Synthesis, Structure, and Reactivity to Nucleophiles of 3-Benzylidene- and 3-Ethylidene-2,3-dihydro-2-methyl-1,2-benzothiazin-4-one 1,1-Dioxides

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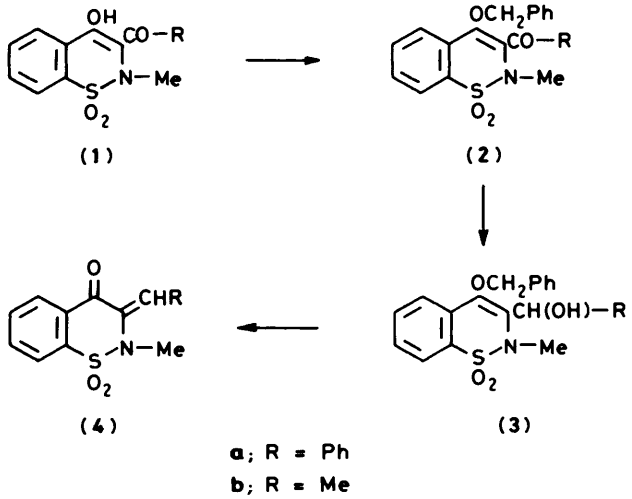
A new approach to (*Z*)-3-benzylidene- and 3-ethylidene-2,3-dihydro-2-methyl-1,2-benzothiazin-4-one 1,1-dioxides (**4**) starting from the corresponding 3-acyl derivatives (**1**) is described. A hypothesis, based on ^{13}C n.m.r. data, that products (**4**) may be considered as α,β-unsaturated carbonyl systems is confirmed experimentally by their chemical behaviour. Reaction with various nucleophiles such as hydrazine, sulphur ylides, and enamines leads to formation of polynuclear heterocyclic systems containing the 1,2-benzothiazine 1,1-dioxide skeleton.

The 1,2-benzothiazin-4-one system has been studied very little. Only recently has the importance of some of its derivatives as anti-inflammatory drugs [1,2] led to research on these heterocycles.

As part of our research into the synthesis of polycyclic heterocycles from unsaturated systems,[3,4] we have used 3-benzylidene- and 3-ethylidene-2,3-dihydro-2-methyl-1,2-benzothiazin-4-one 1,1-dioxides (**4a** and **b**) as starting materials for our syntheses.

H. Zinnes[5] reports two methods for the synthesis of compounds (**4**) starting from 2,3-dihydro-2-methyl-1,2-benzothiazin-4-one 1,1-dioxide by conversion with aldehydes and from 3-acyl-2,3-dihydro-2-methyl-1,2-benzothiazin-4-one 1,1-dioxides by selective reduction of the exocyclic carbonyl group followed by dehydration of the carbinol intermediate. However, there are disadvantages to each of these syntheses: the former is limited to aromatic aldehydes since aliphatic aldehydes self-condense under the reaction conditions, and furthermore the preparation of the 2,3-dihydro-2-methyl-1,2-benzothiazin-4-one 1,1-dioxide is long and laborious. The latter synthesis, despite the results reported by Zinnes, in our attempts led to a complex mixture of products arising from attack on the cyclic carbonyl group as well. These difficulties led us to develop a new approach to compounds (**4**) according to Scheme 1.



Scheme 1.

