ination of TosH was not yet taking place to a measurable extent, since the 5-C integrated for one full proton.
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Synthesis of Heterocycles from Aryl Isothiocyanates and Alkyl Azides

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Benzyl azide reacts with aryl isothiocyanates at 60 °C to produce five types of products (**5–9**). The asymmetric bis adducts of type **6**, formed as major components in the early stage of the reactions, rearrange into the more stable symmetric bis adducts **7** under a variety of conditions. Some derivatives of **6** also undergo partial or complete decomposition into the corresponding benzthiazole **15** upon treatment with Dabco. A precursor of the bis adducts, namely **16**, has been synthesized and shown to react with isothiocyanates at room temperature, giving mainly the asymmetric bis adducts of type **6** (namely **18a** and **18b**). Spectral and mechanistic interpretations are presented.

It is surprising that the behavior of aryl isothiocyanates toward organic azides is unknown, although the chemistry of both classes of compounds has been developed extensively. With inorganic azides, aryl isothiocyanates react to give two types of mono cycloadducts which result from addition of the azide onto the C=S (with HN_3)[1] or C=N bond (with N_3^-, R_3SnN_3, and other organometallic azides).[2]

In a previous article,[3] we have reported that alkyl azides react with arylsulfonyl isothiocyanates at room temperature to give 4-alkyl-5-arylsulfonylimino-1,2,3,4-thiatriazolines (**1**) as the only reaction products. On gentle heating, these adducts decompose into sulfonylcarbodiimides via the intermediacy of iminothiaziridines or their ring-opened dipolar species (**1** → **2** → **3**). Trapping of **2** with many unsaturated compounds (a=b) have led to the synthesis of a large number of other five-membered heterocycles (**4**).[3,4]

Reported here are the results of an extensive investigation on the reactions of aryl isothiocyanates with alkyl azides (in particular benzyl azide), a study complicated by the occurrence of isomerizations during the reaction and also by the number of isomeric reaction products which were difficult to characterize unambiguously by conventional spectroscopic methods (IR, ^{1}H NMR, and MS).[5]

Product Studies. Treatment of benzyl azide with 2 equiv of aryl isothiocyanate at 60 °C led to slow evolution of nitrogen and isolation of five products: a tetrazolinethione **5**, two thiadiazolidines **6** and **8**, and two dithiazolidines **7** and **9**. Since

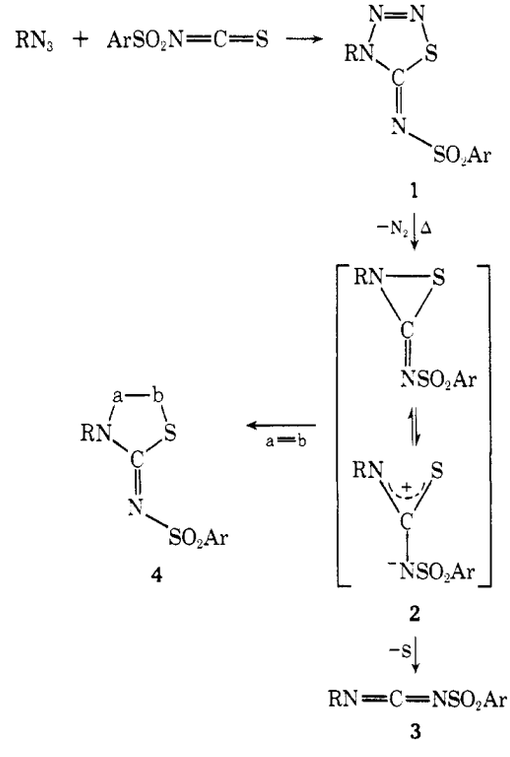
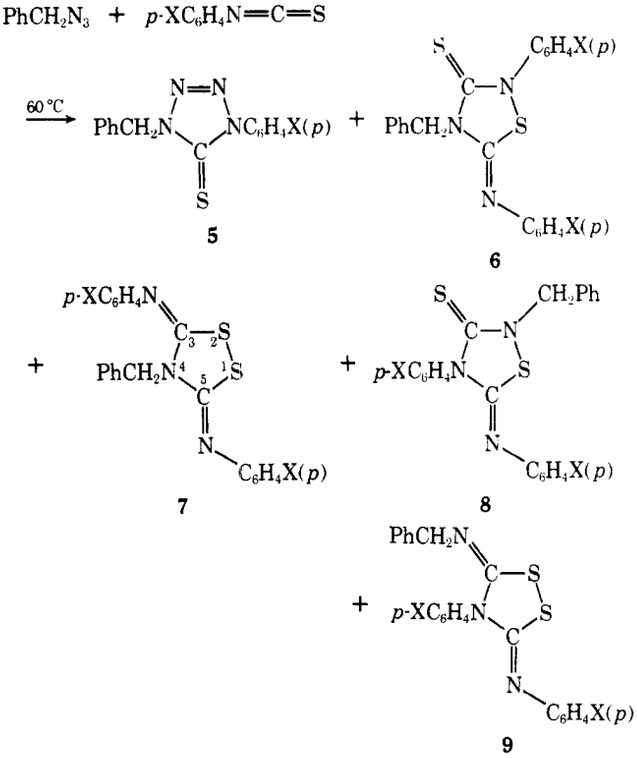


