New NO-Donors with Antithrombotic and Vasodilating Activities, VIII:

Benzothiazole-2(3*H*)-nitrosimines

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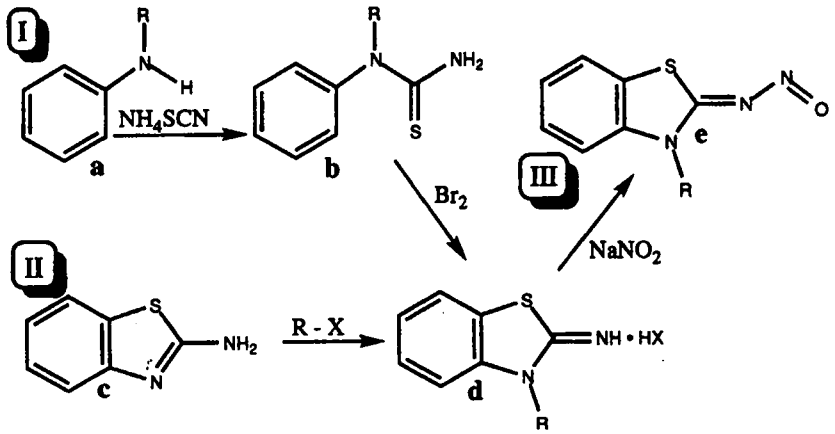
Thirty title compounds were prepared and tested for their antiplatelet activity in the *Born*-test. Five nitrosimines inhibit the aggregation induced by collagen in concentrations below 10 µmol/L halfmaximally. Four compounds were investigated in an *in vivo* thrombosis model. An inhibition of thrombosis between 29 and 53% was observed in mesenteric arterioles of rats 2 h after *p.o.* administration (60 mg/kg). The effect in venoles was less pronounced (10-22%). For one compound these effects could still be demonstrated 4 h after oral application.

Neue NO-Pharmaka mit antithrombotischen und gefäßerweiternden Eigenschaften, 8. Mitt.: Benzothiazol-2-(3*H*)-nitrosimine

30 Titelverbindungen wurden dargestellt und im *Born*-Test auf ihre Fähigkeit geprüft, die Thrombocytenaggregation zu hemmen. Fünf Nitrosimine zeigten eine halbmaximale Hemmung der durch Collagen ausgelösten Aggregation in Konzentrationen <10 µmol/L. Vier Substanzen wurden tierexperimentell auf antithrombotische Eigenschaften geprüft. In Mesenterialarteriolen von Ratten wurde 2 h nach Verabreichung von 60 mg/kg eine 29-53proz. Hemmung der Thrombusbildung gefunden. In Venolen war die Wirkung weniger ausgeprägt (10-22%). Bei einer Verbindung waren diese Effekte auch noch nach 4 h zu beobachten.

Recently we have reported strong antiplatelet effects *in vitro* and antithrombotic properties *in vivo* for thiazole-2-nitrosimines. The positive results prompted us to have a look on the corresponding benzothiazole-2-nitrosimines. The first compounds in this series were prepared by *Besthorn* in 1910[1] The principles of the synthesis are shown in Scheme 1.

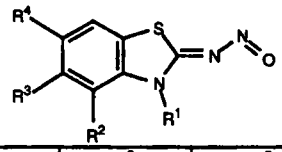
The most convenient way to benzothiazol-2-imines is the synthesis of benzothiazole-2-amines from *N*-phenylthiosemicarbazides[2,5] followed by alkylation. The alternative route I *via* oxidative cyclisation of phenylthioureas was only used for the preparation of **17**. In all cases the superior two phase nitrosation method developed by *Rehse* and *Lüdtke* was applied (III)[6]. The most obvious criterion for the successfull synthesis of the nitrosimines from the corresponding imines is the colour of the reaction products: it varies from orange to pink. This is due to an n → π* transition at 458 (**11**) - 484 (**1**) nm the intensity of which is low [log ε = 1.72 (**1**) - 1.88 (**23**)]. The π → π* transition is observed at 344 (**13**) - 358 (**26**) nm. The log ε values vary from 3.65 (**13**) to 4.24 (**1**). In the ^{1}H-NMR-spectra the chemical shifts of the imine salts and the nitrosimines are very similar. The striking difference is the absence of exchangeable protons in the latter. In the IR-spectrum the N=O valence vibration is found as a strong absorption at 1400-1410 cm^{-1}. The high (thermal) stability of the benzothiazol-2-nitrosimines is underlined by the intense molecular ion even when elevated evaporization temp. are

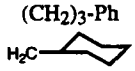


Scheme 1: Synthesis of 3H-benzothiazole-2-nitrosimines

*) Part of the PhD thesis, E. Lüdtke, Berlin 1992

Tab. 1: Inhibition of blood platelet aggregation by 3*H*-benzothiazole-2-nitrosimines



Compound no	R^1	R^2	R^3	R^4	IC_{50} [µmol/L]
1	CH_3	H	H	H	7.5
2	C_2H_5	H	H	H	9
3	C_3H_7	H	H	H	4
4	C_4H_9	H	H	H	22
5	C_5H_{11}	H	H	H	85
6	C_6H_{13}	H	H	H	74
7	C_7H_{15}	H	H	H	41
8	C_8H_{17}	H	H	H	38
9	C_9H_{19}	H	H	H	12
10	$C_{10}H_{21}$	H	H	H	4
11	$C_{12}H_{25}$	H	H	H	50
12	allyl	H	H	H	6
13	2-propinyl	H	H	H	69
14	2-butenyl	H	H	H	52
15	3-butenyl	H	H	H	30
16	CH_2-CH=CH-Ph	H	H	H	42
17	Ph	H	H	H	30
18	benzyl	H	H	H	20
19	$(CH_2)_3$-Ph	H	H	H	44
20		H	H	H	89
21	CH_3	CH_3	H	H	22
22	CH_3	Cl	H	H	90
23	CH_3	OCH_3	H	H	56
24	C_2H_5	OCH_3	H	H	10
25	CH_3	H	H	OC_2H_5	23
26	C_2H_5	H	H	OC_2H_5	56
27	allyl	H	H	OC_2H_5	25
28	CH_3	H	CH_3	CH_3	89
29	C_2H_5	H	CH_3	CH_3	46
30	allyl	H	CH_3	CH_3	41

Tab. 2: Inhibition of thrombus formation in an *in vivo* thrombosis model. Statistics: *Man* and *Whitney* U-test[12].

