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Reactions of Some 2*H*-Chromenes and 2*H*-Thiochromenes with Triazolinediones.

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Dedicated to Professor Hans Suschitzky on the occasion of his 80th birthday.

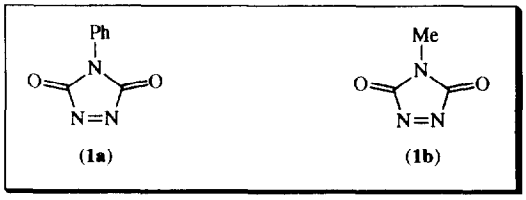
Abstract: Simple 2*H*-chromenes and 2*H*-thiochromenes form the [2+2]-adducts, tetrahydro[1]benzo(thio)pyrano[3,4-*c*][1,2]diazeto[1,2-*a*][1,2,4]triazoles, with triazolinediones, whereas their 3- and 4-bromo and the corresponding cycloalkylamino derivatives undergo an overall electrophilic substitution sequence.

INTRODUCTION

The chemistry of triazolinediones (**1a,b**) has evoked considerable interest in recent years.[1] Their participation as dienophiles in Diels-Alder reactions with conjugated dienes to afford a diversity of nitrogen containing heterocycles is particularly well documented.[2] With certain alkenes the principal products are *N*-allylurazoles which result from an ene type reaction.[3] However, products which are formally derived from a [2+2]-cycloaddition reaction are also frequently encountered.[4] It is this last type of reaction which has stimulated much interest since thermal [$\pi 2_s + \pi 2_s$] cycloadditions are symmetry forbidden. Opinions have been expressed that this reaction involves 1,4-dipoles,[5] aziridinium ions[6] or radicals[7] and evidence has been produced in support of all of these species.

Triazolinediones have been shown to add to 1,3-dicarbonyl compounds[8] and ketones which are appreciably enolised to afford the α-urazolyl ketones.[9] Oxidation of these compounds and subsequent hydrolysis has proved to be a fruitful route to α-diketones[10] and further enhances the synthetic potential of these reagents.

Our programme of research has provided us with a range of substituted 2*H*-chromenes and their sulfur analogues and we now report their behaviour towards phenyltriazolinedione (PTAD) (**1a**) and methyltriazolinedione (MTAD) (**1b**).



(1a) **(1b)**

DISCUSSION

Simple 2*H*-chromenes (**3a,b**) and 2*H*-thiochromenes (**3c,d,e,g,h**) were obtained by standard protocol involving the reduction of the (thio)chroman-4-ones (**2**) with sodium borohydride in refluxing ethanol and dehydration of the resulting (thio)chroman-4-ols with 4-toluenesulfonic acid in refluxing toluene.[11,12] The 2*H*-thiochromene 1,1-dioxide (**3f**) was also obtained by this route starting from the thiochroman-4-one 1,1-dioxide (**2f**) prepared by oxidation of (**2g**) with peroxyacetic acid.[12] However, the 2*H*-thiochromene 1-oxide (**4**) was more conveniently prepared by direct oxidation of (**3g**) with 3-chloroperoxybenzoic acid in dichloromethane at 0 °C.[12,13]

The 4-methylenethiochroman (**8**) was obtained in moderate yield by the addition of (**2g**) to a solution of methylenetriphenylphosphorane, generated from methyltriphenylphosphonium bromide and n-BuLi in THF. The low yield of the compound is attributed to competitive deprotonation by the phosphorus ylide to afford an enolate which regenerates the thiochroman-4-one on aqueous work-up.

The *N*-tosylsulfimide (**9**) was conveniently prepared by refluxing an ethanolic solution of (**3g**) with a slight excess of chloramine-T trihydrate.[14]

3-Bromo-2,2-dimethylchromene (**6**) was obtained by addition of *N*-bromosuccinimide to the 2*H*-chromene (**3a**) in wet dimethyl sulfoxide to afford the *trans*-bromohydrin (**5**) which readily eliminated water on refluxing in toluene containing a catalytic amount of 4-TsOH.[15] The isomeric 4-bromochromene (**7a**) and the sulfur analogue (**7b**) were obtained directly from the respective chroman-4-ones (**2a, 2c**) by refluxing them in phosphorus tribromide.[16] The above routes are summarised in Scheme 1.

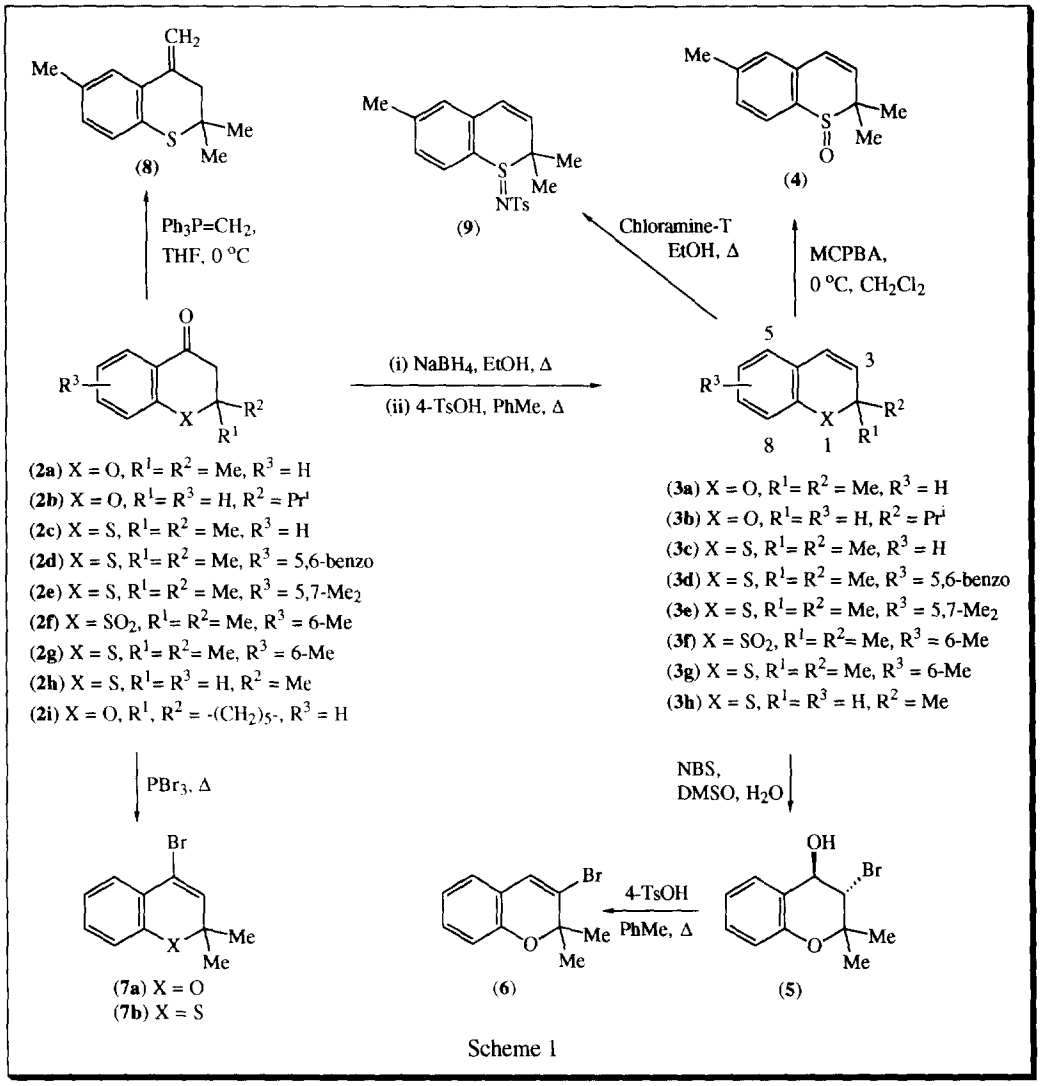
The dropwise addition of a solution of (**1a** or **b**) to a cold stirred solution of the 2*H*-(thio)chromenes (**3a-c**) in CH_2Cl_2 proceeded with the rapid discharge of the intense maroon colour associated with the triazolinedione and evaporation of the CH_2Cl_2 gave gums which yielded the adducts (**10a-d**) on trituration with Et_2O/light petroleum mixtures.

