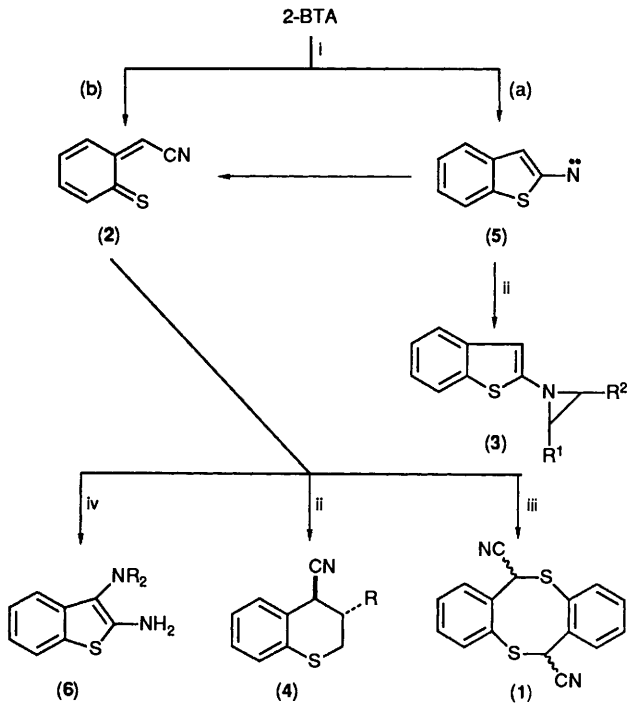
Thermal Reactivity of 2-Azido- and 3-Azido-benzo[*b*]thiophene with Alkenes

Maria Funicello and 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

Thermal decomposition of 2-azidobenzo[*b*]thiophene (2-BTA) in the presence of various (*E*)- and (*Z*)-alkenes, at room temperature, affords thiochroman-4-carbonitriles resulting from cycloaddition of an *ortho*-quinoidal enethione intermediate (**2**) to the olefin double bonds and/or 1-(2-benzothienyl)aziridines which generally occur in a non-stereospecific fashion. In one case, *i.e.* with diethyl fumarate, clear-cut spectroscopic and chemical evidence for the intermediacy of a triazoline adduct in the formation of the observed *trans*- and *cis*-aziridines has been obtained. In the presence of 1-pyrrolidinyl-cyclopentene or -cyclohexene the azide furnishes an isolated triazoline in quantitative yield, whereas with methyl (*E*)-3-(*N*-pyrrolidinylacrylate leads to methyl 1-(2-benzothienyl)triazole-4-carboxylate arising from an intermediate triazoline by readily occurring elimination of pyrrolidine. Results suggest that 2-BTA generally undergoes cycloaddition reactions to give triazoline adducts, from which aziridines can be eventually produced, in competition with unimolecular ring-cleavage fragmentation leading to the enethione (**2**) probably *via* concerted ring opening and nitrogen extrusion. Suitable support has been provided by the finding that 3-azidobenzo[*b*]thiophene (3-BTA) can exhibit analogous cycloaddition reactions with alkenes under the same reaction conditions. The present evidence contradicts our previous claim that a singlet nitrene should be an intermediate in the formation of aziridine and ring-cleavage products arising from decomposition of 2-BTA in the presence of alkenes.

Considerable attention has been devoted in recent years to the study of the thermal reactions of five-membered heteroaromatic azides, mostly due to the fact that these azides exhibit a chemical reactivity largely dependent upon the nature of the heteroaromatic ring and especially the position of the azido substituent.[1,2] The general trend that emerged from these studies indicated that the thermal reactivity of 3-azido-substituted heteroaromatics is not essentially dissimilar from that of aryl azides, whereas a peculiar reactivity is associated with the 2-azido-substituted ones which on thermolysis can undergo smooth ring-cleavage fragmentation. These ring-cleavage reactions are generally believed to involve the intermediacy of a singlet nitrene, but experimental evidence in favour of a nitrene mechanism is actually lacking.[2]

We previously showed[3] that mild thermal fragmentation of 2-azidobenzo[*b*]thiophene (2-BTA) in benzene smoothly afforded a mixture of geometrical isomers of the 6*H*,12*H*-dibenzo[*bf*'][1,5]dithiocine-6,12-dicarbonitrile (**1**) ascribable to cyclodimerization of an intermediate *ortho*-quinoidal enethione (**2**). In the presence of terminal electron-rich and -poor olefins at 25–60 °C 2-BTA gave 4-cyanothiochromans (**4**), arising from cycloaddition of the intermediate (**2**) to the alkenes, and aziridines (**3**). Our general failure to detect triazolines (and/or diagnostic products expected from their decomposition) led us to postulate a common singlet nitrene intermediate (**5**) in the formation of ring-cleavage and aziridine products (Scheme, path a). Our postulate was believed to be supported by *cis*-stereospecific aziridine formation from thermolysis of 2-BTA in (*Z*)- or (*E*)-but-2-ene. We subsequently showed[2b] that on thermolysis in diethyl- or dimethyl-amine both 2-BTA and 3-azidobenzothiophene (3-BTA) afforded the appropriate 2-amino-3-(dialkylamino)benzothiophene (**6**) in good yield. The *ortho*-diamine compounds (**6**) were envisaged as resulting from trapping of, respectively, the ring-cleavage product (**2**) and the tricyclic azirine (**7**), the valence tautomer of



Scheme. *Reagents and conditions:* i, $-N_2$, 25–60 °C; ii, + alkene; iii, + (**2**); iv, R_2NH.

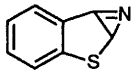
3-nitrenobenzothiophene, by the dialkylamine present. No product formally ascribable to an azirine (**8**) or its nitrene tautomer (**5**) could be observed in these thermolyses of 2-BTA. These findings led us to suspect that 2-BTA might lead to the

Table 1. Product yields[a] (%) for the thermal reaction of 2-BTA with alkenes at room temperature.[b]

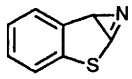
Entry	Alkene	Time[c] (days)	Aziridine	Thiochroman	Other
1	Ethylene	16	(**3a**) (75)	(**4a**) (22)	
2	(*E*)-But-2-ene	20	*trans*-(25) + *cis*-(**3d**) (10)	(**10a**) (47)	
3	(*Z*)-But-2-ene	20	*trans*-(17) + *cis*-(**3d**) (16)	(**9a**) (22) + (**9b**) (22)	*f*
4	Acrylonitrile	7	(**3b**) (85)	(**4b**) (10)	
5	Methyl acrylate	4	(**3c**) (90)	(**4c**) (3)	
6	Trimethyl(vinyl)silane	5	(**3h**) (93)		
7	Dimethyl maleate	20	*trans*-(21) + *cis*-(**3e**) (26)	(**9c**) (25) + (**10c**) (6)	*f*
8	Diethyl maleate	20	*trans*-(16) + *cis*-(**3f**) (23)	(**9d**) (24) + (**10e**) (5)	*f*
9	Dimethyl fumarate[d]	15	*trans*-(34) + *cis*-(**3e**) (2)	(**10b**) (27) + (**10c**) (24)	
10	Diethyl fumarate	3	*trans*-(81) + *cis*-(**3f**) (9)		
11	Diethyl fumarate[e]	15	*trans*-(56) + *cis*-(**3f**) (5)		(**15a**) (30)
12	Diethyl fumarate[g]	45	*trans*-(48) + *cis*-(**3f**) (4)		(**15a**) (40)
13	Methyl (*E*)-crotonate	12	*trans*-(**3g**) (48)	(**10d**) (35)	
14	Methyl (*Z*)-crotonate	20	*trans*-(11) + *cis*-(**3g**) (34)	(**9e**) (29) + (**9f**) (15)	
15	Methyl (*E*)-crotonate[h]	6 h	*trans*-(**3g**) (14)	(**10d**) (81)	
16	Methyl (*Z*)-crotonate[h]	6 h	*trans*-(1) + *cis*-(**3g**) (4)	(**9e**) (38) + (**9f**) (30)	
17	Methyl (*E*)-3-(*N*-Pyrrolidinyl)acrylate[i]	4			
18	1-(*N*-Pyrrolidinyl)cyclopentene[i]	5 min			(**14a**) (91)
19	1-(*N*-Pyrrolidinyl)cyclohexene[i]	5 min			(**12a**) (99) (**12b**) (99)

