (**14a**) were produced as major products to the same extent together with minor amounts of the *cis*-dimethylaziridine (**8i**) (Table 1).

Thus, the formation of the aziridines (**8h,i**) and the thiochromans (**12**), (**13a**), and (**14a**) occurs with retention of the configuration of the starting alkene. Thermolysis of the azide (**4**) in cyclohexene led to results comparable to those obtained with *cis*-but-2-ene (Table 1). Thermal decomposition of the azide (**4**) carried out in the presence of electron-poor olefins such as methyl acrylate and acrylonitrile gave results markedly different from those above obtained with electron-rich olefins. Methyl acrylate and acrylonitrile gave considerable quantities of the aziridines (**8e,f**): thus reaction of the azide (**4**) with methyl acrylate at 60 °C gave the aziridine (**8e**) in 65% yield as well as *t*-3-methoxycarbonylthiochroman-4-carbonitrile (**9e**) (Table 1). Under the same conditions, the azide (**4**) with acrylonitrile afforded a 1:1 mixture of the aziridine (**8f**) and *trans*-thiochroman-3,4-dicarbonitrile (**9f**) in a quantitative yield (Table 1). Structural assignments for the aziridines (**8**) and the thiochromans (**9**), (**10**), (**12**)—(**14**)[7c,8] were made on the basis of i.r., n.m.r., and mass spectral evidence. In particular, the regiochemistry of the compounds (**9a**—**f**) and (**10a,b**) was readily established on the basis of the 4-H splitting pattern in the ^1H n.m.r. spectra. This proton occurred as a doublet with the compounds (**9a,b,d,e,f**), as a singlet with compound (**9c**), and as a triplet with thiochromans (**10a,b**). The *trans*-configuration of the 3,4-disubstituted thiochromans (**9a,b,d,e,f**) was assigned on the basis of the 3-H, 4-H coupling constant for each which occured in the expected range, J 6—8.7 Hz, for vicinal *trans*-coupling. Similarly, configurational assignments for the thiochromans (**12**)—(**14**) came from the observed values of the coupling constants for vicinal 2-H and 3-H, and 3-H and 4-H.[9] However ^1H n.m.r. spectral data did not allow assignment of the stereochemistry for the 2,4-disubstituted thiochromans (**10a,b**) to be made with confidence.

Table 2. Product yields[a] (%) for the thermal reaction of the azide (**4**) with alkenes at room temperature

Alkene	Aziridine	Thiochroman
Ethylene	(**8g**) (77)	(**9g**) (19)
trans-But-2-ene	(**8h**) (34)	(**12**) (51)
Acrylonitrile	(**8f**) (85)	(**9f**) (10)
Methyl acrylate	(**8e**) (90)	(**9e**) (4)

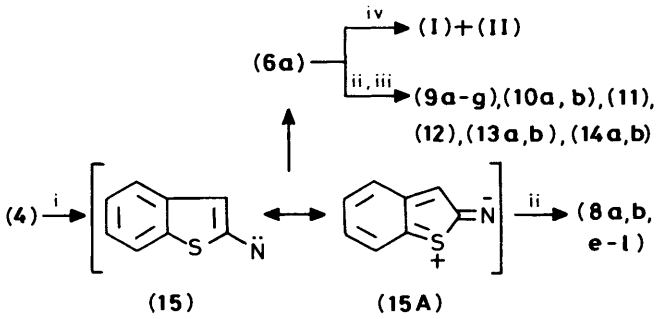
[a] Isolated yields based on starting azide (**4**).

Table 3. First-order rate constants for the decomposition of the azide (**4**) at 60 °C in various solvents

Solvent	$k \times 10^5/s^{-1}$
Cyclohexane	8.1
Cyclohexene	7.9
Benzene	8.4
Acetonitrile	11.6
Acrylonitrile	15.6

A decrease in the reaction temperature can favour the formation of aziridines at the expense of the corresponding thiochromans. This appears to be suggested by our observation that a remarkable increase in the yield of the aziridines (**8e,f,h**) and a concomitant decrease in the yield of the thiochromans (**9e,f**) and (**12**) occurred when the azide (**4**) was allowed to react with methyl acrylate, acrylonitrile, or *trans*-but-2-ene at room temperature (Table 2). Under these conditions the azide (**4**) with ethylene gave essentially the corresponding aziridine (**8g**) (77%), which was accompanied by lesser amounts of thiochroman-4-carbonitrile (**9g**) (Table 2). Conversely, an enhancement of the thiochroman (**9e**) yield at the expense of the aziridine (**8e**) was observed when the azide (**4**) was allowed to react with methyl acrylate at 80 °C rather than 60 °C (Table 1). From the general evidence provided by the findings reported in Tables 1 and 2 it is clear that a progressive decrease in the nucleophilic character of the alkene employed brings about an enhancement of the resulting aziridines and a concomitant decrease in the corresponding thiochromans.

