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STEREOSELECTIVE SYNTHESIS OF VINYLBENZOTHIAZOLES AND THEIR EPOXIDES.

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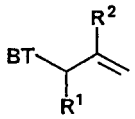
Abstract: Vinylbenzothiazoles 2 were stereoselectively prepared through isomerization of allylbenzothiazoles 1. Oxiranes 5 and 8 were synthesized from 2 and 1 via cyclization of the corresponding bromohydrins 3, 4, 6 and 7.

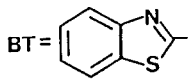
2-Vinylbenzothiazoles (vinyl BT's), known masked α,β-unsaturated carbonyl compounds[1] and ideal Michael acceptors,[2] can be prepared by condensation of 2-lithiobenzothiazole with carbonyls or by the reaction of 2-trimethylsilylmethylbenzothiazole with carbonyls followed by Peterson olefination.[2] Such strategies were mainly concerned with endocyclic vinyl BT's. A more recent route to vinyl BT's was based on the Wittig-type reaction of benzothiazolylmethyltriphenylphosphorane.[3] The epoxidation of such vinyl BT's on the other hand has never been reported so far.

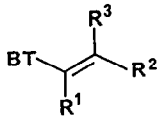
The present paper deals with a high yield and stereoselective route to vinyl BT's based on the allylation of 2-heterosubstituted benzothiazoles and subsequent isomerization. The stereospecific conversion of the vinyl- and allyl-BT's to the corresponding oxiranes has also been successfully carried out.

2-Allyl BT's 1, readily available by cross-coupling of 2-chlorobenzothiazole with allylic Grignard reagents,[4] were converted to vinyl BT's 2 upon treatment with bases. The isomerization 1-->2 could be made satisfactorily stereoselective depending upon the experimental conditions in terms of solvent and base (see table 1). Indeed, while the reaction of 2-allylbenzothiazole 1a with Et_3N in CH_2Cl_2 gave a 1:1 mixture of the E and Z isomers 2a and 2b, treatment of the same alkene 1a with MeONa in MeOH afforded almost exclusively compound 2a. Similarly, 2-allyl BT's 1b-d were isomerized to 2-vinyl BT's 2c-g (See Table 1). Vinyl BT's 2 were fully

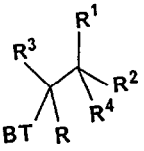


1a: $R^1=R^2=H$
1b: $R^1=Me;R^2=H$
1c: $R^1=H;R^2=Me$
1d: $R^1=Ph;R^2=H$

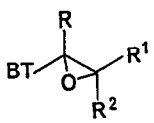




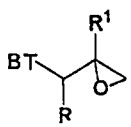
2a: $R^1=R^3=H;R^2=Me$
2b: $R^1=R^2=H;R^3=Me$
2c: $R^1=R^2=Me;R^3=H$
2d: $R^2=H;R^1=R^3=Me$
2e: $R^1=H;R^2=R^3=Me$
2f: $R^1=Ph;R^2=Me;R^3=H$
2g: $R^1=Ph;R^2=H;R^3=Me$



3a: $R=R^1=H;R^2=Me;R^3=Br;R^4=OH$
3b: $R=R^2=H;R^1=Me;R^3=Br;R^4=OH$
3c: $R^1=H;R=R^2=Me;R^3=Br;R^4=OH$
3d: $R=R^1=Me;R^2=H;R^3=Br;R^4=OH$
3e: $R=H;R^1=R^2=Me;R^3=OH;R^4=Br$
3f: $R=Ph;R^1=H;R^2=Me;R^3=Br;R^4=OH$
3g: $R=Ph;R^1=Me;R^2=H;R^3=Br;R^4=OH$
4a: $R=R^1=H;R^2=Me;R^3=OH;R^4=Br$
4b: $R=R^2=H;R^1=Me;R^3=OH;R^4=Br$
4f: $R=Ph;R^1=H;R^2=Me;R^3=OH;R^4=Br$
4g: $R=Ph;R^1=Me;R^2=H;R^3=OH;R^4=Br$
6a: $R=R^1=R^3=H;R^2=CH_2OH;R^4=Br$
6b: $R=R^3=H;R^1=Me;R^2=CH_2OH;R^4=Br$
7: $R=R^1=R^3=H;R^2=CH_2Br;R^4=OH$