Table I. Product Distribution in the Reaction[a] of Benzyl Azide with 2 Equiv of Isothiocyanate at 60 °C

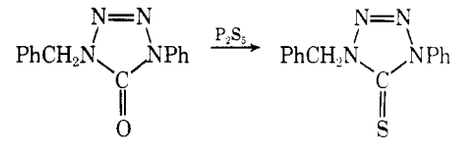
X	Time, days	% 5 (δ 5.5)	% 6 (δ 5.6)	% 7 (δ 5.4)	% 9 (δ 4.6)	% $PhCH_2N_3$ (δ 4.4)
a, NO_2	5	6.5	33	11	5.5	25
	9	5.5	32	16	6.5	18.5
	49[b]	12.5	12.5	>35[c]	15	2.5
	70[b]	11	10	>50[c]	14	
b, Cl	3	2.5	12	5		78
	14	5	25	40		27
	21	5	13	55		16
	30	5	12	66	*d*	11
c, H	4	2	10.5	6		70
	9	2.5	13	13.5		64
	17	5	15	25		55
	42	6	7	43	*d*	21
d, CH_3	8	1	8	3		83
	14		10	13		62
	21	5	10	34		50
	49	5.5	6.5	52	*d*	25

[a] No solvent, except in the case of X = NO_2, which was carried out in $CDCl_3$. [b] A singlet absorption at δ 5.2 ppm (6–7%) is also observed, corresponding to structure **8a**. [c] Compound **7a** is only partly soluble in $CDCl_3$. [d] Small absorptions (2–3%) are observed at ca. δ 4.6 which may correspond either to **9** or to the benzthiazole **15**.

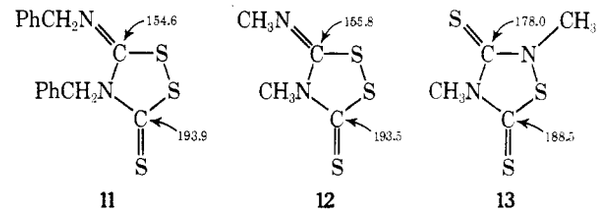
the yields of isolated **6** and **7** were much affected by the reaction conditions, time, and workup procedure, the relative amounts of products were estimated from the crude NMR spectra by integration of the benzyl methylene protons in the region δ 4.4–5.6. This was done at different stages of the overall conversion and the data are summarized in Table I. From this table it is noteworthy that the asymmetric bis adduct **6** was formed as the major product in the beginning of the reaction, whereas the symmetric product **7** predominated at the end of the reaction. This is due to the proclivity of **6** to undergo facile rearrangement into **7** under the reaction conditions (vide infra).