No triazolines, which might have resulted from cycloaddition of the azide (**4**) with the alkene present,[10] were detected although they might be expected to survive our very mild reaction conditions; they are known, however, to afford aziridines under thermal fragmentation.[10a,11] From this evidence it is inferred that a nitrene rather than a triazoline is the intermediate leading to aziridine (**8**) formation. The former are known to add to C=C double bonds to give aziridines, although these reactions are not generally performed by arylnitrenes.[2,12–14] Kinetic evidence leads to the same conclusion. The rate of disappearance of the azide (**4**) in benzene, cyclohexene, or acrylonitrile at 60 °C was first-order. The rate was essentially the same in cyclohexane, cyclohexene, and benzene, but accelerated in acetonitrile and roughly doubled in acrylonitrile (Table 3). Despite the observed dependence of the rate upon the solvent employed, which remains somewhat unclear at this stage, kinetic data seem to be consistent with the general occurrence of a discrete nitrene resulting from the azide (**4**) by unimolecular loss of nitrogen. Thus, we suggest that the initially formed singlet 2-nitrenobenzothiophene (**15**) is primarily responsible for the products observed in the thermal reactions of 2-azidobenzothiophene (**4**). In the presence of the appropriate alkene the singlet nitrene (**15**) would afford the aziridines (**8a,b,e—l**) and/or would undergo ring-opening reaction to give the enethione (**6a**). This intermediate (**6a**) could then undergo cyclodimerization and/or cycloaddition reaction



Scheme 3. *Reagents and conditions:* i, 25—80 °C, $-N_2$; ii, propene, hex-1-ene, methyl acrylate, acrylonitrile, ethylene, *cis*-but-2-ene, *trans*-but-2-ene, or cyclohexene; iii, 2-methylpropene or chloroethylene; iv, benzene or 2-methylpropene, + (**6a**)

with the alkene present leading to the thiochromans (**9a—g**), (**10a,b**), (**12**), (**13a,b**), and (**14a,b**) and the benzothiopyran (**11**) (Scheme 3). An increase in the reaction temperature would favour a ring-opening reaction of the nitrene (**15**), whereas a decrease in the nucleophilic character of the alkene employed would favour trapping of the nitrene itself, which is consistent with the possible intervention of a singlet (and nucleophilic) species rather than a triplet one. In fact, the reactivity of a triplet nitrene is expected to remain largely unaffected by variation in the electron density of the substrate alkene. The observed stereospecificity of the addition to *cis*- and *trans*-but-2-ene is also consistent with the involvement of a singlet species.[14] Further, our general failure to observe any product formally ascribable to a triplet nitrene,[2] while providing additional support for the suggested intermediacy of a singlet nitrene, also suggests that the occurrence of a triplet species is essentially disallowed, at least under our reaction condition. In principle, an alternative route leading to the nitrene (**15**) might be envisaged. This could involve unimolecular ring-cleavage fragmentation of the azide (**4**) followed by ring-closure of the resulting enethione (**6a**). If this were the case, cyclodimerization of the enethione intermediate (**6a**) might occur in competition with ring-closure to give the nitrene (**15**). However, the generally observed formation of the aziridines (**8a,b,e—l**) with concomitant suppression of the cyclodimerization processes should lead to the conclusion that ring-closure of the enethione (**6a**) would be much more feasible. This conclusion would be in contrast with our results obtained from the thermolyses of the azide (**4**) in 2-methylpropene and particularly benzene, in which cases cyclodimerization was found to occur effectively. Moreover, our observation that decomposition of the azide (**4**) at room temperature in methyl acrylate–*trans*-but-2-ene (1:1) leads to results virtually identical with those obtained with neat methyl acrylate (see Experimental section) is not consistent with initial occurrence of the enethione (**6a**). If the enethione (**6a**) had been initially formed, effective trapping by the but-2-ene dienophile should have been observed.

The nucleophilic character apparently exhibited by 2-nitrenobenzo[*b*]thiophene (**15**) can be envisaged, in valence bond terms, as arising from a resonance contribution by the zwitterionic structure (**15A**). This results in stabilization of the nitrene itself and thence in unusually easy decomposition of its azide precursor compared with that of aryl azides, which generally require high temperatures (130—180 °C), unless certain types of *ortho*-substituents are present.[2]

The cycloadditions undergone by the enethione (**6a**) deserve some comments. Our findings with terminal electron-rich and -poor olefins indicate that these cycloadditions proceed with high regioselectivity, generally leading to exclusive (or

preferential) formation of those cycloadducts which bear the olefin substituent(s) in the β-position to the sulphur.