5a: $R=R^2=H;R^1=Me$
5b: $R=R^1=H;R^2=Me$
5c: $R=R^1=Me;R^2=H$
5d: $R=R^2=Me;R^1=H$
5e: $R=H;R^1=R^2=Me$
5f: $R=Ph;R^1=Me;R^2=H$
5g: $R=Ph;R^1=H;R^2=Me$

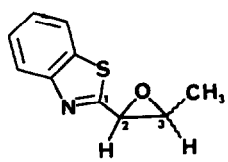


8a: $R=R^1=H$
8b: $R=H;R^1=Me$

characterized by ^{1}H-NMR spectroscopy and CG-MS spectroscopy. The configuration E or Z of olefins 2 was assigned on the basis of the coupling constants between the vinylic protons and/or the chemical shift of the methyl group β to the BT moiety. The trans isomer 2a shows a larger coupling constant between the vinylic protons (J = 15.5 Hz) than the cis isomer 2b (J = 11.6 Hz). The chemical shift of the methyl group in 2b which lies syn to the benzothiazolyl group resonates downfield with respect to the methyl group of 2a which is anti to BT, probably due to the deshelding effect of the BT group. Similarly in Z isomers 2d and 2g the methyl group syn to the BT moiety resonates downfield with respect to that of the corresponding

E isomers 2c and 2f.

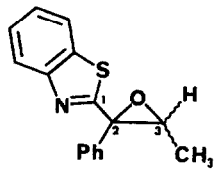
Several attempts to convert vinyl BT's 2 to the corresponding oxiranes 5 and 8 with m-chloroperbenzoic acid were unsuccessful. We may suppose, according the literature,[5] that the oxidation of the heterocyclic moiety giving benzothiazole N-oxides occurs instead of the epoxidation of the C-C double bond. In view of the significant synthetic potential of the above mentioned epoxides 5 and 8,not described so far, we looked for an indirect approach to them and we were pleased to find that a stereospecific synthesis of benzothiazolyl substituted oxiranes can be performed by cyclization of the halohydrins of alkenes 2.[6] Indeed, the reaction of vinyl BT 2a with N-bromosuccinimide (NBS) furnished a mixture of the regioisomeric bromohydrins 3a and 4a which, without isolation, were directly cyclized to give the sole epoxide 5a upon treatment with NaOH in isopropanol. Taking into account the stereochemical features of the halohydrin formation by using NBS under protic conditions, the bromohydrins 3a and 4a obtained from 2a should have erythro configuration. Similarly, vinyl BT's 2b, 2f and 2g were stereospecifically converted into epoxide 5b, 5f and 5g via regioisomeric bromohydrins 3b (threo), 4b (threo), 3f (erythro), 4f (erythro), 3g (threo) and 4g (threo) respectively. Reactions of vinyl BT's 2c, 2d, and 2e with NBS led exclusively to the bromohydrin 3c (erithro), 3d (threo) and 3e respectively, which were isolated, characterized and, upon treatment with NaOH in Pr^iOH, gave the epoxide 5c, 5d, and 5e (see table 2). All the epoxides 5 were fully characterized by ^{1}H-NMR, ^{13}C-NMR and GC-MS spectroscopy. The assignment of the configuration E or Z to the epoxides 5a and 5b was made on the basis of the ^{1}H-NMR coupling constants between the protons on the two ring carbons which turned out to be lower in the E isomer 5a (J = 1.9 Hz) with respect to that of the Z isomer 5b (J = 4.2 Hz). The ^{13}C-NMR spectrum of 5a and 5b confirms the assignment made on the basis of the proton spectrum. Indeed, in the ^{13}C-H coupled spectrum the $^3J_{CH_3\text{-}H2}$ (1.98 Hz) of epoxide 5a (having CH_3 and H-2 cis with respect to the ring) was larger than that of 5b ($^3J_{CH_3\text{-}H2} \sim 0$ Hz).