[a] Isolated yields based on starting 2-BTA. [b] Reactions were run in neat alkenes unless otherwise stated. [c] Approximate reaction time corresponding to complete consumption of starting 2-BTA. [d] Reaction carried out in benzene in the presence of 3 mol equiv. of the alkene. [e] Reaction carried out at 5 °C. [f] A mixture of *trans*- and *cis*-isomers of the dithiocine (**1**) was also obtained (3–7%). [g] Reaction carried out at −20 °C. [h] Reaction carried out at 60 °C. [i] Reaction carried out in benzene in the presence of equiv. amounts of the alkene.

enethione (**2**) by concerted ring opening and nitrogen loss rather than *via* a nitrene intermediate (**5**) (Scheme, path b). If this should be the case, the previously observed aziridines (**3**) might have actually resulted from undetected triazoline adducts arising from 2-BTA–olefin cycloadditions.



(**7**)



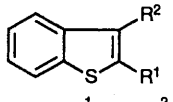
(**8**)

Hence, we felt that additional experimental evidence was required to elucidate the real mechanism of the thermal fragmentation of 2-BTA. With this in mind we undertook a study of the thermal reaction of 2-BTA with various 1,2-disubstituted alkenes such as dimethyl and diethyl maleate, dimethyl and diethyl fumarate, methyl (*E*)- and (*Z*)-crotonate, and methyl (*E*)-3-(*N*-pyrrolidinyl)acrylate. We chose to perform these reactions generally at room temperature with the aim of favouring formation of aziridine (**3**) at the expense of the competing ring-cleavage reaction.[3] Our primary aim was to explore the stereochemistry of the resulting aziridines (**3**) in the hope of gaining conclusive evidence in favour for (or against) the possible intervention of a singlet nitrene (**5**). It was also of interest to us to investigate the reaction of 2-BTA with 1-(*N*-pyrrolidinyl)-cyclopentene or -cyclohexene in view of the particularly high reactivity of these alkenes in cycloadditions with aryl azides.[4] We reasoned that with such cycloalkenes we might well succeed in detecting any triazoline adducts which had been formed. A related investigation of the reaction of 3-azidobenzothiophene (3-BTA) with a number of electron-poor and -rich alkenes at room temperature was additionally undertaken. We thought that such a study should contribute to our understanding of the thermal reactivity of 2-BTA with alkenes. In particular, it seemed to us of interest to compare the chemical reactivity which might exhibit 3-BTA under the same mild thermal conditions, under which the possible occurrence of a corresponding nitrene would be surely prevented.[2b]

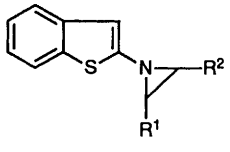
Results and Discussion

In neat methyl (*E*)-crotonate 2-BTA underwent complete decomposition at room temperature within 12 days (as monitored by TLC) to lead, after column chromatography, to the separation of a single aziridine isomer, *i.e.* *trans*-(**3g**) (48%), in addition to smaller amounts of methyl *trans*-4-cyano-*trans*-2-methyl(thiochroman)-3-carboxylate (**10d**) (Table 1, entry 13). On the other hand both geometrical aziridines *cis*- and *trans*-(**3g**) could be isolated in *ca.* 3:1 ratio and in 45% overall yield when 2-BTA was allowed to decompose in neat methyl (*Z*)-crotonate (*ca.* 20 days). In such cases a similar amount of a diastereoisomeric mixture of the *cis,cis*- and *cis,trans*-thiochroman-4-carbonitriles (**9e**) and (**9f**) was also obtained (Table 1, entry 14).

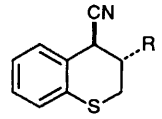
As might have been expected,[3] a remarkable increase in the



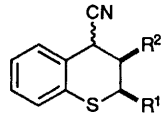
2-BTA $R^1 = N_3$, $R^2 = H$
3-BTA $R^1 = H$, $R^2 = N_3$



(**3**) **a**; $R^1 = R^2 = H$
b; $R^1 = H$, $R^2 = CN$
c; $R^1 = H$, $R^2 = CO_2Me$
d; $R^1 = R^2 = Me$
e; $R^1 = R^2 = CO_2Me$
f; $R^1 = R^2 = CO_2Et$
g; $R^1 = Me$, $R^2 = CO_2Me$
h; $R^1 = H$, $R^2 = SiMe_3$



(**4**) **a**; R = H
b; R = CN
c; R = CO_2Me



(**9**) **a**; $R^1 = R^2 = Me$ (*cis, cis*)
b; $R^1 = R^2 = Me$ (*cis, trans*)
c; $R^1 = R^2 = CO_2Me$ (*cis, trans*)
d; $R^1 = R^2 = CO_2Et$ (*cis,trans*)
e; $R^1 = Me$, $R^2 = CO_2Me$ (*cis, cis*)
f; $R^1 = Me$, $R^2 = CO_2Me$ (*cis, trans*)

yield of the resulting thiochromans (**10d**) and (**9e** and **f**) and a concomitant decrease in the yield of the resulting aziridines (**3g**) occurred when the thermolysis of 2-BTA in the above geometrical alkenes was carried out at 60 °C. However, under these circumstances the (*E*)-crotonate still led to the aziridine *trans*-(**3g**), exclusive of the *cis*-isomer, whereas a mixture of *cis*- and *trans*-(**3g**) still occurred, albeit in very low yield, with the (*Z*)-crotonate (Table 1, entries 15 and 16). In dimethyl and diethyl maleate 2-BTA furnished virtually identical results. In such solvents total azide decomposition took place within *ca.* 20 days to afford comparable amounts of the geometrical aziridines *cis*-and *trans*-(**3e** and **f**) in 39–47% overall yield, together with the *trans*-4-cyanothiochroman-*cis*-2,3-dicarboxylates (**9c** and **d**) to a minor extent (24–25%). Interestingly, in both cases small amounts of the corresponding diastereomeric *cis*-4- cyanothiochroman-*trans*-2,3-dicarboxylate adducts (**10c** and **e**), which did not retain the (*Z*)-configuration of the starting maleate, were additionally obtained (Table 1, entries 7 and 8). In neat diethyl fumarate the decomposition of 2-BTA was significantly faster, being virtually complete after 3 days. The aziridine *trans*-(**3f**) and its geometrical isomer *cis*-(**3f**) were isolated in 81 and 9% yield, respectively, as the exclusive identifiable products (Table 1, entry 10). Clear-cut spectroscopic and chemical evidence for the triazoline (**13b**) intermediate could be obtained when the same reaction was repeated at −20 and 5 °C. At −20 °C virtually complete reaction occurred during 45 days. After this time an aliquot of the resulting reaction mixture was examined by ^{1}H NMR spectroscopy. The NMR spectrum revealed the presence of an AB system (δ_A 5.07 and δ_B 5.81, J_{AB} 7.7 Hz), consistent with the triazoline ring protons of structure (**13b**), and of two singlets at δ 3.61 and 3.25, corresponding to the aziridine ring protons of *trans*- and *cis*-(**3g**), in *ca.* 8:10:1 proportions respectively. The AB quartet was subsequently shown to convert into the two aziridine singlets within 40 h at room temperature. The remaining part of the reaction mixture was immediately adsorbed on silica gel and, after storage at −20 °C for several hours, was chromatographed. Chromatography afforded the diazo diester (**15a**) in 40% yield, in addition to the *trans*- and *cis*-aziridines (**3f**) in 52% overall yield (Table 1, entry 12). The diazo compound (**15a**) evidently resulted from SiO_2-promoted isomerization of the triazoline (**13b**) which had partly survived the reaction conditions. Acid- or base-promoted isomerizations of triazolines bearing an electron-withdrawing group at C-4 along with a free hydrogen to give diazo compounds are well documented.[5]

Similar results were obtained at 5 °C after analogous work-up of the resulting reaction mixture, but in such a case a lower yield of the diazo diester (**15a**) in favour of the *trans*- and *cis*-aziridine (**3f**) was observed (Table 1, entry 11).

