Reaction of Benzothiazole and Substituted Benzothiazoles with Dimethyl Acetylenedicarboxylate. A Novel Heterocyclic Ring Transformation[1]

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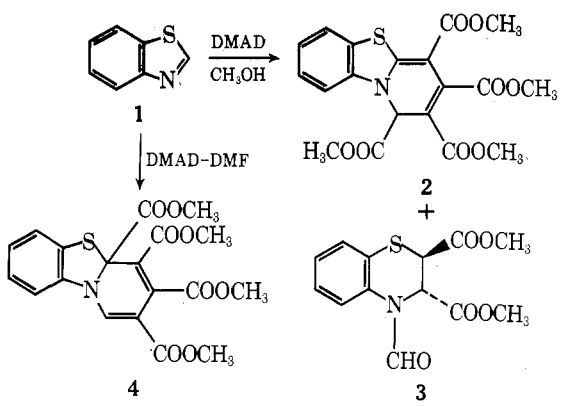
Reaction of benzothiazole with dimethyl acetylenedicarboxylate in aqueous methanol gives *trans*-dimethyl 4-formyl-2,3-dihydro-1,4-benzothiazine-2,3-dicarboxylate in high yield, and a mechanism is proposed for this novel transformation. The scope and limitations of the process have been defined by examination of the reactions of a wide range of substituted benzothiazoles with dimethyl acetylenedicarboxylate in aqueous methanol; the results are fully consistent with the postulated mechanism.

The reactions of benzothiazole **1** with dimethyl acetylenedicarboxylate (DMAD) have been studied by various groups of workers during the last 12 years, but only recently have the structures of the various products been unambiguously assigned by Ogura and his colleagues.[2] At least three products can be obtained, depending on the nature of the solvent used; thus, **2** and **3** are formed in 5 and 8% yield, respectively, when methanol is employed, whereas **4** is produced in 10% yield when DMF is used.



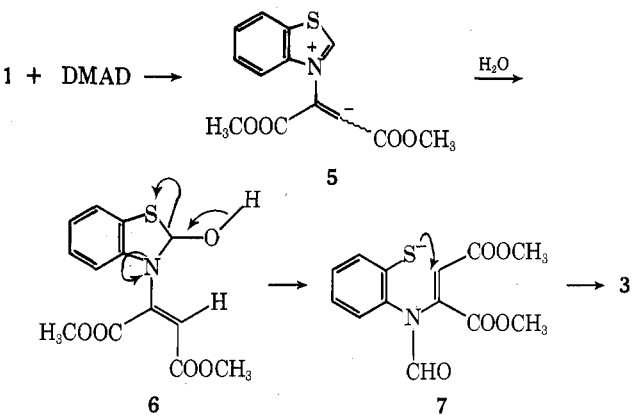
We have recently investigated the unusual transformation involved in the formation of **3** and demonstrated that (a) this product is *only* formed when the methanol contains water, and (b) it is produced in virtually quantitative yield when aqueous methanol is used in excess as solvent.[1] Moreover, the cleanness with which this ring transformation takes place is remarkable. Addition of benzothiazole to DMAD gives a deep red colored solution, and reaction to produce **2** proceeds with formation of considerable amounts of tarry, polymeric materials. Reactions carried out in absolute methanol or in methanol containing small amounts of water similarly give rise to deep red colored solutions and formation of polymeric products. In the presence of a large excess of water, however, the reaction mixture is pale yellow in color throughout and **3** crystallizes from it as a colorless solid. TLC examination of the crude product thus obtained showed that the only impurities present were trace amounts of benzothiazole and DMAD.

These results are fully consistent with the mechanism outlined in Scheme I for the conversion of **1** into **3**. That is, the initial addition product **5** formed from benzothiazole and DMAD can be trapped very effectively with water rather than DMAD, and the overall course of reaction is thus diverted to production of **3**.