Compound	IC_{50} [µmolL]	dose [mg/kg]	time after p.o. appl.[h]	venoles % inhibition	α	arterioles % inhibition	α
2	9	60	2	1 ± 4	n.s	16 ± 8	0,2
3	4	30	2	11 ± 4	0,02	23 ± 5	0,01
		60	2	22 ± 8	0,05	42 ± 11	0,002
		60	4	3 ± 2	n.s.	37 ± 11	0,01
10	4	60	2	10 ± 5	0,2	29 ± 20	n.s.
		60	4	17 ± 7	0,01	39 ± 10	0,02
12	6	30	2	5 ± 6	n.s.	17 ± 6	0,02
		60	2	17 ± 10	0,2	53 ± 12	0,002

needed, e.g.: **1**, 120°, 54%; **2**, 100°, 100%; **24**, 110°, 94%. The results obtained in the *Born*-test for thirty title compounds are summarized in Table 1. In the series of 3-alkyl derivatives (**1-11**) there are peak activities with C_1-C_3 (**1-3**) and $C_{9\text{-}10}$ (**9**, **10**) substituents. This was surprising because in the nitroso sydnone imine series C_6-C_8 substituents had proved to yield optimum effects. The introduction of double bonds (**12-16**) only in the allyl compound **12** gives rise to high activity. This again is very astonishing because compound **13** which bears a triple bond instead of a double bond in 2-position of the substituent shows only 10% of the activity of **12**. The aryl- and arylalkyl substitution which had been as well useful in other series[9,10] was without improvement (**17-20**). Additional substituents in the benzene ring (**21-30**) was with one exception (**24**) less favourable than the unsubstituted analogs. The most potent compounds (**2**, **3**, **10**, **12**) were assayed for their antithrombotic properties in an *in vivo* thrombosis model. In this device the formation of thrombi is induced in mesenteric arterioles and venoles of rats by means of a laser beam (35 mW, 50 ms). If a compound is antithrombotic a higher number of expositions to the laser light is needed for thrombus formation. From the difference to the control values the percentage of inhibition of thrombosis is calculated. The results are summarized in Tab. 2. In general more pronounced effects are found in arterioles. This indicates that predominantly the aggregation of platelets is inhibited. Compound **2** only in arterioles shows a small but significant antithrombotic effect. In contrast, **3** two h after application of 60 mg/kg shows a very marked effect in arterioles (42%) and venoles (22%). This effect is dose dependent. When a dose of 30 mg/kg is given, still a significant effect is retained. When the antithrombotic properties were assayed 4 h after *p.o.* application only in arterioles a pronounced effect was observed (37% inhibition). Compound **12** shows a similar profile 2 h after administration. The *N*-decyl derivative **10** seems to have a longer duration of action which is in accordance with the higher lipophilicity of **12** compared to **10**. In summary compounds **3**, **10**, and **12** have to be classified as antithrombotics of medium activity.

Experimental part

The test compounds were prepared with methods already communicated[1-5]. The spectroscopical and analytical data were obtained as usual[6]. The yields refer to the nitrosation step.- ^{1}H-NMR spectra: 300 MHz in [D_6]DMSO (Bruker AC 300).- IR spectra: in KBr.

3-Methyl-N-nitroso-2(3H)-benzothiazole imine (**1**)

Orange crystals (isopropanol), mp. 145° (dec.) (lit.[1]: 147°). Yield 76%.- $C_8H_7N_3OS$ (193.2) Calcd. C 49.7 H 3.65 N 21.8 Found C 49.9 H 3.51 N 21.7.- IR: 3434; 3077; 1581; 1541; 1469; 1464; 1433; 1407; 1390; 1350; 1327; 1301; 1256; 1141; 1131; 1096; 1074; 1027; 862; 758; 750; 719; 708; 637 cm^{-1}.- UV (CH_3OH): λ max (log ε) = 208 (4.43), 218 (4.46), 258 (3.84), 286 (3.86), 346 (4.24), 484 nm (1.72).- ^{1}H-NMR: δ (ppm) = 8.02 (d, J = 8 Hz, 1H, 7-H), 7.89 (d, J = 8 Hz, 1H, 4-H), 7.62 (dd, J = 8/8 Hz, 1H, 6-H), 7.50 (dd, J = 8/8 Hz, 1H, 5-H), 3.87 (s, 3H, 3-CH_3).- MS (120°): m/z = 193 (54%, $[M]^{+\cdot}$), 165 (14), 163 (58), 149 (36), 136 (100), 109 (60), 77 (13), 69 (13), 65 (16), 45 (11).

3-Ethyl-N-nitroso-2(3H)-benzothiazole imine (**2**)

Orange needles (isopropanol), mp. 150° (dec.) (lit.[7]: 150°). Yield 76%.- $C_9H_9N_3OS$ (207.3) Calcd. C 52.2 H 4.38 N 20.3 Found C 51.8 H 4.34 N 20.1.- IR: 3440; 3082; 3061; 2970; 2924; 1619; 1582; 1532; 1461; 1450; 1408; 1342; 1312; 1307; 1282; 1239; 1159; 1136; 1095; 1084; 1067; 1035; 1020; 944; 863; 803; 777; 755; 708 cm^{-1}.- UV (CH_3OH): λ max (log ε) = 206 (4.42), 218 (4.44), 260 (3.92), 286 (3.76), 350 (4.24), 466 nm (1.88).- ^{1}H-NMR: δ (ppm) = 8.04 (d, J = 8 Hz, 1H, 7-H), 7.96 (d, J = 8 Hz, 1H, 4-H), 7.63 (dd, J = 8/8 Hz, 1H, 6-H), 7.51 (dd, J = 8/8 Hz, 1H, 5-H), 4.45 (q, J = 7.1 Hz, 3-CH_2-CH_3), 1.34 (t, J = 7.1 Hz, 3H, CH_3).- MS (100°): m/z = 207 (100%, $[M]^{+\cdot}$), 208 (12), 179 (20), 178 (13), 177 (88), 163 (17), 151 (15), 150 (61), 149 (36), 136 (61), 135 (51), 122 (14), 117 (24), 109 (90), 108 (25), 105 (18), 96 (11), 91 (12), 90 (11), 78 (14), 69 (20), 65 (20), 63 (13), 51 (11), 45 (20), 39 (14), 29 (18).

N-Nitroso-3-propyl-2(3H)-benzothiazole imine (**3**)

Orange needles (isopropanol), mp. 156° (dec.) (lit.[7]: 155°). Yield 95%.- $C_{10}H_{11}N_3OS$ (221.3) Calcd. C 54.3 H 5.01 N 19.0 Found C 54.5 H 5.05 N 18.9.- IR: 2963; 2931; 2875; 1581; 1530; 1465; 1455; 1445; 1400; 1341; 1307; 1296; 1290; 1260; 1230; 1159; 1142; 1084; 1068; 1036; 1019; 975; 939; 910; 895; 844; 753; 705 cm^{-1}.- UV (CH_3OH): λ max (log ε) = 212 (4.43), 262 (3.79), 300 (3.58), 346 (3.98), 468 nm (1.86).- ^{1}H-NMR: δ (ppm) = 8.05 (d, J = 8 Hz, 1H, 7-H), 7.97 (d, J = 8 Hz, 1H, 4-H), 7.62 (dd, J = 8/8 Hz, 1H, 6-H), 7.50 (dd, J = 8.8 Hz, 1H, 5-H), 4.37 (t, J = 7.2 Hz, 3-CH_2-CH_2), 1.79 (m, 2H, $C\underline{H}_2$-CH_3), 0.92 (t, J = 7.2 Hz, 3H, CH_3).- MS (120°): m/z = 221 (35%, $[M]^{+\cdot}$), 193 (9), 191 (33), 176 (10), 164 (13), 151 (27), 150 (66), 149 (56), 136 (100), 123 (11), 109 (23), 105 (15), 96 (8), 69 (8), 65 (9), 45 (10), 41 (16), 31 (19).

