gel), only a small amount of 1-phenyl-3-benzoyltriazene (**2**) was obtained. After recrystallization from *n*-hexane, it melted at 83–84° dec (lit.[4] mp 84° dec). Its ir spectrum was identical with that of an authentic sample.

The ir spectrum of the insoluble solid (c) was identical with that of authentic benzaldehyde benzoylhydrazone (**4**); recrystallization of c from methanol gave **4**, mp 204–205° (lit. mp 204–205°). When c was considered pure, the yield of **4** was 4.5 mmol (9%).

Registry No.—**1**, 586-96-9; **2**, 29411-28-7; **3**, 613-94-5.

The Cyclization Reaction of Alkylthiomercaptoenethioamide with Carbonyl Compounds

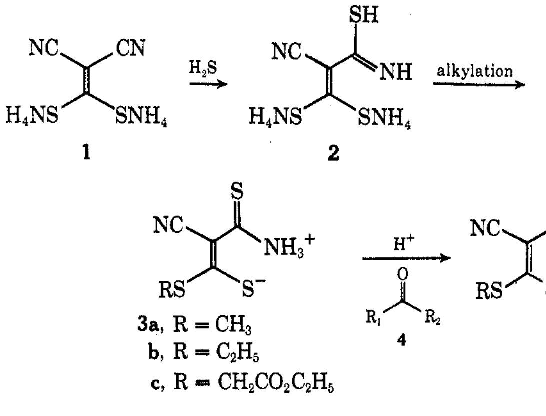
MASATAKA YOKOYAMA

Department of Chemistry, Faculty of Science, Chiba University, Yayoi-cho, Chiba, Japan

Received October 5, 1970

In the course of the investigation of the behavior of enedithiol compounds,[1,2] the reaction of the alkylthiomercaptoenethioamide compound has been studied.

It has been found that 2,2-disubstituted 5-cyano-6-alkylthio-2,3-dihydro-4*H*-1,3-thiazine-4-thione (**5**) type compounds could be isolated from the reaction of an alkylthiomercaptoenethioamide, such as 3-alkylthio-3-mercapto-2-cyanothioacrylamide (**3**), with a variety of carbonyl compounds in acidic medium. The derivatives of 4*H*-1,3-thiazine-4-thione have heretofore not been isolated, although there have been many reports on the preparation of 2*H*-1,3-thiazine-2-thione derivatives[3-6] and 6*H*-1,3-thiazine-6-thione derivatives.[7-10]



1 **2**

3a, R = CH_3
b, R = C_2H_5
c, R = $CH_2CO_2C_2H_5$

4 **5**

Compound **3** was obtained from bisammonium 2,2-dicyanoethenedithiol (**1**) with hydrogen sulfide followed by alkylation of the intermediate 3,3-bis(ammoniumthio)-2-cyanothioacrylamide (**2**). A zwitterion structure was assigned to compound **3a** on the basis of the nmr spectrum (a broad peak at δ 5.00 is characteristic for NH_3^+ group). Compound **5** was obtained in the form of yellow crystals from the reaction of compound **3** and a carbonyl compound **4** by refluxing in alcohol in the presence of sulfuric acid. The physical data of the new compounds are summarized in Table I.

The structure of 2,2-disubstituted 5-cyano-6-alkylthio-2,3-dihydro-4*H*-1,3-thiazine-4-thione was established on the basis of spectroscopic evidence together with elemental analyses (see Table II). Thus the ir spectrum revealed the presence of an amino (3120 cm^{-1}) and conjugated cyano (2210 cm^{-1}) group. The nmr spectrum showed the presence of an NH group (a broad peak at *ca.* δ 10.60). The presence of NH was also seen by its effect on the neighboring proton of the R_1 group, causing a split (J = *ca.* 1 Hz). The mass spectrum of **5** showed a characteristic fragment at the mass number of 126, which was considered to be a fragment of the ($M - SR - NHR_1R_2$) ion (see Table III). The uv spectrum of **5** showed several characteristic absorptions (see Table IV).