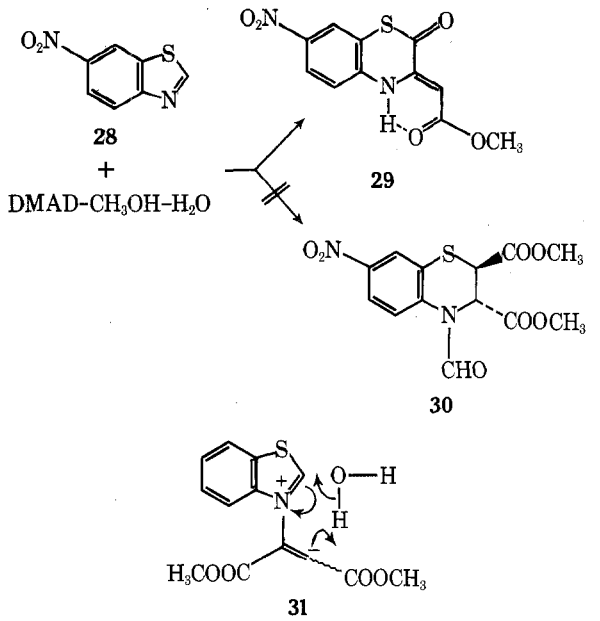
Discussion

The nature of the reaction of benzothiazole with DMAD to produce **3** having been clarified, it remained to determine the generality of this ring transformation. A wide range of substituted benzothiazoles was therefore prepared and treated with DMAD in aqueous methanol; the scope and limitations of the process were then readily deduced from the results obtained. Thus, with the exceptions of 6-nitro-, 5-acetoxy-, and 5,6-dimethoxybenzothiazole, benzothiazoles substituted in the 5, 6, and 7 positions with either electron-donating or electron-withdrawing groups were smoothly converted into the corresponding substituted *trans*-dimethyl 4-formyl-2,3-dihydro-1,4-benzothiazine-2,3-dicarboxylates; yield and experimental data for the various conversions are summarized in Table I.

Scheme I



Reaction of 5-acetoxy- (**26**) and 5,6-dimethoxybenzothiazole (**27**) with DMAD in aqueous methanol resulted only in formation of deep colored, polymeric tars. Neither of the starting benzothiazoles, however, is particularly stable; the dimethoxy compound, for example, rapidly discolored and decomposed on storage at room temperature, and decomposition was extremely rapid if the compound was exposed to light. Consequently, the failure of these compounds to react with DMAD to give identifiable products is almost certainly merely a result of their inherent instability. Reaction of 6-nitrobenzothiazole **28** with DMAD in aqueous methanol proceeded smoothly; the product, however, which was obtained in 60% yield, was easily shown by analytical and spectroscopic means (Experimental Section) to be the thiolactone **29**, and not the *N*-formyl-1,4-benzothiazine **30**. As is indicated below, formation of **29** is not entirely unexpected; moreover, consideration of the probable mechanism for this transformation provides further information on the relative stereochemistry of the two ester groups, both in this case and in the conversion of **1** into **3**. Thus, in the latter case, protonation of the intermediate **5** would be expected to be rapid, and may possibly occur in an intra-



molecular fashion as shown in **31**. Consequently, the ester groups in the subsequent intermediates **6** and **7** would be expected to be cis. Examination of molecular models clearly reveals that this stereochemistry *must* pertain for ring closure to occur in the observed manner; when the ester groups are trans there is severe steric hindrance to conjugate addition of the thiolate anion to the α,β-unsaturated ester system and some steric hindrance to nucleophilic attack of the thiolate anion at the nearer of the two ester carbonyl functions. There is, however, very little steric hindrance to conjugate addition when the two ester groups are cis.

A plausible mechanism for the conversion of **28** into **29** is outlined in Scheme II. In this case, decomposition of the intermediate ortho ester **32** occurs by C–N bond cleavage, and not by C–S bond cleavage as was observed with benzothiazole and the substituted benzothiazoles listed in