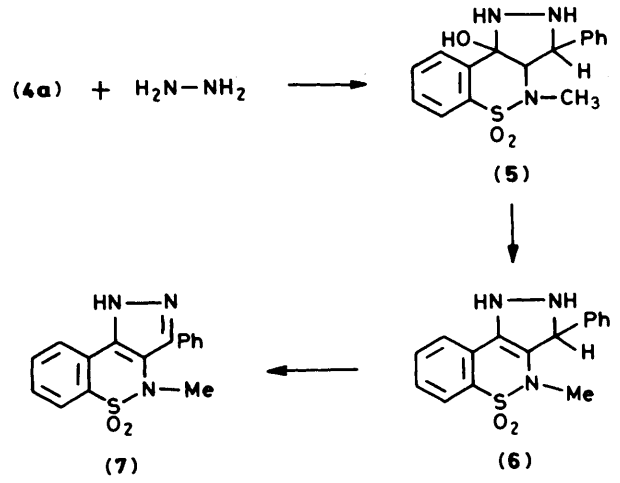
The starting materials (**1**) are readily prepared from saccharin [1,2-benzothiazol-3(2*H*)-one 1,1-dioxide] by means of conventional reactions[5] and are converted into the corresponding enol ethers (**2**) under phase-transfer conditions. These are then reduced to the carbinols (**3**) with sodium borohydride. Treatment of the latter with 10% sulphuric acid gives the products (**4**) directly and in high yield. With regard to the previously unreported steric configuration of compounds (**4**), it should be noted that the synthesis according to Scheme 1 gives only one of the two possible stereoisomers: that with *Z* configuration. This assignment was based on the chemical-shift value for the olefinic proton [δ_H 7.85 for (**4a**)] and by analogy with arylidene derivatives of ketomethylene compounds.[6] However, correct steric assignment requires the availability of spectroscopic data for both stereoisomers. In the case of (**4a**), the $Z \rightleftarrows E$ isomerization was effected photochemically in acetone solution by irradiation at 3 650 Å for 6 h at room temperature. The *Z*:*E* ratio in the reaction mixture was calculated to be 10:90 from the ^1H n.m.r. spectrum, based on the intensity of the olefinic proton signals at δ_H 7.85 and 7.36 respectively for the *Z* and *E* configurations.† This is consistent with the observation that in the *E* configuration the olefinic proton is not deshielded by the carbonyl group and so is shifted upfield. The chemical-shift values for the nitrogen methyl groups (δ_H 3.25 and 3.05 respectively for the *E* and *Z* isomers) also confirm the assignment.

The heterocyclic ring is not planar: molecular models show that an axial N–Me suffers less steric hindrance. In the *Z* configuration, the N–Me and Ph groups are almost perpendicular to one another and this results in the typical anisotropic shielding effect of the benzenic system. On the other hand, there is no such effect in the *E* isomer and the chemical shift of the N–Me group is typical of that in many 2,3-dihydro-2-methyl-1,2-benzothiazin-4-one 1,1-dioxides.

Products (**4**) may be seen as related to an α,β-unsaturated carbonyl compound or to a sulphonylenamine, depending on whether the electron-withdrawing effect of the carbonyl group or the electron-donating effect of the enamine nitrogen is predominant on the β carbon. A comparison of the ^{13}C n.m.r. data for this carbon atom (δ 140 p.p.m.) with the values for an enamine carbon (90—95 p.p.m.) suggests that ketones (**4**) can react with nucleophiles. Therefore the behaviour of ketones (**4**) with hydrazine, sulphur ylides, and enamines was studied.

Upon reaction with hydrazine in ethanol solution at room temperature, ketone (**4a**) gives rise to the hydroxypyrazolidine intermediate (**5**), the unexpected stability of which may be attributed to the rigidity of the tricyclic system. Subsequent

† Attempts to separate the (*E*)-isomer by column chromatography failed owing to its low stability.

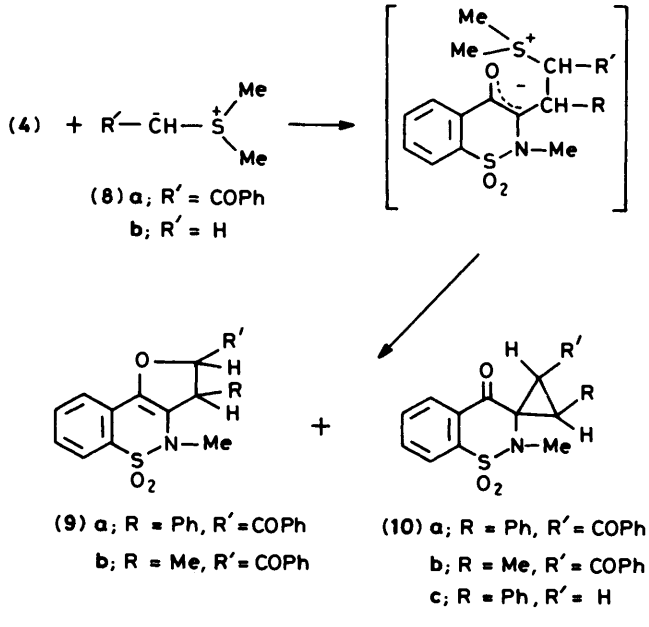


Scheme 2.

reaction with sodium hydroxide affords the pyrazoline (**6**), which may be oxidized to the corresponding pyrazole (**7**) (Scheme 2).