The presence of substituents in the aromatic ring of the 2*H*-thiochromenes (**3d,e**) had little effect on the rate of reaction or the nature of the products. Changing the solvent to acetone for the reaction of (**3e**) with (**1a**) resulted in a marked reduction in the rate of reaction and gentle warming was required to facilitate the discharge of the maroon colour, but the same adduct (**10f**) was obtained albeit in slightly lower yield. The effect of solvent polarity on the rate of reaction of (**1a**) with a variety of alkenes has been investigated.[17] With acetone, interception of a dipolar species was observed and the reaction afforded novel oxadiazines,[5] although not all attempts to trap such species have been successful.[17,18]

In contrast to the reaction of (**1a**) with the monosubstituted 2*H*-chromene (**3b**), 2-methylthiochromene (**3h**) gave only a dark brown multi-component mixture (TLC) which could not be resolved. Anomalous behaviour of 2*H*-thiochromenes having at least one hydrogen atom adjacent to the sulfur heteroatom with oxidising agents has been reported[12,19] and this feature may account for the current behaviour since triazolinediones are known oxidising agents.[20]

Reaction of the oxidised thiochromenes (**4**) and (**3f**) with (**1a**) failed to afford any of the expected products even on refluxing the reaction mixtures for several hours. However, refluxing the reactants in 1,2-dichloroethane (1,2-DCE) (b.p. 82 °C) effected the discharge of the maroon colour after 20 h. and 56 h. for (**4**) and (**3f**) respectively. The crude products were obtained by the usual work up and subsequent elution from silica afforded (**10g**) and (**10i**). Notably, (**10g**) was isolated as a single diastereoisomer (indicated by ^1H NMR

spectroscopy) implying some stereocontrol in the addition process. No thermal decomposition products derived from (**1a**) could be detected despite their well documented formation at elevated temperature.[21] The sulfimide (**9**) also gave a single diastereoisomer (**10h**) on reaction with (**1a**) after boiling in CH_2Cl_2 for 72 h; in 1,2-DCE the same product was formed after only 23 h. reflux.



Scheme 1

The marked effect of the change in oxidation state of the sulfur heteroatom on the rate of formation of the adducts (**10g,i**) can be explained by considering the electron density about the 3,4-double bond in the thiochromenes (**4**) and (**3f**). The addition of triazolindiones to alkenes has been shown to involve electrophilic attack by the triazolinedione on the double bond.[17,22] Thus, in (**3c**) the double bond is conjugated to the electron donating sulfur heteroatom and hence the reaction with (**1a**) proceeds rapidly, but the reverse situation obtains in

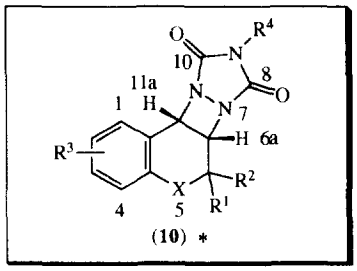
(**3f**) where the double bond is electronically deficient through conjugation with the sulfone. The reactivities of the sulfoxide (**4**) and sulfimide (**9**) fall in between those of **3c** and **3f**.

The ^{1}H NMR spectra of the adducts derived from the simple 2*H*-chromenes and 2*H*-thiochromenes are remarkably similar (Table 1) and display an AX pattern for H-6a/H-11a, with the latter absorbing further downfield in accord with its benzylic disposition. The magnitude of the coupling constant ($J_{\text{H-6a, H-11a}}$) is dependent on the heteroatom, being smaller for the oxygen compounds (**10a,b**) J ~ 8.4 Hz than for the sulfur analogues (**10c,d,e,f**) where J = 8.8 - 8.9 Hz implying subtle changes in the conformation of the hetero-ring. In both simple 2*H*-chromenes and 2*H*-thiochromenes $J_{3,4}$ is *ca.* 10 Hz.[23]

There is a lack of ^{1}H NMR data on 1,2-diazetidines fused to six-membered rings which could help to resolve the stereochemistry at the 6 and 6a positions in (**10b**). An indenodiazetidine has been obtained from PTAD in which coupling between the ring methylene protons and the heteroring protons is larger for *cis* (6.6 Hz) than for *trans* (1.1 Hz),[24] suggesting that the isopropyl group in (**10b**) may be *trans* to H-6a, although it is recognised that the different ring sizes may exert a profound effect on the geometry of the molecules and hence on the magnitude of coupling constants.

The chemical shifts of H-11a in the oxidised sulfur adducts (**10g,h,i**) are almost identical, though there is a considerable difference in the chemical shift of H-6a, with that of the sulfoxide (**10g**) absorbing downfield (δ 5.22) of that of the sulfone (**10i**) (δ 4.87). The magnitude of $J_{\text{H-6a, H-11a}}$ in the sulfone (**10i**) of 10.6 Hz is larger than those of the other adducts and is comparable with $J_{3,4}$ (~10.8 Hz) of the thiochromene 1,1-dioxides.[12,13] The coupling constants for H-6a, H-11a of both the sulfoxide (**10g**) and the sulfimide (**10h**) are 8.2 Hz and are comparable with those obtained for (**10a,b**).

Table 1: Selected ^{1}H NMR Data for Adducts (10).