Compounds **5** synthesized by the present method were 5-cyano-6-methylthio-2,3-dihydro-4*H*-1,3-thiazine-4-thione-2-spirocyclohexane (**5a**), 2,2-dimethyl-5-cyano-6-methylthio-2,3-dihydro-4*H*-1,3-thiazine-4-thione (**5b**), 2-methyl-5-cyano-6-methylthio-2,3-dihydro-4*H*-1,3-thiazine-4-thione (**5c**), 2-phenyl-5-cyano-6-methylthio-2,3-dihydro-4*H*-1,3-thiazine-4-thione (**5d**), 2-furyl-5-cyano-6-methylthio-2,3-dihydro-4*H*-1,3-thiazine-4-thione (**5e**), 5-cyano-6-ethylthio-2,3-dihydro-4*H*-1,3-thiazine-4-thione-2-spirocyclopentane (**5f**), 2-ethyl-2-methyl-5-cyano-6-ethylthio-2,3-dihydro-4*H*-1,3-thiazine-4-thione (**5g**), 2-(3′,4′-methylenedioxyphenyl)-5-cyano-6-ethylthio-2,3-dihydro-4*H*-1,3-thiazine-4-thione (**5h**), and 2,2-dimethyl-5-cyano-6-ethoxycarbonylmethylthio-2,3-dihydro-4*H*-1,3-thiazine-4-thione (**5i**), respectively.

Experimental Section

3-Methylthio-3-mercapto-2-cyanothioacrylamide (**3a**).—Compound **2** was prepared by our method.[11] To the mixture of **2** (17 g, 0.08 mol), sodium hydroxide (6.4 g, 0.16 mol) in water (50 ml), and methanol (50 ml) was added dropwise dimethyl sulfate (7.3 ml, 0.08 mol) under cooling (ice water) and stirring. The reaction mixture was allowed to stand in an icebox for 3 hr. A small amount of solid product was filtered off. It was considered to be 3,3-dimethylthio-2-cyanothioacrylamide by comparison of its ir spectrum with that of the authentic specimen.[11] The yellow filtrate was mixed with 500 ml of water. To the above solution was added 30 ml of concentrated hydrochloric acid. The crude material was filtered, washed with diluted hydrochloric acid, dried in vacuum desiccator for 20 hr, and recrystallized from methanol as yellow needles: yield 15 g, 98%; mp 140–141°; ir (KBr) 3280 (s, NH_3^+), 2200 (vs, conjugated CN), 1593 cm^{-1} (vs, conjugated C═C); nmr (DMSO-d_6) δ 5.00 (br, 3, NH_3^+), 2.48 (s, 3, CH_3); uv $\lambda_{max}^{99\%\ EtOH}$ 246, 286, 341 mμ (log ε 3.60, 3.72, 4.13). *Anal.* Calcd for $C_5H_6N_2S_3$: C, 31.57; H, 3.15; N, 14.72; S, 50.56; mol wt, 190.23. Found: C, 31.68; H, 3.18; N, 14.66; S, 50.60; mol wt, 186 (vapor pressure osmometer, in acetone).

3-Ethylthio-3-mercapto-2-cyanothioacrylamide (**3b**).—The ethylation of **2** was worked up with diethyl sulfate as mentioned in preparation of **3a**. The resulting yellow material was recrystallized from methanol as yellow needles: yield 94%; mp 149–

---

[1] M. Yokoyama, *J. Org. Chem.*, **35**, 283 (1970).

[2] M. Yokoyama, *Bull. Chem. Soc. Jap.*, **43**, 2938 (1970).

[3] J. E. Jansen and R. A. Mathes, *J. Amer. Chem. Soc.*, **77**, 2866 (1955).

[4] M. Kahan, *Chem. Ber.*, **30**, 1318 (1897).

[5] T. L. Gresham, J. E. Jansen, and F. W. Shaver, *J. Amer. Chem. Soc.*, **70**, 1001 (1948).

[6] R. A. Mathes and F. D. Stewart, U. S. Patent 2,514,004 (1950).

[7] T. Takeshima, T. Hayashi, M. Muraoka, and T. Matsuoka, *J. Org. Chem.*, **32**, 980 (1967).