Reaction of 2-BTA with solid dimethyl fumarate was performed in benzene by using a three-fold excess of the alkene. The azide was found to disappear at room temperature within 15 days to give a 17:1 mixture of *trans*- and *cis*-aziridine (**3e**) in 36% yield togethr with a *ca.* 1:1 mixture of the diastereoisomeric thiochroman cycloadducts (**10b**) and (**10c**) in 51% yield (Table 1, entry 9). The occurrence of the cycloadducts (**10a** and **c**) to such a remarkable extent is clearly ascribable to the low concentration of the sparingly soluble fumarate employed in such experiments (see Table 1, entries 9 and 10).

Structural assignments for all new aziridines *trans*- and *cis*-(**3e–g**) and thiochroman-4-carbonitriles (**9c–f**) and (**10b–e**) were made on the basis of IR, ^{1}H NMR, and MS spectral data. In particular, configurational assignments for the thiochromans (**9c–f**) and (**10b–e**) came from the observed values of the coupling constants for vicinal 2-H and 3-H, and 3-H and 4-H in the ^{1}H NMR spectra. These occurred in the expected range, *J* 6.2–9.7 Hz for *trans*-coupling, and *J* 3.2–3.6 Hz for *cis*-coupling.[3]

Our findings with the above disubstituted alkenes appeared to us to conflict with our earlier observation[3] that the reaction of 2-BTA with (*Z*)-but-2-ene (at 45 °C) or (*E*)-but-2-ene (at 45 °C and at room temperature) led to the 2,3-dimethylaziridine (**3d**) with *cis*-stereospecificity. We were therefore prompted to re-examine these reactions at room temperature, and ascertained that, contrary to our previous assertion, formation of the 2,3-dimethylaziridine (**3d**) is by no means stereospecific.

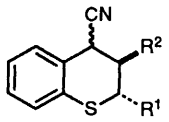
The reaction with (*Z*)-but-2-ene at room temperature led, after 20 days, to the separation of a 1:1 mixture of the dimethylaziridines *trans*- and *cis*-(**3d**) in 33% yield as well as of a diastereoisomeric 1:1 mixture of the dimethylthiochromans (**9a** and **b**) in 44% yield, whereas the corresponding reaction with the (*E*)-alkene allowed us to separate, besides the previously isolated thiochroman (**10a**), the same dimethylaziridine product as previously obtained in 34% yield. However, such an aziridine product, which at that stage had been assigned the structure *trans*-(**3d**), was presently shown to be a mixture of the isomers *trans*- and *cis*-(**3d**) in *ca.* 2.5:1 ratio (Table 1, entries 2 and 3).

Reaction of 2-BTA with methyl 3-(*N*-pyrrolidinylacrylate, *N*-pyrrolidinyl-cyclopentene, and -cyclohexene provided definite evidence for exclusive occurrence of an appropriate triazoline (**13a**) and (**12a** and **b**). In the presence of equimolar amounts of the pyrrolidinylacrylate, 2-BTA in benzene gave no aziridine product, but exclusively led to the triazole-4-carboxylate (**14a**) in 91% yield (Table 1, entry 17). Structural assignment of the triazole (**14a**) came from spectral evidence and was confirmed by an independent synthesis accomplished by reaction of 2-BTA with methyl propiolate (see Experimental section). The triazole (**14a**) evidently arose from an intermediate triazoline (**13a**) by elimination of pyrrolidine, in analogy with that observed with related triazolines resulting from cycloaddition reactions of phenyl azides with methyl 3-(*N*-pyrrolidinyl)acrylate.[6]

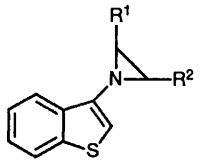
Moreover, 2-BTA in benzene reacted almost instantaneously with equimolar amounts of *N*-pyrrolidinyl-cyclopentene or -cyclohexene to give the corresponding triazolines (**12a** and **b**), which were isolated in quantitative yield (Table 1, entries 18 and 19). The proposed structures (**12a** and **b**) were assigned on the basis of analytical and spectral data and by analogy with the known regiochemistry of the cycloaddition reactions of organic azides with cyclic and acyclic alkenylamines.[5a] To our knowledge the compounds (**12a** and **b**) represent the first instances of isolated triazolines bearing a five-membered 2-heteroaryl substituent at N-1.

In the present work we also briefly re-examined our previous reactions[3] of 2-BTA with ethylene, methyl acrylate, and acrylonitrile at room temperature in order to determine the corresponding reaction times and compare these with those of the above thermal reactions. The observed reaction times are reported in Table 1 (entries 1, 4, and 5). In Table 1 are also reported for comparison the observed yields of the resulting aziridine and thiochroman products, (**3a–c**) and (**4a–c**), which were fully consistent with those determined earlier. In this work we additionally explored the reaction of 2-BTA with trimethyl(vinyl)silane, particularly in the hope that this might offer a straightforward entry to the silyl-substituted aziridine (**3h**). A limited number of *C*-silyl-substituted aziridines are known and the chemistry of these appealing compounds is virtually unexplored.[7] We were pleased to ascertain that 2-BTA reacts cleanly with the silane at room temperature to lead, after 5 days, to the desired aziridine (**3h**) in 93% yield (Table 1, entry 6).

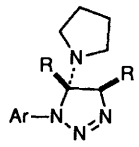
Our general findings obtained from the present study of the thermal reactions of 2-BTA with alkenes argue against our previously suggested intermediacy of a singlet nitrene (**5**) in the formation of aziridines (**3**), whereas they do strongly suggest



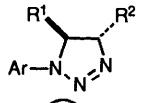
(10) **a**; $R^1 = R^2$ = Me (*trans, trans*)
b; $R^1 = R^2 = CO_2Me$ (*trans, trans*)
c; $R^1 = R^2 = CO_2Me$ (*trans, cis*)
d; R^1 = Me, $R^2 = CO_2Me$ (*trans, trans*)
e; $R^1 = R^2 = CO_2Et$ (*trans, cis*)



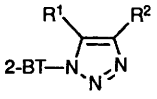
(11) **a**; R^1 = H, $R^2 = CO_2Me$
b; R^1 = H, $R^2 = SiMe_3$
c; $R^1 = R^2 = CO_2Et$
d; R^1 = Me, $R^2 = CO_2Me$



(12) **a**; RR = $-[CH_2]_3-$, Ar = 2-BT
b; RR = $-[CH_2]_4-$, Ar = 2-BT
c; RR = $-[CH_2]_3-$, Ar = 3-BT
d; RR = $-[CH_2]_4-$, Ar = 3-BT

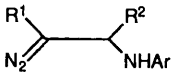


(13) **a**; $R^1 = [CH_2]_4N$, $R^2 = CO_2Me$, Ar = 2-BT
b; $R^1 = R^2 = CO_2Et$, Ar = 2-BT
c; $R^1 = R^2 = CO_2Et$, Ar = 3-BT
d; R^1 = Me, $R^2 = CO_2Me$, Ar = 3-BT
e; R^1 = H, $R^2 = CO_2Me$, Ar = 3-BT