The results obtained with *cis*- and *trans*-butene suggest that these reactions also proceed with *cis*-stereospecificity, at least in these two instances. The observed regioselectivity and stereospecificity is not consistent with Meier's findings from related cycloadditions of the parent enethione (**6b**). In these, the orientation appears to be controlled by the polar nature of the olefin substituents. In fact, electron-releasing substituents have preference in the resulting cycloadducts for the α-position to the sulphur, whereas a preference for the β-position is observed with the electron-withdrawing substituents. Furthermore, non-stereospecific addition occurs with *Z*-olefins. These observations were explained assuming that the enethione (**6b**) might behave like a weakly polar diradical, which would add to olefin double bonds to give 1,6-diradical intermediates.[7c]

Although further study is required, at this stage we suggest that Diels–Alder reaction of the enethione intermediate (**6a**) might proceed in a concerted fashion through that transition state, in which the build up of diradical character, due to unequal bond formation, is best stabilized by the substituents. With terminal alkenes best stabilization would be expected with that diradical-like transition state, in which more advanced radical bond formation between the sulphur of (**6a**) and the terminal carbon occurs.

Finally, the observed *trans*-stereochemistry of the cycloadducts (**9a**,**b**,**d**—**f**) and (**12**) at first sight might suggest general preference for *endo*-addition.[15] However, *exo*- and *endo*-addition products are apparently formed to the same extent with *cis*-but-2-ene and cyclohexene. No explanation of such a stereochemical trend is attempted, since the present evidence does not exclude the possibility of equilibration of (**6a**) with its geometrical *E*-isomer.

Experimental

Materials.—Gaseous olefins were purchased from Matheson, except ethylene and chloroethylene which were available from Fluka AG. Liquid olefins were purchased from Aldrich-Chemie. Chromatography was carried out on Merck silica gel (0.040—0.063 mm) particle size.

Spectra.—I.r. spectra were recorded with a Perkin-Elmer 257 instrument. ^{1}H N.m.r. data were obtained with a Varian EM 360 L 60 MHz or Gemini 200 MHz instruments for solutions in $CDCl_3$ using TMS as internal standard. Mass spectra were recorded on a VG Analytical 7070 E Organic Mass Spectrometer.

Preparation of 2-Azidobenzo[b]*thiophene* (**4**).—This azide (**4**) was prepared in 75% yield by a slight modification of our previously reported method.[16] A solution of benzo[*b*]thiophene (0.05 mol) in dry diethyl ether (20 ml) was added with stirring under nitrogen, at room temperature, to butyl-lithium (1.6M in n-hexane; 35 ml). The reaction mixture was stirred and refluxed for 1 h, after which it was cooled to −70 °C and added dropwise to a solution of tosyl azide (0.055 mol) in ether (100 ml). After the addition was complete the resulting mixture was stirred for 5 h at −70 °C and then allowed to reach 0 °C. The yellow triazene salt which had formed was rapidly filtered off and washed several times with dry ether. This material was suspended in dry ether (150 ml) and treated at 0 °C with a solution of tetrasodium pyrophosphate decahydrate (0.05 mol) in water (250 ml). After a few minutes a pink solid was formed and this was filtered off, suspended in hexane (60 ml) and stirred at room temperature overnight. The hexane layer was filtered and the excess of solvent eliminated by suction to give a residue which was chromatographed on a Florisil column using light petroleum (b.p. 30—60 °C) as eluant. Chromatography gave the title azide (**4**) (0.037 mol, 75%), m.p. 38—40 °C (lit.,[16] 38—40 °C).

Decomposition of 2-Azidobenzo[b]*thiophene* (**4**) *in Benzene at* 60 °C.—A solution of the azide (**4**) (0.35 g, 2 mmol) in benzene (4 ml) was heated at 60 °C for 10 h. On cooling, a white solid mixture of the cyclodimers (**I**) and (**II**) separated (0.28 g, 95%). This, after being filtered off and washed with diethyl ether, had m.p. 193—197 °C (decomp.); $\nu_{max.}$ 3 080, 2 930, 2 260 (CN), 2 250 (CN), and 775 cm^{-1}; δ_H(200 MHz; $CDCl_3$) 7.7—7.5 (8 H, br m), [6.68 (s) and 6.65 (s) (0.8 H)], and [6.25 (s) and 6.15 (s) (1.2 H)]; *m*/*z* 294 (M^+, 64), 261 (64, M − SH), and 229 (100) (Found: M^+, 294.028 67. $C_{16}H_{10}N_2S_2$ requires M, 294.028 54).

Reactions of 2-Azidobenzo[b]*thiophene* (**4**) *with Alkenes: General Procedure.*—A solution of the azide (**4**) (0.35 g, 2 mmol) in the appropriate alkene (4 ml) was allowed to react in a sealed tube at 45 °C for *ca.* 50 h [until t.l.c. showed the absence of the starting azide (**4**)], unless stated otherwise. The residue obtained after careful evaporation of the excess of olefin was chromatographed on a silica gel column using hexane with increasing amounts of diethyl ether (up to 100%) as eluant.