3-Butyl-N-nitroso-2(3H)-benzothiazole imine (**4**)

Orange crystals (isopropanol), mp. 104° (dec.) (lit.[7]: 109°). Yield 89%.- $C_{11}H_{13}N_3OS$ (235.3) Calcd. C 56.2 H 5.57 N 17.9 Found C 56.0 H 5.52 N 17.6.- IR: 3082; 3060; 2952; 2927; 2870; 1581; 1535; 1465; 1443; 1408; 1340; 1308; 1253; 1213; 1159; 1145; 1081; 1064; 1047; 1032; 1019; 1004; 945; 900; 864; 801; 784; 752; 737; 723; 707; 663; 639 cm^{-1}.- UV (CH_3OH): λ max (log ε) = 206 (4.32), 220 (4.49), 260 (3.88), 288 (3.60), 348 (4.10), 470 nm (1.75).- ^{1}H-NMR: δ (ppm) = 8.05 (d, J = 8 Hz, 1H, 7-H), 7.97 (d, J = 8 Hz, 1H, 4-H), 7.63 (dd, J = 8/8 Hz, 1H, 6-H), 7.52 (dd, J = 8/8 Hz, 1H, 5-H), 4.42 (t, J = 7.5 Hz, 2H, 3-$C\underline{H}_2$-CH_2), 1.76 (tt, J = 7.5/7.5 Hz, 2H, 3-CH_2-$C\underline{H}_2$-CH_2), 1.37 (m, J = 7.5/7.5 Hz, 2H, $C\underline{H}_2$-CH_3), 0.92 (t, J = 7.5 Hz, 3H, CH_3).- MS (110°): m/z = 235 (9%, $[M]^{+\cdot}$), 207 (38), 205 (12), 190 (23), 174 (35), 165 (24), 164 (18), 163 (21), 151 (79), 150 (41), 149 (27), 136 (100), 123 (49), 109 (48), 105 (10), 96 (26), 78 (13), 69 (25), 65 (27), 55 (19), 51 (18), 45 (21), 41 (40).

N-Nitroso-3-pentyl-2(3H)-benzothiazole imine (**5**)

Orange crystals (isopropanol), mp. 98°. Yield 79%.- $C_{12}H_{15}N_3OS$ (249.3) Calcd. C 57.8 H 6.06 N 16.9 Found C 57.8 H 6.16 N 17.0.- IR: 2952; 2923; 2856; 2214; 1580; 1535; 1460; 1341; 1306; 1276; 1248; 1202; 1159; 1148; 1081; 1064; 1038; 1018; 1005; 970; 896; 877; 834; 758; 723; 708; 639 cm^{-1}.- UV (CH_3OH): λ max (log ε) = 210 (4.41), 268 (3.72), 348 (4.05), 470 nm (1.81).- ^{1}H-NMR: δ (ppm) = 8.04 (d, J = 8 Hz, 1H, 7-H),

7.95 (d, J = 8 Hz, 1H, 4-H), 7.62 (dd, J = 8/8 Hz, 1H, 6-H), 7.51 (dd, J = 8/8 Hz, 1H, 5-H), 4.40 (t, J = 7 Hz, 2H, 3-C$\underline{H}_2$-CH_2), 1.76 (bs, 2H, 3-CH_2-C$\underline{H}_2$), 1.32 (bs, 4H, ($C\underline{H}_2$)$_2$-CH_3), 0.84 (bs, 3H, CH_3).- MS (120°): m/z = 249 (50%, $[M]^{+\cdot}$), 221 (13), 220 (17), 219 (82), 204 (16), 188 (13), 175 (19), 164 (20), 163 (90), 151 (100), 150 (65), 149 (86), 136 (74), 135 (28), 123 (11), 109 (34), 105 (22), 96 (8), 78 (8), 69 (44), 65 (11), 55 (8), 45 (9), 43 (20), 41 (70).

3-Hexyl-N-nitroso-2(3H)-benzothiazole imine (**6**)

Orange crystals (isopropanol), mp. 92°. Yield 70%.- $C_{13}H_{17}N_3OS$ (263.4) Calcd. C 59.3 H 6.51 N 16.0 Found C 59.2 H 6.60 N 16.0.- IR: 2946; 2923; 2853; 1580; 1528; 1465; 1408; 1345; 1327; 1305; 1264; 1240; 1194; 1156; 1147; 1082; 1067; 1040; 1016; 1002; 940; 899; 852; 748; 722; 700 cm^{-1}.- UV (CH_3OH): λ max (log ε) = 222 (4.51), 260 (3.91), 288 (3.62), 350 (4.00), 472 nm (1.45).- ^{1}H-NMR: δ (ppm) = 8.04 (d, J = 8 Hz, 1H, 7-H), 7.95 (d, J = 8 Hz, 1H, 4-H), 7.62 (dd, J = 8/8 Hz, 1H, 6-H), 7.51 (dd, J = 8/8 Hz, 1H, 5-H), 4.40 (t, J = 7 Hz, 2H, 3-C$\underline{H}_2$-CH_2), 1.74 (tt, J = 7/7 Hz, 2H, 3-CH_2-C$\underline{H}_2$), 1.26 (m, 6H, ($C\underline{H}_2$)$_3$-CH_3), 0.83 (t, J = 7 Hz, 3H, CH_3).- MS (110°): m/z = 263 (27%, $[M]^{+\cdot}$), 235 (19), 233 (63), 218 (18), 202 (30), 190 (7), 175 (14), 165 (14), 165 (26), 163 (68), 151 (100), 150 (65), 149 (57), 136 (70), 135 (19), 123 (17), 109 (32), 105 (16), 96 (10), 83 (11), 65 (11), 55 (9), 43 (34), 28 (34).

3-Heptyl-N-nitroso-2(3H)-benzothiazole imine (**7**)

Orange prisms (isopropanol), mp. 98°. Yield 64%.- $C_{14}H_{19}N_3OS$ (277.4) Calcd. C 60.6 H 6.90 N 15.2 Found C 60.1 H 6.99 N 15.1.- IR: 3054; 2911; 2850; 1578; 1527; 1459; 1404; 1319; 1300; 1257; 1142; 1080; 1061; 1024; 1011; 919; 864; 760; 704; 662; 638 cm^{-1}.- UV (CH_3OH): λ max (log ε) = 222 (4.51), 260 (3.90), 288 (3.61), 348 (3.96), 470 nm (1.81).- ^{1}H-NMR: δ (ppm) = 8.04 (d, J = 8 Hz, 1H, 7-H), 7.95 (d, J = 8 Hz, 1H, 4-H), 7.62 (dd, J = 8/8 Hz, 1H, 6-H), 7.51 (dd, J = 8/8 Hz, 1H, 5-H), 4.40 (t, J = 7.2 Hz, 2H, 3-C$\underline{H}_2$-CH_2), 1.76 (tt, J = 7.2/7.2 Hz, 2H, 3-CH_2-C$\underline{H}_2$-CH_2), 1.30 (m, 8H, ($C\underline{H}_2$)$_4$-CH_3), 0.83 (t, J = 7.2 Hz, 3H, CH_3).- MS (60°): m/z = 277 (8%, $[M]^{+\cdot}$), 249 (52), 247 (21), 232 (22), 217 (11), 216 (70), 193 (13), 165 (27), 164 (27), 151 (100), 150 (29), 138 (11), 136 (89), 123 (23), 109 (30), 96 (12), 65 (11), 57 (13), 55 (41), 43 (32), 41 (46), 39 (11), 28 (60).