(**10**) *

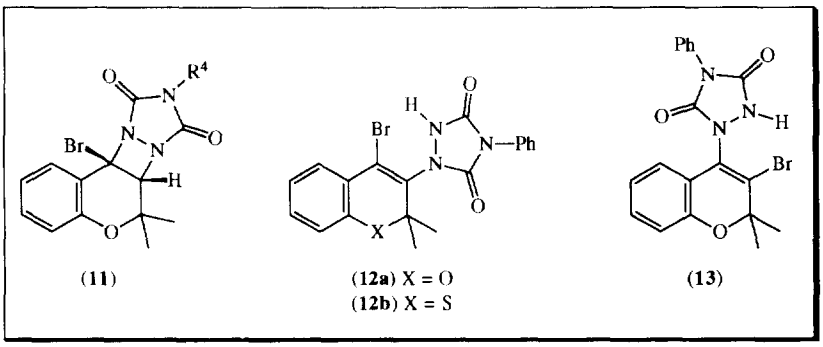
	X	R^1	R^2	R^3	R^4	δ H-6a	δ H-11a	$J_{6a,11a}$ (Hz)
10a	O	Me	Me	H	Ph	4.65	5.45	8.3
10b	O	H	Pr^i	H	Ph	5.23	5.61	8.5
10c	S	Me	Me	H	Ph	4.69	5.51	8.9
10d	S	Me	Me	H	Me	4.52	5.34	8.8
10e	S	Me	Me	1,2-benzo	Ph	4.87	6.48	8.9
10f	S	Me	Me	1,3-Me$_2$	Ph	4.68	5.84	8.9
10g	SO	Me	Me	2-Me	Ph	5.22	5.65	8.2
10h	S=NTs	Me	Me	2-Me	Ph	4.87	5.66	8.2
10i	SO$_2$	Me	Me	2-Me	Ph	4.94	5.67	10.6

* Only relative stereochemistry shown for (**10**).

During the recording of the melting point of adduct (**10i**), the compound darkened and once melted appeared to give off a gas. In order to investigate this observation, a sample was heated above its melting point for ~30 min. The resulting dark brown solid was eluted from silica with 30% ethyl acetate in hexane to afford two major components, the more polar of which was unchanged (**10i**). The ^{1}H NMR spectrum of the less polar pale yellow compound displayed a singlet at δ 2.34 (3H) and doublet at δ 2.53 (3H, J = 1.1 Hz). The remaining signals appear in the range δ 6.92 to δ 8.27 and account for a further 9 protons. Of these, three are readily assigned as they form the characteristic double doublet (δ 7.04, J = 8.6, 1.9 Hz), doublet (δ 7.12, J = 1.9 Hz) and doublet (δ 8.27, J = 8.6 Hz) pattern associated with the aromatic protons of a 6-substituted thiochroman unit. The remaining multiplet at δ 7.41 - 7.60 accounts for 5 protons, attributed to the *N*-phenyl function, and a poorly resolved signal at δ 6.92 accounts for a further proton. High resolution mass spectrometry gave a molecular ion at *m/z* 361.0890 with the base peak at *m/z* 214 corresponding to [M - PhN(CO)$_2$]. The various spectroscopic data indicate that the loss of two molecules of water during heating is accompanied by a rearrangement during which the *gem* dimethyl group is lost. Elemental analysis and mass spectral data indicate a formula $C_{20}H_{15}N_3O_2S$. The nature and mode of formation of this product are under active investigation.

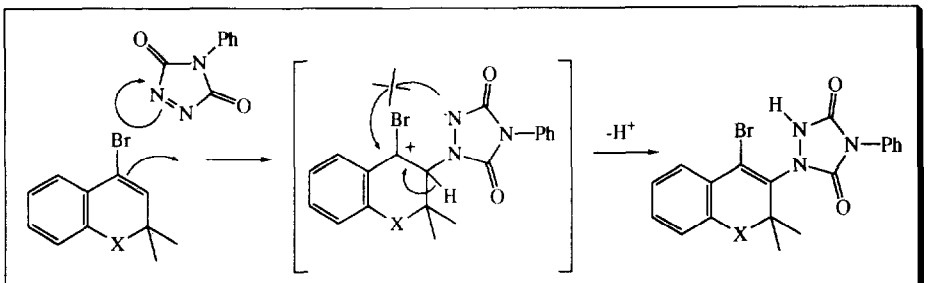
The addition of (**1a**) to the 4-bromochromene (**7a**) required gentle warming to effect complete reaction (TLC) in under 30 min. The ^{1}H NMR spectrum of the crude product indicated that two components had been formed, the major component being the diazetidine (**11**), indicated by the presence of a signal at δ 5.02 assigned to H-6a and singlets at δ 1.35 and δ 1.66 of the diastereotopic methyl groups. The minor component was thought to be (**12a**) (δ_{NH} = 4.4) which results from an electrophilic substitution process. Eluting the mixture from silica gave pure (**11**) but (**12a**) remained contaminated with some (**11**). The corresponding reaction with the sulfur analogue (**7b**) resulted in the formation of a single product (TLC) after a 1.5h reflux, which was characterised as (**12b**). The ^{1}H NMR spectrum product displayed a broad exchangeable signal at δ 4.7 assigned to the NH group and the geminal methyl groups gave rise to signals at δ 1.52 and δ 1.54.

The addition of (**1a**) to the 3-bromochromene (**6**) required the longest reaction time of all of the bromo derivatives, discharge of the maroon colour being complete after refluxing in CH_2Cl_2 for 8 h., but led to a multicomponent mixture from which none of the predicted product (**13**) could be isolated.



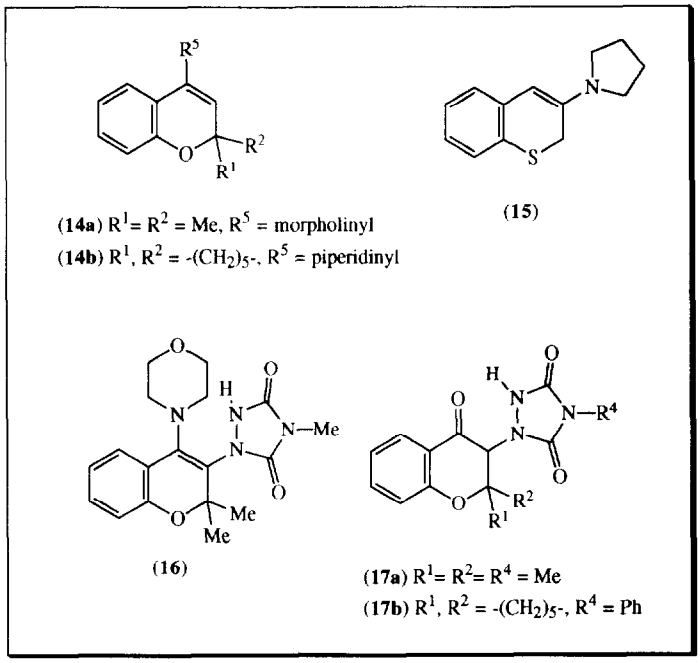
(**11**) (**12a**) X = O (**12b**) X = S (**13**)

The favoured electrophilic substitution process resulting in the formation of (**12**) can be attributed to steric factors. The bulky bromine substituent prevents the intramolecular capture of the carbocation generated by the initial attack of the triazolinedione and instead elimination of a proton completes the sequence to regenerate the double bond (Scheme 2).