Scheme II

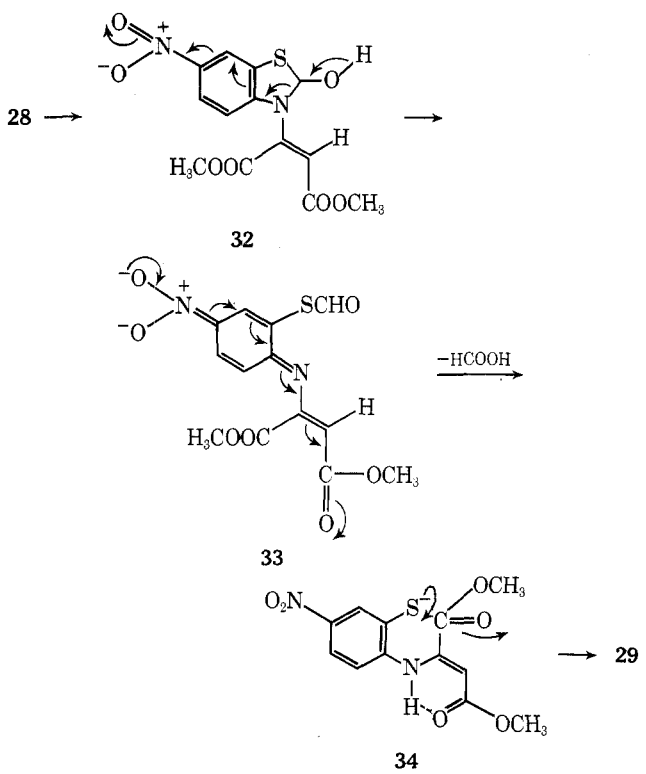
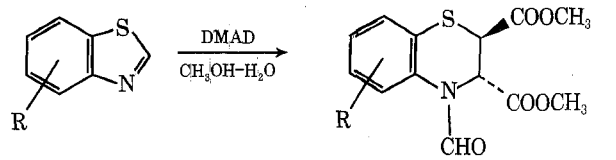


Table I. Conversion of Benzothiazoles into *trans*-Dimethyl 4-Formyl-2,3-dihydro-1,4-benzothiazine-2,3-dicarboxylates[a]

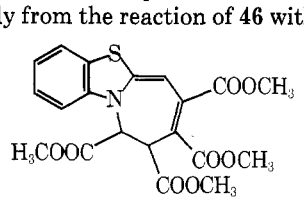


Benzothiazole		Benzothiazine		
Compd	R	Compd	Yield, %[b]	Mp, °C
1	H	3	85	135–136
8	5-CN	9	60	122–123
10	5-CH_3CONH	11	76	155–156
12	5-NO_2	13	80	135–136
14	5-Br	15	70	123–124
16	6-CN	17	60	123–124
18	6-CH_3CONH	19	82	129–130
20	6-CH_3O	21	72	124–125
22	6-Br	23	70	145–146
24	6-CH_3O-7-NO_2	25	70	163–165

[a] Full analytical and spectroscopic data (ir, NMR) for the benzothiazines are listed in Tables II and III (see paragraph at end of paper regarding supplementary material). [b] Refers to pure, recrystallized material.

Table I. That is, the mesomeric effect of the 6-nitro substituent is sufficiently powerful to render the C–N bond in the intermediate **32** weaker than the C–S bond (normal bond energies are C–N 69–75 kcal/mol[3] and C–S 66 kcal/mol[4]). Conversion of **32** into **34** via the resonance stabilized intermediate **33** would be expected to result in formation of the thermodynamically more stable trans diester,[5] lactonization of which leads to the observed product.[6]

The reactions of a variety of 4- and 2-substituted benzothiazoles were then examined. 4-Nitro-6-methoxy-, 4-acetamido-6-methoxy-, 4,6-dichloro-, 4,6-dichloro-7-nitro-, and 4,6-dichloro-7-acetamidobenzothiazole **35–39** were treated with DMAD in aqueous methanol; even after reflux periods of up to 25 h, however, no reaction had taken place, and the starting materials were recovered in virtually quantitative yield in every case. A similar situation was encountered with respect to 2-substituted benzothiazoles. Thus, 2-chloro-, 2-fluoro-, 2-methoxy-, 2-phenyl-, and 2-*p*-methoxyphenylbenzothiazole **40–44** were recovered unchanged even after prolonged reaction times; 2-benzothiazolone **45** also failed to react, even in the presence of sodium hydroxide. 2-Methylbenzothiazole **46** did react, but the product was the known azepine **47**, which has been obtained previously from the reaction of **46** with DMAD.[7]