It is well known that sulphur ylides undergo several different types of reaction with α,β-unsaturated carbonyl compounds: (i) 1,2-addition; (ii) 1,4-conjugate addition; and (iii) 1,4-dipolar addition, with formation of oxiranes, cyclopropanes, or dihydrofurans, respectively. The product formed is dependent both on the type of ylide (stabilized or not) and on the unsaturated carbonyl system, and is therefore difficult to predict *a priori*.

Our results are consistent with these considerations in that two different reaction pathways were observed, depending on the type of ylide used. Reaction between ketones (**4**) and dimethyl(phenacylidene)sulphonium ylide (**8a**) afforded a 70:30 mixture (as determined by n.m.r. spectrometry) of the dihydrofuran (**9**) and the spirocyclopropane (**10**) derivatives. On the other hand, reaction with dimethyl(methylene)sulphonium ylide (**8b**) gave the cyclopropane derivatives (**10c**) only (Scheme 3).

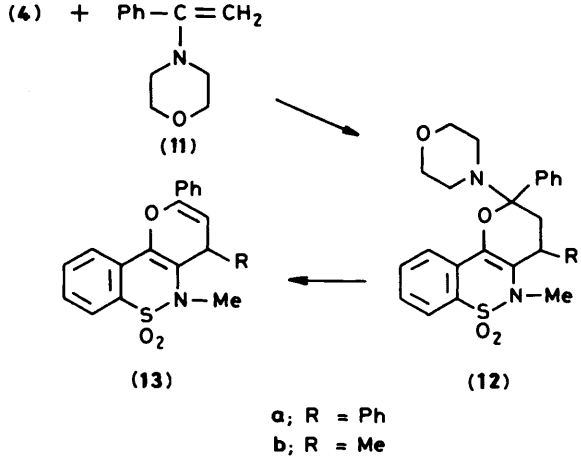


Scheme 3.

The products of the first reaction were separated by column chromatography, and the structure of the products was confirmed by ^{1}H n.m.r. spectrometry. The spectrum of (**9a**) has two doublets at δ_H 5.1 and 5.7 ($J_{2,3}$ 6.5 Hz) which may be assigned to the hydrogen atoms in the 2,3 positions of the dihydrofuran system. The observed values are consistent with those reported for other 2-acyl-substituted 2,3-dihydrofuran systems [7] and lead to a *trans* assignment on the basis of the $J_{2,3}$ value. As expected, the spirocyclopropane derivative (**10a**) has higher-field chemical shift values (δ_H 4.0 and 4.7). In this case as well, the coupling constant leads to a *trans* configuration assignment.*

The addition of ylides to ketones (**4**) is a typical two-step process: nucleophilic attack to form the resonance-stabilized (α) betaine, followed by reaction of the carbanion or oxa-anion with the carbon bearing the leaving group (dimethyl sulphide) to give a three- or five-atom ring respectively. The (**9**):(**10**) ratio is a function of the different contributions of the various mesomeric forms, their relative stability as determined by the presence or absence of an electron-withdrawing group, and the steric interactions in the transition phase between the betaine and the final products.

Finally, reaction of compounds (**4**) with α-morpholinostyrene (**11**) in toluene at 80 °C for 12 h leads to the formation of cycloaddition products (**12**) whose formation can be seen as a further example of a [4 + 2] heterodiene synthesis. Treatment of adducts (**12**) with hydrogen chloride in dioxane affords the corresponding pyranobenzothiazines (**13**) through elimination of the morpholine residue (Scheme 4). The structures assigned



Scheme 4.

to products (**12**) and (**13**) agree with the n.m.r. data (see Experimental section); unfortunately, the chemical-shift values for compounds (**12**) do not allow us to determine the relative configuration between the Ph and R substituents at positions 3 and 5.

