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References and Notes

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(13) In the simplified treatment

$$RO{-}OH \xrightarrow{k_1} RO\cdot + HO\cdot \quad (6)$$

$$RO\cdot\ (\text{or } HO\cdot) + SH \longrightarrow S\cdot + ROH\ (\text{or } H_2O) \quad (7)$$

where SH = solvent

$$S\cdot + RO_2H \xrightarrow{k_2} S'\cdot\ (\text{or } SH + RO_2\cdot) \quad (8)$$

where $S'\cdot$ in this case might be

$$S{-}CH_2{-}\dot{C}MeMe_2O_2H$$

$$RO_2\cdot + RO_2H \xrightarrow{k_2'} S''\cdot \quad (9)$$

where $S''\cdot = RO_2CH_2\dot{C}MeCMe_2O_2H$

$$S\cdot + S\cdot\ (\text{or } S'\cdot \text{ or } S''\cdot) \xrightarrow{k_3} \text{nonradical products} \quad (10)$$

If $k_2 \simeq k_2'$ and k_3 is about the same for all terminations, then steady state gives

$$-d[RO_2H]/dt = k_1[RO_2H] + k_2(k_1/k_3)^{1/2}[RO_2H]^{3/2} \quad (11)$$

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(20) Fortuitously the decrease in $[RO_2H]$ closely paralleled the decrease in $[t\text{-}Bu_2O_2]$ so that a 10% contribution of radicals from RO_2H would not have altered the fit to eq 13.

(21) In general, peroxy radicals prefer to abstract an allylic hydrogen from olefins rather than add to the double bond. However, 1,1-disubstituted olefins, and tetramethylethylene particularly, tend to be exceptional in this regard. Thus TMEH may be considered an unrepresentative hydroperoxide vastly different in behavior from, say, cyclohexenyl hydroperoxide. Our unpublished work with cyclohexenyl hydroperoxide indicates otherwise. The products are a very complex mixture, but there is ample evidence that *addition to*, not abstraction from, the hydroperoxide's allylic system predominates. A driving force for addition to allylic hydroperoxides, absent in the case of simple olefins, is the generation of a free valence on carbon next to oxygen. One has, in effect, the free radical analog to the Michael reaction. This hypothesis needs further testing, of course.

Oxidation of Thioureas in Protic Media. The Structures of Hector's, Dost's, and Hugershoff's Bases

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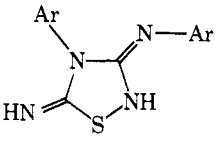
Abstract: The products arising from oxidation of some *N*-alkyl-*N'*-arylthioureas are shown to be 2,4-dialkyl-3,5-bis(arylimino)-1,2,4-thiadiazolidines. In the case of 2,4-dimethyl-3,5-bis(phenylimino)-1,2,4-thiadiazolidine, a three-dimensional single-crystal X-ray structure determination has been carried out. The compound crystallizes in the orthorhombic space group *Pccn* with cell dimensions a = 15.469 (7), b = 23.813 (7), c = 8.114 Å (4). There are eight molecules per unit cell. The positional and anisotropic thermal parameters of the nonhydrogen atoms have been refined to a conventional R index of 4.8% for 1683 reflections. Acid-catalyzed rearrangements were found in two cases to lead to substituted 2-aminobenzothiazole derivatives, the structures of which were assigned partly on the basis of their ^{13}C NMR spectra. From these results, new and conclusive evidence has been brought into the 85 year long discussion of the structures of the so-called Hector's, Dost's, and Hugershoff's bases.

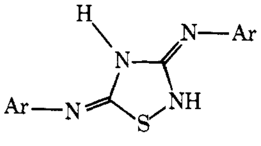
One of the most confusing oxidation reactions in organic chemistry is the oxidation of thioureas. Depending on the substitution pattern of the thiourea, the oxidizing agent, the polarity of the medium, and the conditions used, a variety of products have been isolated.[2] A few examples will suffice to show the complexity and versatility of the reaction which, under certain conditions, leads to ureas, formamidine disulfides, formamidinesulfinic acids, formamidinesulfonic acids, 1,2,4-thiadiazoles, and various benzothiazole derivatives.

Monoarylthioureas are known to give rise to heterocyclic compounds on oxidation under certain conditions. The structures of these compounds have been the subject of several reviews.[3-5] The compounds are usually named after their discoverer as "Hector's bases".[6] A variety of structures have been advanced, but the most favored representation now seems to be that of 4-aryl-3-arylimino-5-imino-1,2,-4-thiadiazolidines (**1**).[5] This structural assignment is based on considerable chemical evidence which is, however, not fully conclusive.[5] A strong argument in favor of **1** is the fact that a base-catalyzed rearrangement gives rise to what are now thought to be 3,5-bis(arylamino)-1,2,4-thiadiazoles (**2**);[7-9] this type is often referred to as "Dost's bases".[7] If the structural type **2** can be firmly secured, it seems that structure **1** must also be accepted.