(14) **a**; R^1 = H, $R^2 = CO_2Me$
b; $R^1 = CO_2Me$, R^2 = H

BT = benzo[*b*]thienyl



(15) **a**; $R^1 = R^2 = CO_2Et$, Ar = 2-BT
b; $R^1 = CO_2Me$, R^2 = H, Ar = 3-BT
c; $R^1 = R^2 = CO_2Et$, Ar = 3-BT
d; $R^1 = CO_2Me$, R^2 = Me, Ar = 3-BT

Table 2. Product yields[a] (%) for the thermal reaction of 3-BTA with alkenes at room temperature.[b]

Entry	Alkene	Time[c] (days)	Aziridine	Diazo compound	Triazoline
1	Methyl acrylate	12	(**11a**) (96)		
2	Methyl acrylate[d]	100	(**11a**) (86)	(**15b**) (8)	
3	Trimethyl(vinyl)silane	15	(**11b**) (95)		
4	Methyl (*E*)-crotonate	60	*trans*-(**11d**) (40)	(**15d**) (18)	
5	Diethyl fumarate	5	*trans*-(75) + *cis*-(**11c**) (5)	(**15c**) (17)	
6	Diethyl fumarate[e]	18	*trans*-(11) + *cis*-(**11c**) (1)	(**15c**) (82)	
7	1-(*N*-Pyrrolidinyl)cyclopentene[f]	15 min			(**12c**) (99)
8	1-(*N*-Pyrrolidinyl)cyclohexene[f]	15 min			(**12d**) (99)
9	(*E*)-But-2-ene	120[g]			

[a] Isolated yields based on starting 3-BTA. [b] Reactions run in neat alkenes unless otherwise stated. [c] Approximate reaction time corresponding to complete consumption of starting 3-BTA. [d] Reaction carried out at −20 °C. [e] Reaction carried out at 5 °C. [f] Reaction carried out in benzene in the presence of 1 mol equiv. of the alkene. [g] Unchanged 3-BTA was recovered after this time in 95% yield.

that these compounds (**3**) should generally arise from eventual fragmentation of unstable triazoline adducts which would initially result from 2-BTA–olefin cycloadditions. With all the (*E*)- and (*Z*)-olefins currently examined [but one, *i.e.* methyl (*E*)-crotonate] the formation of the resulting aziridines (**3e–g**) was found to occur in a non-stereospecific fashion. This finding is clearly inconsistent with the possible addition of singlet nitrene (**5**) to C=C double bond.

On the other hand, we succeeded in gaining clear-cut evidence for the intermediacy of a triazoline (**13b**) in the formation of the geometrical aziridines *trans*- and *cis*-(**3f**) arising from reaction of 2-BTA with diethyl fumarate. Additionally, unequivocal evidence for azide–olefin cycloaddition resulting in triazoline formation was provided by reaction of 2-BTA with methyl *N*-pyrrolidinylacrylate, and *N*-pyrrolidinyl-cyclopentene, and -cyclohexene. Such overall evidence lends firm support to a general intervention of triazoline intermediates in the observed formation of aziridines (**3**). Moreover, as can be seen in Table 1, both electron-deficient and electron-rich alkenes were found to be effectively capable of enhancing the rate of disappearance of 2-BTA, concomitantly enhancing the formation of aziridines or triazolines at the expense of the corresponding thiochroman-4-carbonitriles. Such a chemical trend, while being fully consistent with possible competition between bimolecular azide–olefin cycloaddition and unimolecular azide ring-cleavage, would suggest that the addition of 2-BTA with alkenes might be suitably favoured by both electron-deficient and electron-rich alkenes. This evidence would be in line with the known U-shaped reactivity curve exhibited by alkenes in cycloadditions with phenyl azide.[8]

Our subsequent study of the reactivity of 3-azidobenzothiophene (3-BTA) with methyl acrylate, diethyl fumarate, methyl (*E*)-crotonate, vinyltrimethylsilane, and *N*-pyrrolidinyl-cyclopentene, and -cyclohexene showed this azide to be generally capable of undergoing cycloaddition to these alkenes at room temperature.

Similarly to 2-BTA, 3-BTA was found to decompose at room temperature in neat methyl acrylate to give, after *ca.* 12 days, the aziridine (**11a**) in almost quantitative yield (Table 2, entry 1). Repetition of this reaction at −20 °C (*ca.* 100 days) allowed the isolation of small amounts of the diazo ester (**15b**) (8%), in addition to the aziridine (**11a**) (Table 2, entry 2). The observed occurrence of the diazo compound (**15b**) evidently suggests intermediacy of the triazoline adduct (**13e**). Preferential (if not exclusive) formation of this regioisomer (**13e**) would be expected in the light of the known regiochemistry of the cycloaddition reactions of organic azides to alkenes bearing one electron-withdrawing group.[9]

Reaction of 3-BTA with neat methyl (*E*)-crotonate or diethyl fumarate led, after column chromatography, to the isolation of significant amounts of diazo product, (**15d**) (18%) and (**15c**) (17%) respectively, even at room temperature. The diazo ester (**15d**), which was the presumable isomerization product of the triazoline (**13d**), was accompanied by the *trans*-aziridine (**11d**), exclusive of its *cis*-isomer, whereas a 15:1 mixture of the *trans*- and *cis*-aziridine (**11c**) accompanied the diazo diester (**15c**), the ring-opened product of the triazoline (**13c**) (Table 2, entries 4 and 5). Spectroscopic and further chemical evidence for the intermediacy of this latter compound (**13c**) in the formation of both compound (**15c**) and the aziridines *trans*- and *cis*-(**11c**) was gained from the reaction of 3-BTA with diethyl fumarate carried out at 5 °C for *ca.* 18 days. After this time an aliquot of the reaction mixture was directly analysed by ^{1}H NMR spectroscopy which showed the presence of an AB quartet (δ_A 5.12 and δ_B 5.63, J_{AB} 8.7 Hz), ascribable to the triazoline ring protons of compound (**13c**), and a singlet corresponding to the aziridine ring protons of *trans*-(**11c**) in *ca.* 14:1 ratio, respectively. The AB quartet was shown to disappear at room temperature during *ca.* 72 h to give exclusively the two aziridine ring singlets of *trans*- and *cis*-(**11c**) in *ca.* 10:1 ratio. The remaining part of the reaction mixture was adsorbed on silica gel and, after several hours, chromatographed to give the diazo diester (**15c**) in 82% yield along with small amounts of an isomeric mixture of *trans*- and *cis*-(**11c**) (Table 2, entry 6). Analogously to 2-BTA, but at a significantly lower rate, 3-BTA reacted with neat trimethyl(vinyl)silane to afford the corresponding 2-silylaziridine (**11b**) in very high yield (Table 2, entry 3). Moreover, similarly to 2-BTA, 3-BTA underwent a very fast reaction with both *N*-pyrrolidinyl-cyclopentene and -cyclohexene in benzene to afford the corresponding triazolines (**12c** and **d**) in quantitative yield (Table 2, entries 7 and 8). However, 3-BTA exhibited no reaction with (*E*)-but-2-ene at room temperature even after 4 months (Table 2, entry 9).

The chemical trend that emerged from the above reactions of 3-BTA with alkenes showed a marked resemblance with that observed with 2-BTA, though the former azide would generally appear to react with alkenes at a comparatively slower rate. This evidence is therefore consistent with the above conclusions drawn for the similar thermal reaction of 2-BTA with alkenes.

In the light of the general evidence presented by our present findings, in addition to that previously obtained by our study of the thermal decomposition of 2-BTA and 3-BTA in the presence of dialkylamines,[2b] it might be concluded that unimolecular thermal fragmentation of 2-BTA is likely to proceed *via* a low-energy process involving concerted ring opening and nitrogen loss, rather than *via* a singlet nitrene (**5**) as previously suggested. In fact, at this stage experimental evidence supporting a possible intervention of the nitrene (**5**) is totally lacking. In our opinion, our previous kinetic findings[2b] that the first-order thermal decomposition of 2-BTA is significantly faster than that of 3-BTA can be interpreted in the same way.