N-Nitroso-3-octyl-2(3H)-benzothiazole imine (**8**)

Orange crystals (isopropanol), mp. 97°. Yield 65%.- $C_{15}H_{21}N_3OS$ (291.4) Calcd. C 61.8 H 7.26 N 14.4 Found C 61.7 H 7.50 N 14.3.- IR: 2951; 2923; 2852; 1579; 1534; 1450; 1406; 1380; 1340; 1308; 1272; 1249; 1174; 1157; 1147; 1139; 1081; 1061; 1032; 1016; 982; 948; 883; 843; 761; 723; 707 cm^{-1}.- UV (CH_3OH): λ max (log ε) = 208 (4.37), 262 (3.70), 346 (3.96), 468 nm (1.83).- ^{1}H-NMR: δ (ppm) = 8.04 (d, J = 8 Hz, 1H, 7-H), 7.95 (d, J = 8 Hz, 1H, 4-H), 7.62 (dd, J = 8/8 Hz, 1H, 6-H), 7.51 (dd, J = 8/8 Hz, 1H, 5-H), 4.40 (t, J = 7 Hz, 2H, 3-C$\underline{H}_2$-CH_2), 1.74 (m, 2H, 3-CH_2-C$\underline{H}_2$), 1.26 (bs, 10 H, ($C\underline{H}_2$)$_5$-CH_3), 0.83 (t, J = 7 Hz, 3H, CH_3).- MS (90°): m/z = 291 (6%, $[M]^{+\cdot}$), 263 (54), 261 (21), 246 (24), 230 (80), 207 (12), 193 (17), 165 (27), 164 (31), 152 (19), 151 (100), 150 (24), 149 (14), 136 (82), 123 (20), 109 (25), 96 (10), 69 (20), 65 (9), 55 (30), 43 (37), 41 (59).

N-Nitroso-3-nonyl-2(3H)-benzothiazole imine (**9**)

Orange crystals (isopropanol), mp. 95°. Yield 76%.- $C_{16}H_{23}N_3OS$ (305.4) Calcd. C 62.9 H 7.59 N 13.8 Found C 62.9 H 7.77 N 13.9.- IR: 2954; 2918; 2853; 2710; 1580; 1534; 1459; 1403; 1339; 1307; 1261; 1244; 1158; 1148; 1140; 1081; 1061; 1031; 1017; 983; 956; 898; 859; 816; 760; 707 cm^{-1}.- UV (CH_3OH): λ max (log ε) = 222 (4.51), 260 (3.90), 288 (3.62), 348 (3.91), 470 nm (1.72).- ^{1}H-NMR: δ (ppm) = 8.04 (d, J = 8 Hz, 1H, 7-H), 7.95 (d, J = 8 Hz, 1H, 4-H), 7.62 (dd, J = 8/8 Hz, 1H, 6-H), 7.51 (dd, J = 8/8 Hz, 1H, 7-H), 4.40 (t, J = 7 Hz, 2H, 3-C$\underline{H}_2$-CH_2), 1.74 (m, 2H, 3-CH_2-C$\underline{H}_2$), 1.26 (bs, 12 H, ($C\underline{H}_2$)$_6$-CH_3), 0.83 (t, J = 7 Hz, 3H, CH_3).- MS (150°): m/z = 305 (9%, $[M]^{+\cdot}$), 288 (11), 277 (224), 275 (100), 260 (22), 244 (26), 175 (11), 164 (25), 163 (67), 151 (96), 150 (50), 136 (52), 123 (10), 109 (20), 83 (20), 69 (42), 55 (55).

3-Decyl-N-nitroso-2(3H)-benzothiazole imine (**10**)

Orange crystals (isopropanol), mp. 71°. Yield 54%.- $C_{17}H_{25}N_3OS$ (319.5) Calcd. C 63.9 H 7.89 N 13.2 Found C 63.6 H 8.03 N 13.4.- IR: 2946; 2921; 2852; 1580; 1534; 1460; 1405; 1341; 1306; 1255; 1149; 1082; 1063; 1032; 1014; 914; 871; 838; 783; 760; 720; 706 cm^{-1}.- UV (CH_3OH): λ max (log ε) = 222 (4.56), 260 (3.99), 288 (3.74), 348 (3.99), 470 nm (1.70).- ^{1}H-NMR: δ (ppm) = 8.04 (d, J = 8 Hz, 1H, 7-H), 7.95 (d, J = 8 Hz, 1H, 4-H), 7.62 (dd, J = 8/8 Hz, 1H, 6-H), 7.51 (dd, J = 8/8 Hz, 1H, 5-H), 4.40 (t, J = 7 Hz, 2H, 3-C$\underline{H}_2$-CH_2), 1.74 (m, 2H, 3-CH_2-C$\underline{H}_2$), 1.20 (bs, 14 H, ($C\underline{H}_2$)$_7$-CH_3), 0.84 (t, J = 7 Hz, 3H, CH_3).- MS (80°): m/z = 319 (5%, $[M]^{+\cdot}$), 291 (47), 289 (11), 274 (27), 258 (97), 220 (12), 207 (20), 193 (22), 174 (7), 165 (27), 164 (32), 152 (22), 151 (100), 150 (17), 138 (12), 136 (77), 123 (17), 109 (17), 96 (7), 83 (7), 69 (13), 55 (38), 43 (45), 41 (50), 29 (34).

3-Dodecyl-N-nitroso-2(3H)-benzothiazole imine (**11**)

Orange crystals (isopropanol), mp. 62°. Yield 62%.- $C_{19}H_{29}N_3OS$ (347.5) Calcd. C 65.7 H 8.41 N 12.1 Found C 65.7 H 8.30 N 12.0.- IR: 3087; 3061; 2947; 2911; 2852; 2355; 1580; 1535; 1470; 1460; 1406; 1342; 1308; 1262; 1247; 1159; 1151; 1140; 1082; 1065; 1037; 1027; 1017; 985; 942; 896; 867; 832; 762; 723; 708 cm^{-1}.- UV (CH_3OH): λ max (log ε) = 220 (4.53), 260 (3.92), 288 (3.64), 348 (4.02), 458 nm (1.72).- ^{1}H-NMR: δ (ppm) = 8.04 (d, J = 8 Hz, 1H, 7-H), 7.95 (d, J = 8 Hz, 1H, 4-H), 7.62 (dd, J = 8/8 Hz, 1H, 6-H), 7.51 (dd, J = 8/8 Hz, 1H, 5-H), 4.40 (t, J = 7 Hz, 2H, 3-C$\underline{H}_2$-CH_2), 1.74 (m, 2H, 3-CH_2-C$\underline{H}_2$), 1.20 (bs, 18 H ($C\underline{H}_2$)$_9$-CH_3), 0.84 (t, J = 7 Hz, 3H, CH_3).- MS (120°): m/z = 347 (2%, $[M]^{+\cdot}$), 319 (20), 317 (12), 302 (15), 286 (42), 206 (18), 193 (14), 165 (24), 164 (54), 152 (24), 151 (95), 150 (100), 136 (93), 123 (23), 109 (33), 96 (14), 83 (14), 77 (10), 69 (34), 65 (15), 57 (29), 55 (74), 41 (91).