Scheme 2

In view of the contrasting results obtained for the reaction of PTAD with the bromochromenes, this work was extended to the aminochromenes (**14a,b**) and (**15**). The former were readily obtained from the condensation of a cyclic secondary amine with the substituted chromanone promoted by titanium tetrachloride.[25] The sulfur analogue (**15**) was obtained by refluxing thiochroman-3-one in benzene containing pyrrolidine and a catalytic amount of 4-TsOH.[26]



(**14a**) $R^1 = R^2$ = Me, R^5 = morpholinyl
(**14b**) R^1, R^2 = -$(CH_2)_5$-, R^5 = piperidinyl

(**15**)

(**16**)

(**17a**) $R^1 = R^2 = R^4$ = Me
(**17b**) R^1, R^2 = -$(CH_2)_5$-, R^4 = Ph

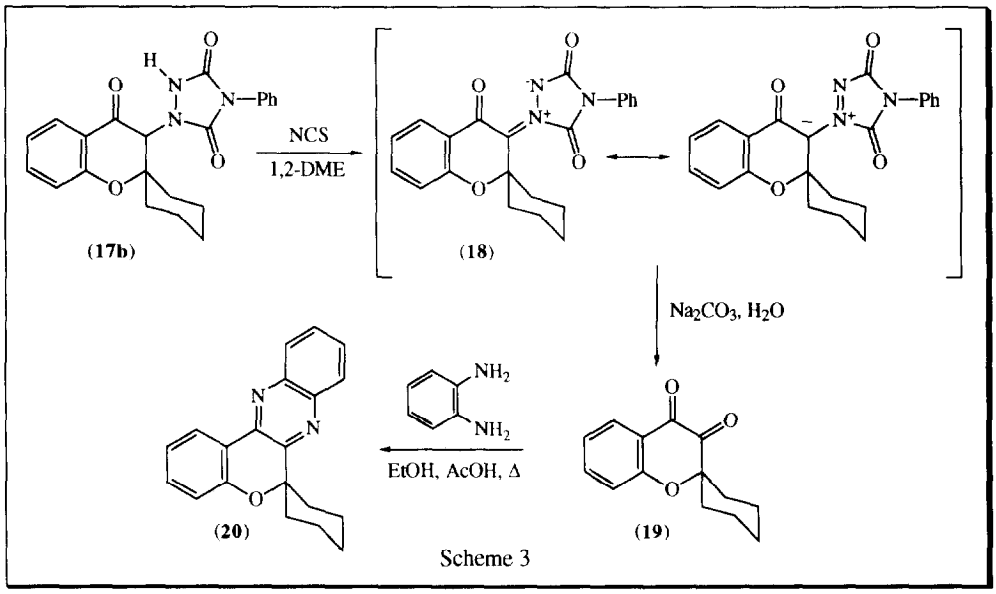
The reaction of (**14a**) with (**1b**) proceeded smoothly at 0 °C and after the solution had warmed to RT the solvent was removed to leave a solid product. The ^{1}H NMR of the product (**16**) was remarkably similar to that of the enamine (**14a**), but with the presence of a signal at δ 3.13 (N-Me) and a broad exchangeable signal at δ 9.25 (NH). Once again, an electrophilic substitution reaction takes preference over formation of the diazetidine adduct. Shaking this sample with dilute aq. HCl hydrolysed the enamine function to the urazolyl ketone (**17a**). The PTAD analogue (**17b**) was obtained directly from (**14b**) by incorporation of an acid wash into the work-up. The

^{1}H NMR of these ketones displayed a signal at δ 5.31 (**17a**) and δ 5.23 (**17b**) for H-3; the NH proton in both examples is broad and overlaps with the aromatic signals.

The addition of PTAD to the enamine (**15**) gave a multicomponent mixture which could not be separated, a similar result to that noted for the addition of PTAD to 2*H*-thiochromene (**3h**).

The direct formation of α-urazolyl ketones from ketones and PTAD has been reported,[8,9] but using this procedure, the chroman-4-one (**2i**) gave no urazolyl ketone (**17b**) even when the reaction mixture incorporated trifluoracetic acid as a catalyst. This lack of reactivity is probably a result of the fact that the chroman-4-ones exist as their keto-tautomers and are reluctant to enolise, thereby inhibiting electrophilic attack by the triazolinedione.

Considering the interest in chroman-[27] and thiochroman-3,4-diones,[28] it seemed worthwhile to exploit the methodology reported by Wilson and Hengge[10] for the transformation of phenylurazolyl ketones into 1,2-diketones using *t*-butyl hypochlorite in DMSO. Stirring a solution of the urazolyl ketone (**17b**) in 1,2-dimethoxyethane with *N*-chlorosuccinimide, a convenient alternative to *t*-BuOCl, gave a dark brown solution, presumably containing the dipolar species (**18**), which on hydrolysis with saturated aq. Na_2CO_3 gave a pale orange viscous oil which could not be induced to crystallise. The ^{1}H NMR spectrum of this crude oil was particularly informative. The absence of a signal at δ 5.23, indicative of H-3 in the starting material, confirms that a new product had been formed and furthermore, the absence of a signal at δ 2.6 - 3.0 indicates that the new product is not a chroman-4-one since the C-3 protons in chroman-4-ones routinely resonate at δ 2.8.[29] From these spectroscopic data, it seems that this product could be the chroman-3,4-dione (**19**). Refluxing a solution of (**19**) and *o*-phenylenediamine in ethanol containing a few drops of glacial acetic acid for 45 min. gave bright yellow crystals of the benzopyrano[3,2-*b*]quinoxaline (**20**), confirming the formation of the dione (**19**) (Scheme 3). The ^{1}H NMR spectrum of the quinoxaline compared favourably with those of other benzopyrano-[30] and benzothiopyrano[3,2-*b*]quinoxalines.[28]



Scheme 3

The reaction of the exocyclic alkene (**8**) with PTAD afforded a complex mixture of products from which no single compound could be isolated. In this case, products arising from a [2+2] cycloaddition and from an ene-

reaction, alone or followed by a further addition reaction are possible but none of these products could be identified by examination of the ^1H NMR spectrum of the crude product.