Product Characterization. The mono cycloadducts **5**, isolated in small amounts from the reactions, were easily characterized by spectral data, particularly by the C=S carbon absorption[6] at δ 163.6 ppm in the ^{13}C NMR spectra (see Table II). Unequivocal proof for **5c** was provided by an independent synthesis from the corresponding ketone[7] **10** upon



treatment with P_2S_5. The mass spectra and analyses of the products **6–9** (called bis adducts) are consistent with addition of two molecules of isothiocyanate onto a benzyl nitrene moiety. Their IR spectra (KBr disk) substantiate the presence of C=N functions with absorptions at 1610–1630 cm^{-1}. To distinguish between the isomeric structures **6–9**, we have analyzed their ^{13}C NMR spectra and compared the ring carbon absorptions with those of three model compounds **11, 12,** and **13,** prepared by the method of Freund[8] (the δ values are indicated on the structures). Compounds **7b–d,** which resonate at δ 5.4 ppm (CH_2) in the ^1H NMR spectra, exhibit C_3 absorptions at δ 153–154 ppm (see Table II), comparable with those in model compounds **11** and **12.** In addition, the symmetric structure of **7a,b,d** is apparent from the presence of two identical para-substituted phenyl groups in the ^1H and ^{13}C NMR spectra.



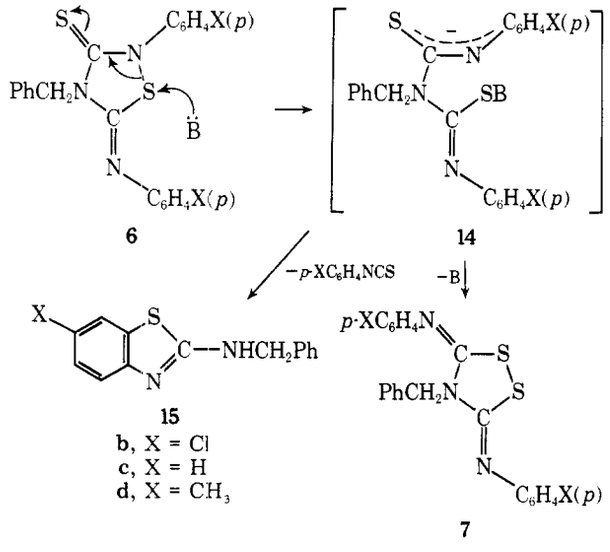
The synthesis of model compound **13,** for which an x-ray analysis has recently been determined,[9] enables us to assign a thiadiazolidine structure **6** to the bis adducts which resonate at δ 5.6 (CH_2) in the ^1H NMR spectra. Indeed, all these compounds exhibit a diagnostic C_3 absorption at δ 177–178 ppm in the ^{13}C NMR spectra (see Table II). The C_5 absorptions occur at δ 153 ppm in accordance with those in structures **7b–d.**

The thiadiazolidine **8a,** isolated in one case and absorbing at δ 5.25 ppm (CH_2) in the ^1H NMR spectrum, is similar in

structure to **6** with ^{13}C NMR ring carbon absorptions at δ 176.6 and 154 ppm. Besides the chemical shift value of the benzyl methylene protons, the only other NMR difference observed between **8a** and **6a–d** is the pattern of the phenyl protons of the benzyl group, being a singlet at δ 7.4 ppm for **8a** (as well as for **18b**!) and two multiplets centered at δ 7.35 and 7.7 ppm for **6a–d.** Conclusive distinction between **6** and **8** comes from rearrangement experiments as discussed in the next section.

Compound **9a** shows in the ^1H NMR spectrum two different aryl groups and a benzyl methylene signal at δ 4.60. The latter is shifted upfield with respect to the methylene protons in **6** (δ 5.6), **7** (δ 5.4), and **8a** (δ 5.2), which is reasonable since the electron density on N_4 in **6** and **7,** and on N_2 in **8a** is strongly decreased by resonance. The same influence on shift value is found for the methylene protons in model compound **11** (δ values at 4.47 and 5.01 ppm). Further confirmation of the assigned structure **9a** comes from measurements of the coupling constant $^1J_{C-H}$ of the benzyl methylene group, whose value is known to be related to the extent of charge localization on the nitrogen atom.[10] In compound **9a** as well as in model compound **11,** the benzylimino methylene group in position 3 exhibits a coupling constant of 133 Hz, compared to $^1J_{C-H}$ = 143 Hz for the benzyl methylene group at the electron-deficient 4 position of our heterocycles.