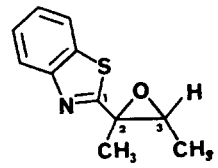
(5a or 5b)

Similarly, the long-range $^3J_{C1\text{-}H3}$ (1.75 Hz) of 5a (putting the BT group and H-3 on the same side of the ring) was larger than that of the epoxide 5b ($^3J_{C1\text{-}H3} \sim 0$).

The assignment of the configuration to the epoxides 5f and 5g could be made only on the basis of the ^{13}C-NMR proton coupled spectra. The epoxide 5f showed a long-range ^{13}C-H coupling constant larger than that corresponding to the isomer 5g ($^3J_{C1-H3}$ = 1.69 Hz for 5f and $^3J_{C1-H3} \sim 0$ for 5g).



(5f or 5g)



(5c)

By analogy, to the epoxide 5c was assigned the E configuration on the basis the vanishingly small long-range ^{13}C-H coupling constant ($^3J_{CH-H2} \sim 0$).

Similarly, 2-allyl BT's 1 could be converted to oxiranes 8, through the corresponding halohydrins 6 and 7. Indeed, the reaction of 2-methallyl BT 1c with NBS gave exclusively bromohydrin 6b which was promptly cyclized to epoxide 8b. The reaction of 2-allyl BT 1a afforded low yields of bromohydrins 6a and 7 which, without isolation, were cyclized to epoxide 8a still in low yield.

Table 1: Isomerization of 2-allyl BT's 1 to 2-vinyl BT's 2.

2-allyl BT	Base	Solvent	Temp.	Reaction time h	Reaction products (yield %)
1a	Et_3N	CH_2Cl_2	R.T.	96	2a (61) + 2b (36)
"	MeONa	MeOH	"	24	2a (91) + 2b (9)
"	DABCO	THF	"	72	- -
"	t-BuOK	THF	-78°	24	- -
1b	Et_3N	CH_2Cl_2	R.T.	96	2c (57) + 2d (15)
"	MeONa	MeOH	"	6	2c (98) + 2d (2)
"	t-BuOK	THF	"	72	- -
1c	MeONa	MeOH	"	6	2e (100)
"	NaH	THF	"	72	- -
1d	MeONa	MeOH	"	12	2f (100)
"a					2f (70) + 2g (30)

a) The isomerization was achieved by keeping the allyl derivative at RT for a long period of time. 2f and 2g were then separated by column chromatography.

In conclusion, synthetically useful diastereoisomeric 2-vinyl BT's can be easily prepared by isomerization of promptly available 2-allyl BT's. Moreover, so far undescribed and potentially very useful epoxides 5 and 8 can be easily achieved by cyclization of bromohydrins of 2 and 1.

The study of the reactivity of epoxides 5 and 8 is underway and results will be published in due course.

Table 2: Epoxidation of 2-vinyl BT's 2 and 2-allyl BT's 1 to epoxides 5 and 8 via reaction with NBS and cyclization with NaOH/Pr^iOH at R.T.