The above unsuccessful reactions clearly indicate that the ring transformation summarized in Scheme I is subject to fairly fine control by both steric and electronic effects. The major factor which contributes to lack of reaction in the case of the 4-substituted derivatives **35–39** is almost certainly steric inhibition of the condensation between the heterocyclic ring nitrogen atom and DMAD, although in the case of **35** and **37–39** inductive electron withdrawal by the nitro and chloro substituents might also reduce slightly the basicity of the benzothiazole nitrogen atom. This latter effect is almost certainly the dominant reason for the failure of compounds **40–42** to react, i.e., the benzothiazole ni-

trogen atom is no longer sufficiently basic to participate in the initial conjugate addition to DMAD. Unfortunately pK_a values for the compounds in question are not available, but on a purely qualitative basis comparison with the corresponding pyridine derivatives gives some indication of the magnitude of the effect which might be operative. Thus, relative to pyridine (pK_a = 5.25) the pK_a values for 2-chloro-, 2-fluoro-, and 2-methoxypyridine are 0.49, −0.44, and 3.25, respectively. Steric effects alone are most probably responsible for inhibition of the reaction of DMAD with **43** and **44**, especially as in the latter case the basicity of the ring nitrogen atom would be expected to be greater than that of benzothiazole owing to the mesomeric effect of the *p*-methoxyphenyl group.

Experimental Section

Melting points were determined on a Kofler hot-stage microscope melting point apparatus and are uncorrected. Microanalyses were performed by Mr. A. R. Saunders and Mr. J. Robinson of the University of East Anglia. Infrared spectra were recorded on a Perkin-Elmer Model 257 grating infrared spectrophotometer using the standard Nujol mull, sodium chloride plate, and liquid film techniques. Nuclear magnetic resonance spectra were determined as solutions in either $CDCl_3$ or Me_2SO-d_6 on a Perkin-Elmer Model R-12 60-MHz nuclear magnetic resonance spectrometer using tetramethylsilane as internal standard.

Starting Materials. Crude benzothiazole (BDH) was first purified by vacuum distillation. It was then converted into the sulfate salt which, after crystallization from alcohol, was neutralized with sodium hydroxide solution. The benzothiazole was then extracted and distilled, and the fraction bp 125–128 °C (18 mm) was collected.

The following substituted benzothiazoles were synthesized by literature procedures: **10**,[8] **12**,[8] **16**,[9] **20**,[10,11] **22**,[9] **24**,[11] **28**,[9] **35**,[11] **37**,[12] **38**,[12] **40**,[13] **41**,[14,15] **42**,[16] **43**,[17,18] **45**,[19] **46**.[18]

5-Cyanobenzothiazole (8). This compound was prepared from 5-aminobenzothiazole[8] by exactly the same procedure as has been described for the preparation of 6-cyanobenzothiazole,[9] and was obtained in 61% yield as long, colorless, glistening needles, mp 138–140 °C from aqueous ethanol.

Anal. Calcd for $C_8H_4N_2S$: C, 60.00; H, 2.50; N, 17.50; S, 20.00. Found: C, 59.94; H, 2.60; N, 17.54; S, 19.94.

5-Bromobenzothiazole (14). This compound was prepared from 5-aminobenzothiazole[8] by exactly the same procedure as has been described for the preparation of 6-bromobenzothiazole,[9] and was obtained in 62% yield as colorless, glistening plates, mp 100–102 °C from aqueous ethanol.

Anal. Calcd for C_7H_4BrNS: C, 39.26; H, 1.87; Br, 37.39; N, 6.54; S, 14.95. Found: C, 39.39; H, 1.90; Br, 37.28; N, 6.50; S, 14.91.

6-Acetamidobenzothiazole (18). A solution of 6-aminobenzothiazole[9] (1.5 g, 0.01 mol) in a mixture of acetic acid (5 ml) and acetic anhydride (5 ml) was heated gently under reflux for 1 h. The cooled reaction mixture was then poured onto crushed ice (50 g) and the solid which separated was collected by filtration, washed with cold water, dried, and recrystallized from ethyl acetate–hexane. This gave 1.65 g (86%) of pure **18** as colorless needles, mp 170–171 °C.

Anal. Calcd for $C_9H_8N_2OS$: C, 56.25; H, 4.17; N, 14.58; S, 16.67. Found: C, 56.27; H, 4.12; N, 14.64; S, 16.71.