[8] T. Takeshima, T. Imamoto, M. Yokoyama, K. Yamamoto, and M. Akano, *ibid.*, **33**, 2877 (1968).

[9] T. Takeshima, M. Yokoyama, T. Imamoto, M. Akano, and H. Asaba, *ibid.*, **34**, 730 (1969).

[10] M. Muraoka, M. Yokoyama, K. Yamamoto, and T. Takeshima, *Bull. Chem. Soc. Jap.*, **43**, 2134 (1970).

[11] T. Takeshima, M. Yokoyama, N. Fukada, and M. Akano, *J. Org. Chem.*, **35**, 2438 (1970).

TABLE I

APPEARANCE, MELTING POINTS, AND YIELDS OF COMPOUNDS 5

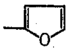
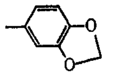
Compd	R	R_1	R_2	Appearance	Mp, °C (cor)	Yield, %
5a	CH_3	$(CH_2)_5$		Yellow plates	219–220 dec	86
5b	CH_3	CH_3	CH_3	Yellow plates	194–195	87
5c	CH_3	H	CH_3	Yellow prisms	174–175	91
5d	CH_3	H	C_6H_5	Yellow prisms	202–203	90
5e	CH_3	H		Yellow plates	184–185 dec	75
5f	C_2H_5	$(CH_2)_4$		Yellow plates	154–155	74
5g	C_2H_5	CH_3	C_2H_5	Yellow plates	161–162	58
5h	C_2H_5	H		Yellow prisms	201–202	89
5i	CH_2CO_2Et	CH_3	CH_3	Yellow prisms	185–186	54

TABLE II

ANALYSES OF COMPOUNDS 5

Compd	Formula	Calcd, %				Found, %			
		C	H	N	S	C	H	N	S
5a	$C_{11}H_{14}N_2S_3$	48.87	5.18	10.36	35.58	48.95	4.99	10.51	35.38
5b	$C_8H_{10}N_2S_3$	41.73	4.34	12.16	41.77	41.93	4.30	12.14	41.55
5c	$C_7H_8N_2S_3$	38.88	3.70	12.95	44.48	38.95	3.68	12.93	44.53
5d	$C_{12}H_{10}N_2S_3$	51.79	3.59	10.06	34.56	51.96	3.39	10.08	34.19
5e	$C_{10}H_8N_2S_3O$	44.73	2.98	10.44	35.85	44.85	3.01	10.64	35.88
5f	$C_{11}H_{14}N_2S_3$	48.87	5.18	10.36	35.58	48.69	5.16	10.50	35.63
5g	$C_{10}H_{14}N_2S_3$	46.47	5.42	10.85	37.25	46.58	5.63	10.93	37.13
5h	$C_{14}H_{12}N_2S_3O_2$	49.97	3.57	8.33	28.61	50.03	3.70	8.50	28.60
5i	$C_{11}H_{14}N_2S_3O_2$	43.68	4.66	9.25	31.80	43.56	4.58	9.40	31.53

TABLE III

MASS SPECTRA OF COMPOUNDS 5[a]

m/e (rel intensity, %)				
5a	**5b**	**5c**	**5d**	**5e**
270 (100, M^+)	230 (76, M^+)	216 (56, M^+)	278 (67, M^+)	268 (55, M^+)
255 (52, $-CH_3$)	215 (48, $-CH_3$)	201 (30, $-CH_3$)	263 (33, $-CH_3$)	253 (13 $-CH_3$)
237 (15, $-HS$)	197 (19, $-HS$)	187 (17)	245 (8, $-HS$)	235 (5, $-HS$)
223 (48, $-SCH_3$)	183 (43, $-SCH_3$)	183 (10, $-HS$)	231 (19, $-SCH_3$)	221 (42, $-SCH_3$)
190 (39, $-SCH_3 - HS$)	174 (19)	169 (21, $-SCH_3$)	199 (21)	189 (5)
174 (30)	126 (100)	140 (17)	172 (8)	138 (12)
126 (85)		126 (100)	126 (100)	126 (100)

[a] Mass spectra were measured with a Nihon Densi JMS-01 mass spectrometer. Ionizing energy was maintained at 75 eV and the total ionizing current of 200 μA.