Experimental

M.p.s were determined with a Buchi apparatus and are uncorrected. ^{1}H N.m.r. spectra were determined at 90 MHz with a Varian EM 390 spectrometer. Chemical shifts are expressed as δ values from tetramethylsilane.

* In the case of spiro derivative (**10a**) a mixture (20:80) of *cis*/*trans* isomers was obtained.

3-Acetyl- and 3-Benzoyl-2,3-dihydro-2-methyl-1,2-benzothiazin-4-one 1,1-Dioxides (**1b** *and* **a**) were prepared according to the reported method.[5]

General Procedure for the Preparation of Compounds (**2a** *and* **b**).—A mixture of the appropriate ketone (**1**) (0.1 mol), potassium carbonate (0.11 mol), and benzyl chloride (0.1 mol) in toluene (300 ml) was stirred and heated at 110 °C for 24 h in the presence of tetrabutylammonium bromide (0.01 mol). The cold reaction mixture was washed with water and the solvent was evaporated off. The residue was purified by crystallization from isopropyl alcohol to give the following ethers (**2**). *3-Benzoyl-4-benzyloxy-2-methyl-2H-1,2-benzothiazine 1,1-dioxide* (**2a**) (80%), m.p. 142—143 °C; $\delta_H(CDCl_3)$ 3.0 (3 H, s, NMe), 4.8 (2 H, s, CH_2), and 7.0—8.1 (14 H, m, ArH) (Found: C, 68.2; H, 4.7; N, 3.5. $C_{23}H_{19}NO_4S$ requires C, 68.14; H, 4.72; N, 3.46%); *3-acetyl-4-benzyloxy-2-methyl-2H-1,2-benzothiazine 1,1-dioxide* (**2b**) (74%), m.p. 104 °C; $\delta_H(CDCl_3)$ 2.4 (3 H, s, Ac), 3.0 (3 H, s, NMe), 5.0 (2 H, s, CH_2), and 7.2—8.0 (9 H, m, ArH) (Found: C, 62.8; H, 4.9; N, 4.0. $C_{18}H_{17}NO_4S$ requires C, 62.97; H, 4.99; N, 4.08%).

General Method for the Reduction of Ketones (**2a** *and* **b**) *to Alcohols* (**3a** *and* **b**).—To a stirred solution of a ketone (**2**) (0.1 mol) in ethanol (300 ml) was added portionwise sodium borohydride (0.05 mol). The mixture was heated to 50 °C for 16 h. The solvent was evaporated off and the residue was treated with 10% aqueous acetic acid to pH 5. The products were recovered by extraction with chloroform followed by evaporation of the solvent. *4-Benzyloxy-3-(α-hydroxybenzyl)-2-methyl-2H-1,2-benzothiazine 1,1-dioxide* (**3a**) (90%) had m.p. 130—132 °C (from di-isopropyl ether); $\delta_H(CDCl_3)$ 2.5 (1 H, d, OH exch. with D_2O), 2.8 (3 H, s, NMe), 4.8 (2 H, s, CH_2), 5.9 (1 H, d, CH), and 7.2—8.0 (14 H, m, ArH) (Found: C, 67.75; H, 5.1; N, 3.4. $C_{23}H_{21}NO_4S$ requires C, 67.80; H, 5.20; N, 3.44%). *4-Benzyloxy-3-(1-hydroxyethyl)-2-methyl-2H-1,2-benzothiazine 1,1-dioxide* (**3b**) (90%) had m.p. 95—97 °C (from cyclohexane); $\delta_H(CDCl_3)$ 1.3 (3 H, d, Me), 2.3 (1 H, d, OH exch. with D_2O), 3.1 (3 H, s, NMe), 4.6—5.0 (3 H, m, CH_2 and CH), and 7.3—8.0 (9 H, m, ArH) (Found: C, 62.65; H, 5.5; N, 4.1. $C_{18}H_{19}NO_4S$ requires C, 62.60; H, 5.55; N, 4.06%).