Alkene	Reaction time h	Bromohydrins	Epoxide yield (%)
2a	9	3a + 4a (erythro)	5a (97)
2b	8	3b + 4b (threo)	5b (93)
2c	6	3c (erythro)	5c (86)
2d	3	3d (threo)	5d (95)
2e	6	3e	5e (84)
2f	6	3f + 4f (erythro)	5f (90)
2g	18	3g + 4g (threo)	5g (88)
1a	5	6a + 7	8a (28)
1c	3	6b	8b (88)

EXPERIMENTAL

^{1}H-NMR spectra were recorded on a Varian XL-200 or EM 360-A; chemical shifts are reported in parts per million (δ) from internal Me_4Si. Proton coupled ^{13}C-NMR spectra were recorded on a Varian XL-200 operating at 50.1 MHz. Melting points were determined on a Electrothermal apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 598 spectrophotometer. Flash chromatographies were done with Merck 230-400 mesh silica gel. GC/mass spectrometry analyses were performed on a Hewlett-Packard 5890A Gas chromatograph equipped with SE-30 capillary column, 30 m, and Hewlett-Packard Mass Selective Detector MSD 5970B operating at 70 eV (E.I.).

Materials: - Tetrahydrofuran (THF) and diethyl ether of commercial grade (RS, Carlo Erba) were purified by distillation (twice) from sodium wire in a N_2 atmosphere. Petroleum ether (RS, C.E.) refers to the 40-60° boiling fraction. CH_2Cl_2, 1,4-dioxane and isopropanol were commercial grade. 2-Chlorobenzothiazole, allylic halides and N-Bromosuccinimide were commercial grade (Fluka) and used without further purification. 2-Allylbenzothiazole 1a, 2-α-methylallylbenzothiazole 1b, 2-methallylbenzothiazole 1c and 2-α-phenylallylbenzothiazole 1d were prepared as reported.[4]

Isomerization of allylic benzothiazoles 1 to vinylic benzothiazoles 2.

General procedure. - The isomerization 1-->2 was carried out on treating the allyl BT's 1 with the appropriate base following the diseappearance of the starting material by TLC or GC. Here is described as an example the isomerization of 1a to 2a and 2b.

To a solution of 1a (1 g, 5.71 mmole) in 10 ml of CH_2Cl_2 1.5 ml of Et_3N was added and the mixture was kept at RT for four days. Evaporation of the solvent left a residue that was a mixture of two components which were separated by column chromatography on silica gel (petroleum ether 8.5, ethyl acetate 1.5). The first eluted compound, 0.36 g, was cis-2-benzothiazolyl--1-propene 2b. The second eluted compound, 0.61 g, was trans-2-benzothiazolyl-1-propene 2a. Yields are reported in table 1. All the new vinylic benzothiazoles 2 showed the data reported below.

2a: - oil. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.63 (d, 3H, J = 5.2 Hz), 6.36-6.51 [(m, 2H; when the signal at 1.63 ppm was irradied the multiplet was transformed in two doublets: 6.47 (d, 1H, J = 15.5 Hz], 6.37 (d, 1H, J = 15.5 Hz), 6.96-7.16 (m, 2H), 7.45-7.49 (m, 1H); 7.66-7.71 (m, 1H). Ms m/e (rel. int.): 175 (M^+, 100), 174 (64), 149 (60), 108 (15), 69 (45), 39 (46).

2b: - oil. ^{1}H-NMR (200 MHz, $CDCl_3$):δ 1.99 (dd, 3H, J = 1.8 Hz, J = 7.4 Hz), 6.02 (dq, 1H, J = 7.4 Hz, J = 11.6 Hz), 6.56 (dq, 1H, J = 1.8 Hz, J = 11.6 Hz), 7.07-7.28 (m, 2H), 7.60-7.65 (m, 1H), 7.79-7.84 (m, 1H). Ms m/e (rel. int.): 175 (M^+, 100), 174 (65), 149 (55), 108 (12), 69 (25), 39 (15).

2c: - m.p. 52-53°C (ether-petroleum ether). ^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.85 (dq, 3H, J = 1.1 Hz, J = 6.1 Hz), 2.20-2.21 (m, 3H), 6.58 (qq, 1H, J = 6.1 Hz, J = 1.4 Hz), 7.23-7.43 (m, 2H), 7.72-7.77 (m, 1H), 7.95-8.00 (m, 1H). Ms m/e (rel. int.): 189 (M^+, 100), 188 (47), 174 (32), 173 (48), 162 (13), 149 (87), 109 (14), 69 (25), 39 (17).