3-Allyl-N-nitroso-2(3H)-benzothiazole imine (**12**)

Orange crystals (isopropanol), mp. 133°. Yield 70%.- $C_{10}H_9N_3OS$ (219.3) Calcd. C 54.8 H 4.14 N 19.2 Found C 54.6 H 4.07 N 19.0.- IR: 1640; 1580; 1530; 1464; 1438; 1403; 1342; 1303; 1288; 1271; 1220; 1140; 1090; 1068; 1032; 1019; 986; 921; 849; 754; 707 cm^{-1}.- UV (CH_3OH): λ max (log ε) = 210 (4.44), 268 (3.81), 296 (3.58), 348 (4.04), 472 nm (1.83).- ^{1}H-NMR: δ (ppm) = 8.05 (d, J = 8 Hz, 1H, 7-H), 7.97 (d, J = 8 Hz, 1H, 4-H), 7.63 (dd, J = 8/8 Hz, 1H, 6-H), 7.52 (dd, J = 8/8 Hz, 1H, 5-H), 6.05-5.93 (m, 1H, C$\underline{H}$=CH_2), 5.26 (d, J = 10 Hz, 1H, *trans* CH=C$\underline{H}_2$), 5.18 (d, J = 17 Hz, 1H, *cis* CH=C$\underline{H}_2$), 5.07 (d, J = 5 Hz, 2H, 3-C$\underline{H}_2$-CH_2).- MS (100°): m/z = 219 (10%, $[M]^{+\cdot}$), 191 (44), 189 (100), 187 (10), 175 (28), 174 (20), 162 (36), 161 (32), 150 (21), 149 (23), 136 (29), 134 (20), 130 (11), 122 (10), 109 (41), 69 (16), 65 (12), 45 (20), 41 (33).

N-Nitroso-3-(2-propinyl)-2(3H)-benzothiazole imine (**13**)

Orange crystals (isopropanol), mp. 153°. Yield 19%.- $C_{10}H_7N_3OS \cdot {}^1/_4$ H_2O (221.8) Calcd. C 54.2 H 3.18 N 19.0 Found C 54.3 H 3.15 N 18.8.- IR: 3428; 3228; 3081; 2964; 2115; 1920; 1620; 1580; 1526; 1464; 1439;

1402; 1363; 1344; 1320; 1304; 1271; 1216; 1159; 1138; 1099; 1074; 1046; 1034; 1020; 984; 942; 851; 755; 725; 719; 684 cm^{-1}.- UV (CH_3OH): λ max (log ε) = 210 (4.60), 344 (3.65), 462 nm (1.83).- ^{1}H-NMR: δ (ppm) = 8.06 (d, J = 8 Hz, 1H, 7-H), 7.95 (d, J = 8 Hz, 1H, 4-H), 7.66 (dd, J = 8/8 Hz, 1H, 6-H), 7.54 (dd, J = 8/8 Hz, 1H, 5-H), 5.29 (s, 2H, 3-CH_2), 3.55 (s, 1H, ≡CH).- MS (220°): m/z = 217 (16%, $[M]^{+\cdot}$), 189 (49), 187 (100), 173 (15), 161 (45), 160 (30), 150 (19), 135 (25), 134 (87), 129 (14), 122 (22), 116 (27), 109 (52), 108 (20), 106 (12), 95 (13), 90 (23), 78 (19), 69 (42), 65 (21), 63 (23), 51 (24), 45 (36), 39 (64).

[E]-N-Nitroso-3-(2-butenyl)-2(3H)-benzothiazole imine (**14**)

Light orange needles (isopropanol), mp. 121° (decompn.). Yield 59%.- $C_{11}H_{11}N_3OS$ (233.3) Calcd. C 56.6 H 4.75 N 18.0 Found C 56.5 H 4.65 N 17.8.- IR: 3425; 1628; 1579; 1528; 1463; 1440; 1414; 1378; 1337; 1304; 1280; 1260; 1211; 1157; 1129; 1080; 1059; 1029; 1014; 971; 909; 855; 754; 706; 657 cm^{-1}.- UV (CH_3OH): λ max (log ε) = 210 (4.12), 322 (4.09), 446 (1.84) nm.- ^{1}H-NMR: δ (ppm) = 8.04 (d, J = 8 Hz, 1H, 7-H), 7.89 (d, J = 8 Hz, 1H, 4-H), 7.61 (dd, J = 8/8 Hz, 1H, 6-H), 7.50 (dd, J = 8/8 Hz, 1H, 5-H), 5.82 (m, 1H, =C<u>H</u>-CH_3), 5.61 (m, 1H, 3-CH_2-C<u>H</u>=), 4.98 (d, J = 6 Hz, 2H, 3-C<u>H</u>$_2$-CH), 1.64 (d, J = 6 Hz, 3H, -CH_3).- MS (100°): m/z = 233 (4%, $[M]^{+\cdot}$), 205 (14), 203 (100), 188 (24), 187 (27), 175 (56), 161 (12), 151 (19), 149 (27), 136 (15), 109 (17), 105 (12), 55 (51), 39 (16), 29 (25).

3-(3-Butenyl)-N-nitroso-2(3H)-benzothiazole imine (**15**)

Orange needles (isopropanol), mp. 101°. Yield 26%.- $C_{11}H_{11}N_3OS$ (233.3) Calcd. C 56.6 H 4.75 N 18.0 Found C 56.6 H 4.70 N 18.0.- IR: 3426; 3080; 3059; 2911; 1637; 1581; 1533; 1465; 1460; 1448; 1426; 1415; 1343; 1329; 1305; 1267; 1213; 1143; 1088; 1066; 1039; 1013; 993; 979; 919; 908; 870; 852; 832; 750; 724; 708; 654; 634; 618 cm^{-1}.- UV (CH_3OH): λ max (log ε) = 220 (4.51), 262 (3.91), 286 (3.65), 346 (3.88), 466 nm (1.61).- ^{1}H-NMR: δ (ppm) = 8.03 (d, J = 8 Hz, 1H, 7-H), 7.97 (d, J = 8 Hz, 1H, 4-H), 7.62 (dd, J = 8/8 Hz, 1H, 6-H), 7.50 (dd, J = 8/8 Hz, 1H, 5-H), 5.90-5.77 (m, 1H, C<u>H</u>=CH_2), 4.98 (m, 2H, CH=C<u>H</u>$_2$), 4.49 (t, J = 8 Hz, 2H, 3-C<u>H</u>$_2$-CH_2), 2.55 (dt, 2H, 3-CH_2-C<u>H</u>$_2$-CH).- MS (40°): m/z = 233 (12%, $[M]^{+\cdot}$), 205 (16), 203 (100), 189 (29), 188 (17), 176 (12), 175 (24), 164 (11), 161 (19), 151 (19), 150 (27), 149 (42), 136 (58), 135 (19), 134 (13), 122 (11), 109 (30), 108 (20), 105 (16), 69 (14), 65 (12), 55 (11), 53 (20), 51 (11), 45 (13), 41 (32), 39 (26), 29 (23).