(Z)-3-Benzylidene- and -3-Ethylidene-2,3-dihydro-2-methyl-1,2-benzothiazin-4-one 1,1-Dioxide (**4a** *and* **b**).—A solution of the alcohol (**3a**) or (**3b**) (0.01 mol) in tetrahydrofuran (THF) (25 ml) was treated with 10% aqueous sulphuric acid (10 ml) and heated at 65 °C for 3 h. The solvent was evaporated off and the residue was extracted with chloroform. After drying (anhyd. Na_2SO_4) and evaporation of the solvent the residue was crystallized from isopropyl alcohol to give respectively the ketone (**4a**) (95%), m.p. 163—164 °C or (**4b**) (95%), m.p. 120—121 °C, whose m.p.s and spectroscopic data agree with those previously reported.[5]

1,2,3,3a,4,9b-Hexahydro-4-methyl-3-phenylpyrazolo[4,3-c]-[1,2]benzothiazin-9b-ol 5,5-Dioxide (**5**).—A solution of compound (**4a**) (0.5 g, 1.7 mmol) in ethanol (10 ml) was treated with hydrazine hydrate (0.084 ml, 1.7 mmol) and was set aside at room temperature for 2 h. The precipitate was filtered off and washed with cold ethanol to give the *title alcohol* (**5**) (0.5 g, 95%), m.p. 133—134 °C; $\delta_H[(CD_3)_2SO]$ 2.7 (3 H, s, NMe), 3.4 (1 H, s, OH exch. with D_2O), 4.0 (1 H, d, 3a-H), 4.0—4.7 (2 H, m, NH and 3-H), 6.6 (1 H, s, NH), and 7.4—8.1 (9 H, m, ArH) (Found: C, 58.1; H, 5.1; N, 12.5. $C_{16}H_{17}N_3O_3S$ requires C, 58.00; H, 5.17; N, 12.68%).

1,2,3,4-Tetrahydro-4-methyl-3-phenylpyrazolo[4,3-c][1,2]-benzothiazine 5,5-Dioxide (**6**).—To a mixture of dioxane (20 ml) and 0.5M-sodium hydroxide (20 ml) was added the alcohol (**5**) (0.4 g, 1.2 mmol) and the solution was stirred at room temperature for 12 h. The solvent was evaporated off and the residue was extracted with chloroform. After drying and evaporation of the solvent the residue was crystallized from isopropyl alcohol to give the *title compound* (**6**) (0.6 g, 90%), m.p. 187—188 °C; $\delta_H(CDCl_3)$ 2.9 (3 H, s, NMe), 6.5 (1 H, s, 3-H), and 7.2—8.0 (11 H, m, 2 × NH and ArH) (Found: C, 61.1; H, 4.8; N, 13.2. $C_{16}H_{15}N_3O_2S$ requires C, 61.33; H, 4.83; N, 13.41%).

1,4-Dihydro-4-methyl-3-phenylpyrazolo[4,3-c][1,2]benzothiazine 5,5-Dioxide (**7**).—To a stirred solution of potassium ferricyanide (1 g, 3 mmol) in 1M-sodium hydroxide (25 ml) was added a solution of compound (**6**) (0.4 g, 1.2 mmol) in dioxane (10 ml) and the mixture was stirred at room temperature for 4 h. Addition of water precipitated a solid which was collected by filtration, washed with water, and crystallized from ethanol to give the title compound (**7**) (0.2 g, 65%) m.p. 247—249 °C (lit.,[8] 249—250 °C).