Reaction of the azide (**4**) *with ethylene at* 25 °C. This reaction was carried out following the general procedure except that the reaction mixture was set aside at room temperature for *ca.* 2 weeks. Chromatography gave: (i) 1-(2-*benzo*[b]*thienyl*)*aziridine* (**8g**) (0.20 g, 77%), m.p. 32—34 °C; $\nu_{max.}$(oil) 3 070, 3 000, 1 285, and 750 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 7.5—7.2 (4 H, br m), 6.5 (1 H, s), and 2.2 (4 H, s, 2- and 3-CH_2); *m*/*z* 175 (M^+, 100), 160 (67, M − 15), 147 (37), 120 (11), and 89 (15) (Found: C, 68.5; H, 5.1; N, 8.05; S, 18.25. $C_{10}H_9NS$ requires C, 68.5; H, 5.1; N, 8.0; S, 18.3%); and (ii) *thiochroman*-4-*carbonitrile* (**9g**) (0.05 g, 19%) as an oil; $\nu_{max.}$ 3 050 and 2 950, 2 250 (CN), and 750 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 7.1 (4 H, br m), 4.3 (1 H, t, *J* 5.0 Hz, 4-CH), 3.1 (2 H, m, 2-CH_2), and 2.9 (2 H, m, 3-CH_2); *m*/*z* 175 (M^+, 100), 160 (28, M − 15), 147 (48), 129 (25), 120 (11), and 84 (11) (Found: C, 68.55; H, 5.1; N, 7.95; S, 18.3. $C_{10}H_9NS$ requires C, 68.55; H, 5.1; N, 8.0; S, 18.3%).

Reaction of the azide (**4**) *with propene.* Chromatography afforded (i) 1-(2-*benzo*[b]*thienyl*)-2-*methylaziridine* (**8a**) (0.07 g, 18%) as a pale yellow oil; $\nu_{max.}$ 3 080, 3 000, 2 940, 1 285, and 750 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 7.5—7.2 (4 H, br m), 6.5 (1 H, s), 2.2 (3 H, br m, 2-CH and 3-CH_2), and 1.4 (3 H, d, *J* 5.0 Hz, Me); *m*/*z* 189 (M^+, 100) 174 (10, M − 15), 160 (69), 147 (47), and 120 (25) (Found: M^+, 189.060 92. $C_{11}H_{11}NS$ requires M, 189.061 22); (ii) trans-3-*methylthiochroman*-4-*carbonitrile* (**9a**) (0.24 g, 63%) as a solid, m.p. 53—55 °C; $\nu_{max.}$ 3 080, 2 990, 2 940, 2 255 (CN), and 755 cm^{-1}; δ_H(200 MHz; $CDCl_3$) 7.4—7.2 (4 H, br m), 3.7 (1 H, d, *J* 7.4 Hz, 4-CH), 3.2 (1 H, dd, *J* 12.0 and 3.4 Hz) and 2.8 (1 H, dd, *J* 12.0 and 7.4 Hz) (2-CH_2), 2.5 (1 H, br m, 3-CH), and 1.3 (3 H, d, *J* 6.0 Hz, Me); *m*/*z* 189 (M^+, 100), 174 (22, M − Me), 160 (22), and 147 (52) (Found: C, 69.85; H, 5.85; N, 7.4; S, 16.85. $C_{11}H_{11}NS$ requires C, 69.8; H, 5.85; N, 7.4; S, 16.9%); and (iii) 2-*methylthiochroman*-4-*carbonitrile* (**10a**) (0.05 g, 13%); $\nu_{max.}$ 3 080, 2 990, 2 940, 2 250 (CN), and 755 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 7.7—7.5 (4 H, br m), 4.1 (1 H, br m), 2.9 (1 H, m), and 2.4 (2 H, br m); *m*/*z* 189 (M^+, 100), 174 (22, M − CH_3), 160 (22), and 147 (52) (Found: M^+, 189.060 98. $C_{11}H_{11}NS$ requires M, 189.061 22).

Reaction of the azide (**4**) *with hex*-1-*ene.* Chromatography gave (i) 2-*butyl*-1-(2-*benzo*[b]*thienyl*)*aziridine* (**8b**) (0.06 g, 13%), as a colourless oil; $\nu_{max.}$ 3 085, 2 970, 2 940, 2 880, 1 270, and 745 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 7.5—7.2 (4 H, br m), 6.5 (1 H, s), 2.2 (3 H, br m), 1.5 (6 H, br s), and 0.8 (3 H, br s); *m*/*z* 231 (M^+, 100), 202 (25, M − CH_3CH_2), 188 (20), 175 (100), 161 (88), and 149 (48) (Found: M^+, 231.108 89. $C_{14}H_{17}NS$ requires M, 231.108 17); (ii) trans-3-*butylthiochroman*-4-*carbonitrile* (**9b**)