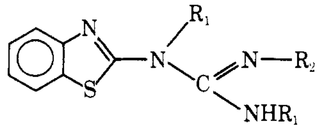
1

(Hector's base)



2

(Dost's base)

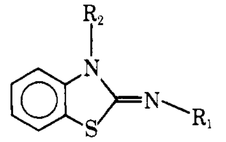


3a, $R_1 = R_2 = C_6H_5$

b, $R_1 = CH_3$; $R_2 = C_6H_5$

c, $R_1 = CH_2CH_3$; $R_2 = C_6H_5$

(Hugershoff's base)



4a, $R_1 = C_6H_5$; $R_2 = C(NC_6H_5)(NHC_6H_5)$

b, $R_1 = CH_3$; $R_2 = C(NC_6H_5)(NHCH_3)$

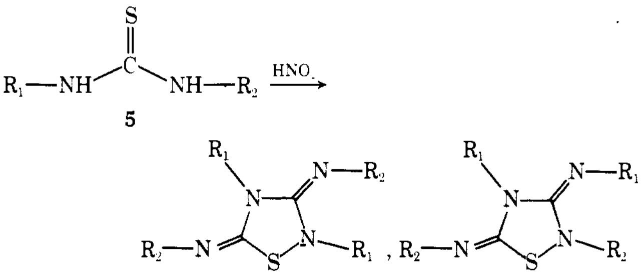
c, $R_1 = CH_3$; $R_2 = CH_3$

d, $R_1 = H$; $R_2 = CH_3$

Some thioureas, e.g., *N,N'*-diphenylthiourea[5] and *N*-phenyl-*N'*-methylthiourea,[10] are oxidized to what are now considered benzothiazole derivatives **3** and termed "Hugershoff's bases".[11] The most convincing argument for structure **3a** is that the compound can be obtained from the reaction of 2-phenylaminobenzothiazole and diphenylcarbodiimide.[12] However, a benzothiazoline structure **4a** has been tentatively assigned to the compound from uv and ir spectral analyses.[13] Structure **4b** has been postulated as an intermediate in the oxidation of **5a**.[10] Furthermore the synthetic pathway considered leading to **3a** does not a priori determine this structure unambiguously since at least one case is known where 2-aminobenzothiazole is alkylated on the endo-cyclic nitrogen, namely the reaction between 2-aminobenzothiazole and methyl iodide.[14]

Results

We have been concerned with the oxidation of *N*-aryl-*N'*-alkylthioureas **5** with nitrous acid in protic media (water–ethanol mixtures). When **5a** is subjected to the oxidation procedure, a compound is isolated, the chemical and spectroscopic properties of which are in accordance with its formulation as 2,4-dimethyl-3,5-bis(phenylimino)-1,2,4-thiadiazolidine (**6a**). The same compound is obtained when 2-methyl-4-phenylthiosemicarbazide is treated with nitrous acid, presumably via the corresponding thiourea **5a** formed as an intermediate.[2b]



a, $R_1 = CH_3$; $R_2 = C_6H_5$

b, $R_1 = CH_2CH_3$; $R_2 = C_6H_5$

c, $R_1 = C_6H_{11}$; $R_2 = C_6H_5$

d, $R_1 = CH_3$; $R_2 = 4\text{-Cl-}C_6H_4$

e, $R_1 = N(CH_3)_2$; $R_2 = C_6H_5$

Acid-catalyzed isomerization of **6a** and **6b** gives rise to products which, according to their spectroscopic properties, are Hugershoff-type derivatives **3** or **4**. To distinguish between **3** and **4** and also to settle the ambiguity in the structure of **3a** (vs. **4a**), we have compared the ^{13}C NMR spectra of the rearrangement product of **6a** with those of **4c**, **4d**, and 2-methylaminobenzothiazole. A detailed assignment of the ^{13}C resonances has not been carried out, but the benzothiazoline derivatives **4c** and **4d** have a very characteristic feature, namely a signal at very high field (δ 108.2 and 109.1 ppm respectively), the analog of which is not observed in either 2-methylaminobenzothiazole or **3b** (highest field aromatic carbon signals at δ 117.7 and 120.2 ppm, respectively). Current ^{13}C NMR theory offers no straightforward explanation of this high-field aromatic carbon resonance, and it is not obvious from chemical considerations why one of the aromatic carbons should have a considerably higher electron density that the rest. However, the phenomenon may be a general feature in this type of system since it was also observed in the case of the selenium analog of **4d**, which has a high-field resonance at δ 110.5 ppm vs. the highest-field aromatic carbon resonance of 2-methylaminobenzoselenazole at δ 119.6 ppm.[15] This phenomenon warrants further study but, in this case, allows a decision in favor of structure **3** for Hugershoff's bases.

The factors governing the benzothiazole formation still need clarification since it was established that **6c** and **6d** give rise to the corresponding ureas under conditions where **6a** and **6b** underwent smooth rearrangement. In the case of **6e**, unidentified hydrolysis products are formed, and Dost's base **2** (Ar = C_6H_5) on long boiling gives only hydrolysis products (phenylguanidine) besides unreacted starting material.