Dimroth Rearrangements. The isomerization of **6** into **7** which occurred during the reaction is a typical Dimroth rearrangement.[11] We have found that **6a** isomerized quantitatively into **7a** under a variety of mild conditions, i.e., upon recrystallization from acetone or upon treatment with 1,4-diazabicyclo[2.2.2]octane (Dabco) in refluxing chloroform. Compound **6b** was found to resist isomerization when heated in acetone for several hours, but rearrangement occurred in the presence of Dabco. After a reaction time of 3 days, an 80:20 mixture of **7b** and the benzothiazole **15b** was obtained. Similarly, **6c** did not isomerize when heated at 60 °C, but in the presence of benzyl azide reaction occurred to give **7c** (66%) and **15c** (11%) after 5 weeks. When a chloroform solution of **6c** was



heated with Dabco, the benzothiazole **15c** was formed exclusively. Finally, **6d** was also converted into **15d** upon heating with Dabco at 60 °C.

Isomerization of **6** into **7** is best accounted for by a mechanism which involves the intermediacy af **14.** This intermediate is stabilized by the presence of a strongly electron-withdrawing *p*-aryl substituent, such as No_2, which promotes the isomerization and deactivates the aromatic ring for electrophilic substitution. In the absence of NO_2, decomposition of **14** into benzothiazole **15** competes with rearrangement. We have shown that **7a–d** were stable under the conditions of isomerization.

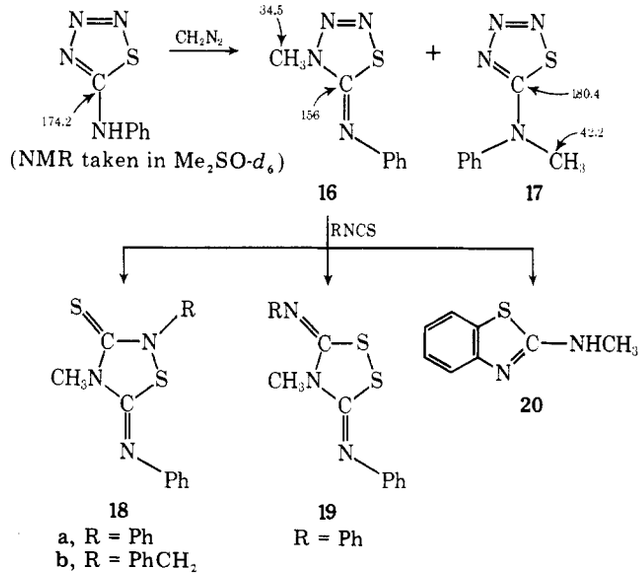
Table II. ^{13}C NMR Data of the Heterocycles[a]

Compd	Mp, °C	C_3	C_5	$PhCH_2N<$
5a	153–154		163.6	51.6
5c	112–112.5		163.8	51.4
6a	176–178	177.2	153.4	52
6b	150–152	177.6	153.3	51.7
6c	108–109	177.4	153	51.4
6d	116–118	177.5	152.7	51.4
7b	178	154	154	51.3
7c	151–152	153.5	153.5	51.1
7d	178–180	153.5	153.5	51.2
8a	229–230	176.6	154	53.7
9a	168–169	150.8	154.3	56.5
18a	86–88	177.6	153.9	
18b	97–98	177.7	153.6	53
19	134–135	154.3	154.3	

[a] The atoms comprising the five-membered rings are all numbered in the same manner as shown in structure **7.** All the spectra (δ values in parts per million from Me_4Si) were recorded in $CDCl_3$. The aromatic carbon absorptions are omitted. The CH_3 signals of **18a, 18b,** and **19** occur at δ 35 ppm.

Rearrangement **6** → **7** provides conclusive evidence for structure **6,** attributed to the asymmetric bis adducts which absorb at δ 5.6 in the ^1H NMR spectra. Indeed, the alternate structure **8** would not be expected to rearrange into **7** as was found experimentally for **8a.** Prolonged reaction time did not change the amount of **8a** formed.