2d: - oil. ^{1}H-NMR (60 MHz, CCl_4): δ 2.22 (d, 3H, J = 8.0 Hz), 2.28 (s, 3H), 6.15 (dq, 1H, J = 1.2 Hz, J = 7.0 Hz), 7.3-7.7 (m, 2H), 7.8-8.2 (m, 2H). Ms m/e (rel. int.): 189 (M^+, 100), 188 (47), 174 (30), 173 (46), 162 (19), 149 (90), 109 (17), 69 (27), 39 (20).

2e: - m.p. 78-79°C (ether-petroleum ether). ^{1}H-NMR (60 MHz, CCl_4): δ 2.06 (s, 3H), 2.32 (s, 3H), 6.5-6.7 (m, 1H), 7.3-7.7 (m, 2H), 7.8-8.2 (m, 2H). Ms m/e (rel. int.): 189 (M^+, 100), 174 (98), 173 (41), 149 (57), 109 (11), 69 (22), 39 (18).

2f: - oil. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.85 (d, 3H, J = 7.2 Hz), 7.15 (q, 1H, J = 7.2 Hz), 7.25-7.50 (m, 7H), 7.70-7.80 (m, 1H), 8.0-8.10 (m, 1H). Ms m/e (rel. int.): 251 (M^+, 100), 250 (77), 236 (18), 149 (81), 115 (44).

2g: - oil. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 2.15 (d, 3H, J = 7.2 Hz), 6.41 (q, 1H, J = 7.3 Hz), 7.31-7.55 (m, 7H), 7.84-7.89 (m, 1H), 8.10-8.15 (m, 1H). Ms m/e (rel. int.): 251 (M^+, 100), 250 (75), 236 (18), 149 (87), 115 (45), 77 (8).

Epoxidation of alkenyl benzothiazoles 2 and 1. General procedure. -

The epoxidation of alkenyl benzothiazoles was performed in two steps. In the first step the alkenyl BT's were transformed, on treatment with NBS in dioxane/water (7:3), into the corresponding bromohydrins. In the second step the bromohydrins were epoxidized upon treatment with NaOH in isopropanol. In the case of vinyl BT's 1a, 2a, 2b, 2f and 2g treatment with NBS led to mixtures of regioisomeric bromohydrins which were then epoxidized without separation. In the case of vinyl BT's 1c, 2c, 2d, 2e, only one bromohydrin was obtained. Yields are reported in Table 2. As an example here is described the epoxidation of 2a to 5a: to a solution of 2a (0.41 g, 2.34 mmole) in 14 ml of 1,4-dioxane and 6 ml of H_2O was added portionwise NBS (0.5 g, 2.81 mmole). After 9h the reaction mixture was poured into water, extracted with Et_2O (3x15 ml), washed with H_2O and dried over $MgSO_4$. Eva-

poration of the solvent under reduced pressure gave a residue that was a mixture of bromohydrins 3a and 4a (0.65 g). 0.61 g of such bromohydrins in 8 ml of isopropanol were added with a few drops of phenolphthalein and titrated with aqueous 1M NaOH. Then the solution was diluted with water, extracted with Et_2O and worked up as usual to give almost pure epoxide 5a 97% yield. ^{1}H-NMR data for new bromohydrins 3, 4, 6 and 7 and all new epoxides 5 and 8 are given below:

3a+4a: - oil. ^{1}H-NMR (60 MHz, $CDCl_3/D_2O$): δ 1.2-1.9 (m, 3H), 3.3-3.8 (m, 1H), 4.6-5.5 (m, 1H), 7.3-7.8 (m, 2H), 7.8-8.4 (m, 2H). IR: 3320 cm^{-1} (OH).

3b+4b: - oil. ^{1}H-NMR (60 MHz, $CDCl_3/D_2O$): δ 1.4-2.1 (m, 3H), 3.5-4.2 (m, 1H), 4.8-5.6 (m, 1H), 7.4-7.9 (m, 2H), 7.9-8.4 (m, 2H). IR: 3340 cm^{-1} (OH).