The correctness of structure **3b**, however, does not secure the structure of **6a** since **3b** could as well arise from **6′a**. Spectroscopic and chemical evidence were deemed ambiguous in distinguishing between **6a** and **6′a**. Therefore a single-crystal X-ray study was undertaken.

Diffraction Section

Experimental. Oscillation and Weissenberg photographs indicated orthorhombic symmetry; all reflections $0kl$ for l odd, $h0l$ for l odd, and $hk0$ for $h + k$ odd were systematically absent, uniquely defining the space group as *Pccn*.

A computer-controlled Syntex-P$\bar{1}$ four-circle diffractometer with graphite-monochromatized Mo$K\alpha$ radiation ($K\alpha_1$, $\lambda = 0.70926$ Å; $K\alpha_2$, $\lambda = 0.71354$ Å) and a pulse-height analyzer was used for preliminary experiments and for the measurement of diffraction intensities. The cell constants and their standard deviations were determined by a least-squares treatment of the angular coordinates of 15 independent reflections with 2θ values less than 23°. The program used was written by R. Sparks and is part of the diffractometer program library. The temperature was maintained at 20 ± 1° throughout the experiments. An egg-shaped crystal of approximate dimensions 0.3 × 0.2 × 0.2

Table I. Fractional Atomic Coordinates and Thermal Parameters for Nonhydrogen Atoms with Estimated Standard Deviations ($\times 10^5$)[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S1	38487 (7)	97157 (3)	69423 (10)	672 (5)	119 (1)	1206 (12)	31 (4)	306 (14)	−27 (7)
N2	39779 (19)	103481 (10)	59115 (29)	514 (14)	119 (4)	1029 (34)	8 (13)	127 (38)	−63 (21)
C3	37887 (19)	108062 (11)	68986 (35)	315 (13)	127 (5)	932 (39)	9 (13)	−37 (41)	3 (24)
N4	36244 (18)	106305 (10)	85079 (29)	395 (13)	124 (5)	937 (36)	−10 (11)	65 (34)	−46 (19)
C5	36159 (19)	100646 (13)	88045 (36)	294 (14)	147 (5)	1039 (42)	20 (13)	−45 (41)	−22 (25)
N6	34896 (18)	98457 (11)	101979 (30)	431 (13)	156 (5)	1073 (38)	1 (13)	9 (37)	91 (23)
N7	37434 (18)	113252 (10)	65425 (30)	471 (13)	127 (4)	1171 (38)	44 (13)	153 (39)	16 (20)
C8	37384 (24)	103268 (15)	41628 (37)	517 (17)	175 (6)	1023 (40)	−102 (18)	28 (44)	−137 (29)
C9	35559 (26)	110299 (14)	98633 (40)	656 (21)	157 (6)	1116 (48)	18 (18)	274 (54)	−140 (28)
C10	34744 (21)	92453 (13)	103008 (36)	359 (15)	159 (6)	1046 (43)	−3 (15)	131 (44)	115 (27)
C11	40863 (23)	89773 (15)	112673 (42)	394 (16)	178 (7)	1409 (51)	2 (16)	−162 (48)	34 (29)
C12	40758 (27)	84028 (16)	114277 (46)	550 (20)	186 (7)	1665 (59)	164 (19)	−271 (59)	245 (33)
C13	34476 (29)	80869 (15)	106743 (50)	624 (21)	156 (6)	1818 (63)	−17 (19)	48 (63)	178 (34)
C14	28320 (26)	83489 (16)	97274 (50)	482 (18)	185 (7)	1865 (66)	−160 (18)	−108 (56)	153 (35)
C15	28470 (23)	89294 (14)	95334 (41)	407 (15)	174 (6)	1396 (53)	−28 (18)	−143 (48)	200 (30)
C16	40371 (23)	115646 (12)	50570 (37)	486 (16)	104 (5)	1106 (44)	−25 (14)	76 (47)	−66 (25)
C17	35051 (24)	119344 (13)	42226 (43)	472 (17)	142 (6)	1502 (53)	0 (16)	−51 (50)	42 (29)
C18	37933 (28)	122162 (14)	28362 (46)	671 (22)	155 (6)	1510 (59)	5 (19)	−217 (63)	223 (29)
C19	46154 (30)	121269 (15)	22531 (42)	775 (25)	141 (6)	1332 (55)	−134 (20)	295 (62)	73 (29)
C20	51588 (25)	117633 (14)	30856 (47)	555 (19)	165 (6)	1604 (55)	−86 (18)	441 (61)	−119 (35)
C21	48740 (24)	114866 (14)	44800 (39)	493 (18)	153 (6)	1287 (50)	55 (16)	83 (49)	7 (29)

[a] See Figure 1 for the identities of the atoms. The temperature factors are given by $\exp\left\{-[(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]\right\}$

mm, prepared by dissolving a larger crystal in solvent to the desired size chosen to avoid systematic errors in atomic positions due to X-ray absorption, was used.