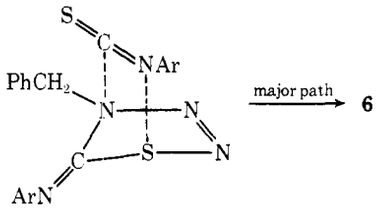
Mechanism. The previously reported[3] formation of **1** from alkyl azides and arylsulfonyl isothiocyanates suggests that the same type of mono cycloadduct (**1,** Ar instead of $ArSO_2$) is involved in the formation of **6–9** from aryl isothiocyanates. One is also tempted to assume the intermediacy of an aryliminothiaziridine, similar to **2,** in the second stage of the reaction.[5] This, however, has been disproved as outlined below. In order to cast light on the mechanism of the reaction, 4-methyl-5-phenylimino-1,2,3,4-thiatriazoline (**16**) was prepared by the method of Neidlein and Tauber.[12] These authors reported the reaction of 5-phenylamino-1,2,3,4-thiatriazole with diazomethane to furnish **16** exclusively. In our hands, the two isomers **16** and **17** were isolated in nearly equal amounts (ca. 37%). Their ^{13}C NMR data are indicated on the structures.



Compound **16** was found to be thermally stable up to 110 °C, at which temperature it decomposed into benzothiazole **20**.[12] In contrast, when **16** was mixed with phenyl isothiocyanate at room temperature, nitrogen evolution occurred and the ^1H NMR spectrum of the crude reaction mixture showed the presence of three methyl signals corresponding to **18a** (δ 3.70), **19** (δ 3.56), and **20** (δ 3.04) in a ratio of 78:18:4 (see Table II for the ^{13}C NMR data). Reaction of **16** with benzyl isothiocyanate at room temperature yielded **18b** (δ 5.2, 70%) along with a small amount of 4-methyl-2-phenyl-5-phenylimino-1,2,4-thiadiazolidin-3-one.[13]

These experiments indicate clearly that a thiaziridinimine, similar to **2**, is not involved in the second stage of the reaction of alkyl azides with aryl isothiocyanates, but that a bimolecular mechanism is operating. The formation of substantial amounts of **18a** and **18b** under the mild conditions is also consistent with our earlier observation that **6** was predominantly formed in the beginning of the reaction at 60 °C (see Table I). As expected, **18a** could be isomerized into **19** upon warming with Dabco, but **18b** failed to do so.

In conclusion, alkyl azides cycloadd preferentially onto the C=S bond of aryl isothiocyanates to give mono adducts (**1**, Ar instead of $ArSO_2$), which are responsible for the formation of **6, 7, 8,** and **9** by further addition of isothiocyanate and loss of nitrogen. Minor amounts of tetrazolinethiones **5**, resulting from addition of the azide onto the C=N bond of the heterocumulenes, are also formed. Whereas the C=N mono adducts are unreactive toward isothiocyanates, the C=S mono adducts react readily to give mainly **6**. This is shown in **21** for



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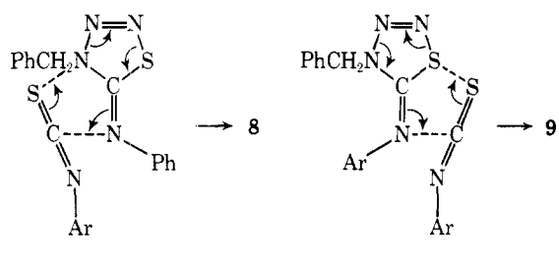
a concerted mechanism, although a stepwise mechanism cannot be excluded at the present time.

The preponderant formation of **7** as the reaction progresses is due to facile isomerization of **6** under the polar and basic conditions. The side products **8** and **9**, which were only isolated in one case (X = NO_2) and in small amounts, may have resulted independently from each other since no interconversion could be observed. Their mode of formation is rationalized below:



Experimental Section

Melting points were determined on a Leitz apparatus and are uncorrected. Infrared spectra were recorded with a Perkin-Elmer 157G spectrometer, mass spectra with an AEI MS-12 instrument, and ^1H NMR spectra with a JEOL MH-100 or Varian XL-100 spectrometer. For ^{13}C NMR spectra, the XL-100 apparatus was equipped with a device for pulsed Fourier transform operation. The chemical shifts given are in δ values in parts per million relative to Me_4Si in $CDCl_3$ solutions unless otherwise stated. The model compounds **11, 12,** and **13** were prepared by the method of Freund.[8] The benzothiazoles **15** obtained in this work were identified by comparison with authentic samples prepared by bromine oxidation of the corresponding thioureas.[14] In the reactions outlined below, no attempts were made to optimize yields.