3c: - oil. ^{1}H-NMR (60 MHz, $CDCl_3/D_2O$): δ 1.70 (d, 3H, J = 7.0 Hz), 1.94 (s, 3H), 4.94 (q, 1H, J = 7.0 Hz), 7.4-7.8 (m, 2H), 7.9-8.3 (m, 2H). IR: 3375 cm^{-1} (OH).

3d: - oil. ^{1}H-NMR (60 MHz, $CDCl_3/D_2O$): δ 1.78 (s, 3H), 1.82 (d, 3H, J = 6.0 Hz), 4.92 (q, 1H, J = 6.0 Hz), 7.4-7.8 (m, 2H), 7.9-8.3 (m, 2H). IR: 3380 cm^{-1} (OH).

3e: - oil. ^{1}H-NMR (60 MHz, $CDCl_3/D_2O$): δ 1.45 (s, 3H), 1.54 (s, 3H), 5.43 (s, 1H), 7.4-7.8 (m, 2H), 7.9-8.3 (m, 2H). IR: 3405 cm^{-1} (OH).

3f: - oil. ^{1}H-NMR (60 MHz, $CDCl_3/D_2O$): δ 1.88 (d, 3H, J = 7.1 Hz), 5.50 (q, 1H, J = 7.1 Hz), 7.2-7.6 (m, 7H), 7.8-8.3 (m, 2H). IR: 3360 cm^{-1} (OH).

3g: - oil. ^{1}H-NMR (60 MHz, $CDCl_3/D_2O$): δ 1.89 (d, 3H, J = 7.3 Hz), 5.50 (q, 1H, J = 7.3 Hz), 7.2-7.6 (m, 7H), 7.8-8.2 (m, 2H). IR: 3370 cm^{-1} (OH).

4f: - oil. ^{1}H-NMR (60 MHz, $CDCl_3/D_2O$): δ 1.85 (d, 3H, J = 6.5 Hz), 3.55 (q, 1H, J = 6.5 Hz), 7.2-7.6 (m, 7H), 7.8-8.2 (m, 2H). IR: 3360 cm^{-1} (OH).

4g: - oil. ^{1}H-NMR (60 MHz, $CDCl_3/D_2O$): δ 1.85 (d, 3H, J = 6.7 Hz), 3.55 (q, 1H, J = 6.7 Hz), 7.2-7.6 (m, 7H), 7.9-8.2 (m, 2H). IR: 3360 cm^{-1} (OH).

6a+7: - oil. ^{1}H-NMR (60 MHz, $CDCl_3/D_2O$): δ 3.3-4.2 (m, 4H), 4.7-4.9 (m, 1H), 7.3-7.8 (m, 2H), 7.8-8.3 (m, 2H). IR: 3360 cm^{-1} (OH).

6b: - oil. ^{1}H-NMR (60 MHz, $CDCl_3/D_2O$): δ 1.50 (s, 3H), 3.50 (s, 2H), 3.75 (s, 2H), 7.3-7.8 (m, 2H), 7.9-8.3 (m, 2H). IR: 3390 cm^{-1} (OH).

5a: - oil. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.22 (d, 3H, J = 5.2 Hz), 3.03 (dq, 1H, J = 1.9 Hz, J = 5.2 Hz); 3.82 (d, 1H, J = 1.9 Hz), 7.04-7.23 (m, 2H), 7.53-7.58 (m, 1H), 7.70-7.75 (m, 1H). Ms m/e (rel. int.): 191 (M^+, 27), 176 (16), 174 (9), 162 (11), 135 (100), 109 (12). ^{13}C-NMR ($CDCl_3$): δ 17.5 (qdd, CH_3, J = 127.6, J = 6.3, J = 1.9 Hz), 57.3 (dqd, C-3, J =182.7, J = 4.9, J = 1.7 Hz), 60.1 (dqd, C-2, J = 176.1, J = 5.6, J = 2.2 Hz), 121.8, 122.8, 125.3, 126.2, 134.2, 153.3, 169.9 (dd, C-1, J = 7.2, J = 1.8 Hz)