TABLE IV

ULTRAVIOLET DATA OF COMPOUNDS 5[a]

Compd	$\lambda_{max}^{99\%\ EtOH}$, mμ (log ε)
5a	255 (3.58), 288 (3.69), 374 (4.11)
5b	263 (3.10), 287 (3.44), 373 (3.99)
5c	263 (3.39), 290 (3.62), 372 (4.21)
5d	263 (3.27), 298 (3.60), 380 (4.12)
5e	264 (3.53), 300 (3.62), 381 (4.12)
5f	255 (3.64), 291 (3.74), 372 (4.15)
5g	255 (3.50), 289 (3.61), 372 (4.05)
5h	264 (3.74), 295 (3.91), 382 (4.25)

[a] The absorbance measurements were made with a Hitachi EPS-3T type spectrophotometer.

150°; ir (KBr) 3280 (s, NH_3^+), 2200 (vs, conjugated CN), 1605 cm^{-1} (vs, conjugated C=C); nmr (DMSO-d_6) δ 4.30 (br, 3, NH_3^+, 3.10 (q, 2, CH_2, J = 6 Hz), 1.18 (t, 3, CH_3, J = 6 Hz); uv $\lambda_{max}^{99\%\ EtOH}$ 241, 287, 344 mμ (log ε 3.61, 3.39, 4.25) *Anal.* Calcd for $C_6H_8N_2S_3$: C, 35.28; H, 3.92; N, 13.71; S, 47.09; mol wt, 204.24. Found: C, 35.22; H, 3.89; N, 13.88; S, 46.98; mol wt, 218 (vapor pressure osmometer, in acetone).

3-Ethoxycarbonylmethylthio-3-mercapto-2-cyanothioacrylamide (3c).—The ethoxycarbonyl methylation was worked up with ethyl bromoacetate as mentioned in the preparation of **3a**. The crude material was recrystallized from acetic acid and washed with ethanol to give orange needles: yield 24%; mp 129–130°; ir (KBr) 3260 (s, NH_3^+), 2200 (s, conjugated CN), 1720 (vs, CO), 1605 cm^{-1} (vs, conjugated C=C). *Anal.* Calcd for $C_8H_{10}N_2S_3O_2$: C, 36.62; H, 3.84; N, 10.67; S, 36.66; mol wt, 262.34. Found: C, 36.36; H, 3.73; N, 10.69; S, 36.61; mol wt, 258 (vapor pressure osmometer, in acetone).

5-Cyano-6-methylthio-2,3-dihydro-4*H*-1,3-thiazine-4-thione-2-spirocyclohexane (5a).—A solution of **3a** (2.5 g, 0.013 mol), cyclohexanone (5 g, 0.05 mol), and a 2% aqueous solution of sulfuric acid (10 ml) in 30 ml of ethanol was refluxed for 5 min. The yellow material was collected and recrystallized from pyridine–water, yield 3 g.

Compounds **5b–i** were prepared in the same method as mentioned in the preparation of **5a**. The ir and nmr spectral data of compounds 5 were summarized in Tables V and VI.

TABLE V

INFRARED DATA (KBr) OF COMPOUNDS 5

Compd	Tentative assignment, frequency, cm^{-1}			
	ν_{NH}	$\nu_{conjd\ CN}$	$\nu_{conjd\ C=N}$	
5a	3120 (s)	2210 (s)	1520 (vs)	
5b	3120 (s)	2210 (s)	1520 (vs)	
5c	3120 (s)	2200 (s)	1530 (vs)	
5d	3180 (s)	2210 (s)	1520 (vs)	
5e	3120 (s)	2200 (s)	1520 (vs)	
5f	3180 (s)	2220 (s)	1520 (vs)	
5g	3120 (s)	2210 (s)	1530 (vs)	
5h	3120 (s)	2210 (s)		1605 (w, benzene)
5i	3130 (s)	2220 (s)	1520 (vs)	1720 (vs, CO)

TABLE VI

CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR COMPOUNDS 5[a]