Three-dimensional intensity data were collected utilizing the θ-2θ scanning mode with scan speed variable from 1 to 24° min^{-1}, depending on the peak intensity of the reflection. (Most reflections were examined at the slowest scan rate.) Background counting time was equal to the scan time, and the scan range varied from 2.0° at low 2θ to 2.7° at $2\theta = 50°$. The variations in the intensities of three check reflections, which were measured after every hundred during data collection, indicated a linear decay to ~93% of the original, and corresponding decay corrections were applied to the intensity data.

Standard deviations were assigned to the intensities of the individual reflections according to the formula

$$\sigma(I) = \{\omega^2(\mathrm{CT} + B_1 + B_2) + (pI)^2\}^{1/2}$$

where ω is the scan rate, CT is the total integrated count, B_1 and B_2 are the background counts, and the intensity is $I = \omega(\mathrm{CT} - B_1 - B_2)$. A value of 0.02 was assigned to the empirical parameter p to account for experimental uncertainties. Of the 2655 space-group-allowed unique reflections measured, those for which $2\theta < 50°$, 1684 had intensities larger than three times their standard deviations. These were regarded as the observed reflections, and all of the remaining reflections were excluded from further calculations. The intensities were corrected[16] for Lorentz and polarization effects; the contribution of the monochromator crystal was calculated assuming that it was half perfect and half mosaic.

The atomic scatting factors used were those of Doyle and Turner[17] for C^0, N^0, and S^0, and those of Stewart et al.[18] for H (bonded).

Crystal Data. 2,4-Dimethyl-3,5-bis(phenylimino)-1,2,4-thiadiazolidine (6a): $C_{16}H_{16}N_4S$, orthorhombic, *Pccn*, $a = 15.469$ (7), $b = 23.813$ (7), $c = 8.114$ Å (4). Figures in parentheses are estimated standard deviations (Å × 10^3). $V = 2989$ (4) Å^3, $M = 296.4$ amu, $z = 8$, $D_{\mathrm{calcd}} = 1.317$ g cm^{-3}, D_{obsd}(flotation) = 1.32 g cm^{-3}, $F(000) = 1248$, mp 124–125°.

Structure Determination. All programs subsequently used are part of a local (University of Oslo) assembly of computer programs for CYBER-74, described in ref 19.

The phase problem was solved by a computer procedure based on direct methods.[20] None of the phase sets generated using normalized structure factors (E's) calculated on the basis of Wilson and Debye statistics gave a satisfactory solution. Normalized structure factors were therefore calculated using an estimated temperature factor (3.0 Å^2) and scale factor (0.7) (final values for these parameters after least-squares refinement are: $B \sim 4.0$ Å^2, scale factor ~0.6). In a Fourier synthesis (E map) using the "best" phase set generated utilizing these E's, 20 of 21 nonhydrogen atoms could be located. The position of the last atom (C19) was calculated.

Least-squares refinement, first with individual isotropic thermal parameters and thereafter with anisotropic thermal parameters for all 21 atoms, proceeded smoothly to converge where

$$R = 0.078\ [R = (\Sigma|F_o - |F_c||)/\Sigma F_o] \text{ and } R_w = 0.073$$

$$\{R_w = [\Sigma w(F_o - |F_c|)^2/\Sigma w F_o^2]^{1/2}\}$$

At this stage, the positions of the 16 hydrogen atoms were calculated and included in the structure factor calculation. Refinement showed one structure factor, 400, the largest of the data set, to be in very poor agreement with its calculated value, apparently because of extinction, and it was therefore excluded (leaving 1683 F_o's).

Full-matrix least-squares refinement of all positional and anisotropic thermal parameters for nonhydrogen atoms resulted in $R = 0.048$, $R_w = 0.052$. The "goodness of fit" $\{[\Sigma w(F_o - |F_c|)^2]/(m - s)\}^{1/2}$ is 1.50. The number of observations is m, and s, the number of parameters, is 189. In the final cycle of least-squares, all shifts were less than 1% of their esd's. The largest peak in a final difference Fourier function had a density of less than 0.2 e Å^{-3}.

The overdetermination ratio, excluding the unrefined hydrogen parameters, is 8.9. Final parameters obtained for nonhydrogen atoms are listed in Table I, and parameters used for hydrogen are given in Table II.[21]

The root-mean-square difference between the observed U_{ij}'s and those calculated from the "rigid-body" model[22] is 0.0048 Å^2, which indicates that the molecule does not behave as a rigid body. Use of parts of the molecule in the TLS approximation resulted in all cases in negative libration axes. Corrections for librational motion were accordingly not included in the calculations of molecular parameters.

Table II. Fractional Atomic Coordinates ($\times 10^3$) and Isotropic Temperature Factors for Hydrogen Atoms[a]

Atom	x	y	z	B
H22	452	919	1182	4.0
H23	451	822	1207	4.0
H24	344	769	1080	4.0
H25	239	813	919	4.0
H26	242	911	887	4.0
H27	292	1200	461	4.0
H28	342	1247	226	4.0
H29	481	1231	129	4.0
H30	574	1171	270	4.0
H31	525	1123	504	4.0
H32	383	1070	364	5.0
H33	312	1021	405	5.0
H34	411	1004	358	5.0
H35	344	1083	1092	5.0
H36	307	1130	965	5.0
H37	411	1125	998	5.0

[a] The identities of the atoms are as follows: H22 bonded to C11–H26 bonded to C15; H27 bonded to C17–H31 bonded to C21; H32–H34 bonded to C8, H35–H37 bonded to C9.