(0.32 g, 68%), as an oil; $\nu_{max.}$ 3 085, 2 970, 2 940, 2 880, 2 250 (CN), and 750 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 7.5—7.2 (4 H, br m), 3.7 (1 H, d, *J* 6.0 Hz, 4-CH), 3.1 (2 H, m, 2-CH_2), 2.3 (1 H, br m, 3-CH), 1.5 (6 H, br s), and 0.8 (3 H, br s); *m/z* 231 (M^+, 100), 174 [44, $M - CH_3(CH_2)_3$], 150 (28), and 148 (34) (Found: C, 72.6; H, 7.35; N, 6.05; S, 13.85. $C_{14}H_{17}NS$ requires C, 72.7; H, 7.4; N, 6.1; S, 13.9%); and (iii) 2-*butylthiochroman*-4-*carbonitrile* (**10b**) (0.03 g, 7%) as an oil; $\nu_{max.}$ 3 085, 2 970, 2 940, and 2 280, 2 250 (CN), and 750 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 7.5—7.2 (4 H, br m), 4.0 (1 H, t, *J* 4.5 Hz, 4-CH), 3.4 (1 H, m, 2-CH), 2.3 (2 H, m, 3-CH_2), 1.5 (6 H, br s), and 0.8 (3 H, br s); *m/z* 231 (M^+, 100), 174 (42, $M - C_4H_9$), 150 (30), and 148 (36) (Found: M^+, 231.108 62. $C_{14}H_{17}NS$ requires *M*, 231.108 17).

Reaction of the azide (**4**) *with* 2-*methylpropene*. Chromatographic separation gave (i) 3,3-*dimethylthiochroman*-4-*carbonitrile* (**9c**) (0.26 g, 65%), as an oil; $\nu_{max.}$ 3 080, 2 980, 2 960, 2 280 (CN), and 750 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 7.1 (4 H, br m), 3.6 (1 H, s, 4-CH), 2.8(2 H, AB q, *J* 13.0 Hz, 2-CH_2), and 1.2 (6 H, s); *m/z* 203 (M^+, 100), 188 (24, $M - CH_3$), 160 (30), 148 (32), and 147 (30) (Found: C, 70.85; H, 6.35; N, 6.85; S, 15.75. $C_{12}H_{13}NS$ requires C, 70.9; H, 6.4; N, 6.9; S, 15.8%); and (ii) a mixture of the cyclodimers (**I**) and (**II**) (0.04 g, 14%), m.p. 193—197 °C (decomp.), identical in all respects with that obtained from the decomposition of the azide (**4**) in benzene.

Reaction of the azide (**4**) *with* cis-*but*-2-*ene*. Chromatography gave (i) 1-(2-*benzo*[b]*thienyl*)-cis-2,3-*dimethylaziridine* (**8i**) (0.04 g, 9%), m.p. 72—73 °C; $\nu_{max.}$ 3 080, 3 020, 2 980, 2 960, 1 270, and 750 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 7.5—7.2 (4 H, br m), 6.5 (1 H, s), 2.4 (2 H, m), and 1.9 (6 H, d, *J* 5.0 Hz); *m/z* 203 (M^+, 100), 188 (33, $M - CH_3$), 174 (53), and 161 (76) (Found: M^+, 203.076 54. $C_{12}H_{13}NS$ requires *M*, 203.076 87). This aziridine (**8i**) was shown by t.l.c. (SiO_2) to be exclusive of the isomeric aziridine (**8h**); (*vide infra*); (ii) cis,cis-2,3-*dimethylthiochroman*-4-*carbonitrile* (**14a**) (0.16 g, 39%), m.p. 76—78 °C; $\nu_{max.}$ 3 060, 2 970, 2 930, 2 230 (CN), and 750 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 7.5—7.2 (4 H, br m), 4.2 (1 H, d, *J* 3.8 Hz, 4-H), 3.6 (1 H, m, 2-CH), 2.5 (1 H, m, 3-CH), 1.4 (3 H, d, *J* 7.0 Hz), and 1.1 (3 H, d, 7.0 Hz); *m/z* 203 (M^+, 100), 188 (32, $M - CH_3$), 174 (50), 161 (55), and 149 (17) (Found: C, 70.85; H, 6.4; N, 6.85; S, 15.75. $C_{12}H_{13}NS$ requires C, 70.9; H, 6.4; N, 6.9; S, 15.8%); and (iii) cis,trans-2,3-*dimethylthiochroman*-4-*carbonitrile* (**13a**) (0.15 g, 38%) as an oil; $\nu_{max.}$ 3 060, 2 970, 2 930, 2 230 (CN), and 750 cm^{-1}; δ_H(200 MHz; $CDCl_3$) 7.5—7.1 (4 H, br s), 3.8 (1 H, d, *J* 4.5 Hz, 4-CH), 3.6 (1 H, m, 2-CH), 2.45 (1 H, m, 3-CH), 1.3 (3 H, d, *J* 7.0 Hz), and 1.1 (3 H, d, *J* 7.0 Hz); *m/z* 203 (M^+, 100), 188 (29, $M - CH_3$) 174 (43), 161 (21), and 149 (34) (Found: C, 70.85; H, 6.4; N, 6.9; S, 15.7. $C_{12}H_{13}NS$ requires C, 70.9; H, 6.4; N, 6.9; S, 15.8%).