EXPERIMENTAL

Melting points were determined in capillary tubes and are uncorrected. Distillations were performed using a Kugelrohr (Buchi GKR-50 Glass Tube Oven) and all boiling points quoted relate to the oven temperature at which the distillation commenced. Fourier Transform infrared spectra were recorded on a Mattson Polaris spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker WM 250 instrument for solutions in $CDCl_3$, *J* values are given in Hz. Flash chromatographic separations were performed on Crossfields Sorbsil C60 silica gel (M.P.D. 60Å, 40-60μ, activated) according to the published procedure.[31]

2,2,6-Trimethylthiochromene 1-oxide (4).

3-Chloroperoxybenzoic acid (5.5 mmol, 55%), was added portionwise to a cooled (10 - 15 °C) stirred solution of the thiochromene (**3g**) (5.5 mmol) in dichloromethane (25 cm^3). After addition of the final portion of 3-chloroperoxybenzoic acid, the cooling bath was removed and the solution was stirred for a further 5 min. and then diluted with water (200 cm^3). The dichloromethane layer was separated and the aqueous layer was extracted with dichloromethane (2 x 50 cm^3). The combined organic extracts were washed successively with aqueous sodium sulphite solution (100 cm^3, ~ 2M), aqueous saturated $NaHCO_3$ solution (5 x 50 cm^3) and with water (100 cm^3). Removal of the dried (Na_2SO_4) solvent gave the **title compound** (89%) as a pale pink solid after elution from silica with 40% ethyl acetate in hexane and recrystallisation from light petroleum (b.p. 40 - 60 °C) and diethyl ether, m.p. 53.5 - 54.5 °C; υ_{max}/(Nujol) 1597, 1043 cm^{-1}; δ_H 1.25, (3H, s, 2-Me), 1.52 (3H, s, 2-Me), 2.37 (3H, s, 6-Me), 5.78 (1H, d, *J* 10.2, 3-H), 6.54 (1H, d, *J* 10.2, 4-H), 7.03 (1H, d, *J* 1.2, 5-H), 7.19 (1H, dd, *J* 7.8, 1.2, 7-H), 7.59 (1H, d, *J* 7.8, 8-H); (Found: C, 70.0; H, 6.9; S, 15.4. $C_{12}H_{14}OS$ requires C, 69.9; H, 6.9; S, 15.5 %).

4-Methylene-2,2,6-trimethylthiochroman (8).

n-Butyllithium (7.8 mmol) was added to a vigorously stirred suspension of methyltriphenylphosphonium bromide (7.0 mmol) in anhydrous THF (30 cm^3) cooled to -10°C under an argon atmosphere. The resulting orange solution was stirred at room temperature for 45 min. The thiochroman-4-one (**2g**) was added in a single portion followed by THF (20 cm^3). After stirring at RT for 1 hour, the solution was poured into water (200 cm^3) and extracted with ethyl acetate (3 x 50 cm^3). Removal of the dried (Na_2SO_4) solvent gave a brown oil which was eluted from silica with 10% ethyl acetate in hexane to afford: fraction 1, the **title compound** (**8**) (41 %), as a colourless oil, b.p. 100 °C at 0.5 mbar; δ_H 1.38 (6H, s, 2-Me), 2.31 (3H, s, 6-Me), 2.59 (2H, s, 3-H), 4.97 (1H, d, *J* 1.0, alkenyl-H), 5.59 (1H, d, *J* 1.0, alkenyl-H), 6.97 (2H, m, Ar-H), 7.46 (1H, m, Ar-H); (Found: C, 76.1; H, 7.9; S, 15.7. $C_{13}H_{16}S$ requires C, 76.4; H, 7.9; S, 15.7%); and fraction 2, **2,2,6-trimethylthiochroman-4-one** (**2g**) (47%).

2,2,6-Trimethylthiochromene 1-tosylsulfimide (9).

A solution of chloramine-T trihydrate (4.4 mmol) and 2,2,6-trimethylthiochromene (**3g**) (4.2 mmol) in ethanol (30 cm^3) was refluxed for 5 h. The cooled reaction mixture was diluted with water (200 cm^3) and extracted with ethyl acetate (5 x 50 cm^3). Removal of the combined dried solvent gave a sticky cream solid which was eluted from silica with 30 % ethyl acetate in hexane to afford a small amount of the 2*H*-thiochromene (**3g**) and the **title compound** (**9**) (78 %) as colourless needles from ethyl acetate, hexane and ethanol, m.p. 160.5 - 162 °C; δ_H 1.31 (3H, s, 2-Me), 1.46 (3H, s, 2-Me), 2.34 (3H, s, Ar-Me), 2.37 (3H, s, Ar-Me), 5.79 (1H, d, *J* 10.1, 3-H), 6.51 (1H, d, *J* 10.1, 4-H), 7.02 (1H, d, *J* 1.4, 5-H), 7.11 (1H, dd, *J* 7.9, 1.4, 7-H), 7.19-7.23 (3H, m, Ar-H), 7.78 (2H, m, Ar-H); (Found: C, 63.2; H, 5.8; N, 3.8; S, 18.1. $C_{19}H_{21}NO_2S_2$ requires C, 63.5; H, 5.9; N, 3.9; S, 17.8%).

General Method (A) for the Preparation of 4-Amino-2*H*-Chromenes (14).

A solution of $TiCl_4$ (26 mmol) in dry benzene (40 cm^3) was added to a vigorously stirred cold (-5 °C) solution of the chroman-4-one (50 mmol) and the amine (300 mmol) in dry benzene (100 cm^3) under N_2 at such a rate as to maintain the temperature of the reaction mixture below 5 °C. On completion of the addition the solution was allowed to warm to RT under N_2 overnight. The resulting viscous solution was filtered through a pad of celite and the pad washed well with dry benzene (200 cm^3). Removal of the solvent afforded a pale brown semi-solid whch was recrystallised to give the pure 4-aminochromene.

1. 2,2-Dimethyl-4-morpholino-2*H*-chromene (**14a**) (75 %) as colourless cubes from light petroleum (b.p. 40 - 60 °C), m.p. 106 - 107.5 °C; δ_H 1.40 (6H, s, 2-Me), 2.84 (4H, t, *J* 4.5, $(CH_2)_2N$), 3.84 (4H, t, *J* 4.5, $(CH_2)_2O$), 4.89 (1H, s, 3-H), 6.83-6.89 (2H, m, Ar-H), 7.13 (1H, m, Ar-H), 7.28 (1H, dd, *J* 7.9, 1.5, 5-H); (Found: C, 73.5; H, 7.8; N, 5.7. $C_{15}H_{19}NO_2$ requires C, 73.4; H, 7.8; N, 5.7 %).