Benzo[*b*]thiophene would be expected to be less capable of donating electron-density to the electron-deficient nitrogen of an ensuing 2- rather than 3-nitrene, according to the fact that such a heteroaromatic is known to undergo preferential electrophilic attack at the 3- over the 2-position. Consequently, if a nitrene were an intermediate in the fragmentation of 2-BTA as apparently is the case with 3-BTA, the former azide should conceivably display a slower decomposition than 3-BTA, contrary to our observations.

Finally, the observed cycloadditions of the ring-cleavage product (**2**) with (*E*)- and (*Z*)-alkenes deserve a brief comment. As can be seen in Table 1, with (*E*)- and (*Z*)-but-2-ene, methyl (*E*)- and (*Z*)-crotonate, and dimethyl fumarate the cycloaddition reaction generally leads to *exo*- and/or *endo*-adducts with *cis*-stereospecificity. On the other hand, non-stereospecific addition appears to occur with dimethyl and diethyl maleate.

These findings are somewhat consistent with those previously reported by Meier *et al.*[10] from related cycloadditions of the parent enethione (**2**; CN = H). In these, (*E*)-olefins have been found to be added strictly stereospecifically, whereas (*Z*)-olefins [including diethyl maleate and methyl (*Z*)-crotonate] have been shown to afford (*Z*)- and/or (*E*)-adducts *via* non-concerted pathways. However, our results seem to suggest a larger preference for our enethione (**2**) to cycloadd in a concerted fashion, but the actual reasons are unclear at this stage.

Experimental

Materials.—Gaseous olefins were purchased from Matheson, the remaining ones were purchased from Aldrich-Chimica Italiana except for methyl (*Z*)-crotonate[11] and methyl (*E*)-3-(*N*-pyrrolidinyl)acrylate,[12] which were prepared according to the literature method. 2-Azido- (2-BTA)[3] and 3-azidobenzo[*b*]thiophene (3-BTA)[13] were previously reported. Reaction products such as the aziridines (**3a**), *trans*- and *cis*-(**3d**), -(**3b**), and -(**3c**), and the 4-cyanothiochromans (**4a**), (**4b**), (**4c**), (**9a**), (**9b**), and (**10a**) were previously described.[3] Chromatographic separations were carried out on Merck silica gel (0.040–0.063 mm particle size).

Spectra.—IR spectra were recorded with a Perkin-Elmer Model 257 instrument. ^{1}H NMR data were obtained with a Varian EM 360 L 60 MHz or Gemini 200 MHz instrument for solutions in $CDCl_3$ with $SiMe_4$ internal standard. Mass spectra were recorded on a VG Analytical 7070 E Organic mass spectrometer.

Reactions of 2-BTA and 3-BTA with Alkenes at Room Temperature. General Procedure.—A solution of 2-BTA or 3-BTA (0.35 g, 2 mmol) in the appropriate neat alkene [ethylene, methyl acrylate, acrylonitrile, trimethyl(vinyl)silane, (*E*)- and (*Z*)-but-2-ene, dimethyl maleate, diethyl fumarate, diethyl maleate, or methyl (*E*)- and (*Z*)-crotonate] (4 ml) was allowed to react in a sealed tube at room temperature [and also at 60 °C in the case of methyl (*E*)- and (*Z*)-crotonate] for the appropriate time, until TLC showed the absence of the starting azide. The reactions of 2-BTA with solid dimethyl fumarate and methyl *trans*-3-(*N*-pyrrolidinyl)acrylate were carried out in benzene (4 ml) containing alkene (3 and 1 mol equiv.), respectively. The residue obtained after careful evaporation of the excess of olefin or benzene (under high vacuum, when appropriate) was chromatographed on a silica gel column with hexane with increasing amounts of diethyl ether (up to 100%) as eluant.

Reactions of 2-BTA or 3-BTA with 1-(*N*-pyrrolidinyl)-cyclopentene or -cyclohexene were carried out by treatment of a solution of the appropriate azide (2 mmol) in benzene (2 ml) with a solution of cycloalkene (2 mmol) in benzene (2 ml) for several minutes. The resulting reaction mixture was evaporated and the residue was repeatedly washed with pure hexane and then characterized.

Approximate reaction times and product yields for the thermal reactions of 2-BTA and 3-BTA with alkenes at room temperature (and at 60 °C) are reported in Tables 1 and 2.

The following new aziridines (**3**) and (**11**) were obtained (i) *Dimethyl* trans-1-(2-*benzo*[b]*thienyl*)*aziridine*-2,3-*dicarboxylate*, trans-(**3e**), m.p. 78–80 °C; ν_{max} 3 060, 2 960, 1 740 (CO), and 750 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 7.7–7.1 (4 H, br m), 6.7 (1 H, s), 3.7 (6 H, s), and 3.6 (2 H, s); *m/z* 291 (12%, M^+), 232 (15, $M - 59$), 172 (6), 155 (6), 85 (100), and 83 (67) (Found: M^+, 291.056 81. $C_{14}H_{13}NO_4S$ requires *M*, 291.056 53).

(ii) *Dimethyl* cis-1-(2-*benzo*[b]*thienyl*)*aziridine*-2,3-*dicarboxylate*, cis-(**3e**), m.p. 88–90 °C; ν_{max} 3 000, 1 760 (CO), and 750 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 7.8–7.1 (4 H, br m), 6.7 (1 H, s),

3.8 (6 H, s), and 3.3 (2 H, s); *m/z* 291 (100%, M^+), 232 (95, $M - 59$), and 172 (40) (Found: M^+, 291.056 70).

(iii) *Diethyl* trans-1-(2-*benzo*[b]*thienyl*)*aziridine*-2,3-*dicarboxylate*, trans-(**3f**), m.p. 62–64 °C; ν_{max} 2 980 and 1 740 cm^{-1} (CO); δ_H(60 MHz; $CDCl_3$) 7.8 (2 H, br m), 7.2 (2 H, br m), 6.6 (1 H, s), 4.1 (4 H, q), 3.6 (2 H, s), and 1.2 (6 H, t); *m/z* 319 (100%, M^+), 290 (10, $M - 29$), 246 (71), 218 (20), 201 (50), 145 (69), and 103 (44) (Found: M^+, 319.087 51. $C_{16}H_{17}NO_4S$ requires *M*, 319.087 83).

(iv) *Diethyl* cis-1-(2-*benzo*[b]*thienyl*)*aziridine*-2,3-*dicarboxylate*, cis-(**3f**), as an oil; ν_{max} 3 000 and 1 760 cm^{-1} (CO); δ_H(200 MHz; $CDCl_3$) 7.62 (2 H, br m), 7.18 (2 H, br m), 6.78 (1 H, s), 4.24 (4 H, q), 3.28 (2 H, s), and 1.30 (6 H, t); *m/z* 319 (100%, M^+), 290 (3, $M - 29$), 246 (88), 201 (54), 172 (30), 160 (25), and 147 (20) (Found: M^+, 319.088 14).

(v) *Methyl* trans-1-(2-*benzo*[b]*thienyl*)-3-*methyl aziridine*-2-*carboxylate*, trans-(**3g**), as an oil; ν_{max} 2 960 and 1 750 cm^{-1} (CO); δ_H(200 MHz; $CDCl_3$) 7.58 (2 H, br m), 7.25 (2 H, br m), 6.60 (1 H, s), 3.75 (3 H, s), 2.88 (1 H, dq, *J* 3.0 and 5.6 Hz, 3-H), 2.84 (1 H, d, *J* 3.0 Hz, 2-H), and 1.29 (3 H, d, *J* 5.6 Hz); *m/z* 247 (60%, M^+), 188 (100, $M - 59$), and 160 (33) (Found: M^+, 247.066 88. $C_{13}H_{13}NO_2S$ requires *M*, 247.066 69).