[E]-N-Nitroso-3-(3-phenyl-2-propenyl)-2(3H)-benzothiazole imine (**16**)

Orange needles (isopropanol), mp. 116°. Yield 57%.- $C_{16}H_{13}N_3OS$ (295.4) Calcd. C 65.1 H 4.44 N 14.2 Found C 65.1 H 4.27 N 14.1.- IR: 3436; 1673; 1587; 1533; 1465; 1411; 1344; 1301; 1179; 1086; 1044; 1019; 970; 850; 750; 695 cm^{-1}.- UV (CH_3OH): λ max (log ε) = 210 (4.60), 238 (4.34), 292 (3.70), 346 (4.00), 470 nm (1.80).- ^{1}H-NMR: δ (ppm) = 8.06 (d, J = 8 Hz, 1H, 7-H), 7.96 (d, J = 8 Hz, 1H, 4-H), 7.64 (dd, J = 8/8 Hz, 1H, 6-H), 7.54 (dd, J = 8/8 Hz, 1H, 5-H), 7.43 (d, J = 7 Hz, 2H, Ph-2-H and 6-H), 7.33-7.22 (m, 3H, Ph-3-H,4-H and 5-H), 6.74 (d, J = 17 Hz, 1H, =C<u>H</u>-Ph), 6.43 (dt, J = 17/6 Hz, 1H, 3-CH_2-C<u>H</u>=CH), 5.23 (d, J = 6 Hz, 2H, 3-C<u>H</u>$_2$-CH).- MS (130°): m/z = 295 (2%, $[M]^{+\cdot}$), 267 (14), 265 (1), 150 (11), 117 (100), 116 (10), 115 (33), 91 (39), 77 (10), 65 (12), 39 (14), 28 (35).

N-Nitroso-3-phenyl-2(3H)-benzothiazole imine (**17**)

Orange needles (isopropanol), mp. 140° (Lit.[8]: 141°). Yield 74%.- $C_{13}H_9N_3OS$ (255.3) Calcd. C 61.2 H 3.55 N 16.5 Found C 60.7 H 3.22 N 16.4.- IR: 1595; 1578; 1515; 1492; 1456; 1406; 1393; 1360; 1291; 1246; 1184; 1157; 1108; 1097; 1061; 1029; 1017; 952; 850; 762; 691; 614 cm^{-1}.- UV (CH_3OH): λ max (log ε) = 212 (4.50), 350 (4.02), 472 nm (1.75).- ^{1}H-NMR: δ (ppm) = 8.10 (d, 1H, 7-H), 7.65 (m, 5H, 3-Ph), 7.51 (m, 2H, 5-H and 6-H), 7.08 (d, 1H, 4-H).- MS (90°): m/z = 255 (4%, $[M]^{+\cdot}$), 228 (16), 227 (100), 225 (14), 200 (11), 199 (55), 198 (96), 167 (23), 122 (14), 96 (10), 77 (25), 69 (19), 51 (26), 28 (19).

3-Benzyl-N-nitroso-2(3H)-benzothiazole imine (**18**)

Light orange needles (isopropanol), mp. 135° (decompn.). Yield 52%.- $C_{14}H_{11}N_3OS$ (269.3) Calcd. C 62.4 H 4.12 N 15.6 Found C 62.2 H 4.03 N 15.5.- IR: 3079; 3021; 3009; 1601; 1580; 1531; 1493; 1464; 1453; 1444; 1397; 1341; 1322; 1301; 1268; 1199; 1142; 1088; 1060; 1033; 1027; 1015; 963; 940; 916; 846; 761; 747; 722; 697; 660; 635 cm^{-1}.- UV (CH_3OH): λ max (log ε) = 210 (4.55), 218 (4.53), 260 (3.86), 286 (3.68), 352 (4.01), 474 nm (1.85).- ^{1}H-NMR: δ (ppm) = 8.06 (d, J = 8 Hz, 1H, 7-H), 7.86 (d, J = 8 Hz, 1H, 4-H), 7.56 (dd, J = 8/8 Hz, 1H, 6-H), 7.49 (dd, J = 8/8 Hz, 1H, 5-H), 7.32 (m, 5H, Ph), 5.68 (s, 2H, 3-CH_2).- MS (130°): m/z = 269 (4%, $[M]^{+\cdot}$), 241 (14), 239 (30), 91 (100), 65 (20).

N-Nitroso-3-(3-phenylpropyl)-2(3H)-benzothiazole imine (**19**)

Light orange needles (isopropanol), mp. 105°. Yield 69%.- $C_{16}H_{15}N_3OS$ (297.4) Calcd. C 64.6 H 5.08 N 14.1 Found C 64.6 H 4.89 N 14.1.- IR: 2937; 2859; 1580; 1534; 1494; 1461; 1435; 1414; 1346; 1328; 1308; 1268; 1247; 1173; 1135; 1095; 1078; 1066; 1046; 1028; 1019; 1008; 915; 881; 852; 829; 754; 721; 701 cm^{-1}.- UV (CH_3OH): λ max (log ε) = 220 (4.52), 260 (3.91), 288 (3.66), 344 (nm (3.27).- ^{1}H-NMR: δ (ppm) = 8.03 (d, J = 8 Hz, 1H, 7-H), 7.89 (d, J = 8 Hz, 1H, 4-H), 7.61 (dd, J = 8/8 Hz, 1H, 6-H), 7.50 (dd, J = 8/8 Hz, 1H, 5-H), 7.29-7.17 (m, 5H, Ph), 4.45 (t, J = 7.3 Hz, 2H, 3-C<u>H</u>$_2$-CH_2), 2.71 (t, J = 8 Hz, 2H, CH_2-C<u>H</u>$_2$-Ph), 2.09 (tt, J = 7.3/8 Hz, 2H, 3-CH_2-C<u>H</u>$_2$-CH_2).- MS (130°): m/z = 297 (12%, $[M]^{+\cdot}$), 270 (16), 269 (86), 236 (11), 165 (100), 151 (47), 136 (63), 123 (11), 117 (39), 109 (21), 91 (67), 77 (12), 65 (23), 41 (12), 28 (77).

3-(Cyclohexylmethyl)-N-nitroso-2(3H)-benzothiazole imine (**20**)

Pink needles (isopropanol), mp. 140°. Yield 34%.- $C_{14}H_{17}N_3OS$ (275.4) Calcd. C 61.1 H 6.22 N 15.3 Found C 60.8 H 6.41 N 14.9.- IR: 3436; 3078; 2922; 2847; 1625; 1529; 1463; 1445; 1406; 1371; 1336; 1302; 1267; 1249; 1208; 1146; 1090; 1065; 1030; 1019; 954; 893; 868; 832; 764; 708; 638 cm^{-1}.- UV (CH_3OH): λ max (log ε) = 222 (4.50), 260 (3.87), 288 (3.56), 350 (3.90), 474 nm (1.76).- ^{1}H-NMR: δ (ppm) = 8.03 (d, J = 7.2 Hz, 1H, 7-H), 7.97 (d, J = 7.2 Hz, 1H, 4-H), 7.61 (dd, J = 7.2/7.2 Hz, 1H, 6-H), 7.50 (dd, J = 7.2/7.2 Hz, 1H, 5-H), 4.27 (d, J = 7.5 Hz, 2H, 3-C<u>H</u>$_2$-CH), 1.96 (bs, 1H), 1.61 (m, 5H), 1.08 (m, 5H).- MS (180°): m/z = 275 (9%, $[M]^{+\cdot}$), 247 (16), 245 (26), 165 (10), 163 (17), 152 (20), 151 (100), 150 (53), 149 (22), 136 (37), 123 (10), 109 (14), 95 (27), 67 (14), 55 (39), 41 (27), 28 (14).