5-Acetoxybenzothiazole (26). A solution of 5-aminobenzothiazole[9] (6 g, 0.04 mol) in a mixture of concentrated hydrochloric acid (15 ml) and water (35 ml) was cooled to 0 °C and carefully diazotized by the dropwise addition of a cold (0 °C) solution of sodium nitrite (3 g) in water (10 ml). The resulting clear, bright orange solution was stirred at 0 °C for 5 min and then added to a cold (0 °C) solution of 9.35 M hydrofluoroboric acid (42.8 ml). The mixture turned deep orange in color and the diazonium fluoroborate began to precipitate. After 1 h at 0 °C the fluoroborate salt was collected by vacuum filtration, washed with ice–water (2 × 20 ml), and dried over phosphorus pentoxide at room temperature, yield 5.9 g (65%).

The fluoroborate salt thus prepared (5.4 g, 0.024 mol) was suspended in glacial acetic acid (100 ml) and the mixture was stirred and heated under reflux for 1 h. The solvent was then removed by evaporation under reduced pressure and the residual red oil diluted with water (200 ml). The resulting solution was extracted with ether (5 × 40 ml) and the combined extracts were washed with aqueous sodium bicarbonate solution and then dried (Na_2SO_4). The ether was removed by evaporation under reduced pressure and the residual yellow oil distilled to give 1.5 g (32%) of **26** as a colorless oil, bp 129–131 °C (0.2 mm), which slowly solidified on standing to colorless needles, mp 61–62 °C.

Anal. Calcd for $C_9H_7NO_2S$: C, 55.96; H, 3.63; N, 7.25; S, 16.58. Found: C, 55.94; H, 3.57; N, 7.17; S, 16.64.

5,6-Dimethoxybenzothiazole (27). The starting material, 6,6′-dinitro-3,3′,4,4′-tetramethoxydiphenyl disulfide, was prepared from 4,5-dinitroveratrole[20] according to the procedure of Ast and Bogert.[10]

Finely powdered 6,6′-dinitro-3,3′,4,4′-tetramethoxydiphenyl disulfide (4.3 g, 0.01 mol) was slurried with glacial acetic acid (40 ml) and the mixture heated to reflux. Zinc dust was then added carefully until a colorless solution was obtained; the solution was heated under reflux for 15 min, the excess zinc dust was removed by filtration under reduced pressure, and the resulting clear green solution was cooled to room temperature. Anhydrous formic acid (200 ml) and granulated zinc (3 g) were added with stirring to this solution of the zinc mercaptide and the resulting blue-green solution was heated under reflux for 28 h. The mixture was then cooled to room temperature, excess formic acid was removed by distillation under reduced pressure, and the residual blue oil was basified with solid sodium hydroxide (30 g). This gave a colorless emulsion containing a purple-blue oil which was extracted with ether (4 × 25 ml). The combined ether extracts were dried (Na_2SO_4) and evaporated under reduced pressure to give a thick purple oil. This was dissolved in chloroform (100 ml) and the solution treated with charcoal; evaporation of the solvent under reduced pressure gave a colorless, crystalline solid which was recrystallized from hexane to give 1.1 g (30%) of pure **27** as colorless, glistening plates, mp 74–75 °C. This compound discolors rapidly on storage at room temperature and very rapidly on exposure to light.

Anal. Calcd for $C_9H_9NO_2S$: C, 55.38; H, 4.62; N, 7.18; S, 16.41. Found: C, 55.30; H, 4.71; N, 7.15; S, 16.38.

4-Acetamido-6-methoxybenzothiazole (36). This compound was prepared by acetylation of 4-amino-6-methoxybenzothiazole[11] in exactly the same manner as is described above for the preparation of 6-acetamidobenzothiazole, and was obtained in 95% yield as colorless needles, mp 157–158 °C from ethyl acetate–hexane.

Anal. Calcd for $C_{10}H_{10}N_2O_2S$: C, 54.05; H, 4.50; N, 12.61; S, 14.41. Found: C, 53.76; H, 4.66; N, 12.53; S, 14.43.