Reaction of the azide (**4**) *with* trans-*but*-2-*ene*. Chromatographic separation gave (i) trans,trans-2,3-*dimethylthiochroman*-4-*carbonitrile* (**12**) (0.33 g, 73%), m.p. 67—68 °C; $\nu_{max.}$ 3 060, 2 970, 2 920, 2 240 (CN), and 750 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 7.5—7.2 (4 H, br m), 3.6 (1 H, d, *J* 9.5 Hz, 4-CH), 3.0 (1 H, m, 2-CH), 2.1 (1 H, m, 3-CH), 1.95 (3 H, d, *J* 6.8 Hz), and 1.9 (3 H, d, *J* 6.8 Hz); *m/z* 203 (M^+, 100), 188 (44, $M - CH_3$), 174 (30), 161 (15), and 149 (30) (Found: C, 70.85; H, 6.4; N, 6.85; S, 15.75. $C_{12}H_{13}NS$ requires C, 70.9; H, 6.4; N, 6.9; S, 15.8%); and (ii) 1-(2-*benzo*[b]*thienyl*)-trans-2,3-*dimethylaziridine* (**8h**) (0.03 g, 7%) as an oil; $\nu_{max.}$ 3 060, 2 960, 2 940, 1 270, and 750 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 7.5—7.2 (4 H, br m), 6.5 (1 H, s), 2.2 (2 H, m), and 1.90 (3 H, d, *J* 4.5 Hz); *m/z* 203 (M^+, 100), 188 (35, $M - CH_3$), 174 (53), and 161 (72) (Found: M^+, 203.076 62. $C_{12}H_{13}NS$ requires *M*, 203.076 87). This aziridine (**8h**) was shown by t.l.c. (SiO_2) to be exclusive of the isomeric aziridine (**8i**).

The same reaction carried out at 25 °C for *ca.* 2 weeks gave the thiochroman (**12**) (51%) and the aziridine (**8h**) (34%).

Reaction of the azide (**4**) *with cyclohexene*. Chromatography gave (i) 7-(2-*benzo*[b]*thienyl*)-7-*azabicyclo*[4.1.0]*heptane* (**8l**) (0.07 g, 12%), m.p. 109—110 °C; $\nu_{max.}$ 3 085, 2 950, 2 880, 1 260, and 745 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 7.4—7.1 (4 H, br m), 6.4 (1 H, s), 2.4 (2 H, br s), 1.9 (4 H, br s), and 1.3 (4 H, br s); *m/z* 229 (M^+, 100), 188 (59), 186 (60), 175 (100), 160 (50), and 149 (99) (Found: C, 73.1; H, 6.6; N, 5.8; S, 13.9. $C_{14}H_{15}NS$ requires C, 73.4; H, 6.5; N, 6.1; S, 14.0%); (ii) cis-1,2,3,4,4a,9a-*hexahydrothioxanthene*-*cis*-9-*carbonitrile* (**14b**) (0.15 g, 33%), m.p. 88—89 °C; $\nu_{max.}$ 3 080, 3 060, 2 950, and 2 870, 2 250 (CN), and 755 cm^{-1}; δ_H(60 MHz; $CDCl_3$), 7.6—7.1 (4 H, br m), 4.0 (1 H, d, *J* 3.8 Hz, 9-H), 3.8 (1 H, br m, 4a-H), 2.4 (1 H, br m, 9a-H), and 1.7 (8 H, br m); *m/z* 229 (M^+, 100), 200 (10, $M - 29$), 186 (14), 172 (12), 160 (7), 149 (27), and 81 (36) (Found: C, 73.4; H, 6.45; N, 6.05; S, 13.8. $C_{14}H_{15}NS$ requires C, 73.4; H, 6.5; N, 6.1; S, 14.0%); and (iii) cis-1,2,3,4,4a,9a-*hexahydrothioxanthene*-trans-9-*carbonitrile* (**13b**) (0.14 g, 32%) as an oil; $\nu_{max.}$ 3 080, 3 060, 2 950, 2 870, 2 250 (CN), and 755 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 7.1 (4 H, br m), 3.6 (1 H, br m, 4a-H), 3.4 (1 H, d, *J* 4.2 Hz, 9-H), 2.4 (1 H, br m, 9a-H), 1.8 (4 H, br m), and 1.4 (4 H, br m); *m/z* 229 (M^+, 100), 200 (10, $M - 29$), 186 (14), 172 (12), 160 (7), 149 (27), and 81 (36) (Found: C, 73.35; H, 6.5; N, 6.05; S, 13.9. $C_{14}H_{15}NS$ requires C, 73.4; H, 6.5; N, 6.1; S, 13.8%).