Table III. Selected Dihedral Angles with Estimated Standard Deviations in Parentheses. The Angles are Positive for a Right-Handed Screw

Dihedral angle	Degrees	Dihedral angle	Degrees
C5–S1–N2–C3	−4.4 (2)	C5–S1–N2–C8	−149.0 (2)
N2–S1–C5–N4	1.9 (2)	N2–S1–C5–N6	−175.9 (3)
S1–N2–C3–N4	5.7 (3)	S1–N2–C3–N7	−173.8 (3)
C8–N2–C3–N4	146.9 (3)	N2–C3–N4–C5	−4.4 (4)
N2–C3–N4–C9	169.2 (3)	N7–C3–N4–C5	175.1 (3)
C3–N4–C5–S1	1.0 (4)	C3–N4–C5–N6	178.9 (3)
C9–N4–C5–S1	−172.6 (3)	N4–C3–N7–C16	168.4 (3)
C3–N7–C16–C17	132.7 (3)	S1–C5–N6–C10	−4.4 (5)
C5–N6–C10–C11	118.3 (3)		

Estimated standard deviations in molecular parameters were calculated from the correlation matrix, ignoring standard deviations in cell parameters.

Discussion

Bond lengths and bond angles found for **6a** are given in Figure 1, where the numbering of the atoms is indicated. Some selected dihedral angles are given in Table III and deviation from least-squares planes through the three rings in Table IV. The central ring is not planar (Table IV), and the two C=N double bonds are essentially "pure" nonconjugated double bonds (C3—N7 1.271 Å, C5—N6 1.260 Å, comparable to the reported nonconjugated C=N double bond distance of 1.278 Å).[23] Despite these facts, the C—N single bonds in the central ring are somewhat shortened from the nonconjugated C—N single bond distance of 1.458 Å[24] (C3—N2 1.385 Å, C3—N4 1.395 Å, and C5—N4 1.369 Å), indicating at least some conjugation in the ring. This conclusion is further supported by a comparison between the C—S bond distance of 1.762 Å and reported nonconjugated C—S single bond distance of 1.811[25] and 1.815 Å.[26] This phenomenon is analogous to findings for sydnones[27] and *N*-[3-phenyl-5-(1,2,3,4-oxatriazolio)]-phenylamide.[28] Apparently the only reported X-ray structure of this heterocyclic system is that of 5-benzoylimino-3-phenyl-2-(4-bromophenyl)-2,5-dihydro-1,2,4-thiadiazole.[29] This latter system is reported to be extensively conjugated as exemplified by a C=N bond length of 1.35 Å, but the standard deviations obtained in that study do not allow a closer comparison with the present structure.

Oxidation of **5** with benzoyl peroxide in methylene chloride is presumably an easier way to **6**. The product from oxidation of **5a** in this way has been assigned the structure 2-phenyl-4-methyl-3-methylimino-5-phenylimino-1,2,4-thiadiazolidine[30] but is in fact **6a**. The formation of **6a** in this reaction casts some doubt on the validity of the hypothesis that Hector's bases (in this case, Dost's bases) are formed only in acidic polar solvents, while nonpolar neutral solvents, favoring a radical mechanism, give rise to benzothiazoles.[9,31]

Table IV. Deviations (Å $\times 10^3$) from Least-Squares Planes through the Three Ring Systems. The Deviations for the Atoms Used to Define the Plane Are Given in Boldface Figures[a]

Atom	Plane A	Plane B	Plane C
S1	−1	2425	
N2	−76		1822
C3	4		639
N4	−6	992	290
C5	6	920	
N6	−21	−53	
N7	88		−104
C8	584		
C9	−166		
C10	36	3	
C11		−9	
C12		8	
C13		−1	
C14		−4	
C15		4	
C16	−125		8
C17			0
C18			−8
C19			8
C20			0
C21			−7

[a] Angle between plane A and plane B, 113.3°. Angle between plane A and plane C, 62.3°.

The observation that only compounds **6a** and **6b** rearranged to Hugershoff bases (**3b** and **3c**) clearly demonstrates that more data are needed before predictions of the course of this reaction can be safely made. This was also substantiated in the case of oxidation of *N,N'*-diphenylthiourea where **3a** could be isolated and no formation of the corresponding Dost compound could be detected (but a substantial amount of *N,N',N''*-triphenylguanidine was formed in analogy with the findings for **6c**).