(vi) *Methyl* cis-1-(2-*benzo*[b]*thienyl*)-3-*methyl aziridine*-2-*carboxylate*, cis-(**3g**), as an oil; ν_{max} 2 960 and 1 740 cm^{-1} (CO); δ_H(200 MHz; $CDCl_3$) 7.58 (2 H, m), 7.20 (2 H, m), 6.63 (1 H, s), 3.82 (3 H, s), 3.06 (1 H, d, *J* 6.9 Hz, 2-H), 2.70 (1 H, dq, *J* 6.9 and 5.8 Hz, 3-H), and 1.45 (3 H, d, *J* 5.8 Hz); *m/z* 247 (60%, M^+), 188 (80, $M - 59$), 166 (62), 160 (27), and 139 (100) (Found: M^+, 247.066 89).

(vii) 1-(2-*Benzo*[b]*thienyl*)-2-*trimethylsilyl aziridine* (**3h**), as an oil; ν_{max} 3 060, 2 960, and 840 cm^{-1} ($SiMe_3$); δ_H(200 MHz; $CDCl_3$) 7.62 (2 H, m), 7.26 (2 H, m), 6.58 (1 H, s), 2.35 (1 H, dd, *J* 7.8 and 1.4 Hz), 2.31 (1 H, dd, *J* 5.2 and 1.4 Hz), 1.55 (1 H, dd, *J* 7.8 and 5.2 Hz), and 0.2 (9 H, s); *m/z* 247 (37%, M^+), 232 (10, $M - 15$), 205 (8), 190 (7), 179 (7), 147 (15), 100 (20), and 73 (100) (Found: C, 63.65; H, 7.0; N, 5.7; S, 12.9. $C_{13}H_{17}NSSi$ requires C, 63.10; H, 6.95; N, 5.65; S, 12.95%).

(viii) *Diethyl* trans-1-(3-*benzo*[b]*thienyl*)*aziridine*-2,3-*dicarboxylate*, trans-(**11c**), m.p. 76–78 °C, ν_{max} 2 980, 1 730 (CO), and 750 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 7.8 (2 H, br m), 7.3 (2 H, br m), 6.7 (1 H, s), 4.1 (4 H, q), 3.6 (2 H, s), and 1.1 (6 H, t); *m/z* 319 (90%, M^+), 246 (100, $M - 73$), 218 (20), 173 (42), 160 (31), and 149 (44) (Found: M^+, 319.087 61. $C_{16}H_{17}NO_4S$ requires *M*, 319.087 83).

(ix) *Diethyl* cis-1-(3-*benzo*[b]*thienyl*)*aziridine*-2,3-*dicarboxylate*, cis-(**11c**), as an oil; ν_{max} 2 940, and 1 740 cm^{-1} (CO); δ_H(60 MHz; $CDCl_3$) 8.2–7.3 (4 H, br m), 6.7 (1 H, s), 4.3 (4 H, q), 3.1 (2 H, s), and 1.3 (6 H, t); *m/z* 319 (92%, M^+), 246 (100, $M - 73$), and 149 (36) (Found: M^+, 319.088 14).

(x) *Methyl* 1-(3-*benzo*[b]*thienyl*)-3-*methyl aziridine*-2-*carboxylate*, trans-(**11d**), as an oil; ν_{max} 2 970 and 1 750 cm^{-1} (CO); δ_H(60 MHz; $CDCl_3$) 7.5 (2 H, br m), 7.4 (2 H, br m), 6.6 (1 H, s), 3.7 (3 H, s), 3.0 (1 H, br m), 2.8 (1 H, d, *J* 3.2 Hz), and 1.2 (3 H, d, *J* 5.8 Hz); *m/z* 247 (52%, M^+), 188 (100, $M - 59$), and 160 (38) (Found: M^+, 247.066 76. $C_{13}H_{13}NO_2S$ requires *M*, 247.066 69).

(xi) *Methyl* 1-(3-*benzo*[b]*thienyl*)*aziridine*-2-*carboxylate* (**11a**), m.p. 73–75 °C; ν_{max} 2 950, 1 750 (CO), 750, and 730 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 7.7 (2 H, m), 7.3 (2 H, m), 6.6 (1 H, s), 3.8 (3 H, s), 2.7 (2 H, m), and 2.3 (1 H, m); *m/z* 233 (100%, M^+), 174 (72, $M - 59$), 160 (68), 147 (52), 133 (19), and 89 (22) (Found: C, 61.4; H, 4.75; N, 6.0; S, 13.7. $C_{12}H_{11}NO_2S$ requires C, 61.80; H, 4.75; N, 6.00; S, 13.75).

(xii) 1-(3-*Benzo*[b]*thienyl*)-2-*trimethylsilyl aziridine* (**11b**), as an oil; ν_{max} 3 070, 2 970, 2 900, 830 ($SiMe_3$), and 740 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 7.7 (2 H, m), 7.3 (2 H, m), 6.4 (1 H, s), 2.1 (2 H, m), 1.3 (1 H, m), and 0.2 (9 H, s); *m/z* 247 (21%, M^+), 232 (10, $M - 15$), 191 (3), 147 (14), and 73 (100) (Found: C, 63.1; H, 6.95; N, 5.8; S, 13.0). $C_{13}H_{17}NSSi$ requires C, 63.10; H, 6.95; N, 5.65; S, 12.95%).

The following new 4-cyanothiochromans (**9**) and (**10**) were obtained: (i) *Dimethyl* trans-4-*cyanothiochroman*-trans-2,3-*dicarboxylate* (**10b**) as an oil; ν_{max} 2 960, 2 240 (CN), 1 740 (CO), 1 440, and 760 cm^{-1}; δ_H(200 MHz; $CDCl_3$) 7.68 (1 H, br m), 7.35 (3 H, br m), 4.30 (1 H, d, *J* 6.2 Hz, 4-H), 4.28 (1 H, d, *J* 9.4 Hz, 2-H), 3.87 (3 H, s), 3.74 (3 H, s), and 3.67 (1 H, dd, *J* 9.4 and 6.2 Hz, 3-H); *m/z* 291 (40%, M^+), 259 (65, $M - 32$), 232 (36), 231 (46), 172 (100), and 149 (46) (Found: C, 57.75; H, 4.45; N, 4.8; S, 10.95. $C_{14}H_{13}NO_4S$ requires C, 57.7; H, 4.5; N, 4.8; S, 11.0%).

(ii) *Dimethyl* cis-4-*cyanothiochroman*-trans-2,3-*dicarboxylate* (**10c**), m.p. 102–104 °C; ν_{max} 2 960, 2 240 (CN), 1 740 (CO), 1 440, and 755 cm^{-1}; δ_H(200 MHz; $CDCl_3$) 7.45–7.15 (4 H, br m), 4.55 (1 H, d, *J* 3.4 Hz, 4-H), 4.52 (1 H, d, *J* 8.9 Hz, 2-H), 3.82 (3 H, s), 3.80 (3 H, s), and 3.58 (1 H, dd, *J* 8.9 and 3.4 Hz, 3-H); *m/z* 291 (25%, M^+), 259 (55, $M - 32$), 232 (18), 231 (20), 172 (100), and 147 (25) (Found: C, 57.7; H, 4.5; N, 4.75; S, 10.95%).