Compd	δ values in DMSO-d_6
5a	10.42 (s, 1, NH), 2.68 (s, 3, SCH_3), 2.04 (br, 4, $C(2', 6')H_2$), 1.62 (br, 6, $C(3', 4', 5')H_2$)
5b	10.48 (s, 1, NH), 2.68 (s, 3, SCH_3), 1.70 (s, 6, $2CH_3$)
5c	10.47 (br, 1, NH), 5.10 (m, 1, CH), 2.68 (s, 3, SCH_3), 1.60 (d, 3, CH_3, $J = 5$ Hz)
5e	10.86 (br, 1, NH), 7.75 (s, 1, CH), 6.48 (s, 3, C_4H_3O), 2.66 (s, 3, SCH_3)
5f	10.68 (s, 1, NH), 3.18 (q, 2, CH_2CH_3, $J = 6$ Hz), 2.12 (br, 4, $C(3', 4')H_2$), 1.76 (br, 4, $C(2', 5')H_2$), 1.32 (t, 3, CH_2CH_3, $J = 6$ Hz)
5g	10.52 (s, 1, NH), 3.20 (q, 2, SCH_2CH_3, $J = 6$ Hz), 1.98 (q, 2, CH_2CH_3, $J = 6$ Hz), 1.62 (s, 3, CH_3), 1.32 (t, 3, SCH_2CH_3, $J = 6$ Hz), 0.92 (t, 3, CH_2CH_3, $J = 6$ Hz)
5h	10.83 (br, 1, NH), 6.96 (d, 3, C_6H_3), 6.22 (d, 1, CH, $J = 4$ Hz), 6.06 (s, 2, CH_2), 3.14 (q, 2, SCH_2CH_3, $J = 6$ Hz), 1.26 (t, 3, SCH_2CH_3, $J = 6$ Hz)
5i	10.70 (s, 1, NH), 4.20 (s, 2, CH_2), 4.10 (q, 2, CH_2CH_3, $J = 6$ Hz), 1.65 (s, 6, $2CH_3$), 1.20 (t, 3, CH_3CH_3, $J = 6$ Hz)

[a] Recorded on a JNM-C-60 high-resolution nmr spectometer operating at 60 MHz using tetramethylsilane as an internal standard.

Registry No.—**3a**, 29082-78-8; **3b**, 29082-79-9; **3c**, 29082-80-2; **5a**, 29082-81-3; **5b**, 29082-82-4; **5c**, 29082-83-5; **5d**, 29082-84-6; **5e**, 29082-85-7; **5f**, 29082-86-8; **5g**, 29082-87-9; **5h**, 39082-88-0; **5i**, 29082-89-1.

Acknowledgment.—The author wishes to express his thanks to Professor Dr. Tatsuo Takeshima and Dr. Hiroshi Midorikawa for their helpful discussion and encouragement throughout the course of this work.

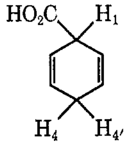
The Conformation of 1,4-Dihydro-1-naphthoic Acid from the Nuclear Magnetic Resonance Spectrum

J. L. MARSHALL* AND T. K. FOLSOM

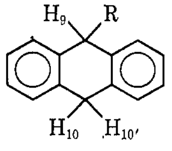
Department of Chemistry, North Texas State University, Denton, Texas 76203

Received August 31, 1970

We recently discussed the long-range splitting between the 1 and 4 protons in 1,4-dihydrobenzoic acid (**1**).[1] This extremely large value of $J_{1,4}$ (8–9 Hz)[2] is somewhat surprising when compared with the negligibly small $J_{9,10}$ values of 9,10-dihydroanthracenes.[3,4] To explain the difference between $J_{1,4}$ in **1** and $J_{9,10}$ in **2**, we considered two possibilities: (1) **1** is flat and **2** is not, and the angular dependence of $J_{1,4}$ is such that the 1 and 4 protons couple when the dihydrobenzene ring is flat, but do not couple when the ring is in the boat conformation;[5] (2) the spin–spin interaction between the 1 and 4 protons is conveyed by an olefin, but not by an aromatic, π system.[6] To decide which explanation is correct, it is necessary to know whether 1,4-dihydrobenzenes and 9,10-dihydroanthracenes are flat. It is known that dihydroanthracenes are not flat (by the nmr chemical nonequivalence of the two 10 protons),[3,4] but, unfortunately, it is not known whether the dihydrobenzene system is relatively flat.[7,8]