Experimental Section[32]

2,4-Dialkyl-3,5-bis(arylimino)-1,2,4-thiazolidines (6). To a mixture of the thiourea (0.05 mol) and concentrated hydrochloric acid (0.15 mol) in 50 ml of ethanol was added, dropwise and under stirring, a solution of sodium nitrite (0.10 mol) in water (25 ml). After 1 hr stirring at room temperature and subsequent removal of the precipitated sulfur by filtration, the reaction mixture was added dropwise to a solution of concentrated aqueous ammonia (0.15 mol) in water and ice (200 ml). The resulting precipitate was washed with water and recrystallized from ethanol. The product **6** was often initially precipitated as an oil together with a colorless crystalline substance, which was distinctly different from **6** (ir) but was converted to **6** on drying at room temperature. The nature of this substance was not further investigated.

The melting points (°C), the yields of crude product (%),[33] and the yields of analytically pure material (%) were: **6a**, 124–125, 68, 34; **6b**, 77–78, 60, 28; **6c**, 141–144, 18, 5; **6d**, 122–124, 71, 71. In the case of **6c**, *N,N'*-diphenyl-*N''*-cyclohexylguanidinium chloride[34] precipitated together with sulfur.

The analytical (%), NMR (δ parts per million from Me_4Si, integral, multiplicity), and spectroscopic data obtained were as follows.

6a. Anal. Calcd for $C_{16}H_{16}N_4S$: C, 64.85; H, 5.44; N, 18.91; S, 10.80. Found: C, 64.75; H, 5.48; N, 18.61; S, 10.93. NMR: 2.67 (3, s), 3.43 (3, s), 6.70–7.45 (10, m).

6b. Anal. Calcd for $C_{18}H_{20}N_4S$: C, 66.65; H, 6.22; N, 17.27. Found: C, 66.40; H, 6.23; N, 17.28. NMR: 0.88 (3, t); 1.33 (3, t); 2.88 (2 q); 3.98 (2, q); 6.58–7.30 (10, m).

6c. Anal. Calcd for $C_{26}H_{32}N_4S$: C, 72.22; H, 7.41; N, 12.96.