Reaction of Ketone (**4**) *with Ylide* (**8**). *General Procedure.*—A solution of the ylide (**8**) (0.01 mol) in THF (25 ml) was added to a stirred solution of ketone (**4**) (0.01 mol) in the same solvent (25 ml) and the mixture was left at room temperature for 16 h. The solvent was evaporated off to give a residue which consisted (t.l.c.) of two products. Separation was achieved by column chromatography [silica gel; toluene–ethyl acetate (95:5)] and/or fractional crystallization. Thus obtained were *2-benzoyl-2,3-dihydro-4-methyl-3-phenyl-4H-furo[3,2-c][1,2]benzothiazine 5,5-dioxide* (**9a**) (2.3 g, 55%), m.p. 136—138 °C; $\delta_H(CDCl_3)$ 3.0 (3 H, s, NMe), 5.1 and 5.7 (2 H, 2 d, $J_{2,3}$ 6.5 Hz, 2- and 3-H), and 7.3—8.2 (9 H, m, ArH) (Found: C, 69.0; H, 4.5; N, 3.3. $C_{24}H_{19}NO_4S$ requires C, 69.06; H, 4.59; N, 3.36%); *2-benzoyl-2'-methyl-4'-oxo-3-phenylspiro [cyclopropane-1,3'-3',4'-dihydro-2'H-1',2'-benzothiazine] 1',1'-dioxide* (**10a**) (1 g, 24%), m.p. 148—150 °C, as a *cis*/*trans* mixture (20:80) from n.m.r. data, $\delta_H(CDCl_3)$ 2.5/2.8 (3 H, s, NMe), 4.0/4.3 [2 H, 2 d, *J* 8.7 Hz (*cis*), 2- and 3-H], 4.5/4.7 [2 H, 2 d, *J* 7.5 Hz (*trans*), 2- and 3-H], and 7.1—8.3 (14 H, m, ArH) (Found: C, 69.1; H, 4.5; N, 3.3. $C_{24}H_{19}NO_4S$ requires C, 69.06; H, 4.59; N, 3.36%); *2-benzoyl-2,3-dihydro-3,4-dimethyl-4H-furo[3,2-c][1,2]benzothiazine 5,5-dioxide* (**9b**) (1.8 g, 52%), m.p. 121—122 °C; $\delta_H(CDCl_3)$ 1.5 (3 H, d, 3-Me), 3.0 (3 H, s, NMe), 3.9 (1 H, m, 3-H), 5.5 (1 H, d, 2-H), and 7.4—8.2 (9 H, m, ArH) (Found: C, 64.0; H, 4.8; N, 3.9. $C_{19}H_{17}NO_4S$ requires C, 64.22; H, 4.82; ; N, 3.94%); *2-benzoyl-2',3-dimethyl-4'-oxospiro [cyclopropane-1,3'-3',4'-dihydro-2'H-1',2'-benzothiazine] 1',1'-dioxide* (**10b**) (0.8 g, 22%), m.p. 151—153 °C; $\delta_H(CDCl_3)$ 1.3 (3 H, d, 3-Me), 2.7 (3 H, s, NMe), 3.2 (1 H, m, 3-H), 4.0 (1 H, d, 2-H), and 7.4—8.3 (9 H, m, ArH) (Found: C, 64.1; H, 4.7; N, 3.9. $C_{19}H_{17}NO_4S$ requires C, 64.22; H, 4.82; N, 3.94%).

2'-Methyl-4'-oxo-2-phenylspiro [cyclopropane-1,3'-3',4'-dehydro-2'H-1',2'-benzothiazine 1',1'-Dioxide (**10c**).—To a stirred suspension of sodium hydride dispersion (60%) in oil (0.4 g, 10 mmol) in dimethyl sulphoxide (20 ml) was added trimethylsulphonium iodide (2.1 g, 10 mmol), under nitrogen, to give the ylide (**8b**). After 15 min a solution of ketone (**4a**) (3.0 g, 10 mmol) in the same solvent (5 ml) was added dropwise and the mixture was stirred for 2 h. The solvent was evaporated off under reduced pressure (0.1 mmHg) and the residue was treated with 5% aqueous acetic acid to pH 5. The precipitate was collected by filtration, washed with water, and crystallized from ethanol to give the *title compound* (**10c**) (2.5 g, 80%), m.p. 139—141 °C; $\delta_H(CDCl_3)$ 1.8 (1 H, dd, 3-H_A), 2.7 (1 H, dd, 3-H_B), 3.1 (3 H, s, NMe), 3.9 (1 H, t, 2-H_X), and 7.8—8.5 (9 H, m, ArH) (Found: C, 65.1; H, 4.7; N, 4.4. $C_{17}H_{15}NO_3S$ requires C, 65.17; H, 4.82; N, 4.47%).