5b: - oil. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.12 (d, 3H, J = 5.4 Hz), 3.27 (dq, 1H, J = 4.2 Hz, J = 5.4 Hz), 4.16 (d, 1H, J = 4.2 Hz), 7.09-7.28 (m, 2H), 7.60-7.65 (m, 1H), 7.76-7.80 (m, 1H). Ms m/e (rel. int.): 191

(M^+, 26), 176 (17), 174 (9), 162 (10), 135 (100), 109 (14). ^{13}C-NMR ($CDCl_3$): δ 13.0 (qdd, CH_3, J = 128.0, J = 6.4, J = 0.5 Hz), 56.0 (dqd, C-3, J = 181.2, J= 4.3, J = 1.1 Hz), 56.4 (dqd, C-2, J = 175.0, J = 5.5, J = 1.7 Hz), 121.6, 122.9, 125.3, 126.3, 134.5, 153.4, 167.6 (dd, C-1, J = 6.1, J = 0.6 Hz).

5c: - oil. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.38 (d, 3H, J = 5.4 Hz), 1.80 (s, 3H), 3.20 (q, 1H, J = 5.4 Hz), 7.21-7.41 (m, 2H), 7.71-7.76 (m, 1H), 7.90-7.95 (m, 1H). Ms m/e (rel. int.): 205 (M^+, 52), 190 (100), 188 (7), 176 (3), 162 (47), 135 (68), 109 (32). ^{13}C-NMR ($CDCl_3$): δ 14.3 (qd, CH_3, J = 127.3, J = 6.1 Hz), 15.5 (q, CH_3, J = 128.9 Hz), 60.5 (C-3), 64.2 (C-2), 121.8, 122.8, 125.1, 126.0, 134.7, 153.6, 175.1 (m, C-1).

5d: - oil. ^{1}H-NMR (60 MHz, $CDCl_3$): δ 1.32 (d, 3H, J = 5.4 Hz), 1.91 (s, 3H), 3.42 (q, 1H, J = 5.4 Hz), 7.3-7.8 (m, 2H), 7.9-8.3 (m, 2H).

5e: - m.p. 57-59°C (ether-petroleum ether). ^{1}H-NMR (60 MHz, $CDCl_3$): δ 1.39 (s, 3H), 1.58 (s, 3H), 4.30 (s, 1H), 7.3-7.8 (m, 2H), 7.9-8.3 (m, 2H). Ms m/e (rel. int.): 205 (M^+, 46), 190 (63), 188 (29), 176 (10), 162 (12), 135 (100), 109 (27).

5f: - oil. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.22 (d, 3H, J = 5.3 Hz), 3.89 (q, 1H, J = 5.3 Hz), 7.26-7.54 (m, 7H), 7.70-7.79 (m, 1H), 7.99-8.06 (m, 1H). Ms m/e (rel. int.): 267 (M^+ 70), 252 (47), 250 (77), 238 (73), 135 (5). ^{13}C-NMR ($CDCl_3$): δ 14.8 (qd, CH_3, J = 127.7, J = 6.2 Hz), 64.2 (dq, C-2, J = 175.9, J = 5.5 Hz), 77.2 (C-3), 121.6, 123.4, 125.2, 126.1, 128.1, 128.2, 128.4, 128.5, 128.6, 132.6, 153.5, 173.0 (d, C-1, J = 1.7 Hz).