2. 4-Piperidinospiro(2*H*-chromen-2,1'-cyclohexane) (**14b**) (51 %) as colourless cubes from light petroleum (b. p. 40 - 60 °C), m.p. 86 - 87 °C, δ_H 1.41-1.90 (16H, m, cyclohexane and piperidine rings), 2.77 (4H, m, $(CH_2)_2N$), 4.87 (1H, s, 3-H), 6.85-6.91 (2H, m, Ar-H), 7.09 (1H, m, Ar-H), 7.27 (1H, dd, *J* 7.8, 1.6, 5-H); (Found: C, 80.6; H, 8.9; N, 5.0. $C_{19}H_{25}NO$ requires C, 80.5; H, 8.9; N, 4.9 %).

General Method (B) for the Reaction of Triazolinediones with 2*H*-Chromenes and 2*H*-Thiochromenes.

A solution of the triazolinedione (5 mmol) in dichloromethane (30 cm^3) was added dropwise over ~ 15 min. to a cold (0 °C) stirred solution of the 2*H*-chromene or 2*H*-thiochromene (5 mmol) in dichloromethane (25 cm^3). On completion of the addition, the pale pink solution was allowed to warm to RT over ~ 1h., whereupon removal of the solvent gave the crude adduct which was washed with a little ice-cold diethyl ether and light petroleum (b.p. 30-40 °C) and collected by vacuum filtration. The following compounds were obtained in this manner.

1. 6,6-Dimethyl-9-phenyl-6a,9,10,11a-tetrahydro-6*H*,8*H*-[1]benzopyrano[3,4-*c*][1,2]diazeto[1,2-*a*][1,2,4]triazole-8,10-dione (**10a**) (91%) from (**3a**) and (**1a**) as an off-white solid, m.p. 173.5 - 175 °C; υ_{max}/(Nujol) 1776(w), 1722(s) cm^{-1}; δ_H 1.11 (3H, s, 6-Me), 1.68 (3H, s, 6-Me) 4.65 (1H, d, *J* 8.3, 6a-H), 5.45 (1H, d, *J* 8.3, 11a-H), 7.05 (2H, m, Ar-H), 7.25-7.52 (7H, m, Ar-H); (Found: C, 68.0; H, 5.0; N, 12.6. $C_{19}H_{17}N_3O_3$ requires C, 68.0; H, 5.1; N. 12.5%).

2. 6-Isopropyl-9-phenyl-6a,9,10,11a-tetrahydro-6*H*,8*H*-[1]benzopyrano[3,4-*c*][1,2]diazeto[1,2-*a*][1,2,4]triazole-8,10-dione (**10b**) (87%) from (**3b**) and (**1a**) as an off-white solid, m.p. 134.5 - 136.5 °C; υ_{max}/(Nujol) 1772(m), 1720(s) cm^{-1}; δ_H 1.10 (6H, m, $CH(C\underline{H}_3)_2$), 1.72 (1H, m, $C\underline{H}(CH_3)_2$), 4.49 (1H, dd, *J* 10.1, 3.1, 6-H), 5.23 (1H, dd, *J* 8.5, 3.1, 6a-H), 5.61 (1H, d, *J* 8.5, 11a-H), 7.06-7.12 (2H, m, Ar-H), 7.32-7.48 (7H, m, Ar-H); (Found: C, 68.7; H, 5.4; N, 12.1. $C_{20}H_{19}N_3O_3$ requires C, 68.7; H, 5.5; N, 12.0%).

3. 6,6-Dimethyl-9-phenyl-6a,9,10,11a-tetrahydro-6*H*,8*H*-[1]benzothiopyrano[3,4-*c*][1,2]diazeto[1,2-*a*][1,2,4]triazole-8,10-dione (**10c**) (93%) from (**3c**) and (**1a**) as an off-white powder from ethyl acetate and hexane, m.p. 175 - 175.5 °C; υ_{max}/(Nujol) 1779(w), 1720(s) cm^{-1}; δ_H 1.23 (3H, s, 6-Me), 1.59 (3H, s, 6-Me), 4.69 (1H, d, *J* 8.9, 6a-H), 5.51 (1H, d, *J* 8.9. 11a-H), 7.25 - 7.55 (9H, m, Ar-H); (Found: C, 64.9; H, 4.9; N, 12.1; S, 9.0. $C_{19}H_{17}H_3O_2S$ requires C, 64.9; H, 4.9; N, 12.0; S, 9.1%).

4. 6a,9,10,11a-Tetrahydro-6,6,9-trimethyl-6*H*,8*H*-[1]benzothiopyrano[3,4-*c*][1,2]diazeto[1,2-*a*][1,2,4]triazole-8,10-dione (**10d**) (89 %) from (**3c**) and (**1b**) as off white microcrystals from ethyl acetate and hexane, m.p. 137 - 139 °C; υ_{max}/(Nujol) 1774(m), 1703(s) cm^{-1}; δ_H 1.20 (3H, s, 6-Me), 1.54 (3H, s, 6-Me), 3.12 (3H, s, 9-Me), 4.52 (1H, d, *J* 8.8, 6a-H), 5.34 (1H, d, *J* 8.8, 11a-H), 7.23 - 7.35 (4H, m, Ar-H); (Found: C, 57.9; H, 5.3; N, 14.6; S, 11.3. $C_{14}H_{15}N_3O_2S$ requires C, 58.1; H, 5.2; N, 14.5; S, 11.1%).

5. 8,8-Dimethyl-11-phenyl-8a,11,12,13a-tetrahydro-8*H*,10*H*-naphtho[2,1-*b*]thiopyrano[3,4-*c*][1,2]diazeto[1,2-*a*] [1,2,4]triazole-10,12-dione (**10e**) (87%) from (**3d**) and (**1a**) as a pale yellow powder from ethyl acetate, m.p. 152 - 156 °C dec.; υ_{max}/(Nujol) 1778(w), 1726(s) cm^{-1}; δ_H 1.29 (3H, s, 8-Me), 1.65 (3H, s, 8-Me), 4.87 (1H, d, *J* 8.9. 8a-H), 6.48 (1H, d, *J* 8.9, 13a-H), 7.45 - 7.57 (8H, m, Ar-H), 7.81 - 7.89 (2H, m, Ar-H), 8.24 (1H, d, *J* 8.1, 1-H); (Found: C, 69.0; H, 4.7; N, 10.4; S, 7.9. $C_{23}H_{19}N_3O_2S$ requires C, 68.8; N, 10.5; S, 8.0%).