Reaction of the azide (**4**) *with chloroethylene*. Chromatography gave (i) 2H-*benzothiopyran*-4-*carbonitrile* (**11**) (0.1 g, 29%), m.p. 44—46 °C; $\nu_{max.}$ 3 080, 2 870, 2 240 (CN), and 765 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 7.4—7.1 (4 H, br m), 6.7 (1 H, t, *J* 5.5 Hz, 3-H), and 3.2 (2 H, d, *J* 5.5 Hz, 2-CH_2); *m/z* 173 (M^+, 80), 172 (100, $M - 1$), and 147 (12) (Found: C, 69.4; H, 4.0; N, 8.05; S, 18.35. $C_{10}H_7NS$ requires C, 69.4; H, 4.0; N, 8.1; S, 18.5%); and (ii) trans-3-*chlorothiochroman*-4-*carbonitrile* (**9d**) (0.27 g, 64%), m.p. 102—104 °C; $\nu_{max.}$ 3 080, 3 000, 2 930, 2 900, 2 250 (CN), and 755 cm^{-1}; δ_H(200 MHz; $CDCl_3$) 7.4—7.2 (4 H, br m), 4.6 (1 H, m, 3-CH), 4.25 (1 H, d, *J* 8.7 Hz, 4-CH), and 3.3 (2 H, m, 2-CH_2); *m/z* 209 (M^+, 100), 173 (98, M – HCl), 147 (64), and 120 (25) (Found: M^+, 209.006 19. $C_{10}H_8ClNS$ requires *M*, 209.006 60).

Reaction of the azide (**4**) *with acrylonitrile*. (a) At 25 °C for a week. Chromatographic separation gave (i) (2-*benzo*[b]*thienyl*)-*aziridine*-1-*carbonitrile* (**8f**) (0.34 g, 85%), m.p. 103—104 °C; $\nu_{max.}$ 3 080, 3 020, 2 940, and 2 270 cm^{-1} (CN); δ_H(60 MHz; $CDCl_3$) 7.4—7.2 (4 H, br m), 6.6 (1 H, s), and 2.7 (3 H, m); *m/z* 200 (M^+, 80), 172 (47, $M - 28$), 160 (100), 147 (45), 146 (48), and 121 (45) (Found: C, 66.1; H, 4.0; N, 13.95; S, 15.9. $C_{11}H_8N_2S$ requires C, 66.0; H, 4.0; N, 14.0; S, 16.0%); and (ii) *thiochroman*-trans-3,4-*dicarbonitrile* (**9f**) (0.04 g, 10%), m.p. 125—127 °C; $\nu_{max.}$ 2 930, 2 265, 2 255 (CN), and 760 cm^{-1}; δ_H(60 MHz; $CDCl_3$), 7.2 (4 H, br m), 4.3 (1 H, d, *J* 6.0 Hz, 4-CH), and 3.4 (3 H, m, 2-CH_2 and 3-CH); *m/z* 200 (M^+, 100), 173 (62, M – HCN), 147 (88), and 121 (43) (Found: C, 66.0; H, 4.0; N, 13.95; S, 15.9. $C_{11}H_8N_2S$ requires C, 66.0; H, 4.0; N, 14.0; S, 16.0%).

(b) At 60 °C for 6 h. Chromatography gave the aziridine (**8f**) (0.20 g, 50%) and the thiochroman (**9f**) (0.20 g, 50%).

Reaction of the azide (**4**) *with methylacrylate*. (a) At 25 °C for a week. Chromatography gave (i) *methyl* 1-(2-*benzo*[b]*thienyl*)-*aziridine*-2-*carboxylate* (**8e**) (0.41 g, 90%), m.p. 96—97 °C; $\nu_{max.}$ 3 080, 3 000, 2 960, 2 940, 1 570, 1 550 (CO_2CH_3), and 750 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 7.7—7.2 (4 H, br m), 6.6 (1 H, s), 3.7 (3 H, s), and 2.7 (3 H, m); *m/z* 233 (M^+, 100), 218 (2, $M - CH_3$), 191 (20), 174 (36), 160 (36), and 147 (45) (Found: C, 61.9 H, 4.7; N, 6.0; S, 13.65. $C_{12}H_{11}NO_2S$ requires C, 61.8; H, 4.7; N, 6.0; S, 13.7%); and (ii) *methyl* 4-*cyanothiochroman*-trans-3-*carboxylate* (**9e**) (0.02 g, 4%), m.p. 101—103 °C; $\nu_{max.}$ 3 080, 2 960, 2 930, 2 250 (CN), 1 750 (CO_2CH_3), and 760 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 7.2 (4 H, br m), 4.4 (1 H, d, *J* 6.0 Hz, 4-CH), 3.4 (3 H, s), and 3.3 (3 H, br m); *m/z* 233 (M^+, 100), 173 (100, $M - HCO_2CH_3$), and 147 (29) (Found: C, 61.8; H, 4.7; N, 5.95; S, 13.6. $C_{12}H_{11}NO_2S$ requires C, 61.8; H, 4.7; N, 6.0; S, 13.7%).