4,6-Dichloro-7-acetamidobenzothiazole (39). This compound was prepared by acetylation of 4,6-dichloro-7-aminobenzothiazole[12] in exactly the same manner as is described above for the preparation of 6-acetamidobenzothiazole, and was obtained in 98% yield as long, colorless needles, mp 270–271 °C from glacial acetic acid.

Anal. Calcd for $C_9H_6Cl_2N_2OS$: C, 41.38; H, 2.30; Cl, 27.20; N, 10.73; S, 12.26. Found: C, 41.14; H, 2.47; Cl, 27.09; N, 10.75; S, 12.39.

2-*p*-Methoxyphenylbenzothiazole (44). This compound was prepared from 2,2′-bis(4-methoxybenzoylamino)diphenyl disulfide by exactly the same procedure as has been described for the preparation of 2-phenylbenzothiazole,[17,18] and was obtained in 75% yield as long, colorless needles, mp 117–118 °C from methanol.

Anal. Calcd for $C_{14}H_{11}NOS$: C, 69.70; H, 4.66; N, 5.80; S, 13.28. Found: C, 69.68; H, 4.67; N, 5.72; S, 13.29.

2,2′-Bis(4-methoxybenzoylamino)diphenyl disulfide was prepared from 2,2′-diaminodiphenyl by the same procedure as has been described for the preparation of 2,2′-diaminodiphenyl disulfide,[17,18] and was obtained in 70% yield as colorless microneedles, mp 110–111 °C.

Anal. Calcd for $C_{28}H_{24}N_2O_4S_2$: C, 65.12; H, 4.65; N, 5.43; S, 12.40. Found: C, 65.02; H, 4.61; N, 5.40; S, 12.50.

***trans*-Dimethyl 4-Formyl-2,3-dihydro-1,4-benzothiazine-2,3-dicarboxylate (3).** A solution of DMAD (1.5 g, 0.0105 mol, redistilled prior to use) in AnalaR methanol (5 ml) was added in one portion to a stirred solution of benzothiazole (1.3 g, 0.01 mol) in a mixture of AnalaR methanol (25 ml) and water (5 ml). The solution immediately turned pale yellow in color and was either heated under reflux for 5 h or stirred at room temperature for 3 days. The resulting mixture, from which some of the product had crystallized, was evaporated to dryness and the semisolid mass thus obtained triturated with a little ethanol at 0 °C. The solid was collected by filtration, washed with a small quantity of ice-cold ethanol, and recrystallized from ethanol. This gave 2.5 g (85%) of pure **3** as colorless rhombohedrons, mp 135–136 °C.

The other 1,4-benzothiazines listed in Table I were prepared in

an analogous fashion. Full analytical and spectroscopic data (ir, NMR) for these compounds are listed in Tables II and III (see paragraph at end of paper regarding supplementary material).

3-Carbomethoxymethylene-3,4-dihydro-7-nitro-2-oxo-2*H*-1,4-benzothiazine (29). A solution of DMAD (1.5 g, 0.0105 mol) in AnalaR methanol (5 ml) was added in one portion to a stirred suspension of 6-nitrobenzothiazole (1.8 g, 0.01 mol) in a mixture of AnalaR methanol (55 ml) and water (10 ml). The mixture was heated under reflux for 5 h, during which time the 6-nitrobenzothiazole gradually dissolved and a bright yellow solid precipitated. The reaction mixture was cooled and the solid collected by filtration, washed with ether, and dried. This gave 1.7 g (60%) of **29** as bright yellow needles: mp 305–310 °C dec; ir (Nujol) ν_{N-H} 3225 cm^{-1}, $\nu_{C=O}$ 1690 (lactone), and 1670 cm^{-1} (unsaturated ester). The NMR spectrum could not be recorded as the solid is completely insoluble in all common solvents.

Anal. Calcd for $C_{11}H_{18}N_2O_5S$: C, 47.14; H, 2.86; N, 10.00; S, 11.43. Found: C, 47.23; H, 2.81; N, 10.12; S, 11.48.

Acknowledgments. Two of us (T.S.B.S. and G.C.A.B.) acknowledge the receipt of Science Research Council Scholarships.

Supplementary Material Available. Full analytical and spectroscopic (ir, NMR) data for compounds **3, 9, 11, 13, 15, 17, 19, 21, 23,** and **25** are listed in Tables II and III (2 pages). Ordering information is given on any current masthead page.