(iii) *Dimethyl* trans-4-*cyanothiochroman*-cis-2,3-*dicarboxylate* (**9c**), m.p. 117–119 °C; ν_{max} 2 950, 2 240 (CN), 1 740 (CO), 1 440, and 750 cm^{-1}; δ_H(200 MHz; $CDCl_3$) 7.50–7.15 (4 H, br m), 4.91 (1 H, d, *J* 7.0 Hz, 4-H), 4.42 (1 H, d, *J* 3.4 Hz, 2-H), 3.79 (3 H, s), 3.78 (3 H, s), and 3.77 (1 H, dd, *J* 7.0 and 3.4 Hz, 3-H); *m/z* 291 (10%, M^+), 259 (4, $M - 32$), 232 (8), 231 (10), 172 (100), and 147 (10) (Found: C, 57.8; H, 4.5; N, 4.85; S, 11.0%).

(iv) *Diethyl* trans-4-*cyanothiochroman*-cis-2,3-*dicarboxylate* (**9d**), as an oil; ν_{max} 2 950, 2 240 (CN), 1 740 (CO), 1 440, and 750 cm^{-1}; δ_H(200 MHz; $CDCl_3$) 7.60–7.15 (4 H, br m), 4.87 (1 H, d, *J* 7.0 Hz, 4-H), 4.41 (1 H, d, *J* 3.3 Hz, 2-H), 4.26 (4 H, q), 3.77 (1 H, dd, *J* 7.0 and 3.3 Hz, 3-H), and 1.28 (6 H, dt); *m/z* 319 (28%, M^+), 273 (6, $M - 46$), 246 (18), 218 (4), 201 (5), 172 (100), and 147 (19) (Found: M^+, 319.087 62. $C_{16}H_{17}NO_4S$ requires *M*, 319.087 83).

(v) *Diethyl* cis-4-*cyanothiochroman*-trans-2,3-*dicarboxylate* (**10e**), δ_H(200 MHz; $CDCl_3$) 7.50–7.15 (4 H, br m), 4.52 (1 H, d, *J* 3.4 Hz, 4-H), 4.50 (1 H, d, *J* 8.8 Hz, 2-H), 4.27 (4 H, dq), 3.47 (1 H, dd, *J* 8.8 and 3.4 Hz, 3-H), and 1.30 (6 H, dt) (Found: M^+, 319.087 75).

(vi) *Methyl* trans-4-*cyano*-trans-2-*methyl*(*thiochroman*)-3-*carboxylate* (**10d**), m.p. 76–78 °C; ν_{max} 2 960, 2 250 (CN), 1 740 (CO), 1 440, and 750 cm^{-1}; δ_H(200 MHz; $CDCl_3$) 7.52–7.15 (4 H, br m), 4.35 (1 H, d, *J* 9.7 Hz, 4-H), 3.82 (3 H, s), 3.50 (1 H, dq, *J* 6.8 and 8.9 Hz, 2-H), 2.94 (1 H, t, *J* 9.7 and 8.9 Hz, 3-H), and 1.35 (3 H, d, *J* 6.8 Hz); *m/z* 247 (63%, M^+), 187 (65, $M - 60$), and 172 (100) (Found: M^+, 247.066 86. $C_{13}H_{13}NO_2S$ requires *M*, 247.066 69).

(vii) *Methyl* trans-4-*cyano*-cis-2-*methyl*(*thiochroman*)-3-*carboxylate* (**9f**), m.p. 117–118 °C; ν_{max} 2 960, 2 250 (CN), 1 740 (CO), 1 440, and 760 cm^{-1}; δ_H(200 MHz; $CDCl_3$) 7.52 (1 H, br m), 7.15 (3 H, br, m), 4.51 (1 H, d, *J* 8.9 Hz, 4-H), 3.83 (3 H, s), 3.73 (1 H, dq, *J* 6.8 and 3.2 Hz, 2-H), 3.50 (1 H, dd, *J* 8.9 and 3.2 Hz, 3-H), and 1.40 (3 H, d, *J* 6.8 Hz) *m/z* 247 (56%, M^+), 187 (63, $M - 60$), and 172 (100) (Found: C, 63.3; H, 5.3; N, 5.6; S, 12.95. $C_{13}H_{13}NO_2S$ requires C, 63.15; H, 5.3; N, 5.65; S, 12.95%).

(viii) *Methyl* cis-4-*cyano* cis-2-*methyl*(*thiochroman*)-3-*carboxylate* (**9e**), m.p. 130–132 °C; ν_{max} 2 950, 2 240 (CN), 1 740 (CO), 1 440, and 750 cm^{-1}; δ_H(200 MHz; $CDCl_3$) 7.50–7.10 (4 H, br m), 4.48 (1 H, d, *J* 5.6 Hz, 4-H), 4.25 (1 H, m, 2-H), 3.78 (3 H, s), 3.40 (1 H, dd, *J* 3.6 and 5.6 Hz, 3-H), and 1.58 (3 H, d, *J* 7.3 Hz); *m/z* 247 (100%, M^+), 232 (6, $M - 15$), 188 (30), and 172 (37) (Found: C, 63.1; H, 5.3; N, 5.6; S, 13.05%).

The following new diazoalkanes (**15**) were obtained. (i) *Diethyl* 2-(3-*benzo*[b]*thienylamino*)-3-*diazosuccinate* (**15c**), as an oil; ν_{max} 3 360 (NH), 2 980, 2 100 (C=N_2), 1 740 (CO), and 750 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 8.0–7.3 (4 H, br m), 6.9 (1 H, s), 5.1 (2 H, br s), 4.4 (2 H, q), 4.3 (2 H, q), 1.4 (3 H, t), and 1.3

(3 H, t); *m/z* 347 (30%, M^+), 319 (100, $M - 28$), 273 (46), 246 (63), 200 (62), 173 (70), and 149 (80) (Found: M^+, 347.093 78. $C_{16}H_{17}N_3O_4S$ requires *M*, 347.093 96).

(ii) *Methyl* 3-(3-*benzo*[b]*thienylamino*)-2-*diazobutanoate* (**15d**), as a resinous oil; ν_{max} 3 390 (NH), 2 980, 2 110 (C=N_2), 1 690 (CO), and 750 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 8.0–7.2 (4 H, br m), 6.2 (1 H, s), 4.5 (1 H, q, *J* 6.4 Hz), 3.8 (3 H, s), 3.4 (1 H, br s), and 1.6 (3 H, d, *J* 6.4 Hz); *m/z* 275 (22%, M^+), 247 (70, $M - 28$), 215 (22), 188 (49), 186 (41), 149 (90), and 84 (100) (Found: M^+, 275.324 84. $C_{13}H_{13}N_3O_2S$ requires *M*, 275.324 76).

The following new triazole was obtained. *Methyl* 1-(2-*benzo*[b]*thienyl*)-1H-1,2,3-*triazole*-4-*carboxylate* (**14a**), m.p. 162–164 °C; ν_{max} 3 120, 3 060, and 1 710 cm^{-1} (CO); δ_H(60 MHz; $CDCl_3$) 8.5 (1 H, s), 7.8 (2 H, br m), 7.6 (1 H, s), 7.1 (2 H, br m), and 4.0 (3 H, s); *m/z* 259 (77%, 231 (100, $M - 28$), 200 (24), 188 (38), 172 (95), 121 (75), and 89 (25) (Found: M^+, 259.041 16. $C_{12}H_9N_3O_2S$ requires *M*, 259.041 54).

The following new triazolines (**12**) were obtained: (i) 1,3a,4,5,6,6a-*Hexahydro*-6a-(N-*pyrrolidinyl*)-1-(2-*benzo*[b]-*thienyl*)*cyclopentatriazole* (**12a**), as an oil; ν_{max} 2 960 and 730 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 7.9 (2 H, br m), 7.3 (2 H, br m), 6.9 (1 H, s), 4.7 (1 H, t), and 3.0–1.5 (14 H, br m); *m/z* 284 (3%, $M - 28$), 279 (19), 175 (10), 167 (27), 149 (100), 136 (95), and 121 (36) (Found: C, 65.7; H, 6.6; N, 17.65. $C_{17}H_{20}N_4S$ requires C, 65.40; H, 6.50; N, 17.95%).