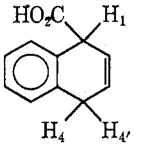


1



2

It was thought that a good test molecule to help resolve these difficulties would be 1,4-dihydro-1-naphthoic acid (**3**). This molecule possesses both an aromatic ring, whose ring currents would cause the two 4 protons to be chemically nonequivalent and would thus demonstrate the molecule to be nonplanar if it indeed were so, and also an olefin to transmit the spin–spin interaction if explanation 2 were operative. Therefore, **3** was synthesized by the Birch reduction[9] of 1-naphthoic acid and an nmr study of **3** was undertaken.



3

The 60-MHz nmr spectrum of **3** showed five regions of signals centered at δ 11.5, 7.3, 6.2, 4.6, and 3.6 that integrated in the respective ratio of 1, 4, 2, 1, and 2. Unlike the case of 1,4-dihydrobenzoic acid,[1] the spectral pattern of **3** was so complex that a complete 60-MHz analysis was impossible. Therefore, the 100-MHz spectrum was taken and studied. Decoupling experiments and use of the LAOCOON III nmr computer program[10] led to a set of parameters for the protons 1, 2, 3, 4, and 4′. These parameters are given in Table I.

---

(1) J. L. Marshall, K. C. Erickson, and T. K. Folsom, *J. Org. Chem.*, **35**, 2038 (1970).

(2) For other examples of large homoallylic couplings in 1,4-dihydrobenzenes, see E. W. Garbisch, Jr., and M. G. Griffith, *J. Amer. Chem. Soc.*, **90**, 3590 (1968); D. J. Atkinson and M. J. Perkins, *Tetrahedron Lett.*, 2335 (1969); L. J. Durham, J. Studebaker, and M. J. Perkins, *Chem. Commun.*, 456 (1965).

(3) D. Nicholls and M. Szwarc, *J. Amer. Chem. Soc.*, **88**, 5757 (1966); R. G. Harvey, L. Arzadon, J. Grant, and K. Urberg, *ibid.*, **91**, 4535 (1969).

(4) A. W. Brinkman, M. Gordon, R. G. Harvey, P. W. Rabideau, J. B. Stothers, and A. L. Ternay, Jr., *ibid.*, **92**, 5912 (1970).

(5) Theory predicts that the size of the homoallylic coupling constant varies as $\cos^2\phi\cdot\cos^2\phi'$ with the two angles ϕ and ϕ' each being the dihedral angle between each C–H bond and the intervening p orbitals of the π system: M. Karplus, *J. Chem. Phys.*, **33**, 1842 (1960); M. Barfield, *ibid.*, **48**, 4463 (1968).

(6) There is a theoretical basis for this explanation. If one assumes that the proton–proton coupling is dominated by a (nuclear-spin)–(electron-spin)–(electron-spin)–(nuclear-spin) coupling mechanism, then coupling *via* olefin bonds can be calculated to rather large and *via* aromatic bonds to be rather small: H. M. McConnell, *ibid.*, **30**, 126 (1959).

(7) See ref 2. See also B. A. Shoulders, R. M. Gipson, R. J. Jandacek, S. H. Simonsen, and W. Shive, *J. Amer. Chem. Soc.*, **90**, 2992 (1968); F. H. Herbstein, *J. Chem. Soc.*, 2292 (1959).

(8) The conformation of 1,4-dihydrobenzene itself is known to be very slightly puckered: H. Oberhammer and S. H. Bauer, *J. Amer. Chem. Soc.*, **91**, 10 (1969).

(9) M. E. Kuehne and B. F. Lambert, *Org. Syn.*, **43**, 22 (1963). For the synthesis of **3**, see the Experimental Section.

(10) A. A. Bothner-By and S. M. Castellano, "Computer Programs for Chemistry," Vol. 1, D. F. DeTar, Ed., W. A. Benjamin, New York, N. Y., 1968, p 10.