Reaction of *p*-Nitrophenyl Isothiocyanate with Benzyl Azide. In a typical experiment *p*-nitrophenyl isothiocyanate (7.2 g, 0.04 mol) and benzyl azide (2.7 g, 0.02 mol) were dissolved in 20 ml of dry chloroform. The reaction flask was wrapped in aluminum foil and allowed to stand at 60 °C for 3 weeks. The solid **7a** (1.33 g), which precipitated upon cooling to room temperature, was removed by filtration, and the filtrate was diluted with 50 ml of ether giving a first fraction of **6a** (1.98 g, 21%) upon cooling to 0 °C and a second fraction (1.85 g) at −20 °C composed of **6a** and **7a** (ratio 60:40). The mother liquor was evaporated in vacuo and the residue was subjected to column chromatography on silica with $CHCl_3$–CCl_4 (ratio 60:40) as the eluent. This furnished unreacted isothiocyanate (1.3 g, 19%), **5a** (0.28 g), **7a** (0.15 g), and a mixture of reaction products (1 g) from which **7a** (0.53 g) and **9a** (0.2 g) were isolated by crystallization from acetone and ether–CH_2Cl_2, respectively.

5a (5%, mp 153–154 °C). Anal. Calcd for $M\cdot^+$ (determined by high-resolution exact-mass measurements): 313.06333. Found: 313.06373.

6a (21%, mp 176–178 °C). Anal. Calcd for $M\cdot^+$: 465.05653. Found: 465.05791.

7a (22%, mp 223–225 °C). Anal. Calcd for $C_{21}H_{15}N_5O_4S_2$ (465): C, 54.18; H, 3.25; N, 15.04; S, 13.78. Found: C, 54.00; H, 3.10; N, 15.20; S, 13.90.

9a (2.2%, mp 168–169 °C). Anal. Calcd for $M\cdot^+$: 465.05654. Found: 465.05760.

In another experiment, the reaction mixture from *p*-nitrophenyl isothiocyanate and benzyl azide was evaporated in vacuo and then subjected to fractional crystallization from acetone, giving respectively **7a** (32%), **9a** (20%), and **8a** (4%, mp 229–230 °C).

Compound **6a** isomerized quantitatively into **7a** upon recrystallization from acetone or upon heating with Dabco in chloroform solution for 0.5 h. On the contrary, **7a** and **9a** did not isomerize under the reaction conditions or under the influence of Dabco.

Reaction of *p*-Chlorophenyl Isothiocyanate with Benzyl Azide. *p*-Chlorophenyl isothiocyanate (3.4 g, 0.02 mol) was treated with benzyl azide (1.33 g, 0.01 mol) in 10 ml of dry chloroform at 55 °C for 30 days (conversion 60% by NMR). The solvent was then removed and the residue was fractionally crystallized from acetone to yield **7b** (0.86 g) and **6b** (0.09 g). A second crop of **6b** (0.37 g) was obtained by crystallization of the residue from ether.

6b (18%, mp 150–152 °C). Anal. Calcd for $C_{21}H_{15}Cl_2N_3S_2$ (444.5): C, 56.76; H, 3.40; N, 9.46; S, 14.43. Found: C, 56.60; H, 3.35; N, 9.35; S. 14.25.

7b (19%, mp 178 °C). Anal. Calcd for $M\cdot^+$: 444.01179. Found: 444.01132.

When benzyl azide was reacted with 2 equiv of *p*-chlorophenyl isothiocyanate at 100 °C for 1 day, **7b** was isolated in 56% yield by crystallization of the reaction mixture from acetone and ether.

When a chloroform solution of **6b** was heated in the presence of Dabco for 3 days, the NMR spectrum revealed the presence of **7b** (δ 5.36) and **15b** (δ 4.6) in a ratio of 80:20. Compound **7b** was heated in toluene at 100 °C for 22 h without any change.