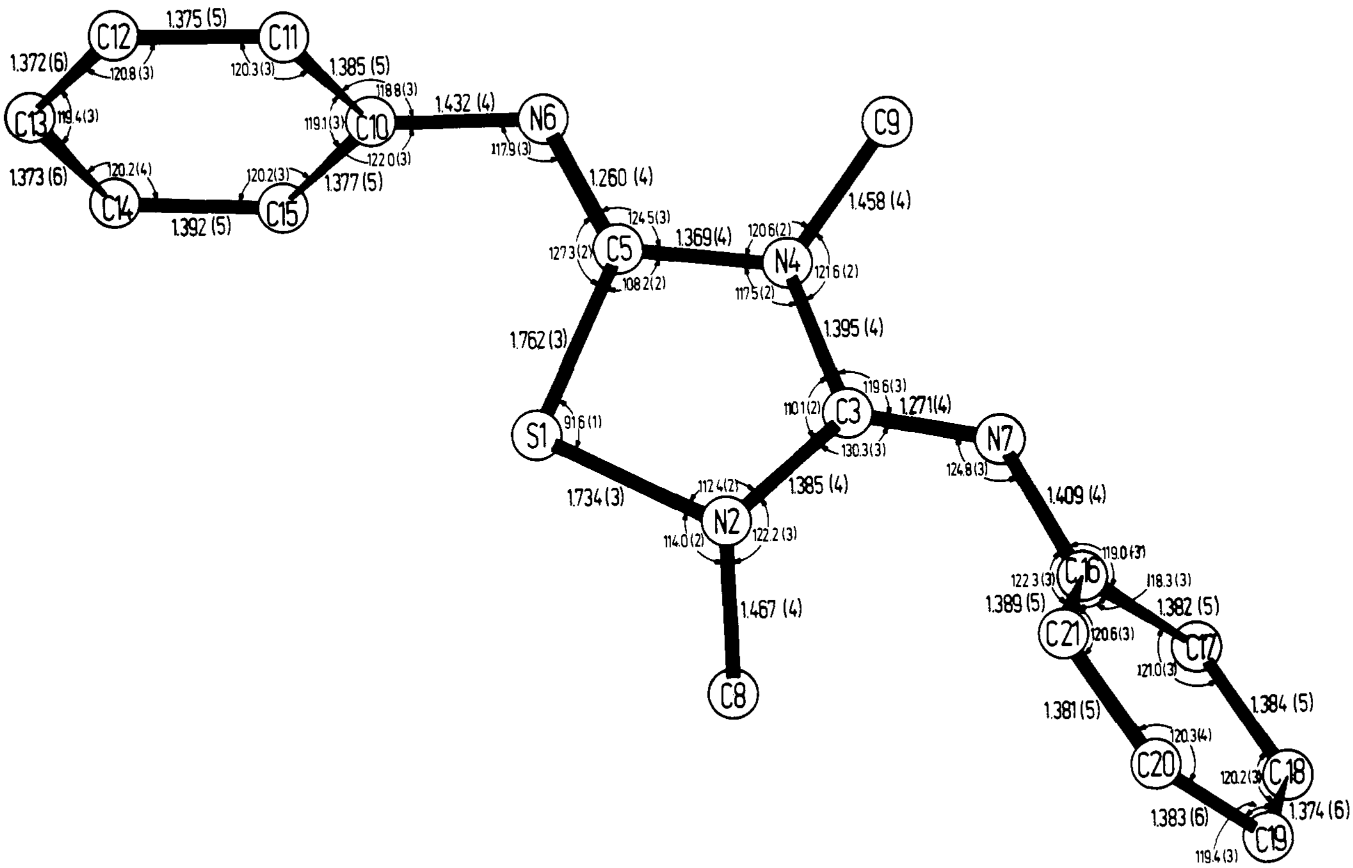


Figure 1. Bond lengths (Å) and bond angles (°) with estimated standard deviations (in parentheses) in the units of the least significant digit given for the corresponding parameter.

Found: C, 72.01; H, 7.63; N, 12.81. NMR 0.82-1.98 (20, m); 2.33-3.00 (1, m); 3.21-3.85 (1, m); 6.63-7.40 (10, m).

6d. Anal. Calcd for $C_{16}H_{14}Cl_2N_4S$: C, 52.62; H, 3.86; N, 15.34. Found: C, 52.58; H, 3.85; N, 15.72. NMR: 2.72 (3, s); 3.40 (3, s); 6.68-7.35 (8, m).

When 2-methyl-4-phenylthiosemicarbazide was treated as described above (only 3 mol of nitrous acid was used per mole of thiosemicarbazide), **6a** was isolated in a crude yield of 65% and a 31% yield of analytical pure product. Replacement of thiourea with 1,1-dimethyl-4-phenylthiosemicarbazide gave rise to **6e**, mp 157° dec, crude yield 51% and analytically pure yield 28%. Anal. Calcd for $C_{28}H_{22}N_6S$: C, 60.99; H, 6.21; N, 23.73. Found: C, 60.80; H, 6.45; N, 23.48. NMR: 2.22 (6, s); 2.52 (6, s); 6.57-7.40 (10, m).

Isomerization of 6a and 6b to 3b and 3c, Respectively. A mixture of **6a** or **6b** (0.01 mol) and hydrochloric acid (50 ml, 1 *M*) was refluxed for 45 min. On addition of base (NaOH, 1 *M*) at 0°, the mixture gave rise to crude **3b** (82%) or **3c** (91%). Recrystallization from ethanol afforded the analytically pure **3b** (50%, mp 118-119°) or **3c** (26%, mp 124-126°).

3b. Anal. Calcd for $C_{16}H_{15}N_4S$: C, 64.85; H, 5.44; N, 18.91. Found: C, 65.02; H, 5.48; N, 18.80. ^1H NMR: 2.78 (3, s); 3.35 (3, s); 6.75-7.72 (9, m); 4.93 (1, broad). ^{13}C NMR: 165.1; 150.8; 147.8; 132.0; 129.1; 125.9; 122.7; 122.5; 122.0; 120.7; 120.2; 37.5; 30.6. Ir: 3230 (s); 1630 (s); 1585 (s) cm^{-1}.

3c. Anal. Calcd for $C_{18}H_{19}N_3S$: C, 66.65; H, 6.22; N, 17.27. Found: C, 66.58; H, 6.42; N, 17.27. NMR: 1.17 (3, t); 1.33 (3, t); 3.21 (4, q); 3.88 (4, q); 4.98 (1, broad); 6.78-7.75 (10, m). Ir: 32.50 (m); 1642 (s); 1588 (s) cm^{-1}.

Hydrolyses of 6c and 6d to the Corresponding Ureas. When **6c** or **6d** was treated as described for **6a** and **6b**, it gave rise to *N*-phenyl-*N'*-cyclohexylurea [50%, mp 184-185° (lit.[35] 182°)] or *N*-(4-chlorophenyl)-*N'*-methylurea [40%, mp 203-204° (lit.[36] 200°)], respectively. Compound **6e** was hydrolyzed to unidentified products.

Attempted Isomerization of Dost's Base (2, Ar = C_6H_5). Refluxing of **2** (Ar = C_6H_5) in concentrated hydrochloric acid-dioxane (5 ml:15 ml) for 72 hr resulted in hydrolysis to phenylguanidine (identified by comparison with an authentic sample) with 46% unaltered starting material.

^{13}C NMR Spectra of 4c, 4d, 2-Methylaminobenzothiazoles, and *N,N'*-Dimethyl-*N''*-phenylguanidine. 4c: 157.1, 141.3, 122.5, 126.1, 120.4, 122.0, 108.2, 40.6, 29.7. **4d**: 162.2 141.2, 122.6, 126.1, 121.5, 121.4, 109.1, 29.2. 2-Methylaminobenzothiazole: 168.3, 152.0, 129.9, 125.5, 120.8, 120.2, 117.7, 31.4. For comparison, the spectra of *N,N'*-dimethyl-*N''*-phenylguanidine were also recorded: 152.9, 150.5, 129.3, 123.8, 121.4, 28.5.