Reaction of Ketones (**4**) *with α-Morpholinostyrene* (**11**). *General Procedure.*—A solution of a ketone (**4**) (5 mmol) and compound (**11**) (10 mmol) in toluene (50 ml) was heated at 80 °C for 12 h. The solvent was evaporated off to give the following products (**12**). 3,4-*dihydro*-5-*methyl*-2-*morpholino*-2,4-*diphenyl*-2H,5H-*pyrano*[3,2-c][1,2]*benzothiazine* 6,6-*dioxide* (**12a**) (2 g, 85%), m.p. 180—181 °C (from ethanol); $\delta_H(CDCl_3)$ 2.6 (3 H, s, NMe), 2.7—3.4 (7 H, m, CH_2NCH_2, 3-H_2, 4-H), 3.9 (4 H, t, CH_2OCH_2), and 7.8—8.8 (14 H, m, ArH) (Found: C, 68.7; H, 5.5; N, 5.6. $C_{28}H_{28}N_2O_4S$ requires C, 68.84; H, 5.78; N, 5.73%); 3,4-*dihydro*-4,5-*dimethyl*-2-*morpholino*-2-*phenyl*-2H,5H-*pyrano*[3,2-c][1,2]*benzothiazine* 6,6-*dioxide* (**12b**) (1.7 g, 83%), m.p. 160—162 °C (from isopropyl alcohol), $\delta_H(CDCl_3)$ 1.2 (3 H, d, 4-Me), 1.8—2.2 (1 H, m, 4-H), 2.3 (2 H, d, 3-H_2), 2.6 (3 H, s, NMe), 2.7—3.2 (4 H, m, CH_2NCH_2), 3.8 (4 H, t, CH_2OCH_2), and 7.2—8.0 (9 H, m, ArH) (Found: C, 64.3; H, 6.5; N, 6.5. $C_{23}H_{26}N_2O_4S$ requires C, 64.67; H, 6.15; N, 6.57%).

General Method for Deamination of Compounds (**12**) *to Alkenes* (**13**).—Hydrogen chloride gas was passed, for 6 h, into a stirred, refluxing solution of an amine (**12**) (3 mmol) in dioxane (20 ml). The solvent was evaporated off and the residue was treated with water and extracted with methylene dichloride. The organic layer was washed with 5% aqueous sodium hydrogen carbonate and dried (anhyd. Na_2SO_4), and the solvent was evaporated off. The residue was crystallized from isopropyl alcohol to give 5-*methyl*-2,4-*diphenyl*-4H,5H-*pyrano*[3,2-c][1,2]*benzothiazine* 6,6-*dioxide* (**13a**) (0.5 g 46%), m.p. 193—195 °C; $\delta_H(CDCl_3)$ 2.9 (3 H, s, NMe), 4.6 and 5.5 (2 H, 2 d $J_{3,4}$ Hz, 3- and 4-H), and 7.2—8.0 (14 H, m, ArH) (Found: C, 71.7; H, 4.6; N, 3.4. $C_{24}H_{19}NO_3S$ requires C, 71.81; H, 4.77; N, 3.49%); 4,5-*dimethyl*-2-*phenyl*-4H,5H-*pyrano*[3,2-c][1,2]*benzothiazine* 6,6-*dioxide* (**13b**) (0.5 g, 50%), m.p. 199—201 °C; $\delta_H(CDCl_3)$, 1.4 (3 H, d, 4-Me), 3.0 (3 H, s, NMe), 3.5 (1 H, m, 4-H), 5.5 (1 H, d, $J_{3,4}$ 4.5 Hz, 3-H) and 7.3—8.0 (9 H, m, ArH) Found: C, 67.1; H, 5.0; N, 4.1. $C_{19}H_{17}NO_3S$ requires C, 67.25; H, 5.05; N, 4.13%).

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