Registry No.—**1,** 95-16-9; **3,** 55052-31-8; **8,** 58249-57-3; **9,** 58249-58-4; **10,** 36894-61-8; **11,** 58249-59-5; **12,** 2942-07-6; **13,** 58268-61-4; **14,** 768-11-6; **15,** 58249-60-8; **16,** 58249-61-9; **17,** 58249-62-0; **18,** 58249-63-1; **19,** 58249-64-2; **20,** 19989-66-3; **21,** 58249-65-3; **22,** 53218-26-1; **23,** 58249-66-4; **24,** 30132-83-3; **25,** 58249-67-5; **26,** 58249-68-6; **27,** 58249-69-7; **28,** 2942-06-5; **29,** 58249-70-0; **36,** 58249-71-1; **39,** 58249-72-2; **44,** 6265-92-5; DMAD, 503-17-3; 5-aminobenzothiazole, 1123-93-9; 6,6′-dinitro-3,3′,4,4′-tetramethoxydiphenyl disulfide, 58249-73-3; 4-amino-6-methoxybenzothiazole, 58249-74-4; 4,6-dichloro-7-aminobenzothiazole, 58249-75-5; 2,2′-bis(4-methoxybenzoylamino)diphenyl disulfide, 58249-76-6; 6-aminobenzothiazole, 533-30-2.

References and Notes

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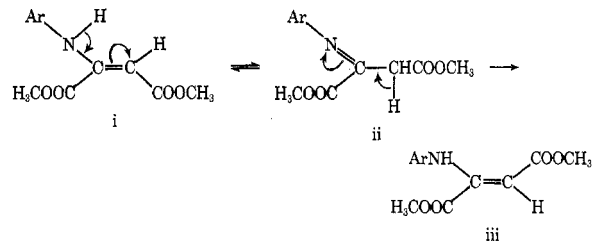

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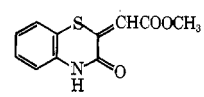

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Reaction of 1,2,3-Benzothiadiazole with Arylthio Radicals†

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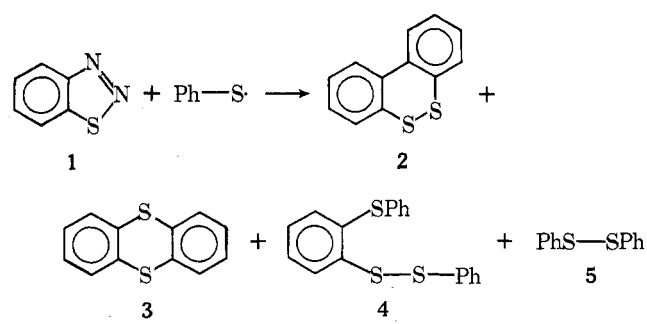
The reaction of 1,2,3-benzothiadiazole (1) with phenylthio radicals afforded dibenzo[*c,e*]-*o*-dithiin, thianthrene, and 2-(phenylthio)diphenyl disulfide. A mechanism is proposed which assumes initial attack of phenylthio radical at the sulfur atom of 1 to give radical 6, a key intermediate in this reaction.

Homolytic aromatic thioarylations have been achieved in a very limited number of cases and only if certain conditions are satisfied. High homolytic reactivity of the substrate and a strongly oxidizing medium allow direct substitution to occur on furan[1] and thiophene[2] rings. Indirect substitution has been observed at high temperatures with halobenzenes,[3] while intramolecular indirect substitutions occur easily when arylthio radical displaces an arylthio, phenoxy, and mercapto group to give a stable product such as dibenzothiophene or thianthrene.[4]

We now have found what is, to the best of our knowledge, the first example of an aromatic SH2 reaction effected by thiyl radicals at heterocyclic sulfur atom. In Scheme I are reported the products obtained from reaction between 1,2,3-benzothiadiazole (1) and phenylthio radicals

Scheme I



1 2 3 4 5

generated both by hydrogen abstraction from thiophenol with 2-cyanopropyl radicals[5] and by thermal decomposition of diphenyl disulfide (at 165 °C).[6] Under the latter

† Dedicated to Professor Martino Colonna on his 70th birthday.