6. 9-Phenyl-6a,9,10,11a-tetrahydro-1,3,6.6-tetramethyl-6*H*,8*H*-[1]benzothiopyrano[3,4-*c*][1,2]diazeto[1,2-*a*] [1,2,4]triazole-8,10-dione (**10f**) (79%) from (**3e**) and (**1a**) as an off-white powder from ethyl acetate and hexane, m.p. 161 - 163 °C; υ_{max}/(Nujol) 1780(m), 1721(s) cm^{-1}; δ_H 1.23 (3H, s, 6-Me), 1.65 (3H, s, 6-Me), 2.21 (3H, s, Ar-Me), 2.44 (3H, s, Ar-Me), 4.68 (1H, d, *J* 8.9, 6a-H), 5.84 (1H, d, *J* 8.9, 11a-H), 6.90 (1H, d, *J* 1.4, Ar-H), 7.06 (1H, d, *J* 1.4, Ar-H), 7.36 - 7.55 (5H, m, 9-Ph); (Found: C, 66.7; H, 5.6; N, 11.1; S, 8.5. $C_{21}H_{21}N_3O_2S$ requires C, 66.5; H, 5.6; N, 11.1; S, 8.5%).

7. 1,2-Dihydro-1-(2,2-Dimethyl-4-morpholino-2*H*-[1]benzopyran-3-yl)-4-methyl-1,2,4-triazoline-3,5-dione (**16**) (97%) from (**14a**) and (**1b**) as an off-white solid from ethyl acetate and hexane, m.p. 198 - 199 °C; δ_H 1.43 (6H, s, 2-Me), 3.00 (4H, m, $N(CH_2)_2$), 3.13 (3H, s, N-Me), 3.79 (4H, m, $O(CH_2)_2$), 6.88 - 6.99 (2H,

m, Ar-H), 7.20 -7.26 (1H, m, Ar-H), 7.41 (1H, m, Ar-H), 9.57 (1H, bs, NH); (Found: C, 60.3; H, 6.2; N, 15.7. $C_{18}H_{22}N_4O_4$ requires C, 60.3; H, 6.2 ; N, 15.6%).
The foregoing solid was dissolved in ethyl acetate (150 cm^3) and washed with aqueous HCl (~2M, 3 x 50 cm^3) and then water (50 cm^3). Removal of the dried (Na_2SO_4) ethyl acetate gave an off-white solid which was recrystallised from ethyl acetate and hexane to afford 1,2-dihydro-1-(2,3-dihydro-2,2-dimethyl-4-oxo-4*H*-[1]benzopyran-3-yl)-4-methyl-1,2,4-triazoline-3,5-dione (**17a**) (91%) as colourless microcrystals, m.p. 197 - 198 °C, υ_{max}/(Nujol) 1768(w), 1687(s) cm^{-1}; δ_H 1.48 (3H, s, 2-Me), 1.56 (3H, s, 2-Me), 3.11 (3H, s, N-Me), 5.24 (1H, s, 3-H), 6.94 - 7.06 (2H, m, Ar-H), 7.50 (1H, m, Ar-H), 7.79 (2H, m, Ar-H); (Found: C, 58.2; H, 5.3; N, 14.7. $C_{14}H_{15}N_3O_4$ requires C, 58.1; H, 5.2; N, 14.5 %).

8. Incorporation of an acid wash (as described in 7 above) into the routine work up described in general method B gave the spiro compound (**17b**) (96%) from (**14b**) and (**1a**) as an off-white powder from hexane and ethyl acetate; m.p. 168.5 - 171 °C (dec.), υ_{max}/(Nujol) 1769(w), 1710(s), 1696(s) cm^{-1}; δ_H 1.22 - 2.20 (10 H, m, $(CH_2)_5$), 5.29 (1H, s, 3-H), 7.05 (1H, m, Ar-H), 7.36 - 7.59 (2H, m, Ar-H), 7.78 (1H, bs, NH), 7.86 (1H, m, Ar-H); (Found: C, 67.4; H, 5.5; N, 10.8. $C_{22}H_{21}N_3O_4$ requires C, 67.5; H, 5.4; N, 10.7%).
N-Chlorosuccinimide (3.0 mmol) was added portionwise over 20 min to a stirred solution of (**17b**) (3.0 mmol) in 1,2-dimethoxyethane (20 cm^3) at RT. On completion of the addition, saturated Na_2CO_3 solution (3 cm^3) was added in a single portion and the brown solution was stirred for a further 30 min. during which time the dark brown colour faded to pale orange. The resulting solution was diluted with water (100 cm^3) and extracted with ethyl acetate (3 x 30 cm^3). The combined organic extracts were washed well with brine (2 x 50 cm^3) and water (50 cm^3). Removal of the dried (Na_2SO_4) solvent gave a sticky orange oil (**19**). This oil was dissolved in ethanol (7.5 cm^3) containing 1,2-diaminobenzene (2.0 mmol) and glacial acetate acetic (0.2 cm^3), and then refluxed for 45 min. On cooling the crude product precipitated as yellow cubes which were collected and t recrystallised from ethyl acetate and hexane to afford spiro[6*H*-[1]benzopyrano[3,4-*b*]quinoxaline-6,1'-cychohexane] (**20**) (83%) as pale yellow cubes, m.p. 127 - 128 °C, δ_H 1.26 - 2.25 (10H, m, $(CH_2)_5$), 7.07 - 7.17 (2H, m, Ar-H), 7.45 (1H, m, Ar-H), 7.64 - 7.75 (2H, m, Ar-H), 8.01 - 8.07 (2H, m, Ar-H) 8.40 (1H, m, Ar-H); (Found: C, 79.2; H, 6.1; N, 9.4. $C_{20}H_{18}N_2O$ requires C, 79.4; H, 6.0; N, 9.3%).

General method (C) for the Reaction of 4-Phenyl-1,2,4-triazoline-3,5-dione with 2*H*-Thiochromenes.

A solution of (**1a**) or (**1b**) (3 mmol) and the 2*H*-thiochromene (3 mmol) (**3f**, **4** or **9**) in 1,2 dichloroethane (40 cm^3) was refluxed until the initial maroon colour was discharged and tlc examination of the reaction mixture indicated that no 2*H*-thiochromene remained. The cooled solvent was evaporated and the resulting sticky solid was then purified. The following compounds were obtained in this fashion.

1. 9-Phenyl-6a,9,10,11a-tetrahydro-2,6,6-trimethyl-6*H*,8*H*-[1]benzothiopyrano[3,4-*c*][1,2]diazeto[1,2-*a*][1,2,4]triazole-8,10-dione 5-oxide (**10g**), (54%) as colourless micro crystals from (**4**) after elution from silica with 50% ethyl acetate in hexane and recrystallisation from ethyl acetate and hexane, m.p. 190 - 195 °C (dec.), υ_{max}/(Nujol) 1770(m), 1709(s), 1039(m) cm^{-1}; δ_H 1.42 (3H, s, 6-Me), 1.80 (3H, s, 6-Me), 2.37 (3H, s, 2-Me), 5.22 (1H, d, *J* 8.2, 6a-H), 5.65 (1H, d, *J* 8.2, 11a-H), 7.23 (1H, dd, *J* 7.9, 1.7, 3-H), 7.33 (1H d,

J 1.7, 1-H), 7.41 - 7.57 (5H, m, 9-Ph), 8.24 (1H, d, *J* 7.9, 4-H); (Found: C, 63.0; H, 5.1; N, 10.7; S, 8.3. $C_{20}H_{19}N_3O_3S$ requires C, 63.0; H, 5.0; N, 11.0; S, 8.41%).