Supplementary Material Available. A listing of observed and calculated structure factors will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JACS-75-5237.

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(33) The crude products were shown by ir spectroscopy not to contain more than 5% impurity.
(34) The free base was identified by elemental analysis (Anal. Calcd for $C_{19}H_{23}N_3$: C, 77.78; H, 7.90; N, 14.32. Found: C, 77.53; H, 8.08; N, 14.34): NMR 0.63–2.23 (10, m), 3.37–4.00 (1, brcad), 4.00–5.67 (broad, 10, m); ir ($CHCl_3$ solution in CaF_2 cells) 3360, 2910, 1635, 1590 cm^{-1}; MW from mass spectrometry M^+ 293; mp 140–141° (mp according to B. Anders, E. Kvehle, H. Freitag, and W. Redetzky, Belgian Patent, 637,357, 1964, 120–132°).
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Dehalogenations of 2,3-Dihalobutanes by Alkali Naphthalenes. A CIDNP and Stereochemical Study

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Abstract: In reactions with alkali naphthalenes, *meso-* and *dl*-2,3-dichloro- and dibromobutanes give *cis-* and *trans*-2-butenes in over 90% yields. With sodium naphthalene in DME, *meso-* and *dl*-2,3-dichlorobutanes give 76% *trans*-2-butene (24% cis). *meso*-2,3-Dibromobutane gives 66–79% *trans*-2-butene (34–21% cis), and *dl*-2,3-dibromobutane gives 39–67% *trans*-2-butene (61–33% cis). When the reactions are carried out in magnetic fields of 60 G, the 2-butenes exhibit CIDNP. These facts are not consistent with two-electron reductive elimination pathways. They are consistent with the following one-electron pathway: $RX_2\ (+NaC_{10}H_8) \rightarrow \cdot RX\ (+NaC_{10}H_8) \rightarrow [^-{:}RX] \rightarrow$ 2-butene. Intermediate 2-chloro-1-methylpropyl radicals probably suffer essentially complete rotameric relaxation, thereby losing their "memories" of the diastereomers from which they were formed. Rotameric relaxation in intermediate 2-bromo-1-methylpropyl radicals may be incomplete, since *meso-* and *dl*-2,3-dibromobutanes give rise to different 2-butene mixtures. Fragmentation of 2-bromo-1-methylpropyl radicals to bromine atoms and 2-butene may account for lower CIDNP intensities from reactions of 2,3-dibromobutanes than from 2,3-dichlorobutanes. Alternatively, or in addition, an initial one-electron transfer with multiple fragmentation may occur: $RX_2\ (+NaC_{10}H_8) \rightarrow$ 2-butene $+ X^- + X\cdot$. Neither of the latter two processes would give rise to CIDNP in the 2-butenes. The form of the observed CIDNP is different from that previously observed for reactions of sodium naphthalene with alkyl halides in low magnetic fields, but it appears that the accepted radical pair CIDNP model can accommodate this.

Sodium naphthalene reacts with vicinal dihalides to give olefins in yields better than 90% even in cases where many conventional reagents fail.[1] Since sodium naphthalene reacts with simple alkyl halides through an initial dissociative electron transfer (eq 1),[2] it seemed likely, a priori, that

$$RX + NaC_{10}H_8 \longrightarrow R\cdot + NaX + C_{10}H_8 \qquad (1)$$

intermediate alkyl radicals are involved in the dehalogenations of vicinal dihalides as well.

Two probes seemed directly and immediately applicable to this question, CIDNP[3] and stereochemistry. The applicability of CIDNP to reactions of sodium naphthalene has been demonstrated recently for reactions with alkyl halides[4] and proton sources.[5] In these cases, high-field CIDNP experiments fail, but polarization does result from appropriate reactions carried out in fields of the order of 100 G. The dehalogenations are a potentially interesting variant of the alkyl halide systems previously studied.

There has been an earlier report of the stereochemistry of dehalogenation by sodium naphthalene.[6] It was found that *erythro-* and *threo*-2,3-dibromo-3-methylpentanes react with sodium naphthalene in DME to give products of anti elimination to the extents of 76 and 92%, respectively.

We have studied reactions of the diastereomeric 2,3-dichloro- and 2,3-dibromobutanes with lithium, sodium, and cesium naphthalenes in DME at room temperature and at −78°.

Experimental Section

Alkali naphthalene solutions were prepared as previously described.[7] Concentrations were determined by quenching aliquots with water and titrating the resulting solutions with dilute hydrochloric acid.[8]

meso-2,3-Dibromobutane was prepared by the addition of bromine to *trans*-2-butene at 0° in carbon tetrachloride. It was purified by distillation on an annular Teflon spinning band column under reduced pressure; bp 55–56° (22 mm). *dl*-2,3-Dibromobutane was prepared similarly from *cis*-2-butene; bp 63° (28 mm). *meso*-2,3-Dichlorobutane and *dl*-2,3-dichlorobutane were similarly prepared from *trans-* and *cis*-2-butenes and chlorine in carbon