Reaction of Phenyl Isothiocyanate with Benzyl Azide. A mixture of phenyl isothiocyanate (5.4 g, 0.04 mol) and benzyl azide (2.7 g, 0.02 mol) was kept at 60 °C for 6 weeks. The reaction mixture was crystallized from chloroform and then from ether to give **7c** in 52% yield. The remaining oil was subjected to column chromatography on silica gel with *n*-hexane–ether as the eluent. This furnished sulfur (30 mg), unreacted azide and isothiocyanate (1 g), **7c** (0.4 g), **5c** (0.3 g), **6c** (0.37 g), and *N,N'*-diphenylurea (0.10 g).

5c (5.5%, mp 112–112.5 °C). Anal. Calcd for $M\cdot^+$: 268.07826. Found: 268.07531.

6c (5%, mp 108–109 °C). Anal. Calcd for $M\cdot^+$: 375.08638. Found: 375.08400.

7c (57%, mp 151–152 °C). Anal. Calcd for $C_{21}H_{17}N_3S_2$ (375): C, 67.20; H, 4.53; N, 11.20. Found: C, 67.10; H, 4.69; N, 10.91.

For the independent synthesis of **5c**, 1-benzyl-4-phenyltetrazolinone (**10**, 1 g, mp 95–96 °C)[7] and P_2S_5 (2 g) were heated in dry toluene (15 ml) at reflux temperature for 2 days. After addition of 50 ml of CCl_4, the reaction mixture was filtered and the filtrate was chromatographed on silica gel using CCl_4–1.5% ethyl acetate as the eluent to give **5c** in 46% yield.

In another experiment, the reaction of benzyl azide with phenyl isothiocyanate was conducted at 100 °C for 72 h, giving **7c** in 55% yield. When **6c** and **7c** were heated in toluene at 100 °C for 1 day, no change was observed in the IR and NMR spectra and the products were recovered in pure form. However, in the presence of benzyl azide in $CDCl_3$ at 60 °C for 5 weeks, **6c** was partly converted into a mixture

of **7c** (66%) and **15c** (11%). A NMR sample of **6c** in $CDCl_3$ was also heated with Dabco to give **15c** (δ 4.55) in quantitative yield. The benzothiazole **15c** has been isolated (mp 166–167 °C) and identified by comparison with an authentic sample.[14]

Reaction of *p*-Tolyl Isothiocyanate with Benzyl Azide. *p*-Tolyl isothiocyanate (5.96 g, 0.04 mol) was allowed to react with benzyl azide (2.66 g, 0.02 mol) at 60 °C for 7 weeks. The reaction mixture was crystallized from ether to give **7d** (2.13 g) and the mother liquor was subjected to column chromatography on silica with *n*-hexane–ethyl acetate as the eluent. This furnished starting materials, a fraction (0.15 g) composed of **5d** (66%, δ 5.46), **6d** (30%, δ 5.56), and **7d** (4%, δ 5.38), and a third fraction of **15d** (0.1 g, mp 176–178 °C from acetone). Crystallization of the second fraction from *n*-hexane–chloroform furnished pure **5d** (15 mg), mp 90–90.5 °C, δ 5.55.

In order to isolate **6d**, the reaction was repeated and the mixture worked up after 12 days (conversion 30%). Column chromatography on silica with *n*-hexane as the eluent furnished starting materials (6.3 g), **7d** (0.7 g, 8.7%), and **6d** (0.84 g, 10.4%).

6d (mp 116–118 °C). Anal. Calcd for $M^{\cdot+}$: 403.11768. Found: 403.12095.

7d (mp 178–180 °C). Anal. Calcd for $C_{23}H_{21}N_3S_2$ (403): C, 68.48; H, 5.21; N, 10.42; S. 15.88. Found: C, 68.33; H, 5.14; N, 10.55; S, 15.77.