(ii) 3a,4,5,6,7,7a-*Hexahydro*-7a-(N-*pyrrolidinyl*)-1-(2-*benzo*-[b]*thienyl*)-1H-*benzotriazole* (**12b**), as an oil; ν_{max} 2 960 and 730 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 7.7 (2 H, br m), 7.4 (2 H, br m), 6.7 (1 H, s), 4.2 (1 H, t), and 3.0–1.5 (16 H, br m); *m/z* 298 (30%, $M - 28$), 239 (30), 237 (30), 199 (27), 150 (100), 136 (43), and 123 (50) (Found: C, 66.4; H, 6.9; N, 16.95. $C_{18}H_{22}N_4S$ requires C, 66.20; H, 6.80; N, 17.20%).

(iii) 1,3a,4,5,6,6a-*Hexahydro*-6a-(N-*pyrrolidinyl*)-1-(3-*benzo*-[b]*thienyl*)*cyclopentatriazole* (**12c**), m.p. 92–94 °C (decomp.); ν_{max} 2 960, 760, and 730 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 8.3 (1 H, br m), 7.9 (1 H, br m), 7.5 (1 H, s), 7.6 (2 H, br m), 4.6 (1 H, t), and 2.6–1.1 (14 H, br m); *m/z* 312 (10%, M^+), 284 (15, $M - 28$), 282 (15), 175 (10), 136 (100), 122 (20), and 70 (30) (Found: M^+, 312.140 98. $C_{17}H_{20}N_4S$ requires *M*, 312.140 87).

(iv) 3a,4,5,6,7,7a-*Hexahydro*-7a-(N-*pyrrolidinyl*)-1-(3-*benzo*-[b]*thienyl*)-1H-*benzotriazole* (**12d**), m.p. 106–108 °C (decomp.); ν_{max} 2 940, 760, and 730 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 8.2 (1 H, br m), 7.8 (1 H, br m), 7.6 (1 H, s), 7.4 (2 H, br m), 4.4 (1 H, t), and 2.6–1.4 (16 H, br m); *m/z* 298 (13, $M - 28$), 229 (20), 199 (14), 175 (42), 151 (100), 150 (90), 136 (50), and 123 (58) (Found: C, 66.5; H, 6.75; N, 17.0).

Reaction of 3-BTA with Diethyl Fumarate at 5 °C.—A solution of 3-BTA (0.5M) in neat diethyl fumarate was allowed to react in a refrigerator at *ca.* 5 °C for 18 days, after which time TLC showed the absence of the starting azide. An aliquot of the crude reaction mixture was diluted with deuteriochloroform and immediately analysed by ^1H NMR spectroscopy at room temperature. The NMR spectrum showed an AB quartet (δ_A 5.63 and δ_B 5.12, J_{AB} 8.7 Hz), and a singlet at δ 3.61, corresponding to the ring aziridine protons of *trans*-(**11c**) in *ca.* 14:1 ratio, respectively. Within *ca.* 72 h the AB quartet was shown to disappear completely, being converted into the two aziridine singlets of *trans*- and *cis*-(**11c**).

The remaining part of the cold reaction mixture was adsorbed on silica gel and, after storage at 5 °C for several hours, chromatographed to give (i) the diazosuccinate (**15c**) (82%); (ii) the aziridine *trans*-(**11c**) (11%); and (iii) the aziridine *cis*-(**11c**) (1%).

Reaction of 2-BTA with Diethyl Fumarate at −20 *and* 5 °C.—A solution of 2-BTA (0.5M) in neat diethyl fumerate was kept in a freezer at *ca.* −20 °C for 45 days, after which time complete disappearance of the starting azide had occurred (TLC). An aliquot of the crude reaction mixture was diluted with deuteriochloroform and analysed by ^1H NMR spectroscopy at room temperature. The NMR spectrum showed an AB quartet (δ_A 5.81 and δ_B 5.07, J_{AB} 7.7 Hz), and two singlets at δ 3.61 and δ 3.25, corresponding to the aziridine ring protons of *trans*- and *cis*-(**3f**) in *ca.* 8:10:1 proportions, respectively. Within *ca.* 40 h the AB quartet was shown to disappear completely, being converted into the two aziridine singlets. The remaining part of the cold reaction mixture was adsorbed on silica gel and, after storage at −20 °C for several hours, chromatographed to give (i) *diethyl* 2-(2-*benzo*[b]*thienylamino*)-3-*diazosuccinate* (**15a**) (0.27 g, 39%) as an oil; ν_{max} 3 360 (NH), 2 980, 2 100 (C=N_2), 1 740 (CO), and 750 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 7.7–7.0 (4 H, br m), 6.2 (1 H, s), 5.04 (1 H, br s), 5.00 (1 H, s), 4.34 (2 H, q), 4.30 (2 H, q), 1.34 (3 H, t), and 1.30 (3 H, t); *m/z* 347 (4%, M^+), 319 (34, $M - 28$), 273 (38), 245 (46), 172 (100), 147 (36), and 29 (40) (Found: M^+, 347.093 87. $C_{16}H_{17}N_3O_4S$ requires *M*, 347.093 96); (ii) the aziridine *trans*-(**3f**) (48%); and (iii) the aziridine *cis*-(**3f**) (4%).

The same reaction carried out in a refrigerator at *ca.* 5 °C for 15 days gave, after analogous work-up, (i) the diazosuccinate (**15a**) (30%); (ii) the aziridine *trans*-(**3f**) (56%); and (iii) the aziridine *cis*-(**3f**) (5%).

Reactions of 3-BTA with Methyl Acrylate at −20 °C.—A solution of 3-BTA (0.5M) in neat methyl acrylate was kept in a freezer at *ca.* −20 °C for 100 days. The resulting reaction mixture was adsorbed on silica gel and, after storage at −20 °C for several hours, was chromatographed to give (i) the aziridine (**11a**) (86%) and (ii) *methyl* 3-(3-*benzo*[b]*thienyl-amino*)-2-*diazopropanoate* (**15b**) (8%) as an oil; ν_{max} 3 390 (NH), 2 930, 2 100 (C=N_2), 1 700 (CO), and 740 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 8.0–7.6 (4 H, br m), 6.2 (1 H, s), 4.3 (2 H, s), and 3.8 (3 H, s), *m/z* 261 (17%, M^+), 233 (88, $M - 28$), 201 (68), 173 (100), 160 (27), and 147 (28) (Found: M^+, 261.057 42. $C_{12}H_{11}N_3O_2S$ requires *M*, 261.057 12).

Reaction of 2-BTA with Methyl Propiolate.—A solution of 2-BTA (2 mmol) and methyl propiolate (20 mmol) in benzene (4 ml) was kept at 60 °C for 4 h. The excess of solvent was removed and the residue was chromatographed. Elution with hexane–diethyl ether (70:30) gave (i) *methyl* 1-(2-*benzo*[b]-*thienyl*)-1H-1,2,3-*triazole*-5-*carboxylate* (**14b**) (0.3 mmol, 15%), m.p. 92–94 °C; ν_{max} 3 120, 3 060, 1 740 (CO), and 750 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 8.3 (1 H, s), 7.8 (2 H, br m), 7.6 (2 H, br m), 7.5 (1 H, s), and 3.9 (3 H, s); *m/z* 259 (100%, M^+), 231 (57, $M - 28$), 216 (22), 200 (20), 188 (33), 172 (86), 160 (29), 121 (86), and 89 (25) (Found: M^+, 259.041 28. $C_{12}H_9N_3O_2S$ requires *M*, 259.04154), and (ii) methyl 1-(2-benzo[*b*]thienyl)-1*H*-1,2,3-triazole-4-carboxylate (**14a**) (1.25 mmol, 62%), identical in all respects with that obtained from reaction of 2-BTA with methyl 3-(*N*-pyrrolidinyl)acrylate.

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