2. 9-Phenyl-6a,9,10,11a-tetrahydro-2,6,6-trimethyl-6*H*,8*H*-[1]benzothiopyrano[3,4-*c*][1,2]diazeto[1,2-*a*][1,2,4]triazole-8,10-dione 5-tosyl sulfimide (**10h**) (66%) as colourless microcrystals from (**9**) after elution from silica with 70% ethyl acetate in hexane and recrystallisation from ethyl acetate in hexane and methanol, m.p. 189 - 193 °C (dec.), υ_{max}/(Nujol) 1773(m), 1705(s) cm^{-1}; δ_H 1.12 (3H, s, 6-Me), 1.36 (3H, s, 6-Me), 2.38 (3H, s, 2-Me), 2.49 (3H, s, Ar-Me), 4.87 (1H, d, *J* 8.2, 6a-H), 5.66 (1H, d, *J* 8.2, 11a-H), 7.24 (1H, dd, *J* 8.0, 1.8, 3-H), 7.41 - 7.57 (8H, m, Ar-H), 7.97 - 8.04 (2H, m, Ar-H), 8.17 (1H, d, *J* 8.0, 4-H); (Found: C, 60.6; H, 4.9; N, 10.4; S, 12.2. $C_{27}H_{26}N_4O_4S_2$ requires C, 60.6; N, 4.9; N, 10.5; s, 12.0%).

3. 9-Phenyl-6a,9,10,11a-tetrahydro-2,6,6-trimethyl-6*H*,8*H*-[1]benzothiopyrano[3,4-*c*][1,2]diazeto[1,2-*a*][1,2,4]triazole-8,10-dione 5,5-dioxide (**10i**) (78%) as colourless microcrystals from ethyl acetate and methanol, m.p. 267 - 272 °C (dec.), υ_{max}/(Nujol) 1773(w), 1707(s), 1281(w), 1113(m) cm^{-1}; δ_H 1.56 (3H, s, 6-Me), 1.85 (3H, s, 6-Me), 2.38 (3H, s, 2-Me), 4.94 (1H, d, *J* 10.6, 6a-H), 5.67 (1H, d, *J* 10.6, 11a-H), 7.14 (1H, d,*J* 1.4, 1-H), 7.28 (1H, dd, *J* 7.7, 1.4, 3-H), 7.41 - 7.52 (5H, m, 9-Ph), 8.36 (1H, *J* 7.8, 4-H); (Found: C, 60.2; H, 4.7; N, 10.6; S, 8.3. $C_{20}H_{19}N_3O_4S$ requires C, 60.4; H, 4.8; N, 10.6; S, 8.1%).

Thermolysis of 9-Phenyl-6a,9,10,11a-tetrahydro-2,2,6-trimethyl-6*H*,8*H*-[1]benzothiopyrano [3,4-*c*][1,2]diazeto[1,2-*a*][1,2,4]triazole-8,10-dione 5,5-dioxide (10i).

The title compound (**10i**) (2.5 mmol) was heated above its melting point for 30 min. On cooling the resulting dark brown solid was eluted from silica with 30% ethyl acetate in hexane to afford: fraction 1 a pale yellow solid (46%) from ethyl acetate and hexane; m.p. 221.5 - 224 °C and fraction 2 unreacted (**10i**).

Addition of 4-Phenyl-1,2,4-triazoline-3,5-dione (1a) to 4-Bromo-2,2-dimethyl-2*H*-chromene (7a).

This method is a modification of general method (B). On completion of the addition, the pale pink solution was warmed until the pink colouration faded (~ 30 minutes). The cooled solvent was removed and the sticky residue eluted from silica with 35% ethyl acetate in hexane to afford: fraction 1 11a-bromo-6,6-dimethyl-9-phenyl-6a,9,10,11a-tetrahydro-6*H*,8*H*-[1]benzopyrano[3,4-*c*][1,2]diazeto[1,2-*a*][1,2,4]triazoline-8,10-dione (**11**) (56%)# as an off-white solid from ethyl acetate, methanol and hexane; m.p. 242 - 248 °C (decomp), υ_{max}/(Nujol) 1773(m), 1708(m), 1697(s) cm^{-1}; δ_H 1.20 (3H, s, 6-Me), 1.68 (3H, s, 6-Me), 5.02 (1H, s, 6a-H), 6.99 (1H, m, Ar-H), 7.11 (1H, m, Ar-H), 7.38 - 7.52 (6H, m, Ar-H), 7.75 (1H, m, Ar-H); (Found: C, 55.1; H, 3.9; N, 10.2; Br, 19.3. $C_{19}H_{16}N_3BrO_3$ requires C, 55.2; H, 4.1; N, 10.2; Br, 19.4 %); and fraction 2 a mixture of (**11**) and 1-(4-bromo-2,2-dimethyl-2*H*-[1]benzopyran-3-yl)-1,2-dihydro-4-phenyl-1,2,4-triazoline-3,5-dione (**12a**), δ_H 1.55 (3H, s, 2-Me), 1.56 (3H, s, 2-Me), 4.40 (1H, bs, NH), remaining signals overlap with those of (**11**).

yield based on pure (**11**) obtained.

Addition of 4-Phenyl-1,2,4-triazoline-3,5-dione (1a) to 4-Bromo-2,2-dimethyl-2*H*-thiochromene (7b).

This method is a modification of general method (B). On completion of the addition the maroon solution was refluxed for 1h during which time the colour faded to pale pink. The cooled solvent was evaporated and the off-white solid was washed with ether/light petroleum (b.p. below 40 °C) and then recrystallised from ethyl acetate and light petroleum (b.p.40 - 60 °C) to afford 1-(4-bromo-2,2-dimethyl-2*H*-[1]benzothiopyran-3-yl)-1,2-dihydro-4-phenyl-1,2,4-triazole-3,5-dione (**12b**) (71%), m.p. 215.5 - 217 °C, υ_{max}/(Nujol) 1769(m), 1697(s) cm^{-1}; δ_H 1.52 (3H, s, 2-Me), 1.54 (3H, s, 2-Me), 4.70 (1H, bs, NH), 7.22 - 7.76 (8H, m, Ar-H), 7.78 (1H, m, Ar-H); (Found: C, 52.9; H, 3.5; Br, 18.9; N, 10.2; S 7.8. $C_{19}H_{16}BrN_3O_2S$ requires C, 53.0; H, 3.8; N, 9.8; Br, 18.6; S, 7.6%).

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