5g: - oil. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.41 (d, 3H, J = 5.4 Hz), 3.57 (q, 1H, J = 5.4 Hz), 7.26-7.54 (m, 7H), 7.70-7.80 (m, 1H), 7.81-8.06 (m, 1H). ^{13}C-NMR ($CDCl_3$): δ 14.7 (qd, CH_3, J = 127.8, J = 6.1 Hz), 64.8 (dq, C-2, J = 175.1, J = 5.3 Hz), 77.2 (C-3), 121.6, 123.3, 125.2, 126.5, 128.1, 128.2, 128.4, 128.6, 135.1, 153.6, 168.7 (C-1).

8a: - oil. ^{1}H-NMR (60 MHz, $CDCl_3$): δ 3.43 (d, 2H, J = 4.4 Hz), 3.58 (d, 2H, J = 5.6 Hz), 4.2-4.7 (m, 1H), 7.3-7.8 (m, 2H), 7.8-8.3 (m, 2H).

8b: - oil. ^{1}H-NMR (60 MHz, $CDCl_3$): δ 1.47 (s, 3H), 2.7-3.0 (m, 2H), 3.42 (s, 2H), 7.4-7.8 (m, 2H), 7.9-8.3 (m, 2H).

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References

1) E.J. Corey and D.L. Boger, Tetrahedron Lett., 5 (1978); ibid, 4041 (1976).
2) E.J. Corey and D.L. Boger, Tetrahedron Lett., 9 (1978); M.J. Crimmin, P.J. O'Hanlon, N.H. Rogers, and G. Walker, J. Chem. Soc. Perkin I, 2047 (1989).
3) A. Dondoni, G. Fantin, M. Fogagnolo, A. Medici, and P. Pedrini, Tetrahedron, 44, 2021 (1988).
4) S. Florio, E. Epifani, and G. Ingrosso, Tetrahedron, 40, 4527 (1984).
5) S. Takahashi and H. Kanö, Chem. Pharm. Bull., 17, 1598 (1969); H.J. Anderson, D.J. Barnes, Z.M. Khan, Can. J. Chem., 42, 2375 (1964).
6) The reaction of 1 and 2 with NBS was carried as in: G. Bellucci, R.Bianchini, G. Ingrosso, E. Mastrorilli. Gazz. Chim. Ital., 108, 643 (1978).

Elemental Analyses for compounds 2a-2g and 5a-5g

	Formula (MW)	Calc. C%	H%	N%	Found C%	H%	N%
2a	$C_{10}H_9NS$ (175.3)	68.5	5.1	8.0	68.7	5.3	8.2
2b	$C_{10}H_9NS$ (175.3)	68.5	5.1	8.0	68.6	5.3	7.9
2c	$C_{11}H_{11}NS$ (189.3)	69.8	5.8	7.4	69.6	5.9	7.5
2d	$C_{11}H_{11}NS$ (189.3)	69.8	5.8	7.4	69.7	5.7	7.6
2e	$C_{11}H_{11}NS$ (189.3)	69.8	5.8	7.4	69.7	5.8	7.5
2f	$C_{16}H_{13}NS$ (251.4)	76.4	5.2	5.6	76.5	5.2	5.7
2g	$C_{16}H_{13}NS$ (251.4)	76.4	5.2	5.6	76.4	5.3	5.8
5a	$C_{10}H_9NOS$ (191.3)	62.7	4.7	7.3	62.5	4.6	7.4
5b	$C_{10}H_9NOS$ (191.3)	62.7	4.7	7.3	62.6	4.8	7.5

5c	$C_{11}H_{11}NOS$ (205.3)	64.3	5.4	6.8	64.5	5.5	6.9
5d	$C_{11}H_{11}NOS$ (205.3)	64.3	5.4	6.8	64.5	5.2	6.7
5e	$C_{11}H_{11}NOS$ (205.3)	64.3	5.4	6.8	64.2	5.5	6.9
5f	$C_{16}H_{13}NOS$ (267.4)	71.8	4.9	5.2	71.9	4.8	5.3
5g	$C_{16}H_{13}NOS$	71.8	4.9	5.2	71.7	4.7	5.4

Microanalyses were performed on a Carlo Erba 1106 elemental analyser.