Identical yields of the aziridine (**8e**) and the thiochroman (**9e**) were essentially obtained when the decomposition of the azide (**4**) was carried out at 25 °C in a mixture of methyl acrylate and *trans*-but-2-ene (1:1).

(b) At 60 °C for 6 h. Chromatographic separation gave the aziridine (**8e**) (0.30 g, 65%) and the thiochroman-4-carbonitrile (**9e**) (0.14 g, 27%).

(c) At 80 °C for 5 h. Chromatography gave the aziridine (**8e**) (0.27 g, 61%) and the thiochroman-4-carbonitrile (0.18 g, 35%).

Rates of Decomposition of 2-Azidobenzo[b]*thiophene* (**4**).—A solution of the azide (**4**) (0.2 mmol) in benzene, cyclohexane, acetonitrile, cyclohexene, or acrylonitrile (10 ml) was allowed to react in a thermostatic bath at 60 °C. The rates of decomposition of the azide (**4**) were determined by i.r. spectroscopic measurement of the neat N_3 band (*ca.* 2 100 cm^{-1}) as a function of time. Results are summarized in Table 3.

Acknowledgements

This research was supported by CNR and 'Ministero della Pubblica Istruzione'.

References

1 T. L. Gilchrist, 'Ring-opening of Five-Membered Heteroaromatic Anions,' in 'Advances in Heterocyclic Chemistry,' eds. A. R. Katritzky and A. J. Boulton, Academic Press, New York, 1987, vol. 41, pp. 42—71.
2 P. A. S. Smith, 'Aryl and Heteroaryl Azides and Nitrenes,' in 'Azides and Nitrenes, Reactivity and Utility,' ed. E. F. V. Scriven, Academic Press, Orlando, 1984.
3 (*a*) S. Gronowitz, P. Spagnolo, and P. Zanirato, *J. Org. Chem.*, 1982, **47**, 3177; (*b*) P. Spagnolo, G. Zanardi, and P. Zanirato, *J. Chem. Soc., Perkin Trans. 1*, 1983, 2551.
4 V. M. Colburn, B. Iddon, H. Suschitzky, and P. T. Challengher, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1337.
5 K. E. Chippendale, B. Iddon, and H. Suschitzky, *J. Chem. Soc., Perkin Trans. 1*, 1973, 129.
6 For a preliminary account of this work see: P. Spagnolo and P. Zanirato, *J. Chem. Soc., Chem. Commun.*, 1985, 1441.
7 (*a*) E. Voigt and H. Meier, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 117; (*b*) K. Kanakarajan and H. Meier, *J. Org. Chem.*, 1983, **48**, 881; (*c*) H. Meier and H.-L. Eckes, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 1046.
8 S. W. Schneller, 'Thiochromanones and Related Compounds,' in 'Advances in Heterocyclic Chemistry,' eds. A. R. Katritzky and A. J. Boulton, Academic Press, London, 1975, vol. 18, pp. 59—96.
9 J. B. Lambert and F. R. Koeng, *Org. Magn. Reson.*, 1971, **3**, 389.
10 (*a*) P. K. Kadaba, B. Stanovnik, and M. Tisler, 'Δ^2-1,2,3-Triazolines,' in 'Advances in Heterocyclic Chemistry,' eds. A. R. Katritzky and A. J. Boulton, Academic Press, London, 1985, **37**, pp. 219—345; (*b*) A. Padwa, '1,3-Dipolar Cycloaddition Chemistry,' Wiley, New York, 1984, vol. 2; (*c*) T. Sheradsky, 'Azides as Synthetic Starting Materials,' in 'The Chemistry of the Azido Group,' ed. S. Patai, Interscience, London, 1971, pp. 359—361.
11 W. Lwowski, 'Acyl Azides and Nitrenes,' in ref. 2, pp. 210—215.
12 P. Scheiner, *Sel. Org. Transform.*, 1970, **1**, 32.
13 L. L. Muller and J. Hamer, '1,2-Cycloaddition Reactions,' Interscience, New York, 1967, pp. 5—43.
14 R. A. Abramovitch and S. R. Challand, *J. Chem. Soc., Chem. Commun.*, 1972, 1160.
15 J. March, 'Advanced Organic Chemistry,' J. Wiley and Sons, New York, 3rd edn., 1985, ch. 15, pp. 745—775.
16 P. Spagnolo and P. Zanirato, *J. Org. Chem.*, 1978, **43**, 3539.

Received 22nd April 1988; *Paper* 8/01589I