3,4-Dimethyl-N-nitroso-2(3H)-benzothiazole imine (**21**)

Orange needles (isopropanol), mp. 141° (decompn.). Yield 53%.- $C_9H_9N_3OS$ (207.3) Calcd. C 52.2 H 4.38 N 20.3 Found C 52.3 H 4.26 N 20.0.- IR: 3048; 3012; 2960; 1590; 1526; 1470; 1448; 1435; 1408; 1392; 1344; 1320; 1268; 1245; 1190; 1164; 1118; 1069; 1033; 1001; 866; 798; 728 cm^{-1}.- UV (CH_3OH): λ max (log ε) = 214 (4.45), 270 (3.63), 346 nm (3.92).- ^{1}H-NMR: δ (ppm) = 7.82 (d, 1H, 7-H), 7.36 (m, 2H, 5-H and 6-H), 4.12 (s, 3H, 3-CH_3), 2.83 (s, 3H, 4-CH_3).- MS (80°): m/z = 207 (27%, $[M]^{+\cdot}$), 179 (42), 177 (28), 163 (20), 150 (100), 148 (10), 136 (10), 123 (14), 117 (10), 91 (11), 79 (11), 77 (16), 69 (10), 65 (14), 51 (10), 45 (26), 39 (14).

4-Chlor-3-methyl-N-nitroso-2(3H)-benzothiazole imine (**22**)

Pink needles (isopropanol), mp. 144° (decompn.). Yield 67%.- $C_8H_6ClN_3OS$ (227.7) Calcd. C 42.2 H 2.66 N 18.5 Found C 42.4 H 2.46 N 18.3.- IR: 3053; 1664; 1574; 1533; 1465; 1450; 1417; 1397; 1346; 1324; 1261; 1206; 1163; 1144; 1097; 1055; 1020; 1010; 863; 832; 799; 717; 657 cm^{-1}.- UV (CH_3OH): λ max (log ε) = 222 (4.46), 274 (3.70), 346 (4.07), 476 nm (1.79).- ^{1}H-NMR: δ (ppm) = 7.98 (d, J = 8 Hz, 1H, 7-H), 7.63 (d, J = 8 Hz, 1H, 5-H), 7.44 (dd, J = 8/8 Hz, 1H, 6-H), 4.16 (s, 3H, 3-CH_3).- MS (100°): m/z = 227 (37%, $[M]^{+\cdot}$), 229 (14), 201 (15), 199 (65), 197 (32), 185 (11), 183 (28), 172 (37), 171 (11), 170 (100), 136 (11), 135 (17), 134 (72), 108 (17), 107 (11), 69 (16), 63 (12), 45 (14), 28 (16).

4-Methoxy-3-methyl-N-nitroso-2(3H)-benzothiazole imine (**23**)

Orange needles (isopropanol), mp. 132°. Yield 67%.- $C_9H_9N_3O_2S$ (223.3) Calcd. C 48.4 H 4.06 N 18.8 Found C 48.1 H 4.04 N 18.7.- IR: 3430; 3089; 3058; 2938; 1590; 1534; 1481; 1443; 1425; 1396; 1346; 1287; 1268; 1117; 1071; 1039; 859; 786; 724; 685 cm^{-1}.- UV (CH_3OH): λ max (log ε) = 218 (4.49), 266 (3.79), 346 (3.95), 460 nm (1.88).- ^{1}H-NMR: δ (ppm) = 7.54 (d, J = 8 Hz, 1H, 7-H), 7.41 (dd, J = 8/8 Hz, 1H, 6-H), 7.22 (d, J = 8 Hz, 1H, 5-H), 4.06 (s, 3H, O-CH_3), 3.97 (s, 3H, 3-CH_3).- MS (150°): m/z = 223 (59%, $[M]^{+\cdot}$), 195 (28), 193 (51), 179 (27), 166 (46), 152 (35), 151 (100), 136 (12), 123 (11), 120 (13), 111 (13), 109 (16), 96 (12), 83 (10), 69 (12), 65 (14), 51 (10), 39 (26).

4-Methoxy-3-ethyl-N-nitroso-2(3H)-benzothiazole imine (**24**)

Orange needles (isopropanol), mp. 126° (decompn.). Yield 59%.- $C_{10}H_{11}N_3O_2S$ (237.3) Calcd. C 50.6 H 4.67 N 17.7 Found C 50.4 H 4.66 N 17.6.- IR: 2971; 2933; 2838; 1591; 1581; 1524; 1481; 1433; 1407; 1339; 1324; 1306; 1274; 1239; 1164; 1126; 1100; 1068; 1038; 944; 859; 790; 783; 768; 723 cm^{-1}.- UV (CH_3OH): λ max (log ε) = 214 (4.41), 266 (3.72), 346 (3.91), 462 nm (1.72).- ^{1}H-NMR: δ (ppm) = 7.58 (d, J = 8 Hz, 1H, 7-H), 7.44 (dd, J = 8/8 Hz, 1H, 6-H), 7.27 (d, J = 8 Hz, 1H, 5-H), 4.64 (q, J = 7 Hz, 2H, 3-$C\underline{H}_2$-CH_3), 4.02 (s, 3H, O-CH_3), 1.35 (t, J = 7 Hz, 3H, 3-CH_2-$C\underline{H}_3$).- MS (110°): m/z = 237 (94%, $[M]^{+\cdot}$), 209 (30), 208 (12), 207 (90), 192 (37), 191 (37), 180 (25), 179 (11), 167 (11), 166 (73), 165 (100), 164 (21), 152 (44), 151 (42), 150 (14), 136 (30), 135 (14), 125 (11), 122 (23), 111 (15), 109 (25), 106 (12), 96 (19), 83 (13), 77 (14), 69 (18), 65 (13), 51 (12), 49 (17), 39 (37), 30 (37), 29 (23), 27 (24).

6-Ethoxy-3-methyl-N-nitroso-2(3H)-benzothiazole imine (**25**)

Orange crystals (isopropanol), mp. 147°. Yield 94%.- $C_{10}H_{11}N_3O_2S$ (237.3) Calcd. C 50.6 H 4.67 N 17.7 Found C 50.4 H 4.67 N 17.3.- IR: 2974; 2932; 1600; 1583; 1541; 1486; 1473; 1452; 1429; 1396; 1357; 1328; 1297; 1275; 1266; 1135; 1110; 1081; 1059; 1017; 943; 869; 835; 823; 798 cm^{-1}.- UV (CH_3OH): λ max (log ε) = 216 (4.47), 358 nm (4.16).- ^{1}H-NMR: δ (ppm) = 7.78 (d, J = 9 Hz, 1H- 4-H), 7.62 (s, 1H, 7-H), 7.17 (d, J = 9 Hz, 1H, 5-H), 4.09 (q, J = 7 Hz, 2H, O-$C\underline{H}_2$-CH_3), 3.83 (s, 3H, 3-CH_3), 1.37 (t, J = 7 Hz, 3H, O-CH_2-$C\underline{H}_3$).- MS (110°): m/z = 237 (28%, $[M]^{+\cdot}$), 209 (28), 208 (14), 207 (54), 181 (19), 180 (19), 179 (24), 152 (100), 97 (11), 29 (17).