Reaction of 4-Methyl-5-phenylimino-1,2,3,4-thiatriazoline (16) with Phenyl Isothiocyanate. The procedure of Neidlein and Tauber[12] for the reaction of 5-phenylamino-1,2,3,4-thiatriazoline with an excess of diazomethane furnished, after column chromatography on silica gel with hexane–ether (70:30) as eluent, 38% of **16** (mp 68–70 °C, δ 3.95 for CH_3) and 36% of **17** (mp 56–58 °C, δ 3.7 for CH_3). Compound **16** (5×10^{-3} mol) was allowed to react with 3 equiv of phenyl isothiocyanate at room temperature for 22 h, followed by warming at 40 °C for another 2 h. The excess of phenyl isothiocyanate and crude benzothiazole **20** (2.5%)[12] were removed by column chromatography on silica gel using *n*-hexane as the eluent. The remaining fraction was crystallized from *n*-hexane–petroleum ether to give **18a** in 57% yield. The filtrate, which contained **18a** and **19** in a ratio of 40:60, was then treated with Dabco in order to isomerize **18a** completely into **19**. Crystallization from chloroform–ether furnished pure **19** in 27% yield.

18a (mp 86–88 °C). Anal. Calcd for $M^{\cdot+}$: 299.05508. Found: 299.05338.

19 (mp 134–135 °C). Anal. Calcd for $M^{\cdot+}$: 299.05508. Found: 299.05564.

Reaction of 16 with Benzyl Isothiocyanate. When compound **16** (5×10^{-3} mol) was allowed to react with 3 equiv of benzyl isothiocyanate at room temperature for 7 days, 1 equiv of nitrogen had evolved. Column chromatography of the reaction mixture on silica gel with *n*-hexane–ethyl acetate as the eluent furnished sulfur (10 mg), starting benzyl isothiocyanate (1.66 g), **18b** (1.1 g, 70.3%), and 4-methyl-2-phenyl-5-phenylimino-1,2,4-thiadiazolidin-3-one [0.1 g, mp 78–79 °C, C=O at 1703 cm^{-1}, CH_3 at δ 3.40, $M^{\cdot+}$ at 283.07939 (calcd, 283.07793)].

18b (mp 97–98 °C). Anal. Calcd for $M^{\cdot+}$: 313.07073. Found: 313.069504.

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Registry No.—**5a,** 61249-30-7; **5b,** 61249-31-8; **5c,** 61249-32-9; **5d,** 61249-33-0; **6a,** 56406-09-8; **6b,** 56406-12-3; **6c,** 50506-90-6; **6d,** 61249-34-1; **7a,** 56406-08-7; **7b,** 56406-11-2; **7c,** 55000-06-1; **7d,** 56406-13-4; **8a,** 61249-35-2; **9a,** 56406-10-1; **10,** 61249-36-3; **15b,** 61249-37-4; **15c,** 21816-82-0; **15d,** 56406-14-5; **16,** 34551-29-6; **17,** 34551-25-2; **18a,** 50506-86-0; **18b,** 61249-38-5; **19,** 61249-39-6; *p*-nitrophenyl isothiocyanate, 2131-61-5; benzyl azide, 622-79-7; *p*-chlorophenyl isothiocyanate, 2131-55-7; phenyl isothiocyanate, 103-72-0; P_2S_5, 1314-80-3; *p*-tolyl isothiocyanate, 622-59-3; benzyl isothiocyanate, 622-78-6; 4-methyl-2-phenyl-5-phenylimino-1,2,4-thiadiazolidin-3-one, 61249-40-9.

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Novel Heterocyclic Synthons, Synthesis and Properties of Thia- and Oxacyclohexane-3,5-diones

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Novel thia- (**1**) and oxacyclohexane-3,5-diones (**2**), as useful starting materials for the total synthesis of steroid S- and O-heterocycles, have been prepared and their physical properties are described. Both series of the heterodiones were prepared by a versatile synthetic route involving base-catalyzed cyclization of methyl 2-(3-alkylacetonylthio)acetates (**4**) and methyl 2-(3-alkylacetonyloxy)acetates (**5**), readily available from thiodiacetic and diglycolic anhydrides, respectively. The IR, NMR, UV, and pK_a data are discussed in terms of the heteroatom and compared to those of cyclohexane-1,3-diones (**3**).

At the outset of our studies directed toward the total synthesis of steroid S- and O-heterocycles, we considered as useful starting materials compounds of types **1** and **2**, isosteres of cyclohexane-1,3-diones (**3**) which have been widely used in the synthesis of natural products. Such novel types of heterodiones may not only be utilized as expedient building blocks