6-Ethoxy-3-ethyl-N-nitroso-2(3H)-benzothiazole imine (**26**)

Orange needles (isopropanol), mp. 140°. Yield 74%.- $C_{11}H_{13}N_3O_2S$ (251.3) Calcd. C 52.6 H 5.21 N 16.7 Found C 52.7 H 5.18 N 16.5.- IR: 2977; 2930; 2873; 1606; 1580; 1539; 1483; 1470; 1438; 1404; 1392; 1367; 1341; 1329; 1276; 1255; 1212; 1152; 1139; 1112; 1104; 1078; 1020; 942; 867; 850, 805; 797 cm^{-1}.- UV (CH_3OH): λ max (log ε) = 216 (4.40), 358 nm (4.10).- ^{1}H-NMR: δ (ppm) = 7.86 (d, J = 9 Hz, 1H, 4-H), 7.65 (s, 1H, 7-H), 7.18 (d, J = 9 Hz, 1H, 5-H), 4.42 (q, 2H, 3-$C\underline{H}_2$-CH_3), 4.10 (q, J = 6.8 Hz, 2H, O-$C\underline{H}_2$-CH_3), 1.35 (m, 6H, 3-CH_2-$C\underline{H}_3$ and O-CH_2-$C\underline{H}_3$).- MS (140°): m/z = 251 (55%, $[M]^{+\cdot}$), 223 (40), 222 (28), 221 (100), 195 (22), 193 (67), 192 (23), 180 (17), 167 (20), 166 (68), 165 (46), 152 (35), 151 (19), 138 (14), 133 (14), 125 (30), 97 (13), 80 (13), 29 (39).

3-Allyl-6-ethoxy-N-nitroso-2(3H)-benzothiazole imine (**27**)

Orange needles (isopropanol), mp. 119°. Yield 67%.- $C_{12}H_{13}N_3O_2S$ (263.3) Calcd. C 54.7 H 4.98 N 16.0 Found C 54.4 H 4.98 N 15.9.- IR: 3871; 3024; 2972; 2919; 2852; 1701; 1649; 1600; 1532; 1487; 1469; 1435; 1400; 1350; 1326; 1303; 1273; 1245; 1203; 1087; 1051; 1014; 990; 936; 872; 834; 769; 721; 630 cm^{-1}.- UV (CH_3OH): λ max (log ε) = 218 (4.41), 266 (3.94), 304 (3.63), 349 nm (3.78).- ^{1}H-NMR: δ (ppm) = 7.75 (d, J = 9 Hz, 1H, 4-H), 7.67 (s, 1H, 7-H), 7.17 (d, J = 9 Hz, 1H, 5-H), 6.03-5.91 (m, 1H, C$\underline{H}$=CH_2), 5.25 (d, J = 10.3 Hz, 1H, CH=C$\underline{H}_2$), 5.16 (d, J = 17 Hz, 1H, CH=C$\underline{H}_2$), 5.03 (d, J = 5 Hz, 2H, 3-CH_2-CH), 4.10 (q, J = 7 Hz, 2H, O-$C\underline{H}_2$-CH_3), 1.37 (t, J = 7 Hz, 3H, O-CH_2-$C\underline{H}_3$).- MS (130°): m/z = 263 (12%, $[M]^{+\cdot}$), 236 (14), 235 (100), 233 (51), 207 (16), 205 (29), 194 (19), 178 (23), 166 (70), 152 (11), 122 (12), 80 (10), 41 (63), 39 (16), 29 (15).

3,5,6-Trimethyl-N-nitroso-2(3H)-benzothiazole imine (**28**)

Orange crystals (isopropanol), mp. 158°. Yield 76%.- $C_{10}H_{11}N_3OS$ (221.3) Calcd. C 54.3 H 5.01 N 19.0 Found C 54.3 H 5.04 N 18.8.- IR: 3011; 2940; 1673; 1574; 1539; 1451; 1433; 1414; 1380; 1305; 1278; 1217; 1190; 1138; 1075; 1053; 998; 971; 883; 848; 733 cm^{-1}.- UV (CH_3OH): λ max (log ε) = 210 (4.54), 220 (4.48), 266 (3.87), 356 nm (4.13).- ^{1}H-NMR: δ (ppm) = 7.76 (s, 1H, 4-H), 7.71 (s, 1H, 7-H), 3.84 (s, 3H, 3-CH_3), 2.39 (s, 3H, 5-CH_3), 2.33 (s, 3H, 6-CH_3).- MS (100°): m/z = 221 (39%, $[M]^{+\cdot}$), 193 (30), 192 (21), 191 (68), 177 (11), 165 (11), 164 (100), 149 (11), 91 (17), 77 (10), 45 (12), 39 (13).

3-Ethyl-5,6-dimethyl-N-nitroso-2(3H)-benzothiazole imine (**29**)

Orange needles (isopropanol), mp. 151°. Yield 43%.- $C_{11}H_{13}N_3OS$ (235.3) Calcd. C 56.2 H 5.57 N 17.9 Found C 56.1 H 5.74 N 17.3.- IR: 3448; 2931; 1641; 1567; 1534; 1474; 1457; 1424; 1396; 1359; 1342; 1319; 1295; 1254; 1232; 1205; 1186; 1138; 1118; 1098; 1065; 1025; 1002; 987; 878; 855; 806 cm^{-1}.- UV (CH_3OH): λ max (log ε) = 210 (4.53), 276 (3.75), 356 nm (4.16).- ^{1}H-NMR: δ (ppm) = 7.78 (s, 1H, 4-H), 7.76 (s, 1H, 7-H), 4.40 (q, 2H, 3-$C\underline{H}_2$-CH_3), 2.39 (s, 3H, 5-CH_3), 2.33 (s, 3H, 6-CH_3), 1.32 (t, 3H, 3-CH_2-$C\underline{H}_3$).- MS (110°): m/z = 235 (52%, $[M]^{+\cdot}$), 207 (25), 205 (100), 179 (12), 178 (46), 177 (18), 164 (52), 163 (25), 145 (14), 137 (19), 91 (23), 77 (14), 45 (34), 39 (10).

3-Allyl-5,6-dimethyl-N-nitroso-2(3H)-benzothiazole imine (**30**)

Orange needles (isopropanol), mp. 134°. Yield 45%.- $C_{12}H_{13}N_3OS$ (247.3) Calcd. C 58.3 H 5.30 N 17.0 Found C 58.0 H 5.34 N 16.8.- IR: 3446; 2919; 1641; 1571; 1527; 1477; 1430; 1395; 1371; 1334; 1312; 1280; 1241; 1138; 1081; 1066; 996; 978; 946; 839; 719; 700; 643 cm^{-1}.- UV (CH_3OH): λ max (log ε) = 212 (4.49), 266 (3.86), 356 nm (3.85).- ^{1}H-NMR: δ (ppm) = 7.76 (s, 1H, 4-H), 7.65 (s, 1H, 7-H), 6.04-5.92 (m, 1H, C$\underline{H}$=CH_2), 5.24 (d, J = 10 Hz, 1H, CH=C$\underline{H}_2$), 5.13 (d, J = 17 Hz, 1H, CH=C$\underline{H}_2$), 5.01 (d, J = 5 Hz, 2H, 3-CH_2-CH), 2.36 (s, 3H, 5-CH_3), 2.32 (s, 3H, 6-CH_3).- MS (120°): m/z = 247 (21%, $[M]^{+\cdot}$), 219 (89), 217 (100), 215 (13), 203 (28), 202 (19), 190 (46), 189 (31), 178 (64), 177 (28), 176 (21), 164 (33), 163 (16), 158 (11), 148 (11), 135 (12), 91 (33), 77 (12), 45 (23), 41 (20), 39 (28).

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