Table II. Constants of Various Refined Oils

Oil	Acid value	Sapon. value	Iodine value	Peroxide value	Hydroxylamine value	Viscosity* (c. p. s.)
Linseed	0.5	192	185	28.1	0.	72
Soybean	0.06	193	126	33.1	0.9	62
Oilve	1.7	190	84.5	20.6	0.8	68
Peanut	0.8	191	96.4	56.8	7.0	63

* At 25° with capillary viscometer.

These points must be examined further by a larger number of measurements. It must be noted, however, that the deterioration of base oils with rancidification brings about various undesirable effects on the rheological behavior of these oil preparations, as observed in the rancid peanut oil–Al–St system.

The authors wish to express their thanks to Dr. T. Saito, Chief Investigater of Miike Dye Works Research Laboratory (Mitsui Chem. Co.), and to Mr. S. Igata, member of the same Laboratory, for supplying polyvinyl chloride films and determining their ultraviolet transmittance.

Summary

In the colloidal system of aluminum stearate–peanut oil, deterioration of oil by rancidification brought about undesirable effects, causing the flow rate to increase and rigidity to lower in the region of small shearing stress.

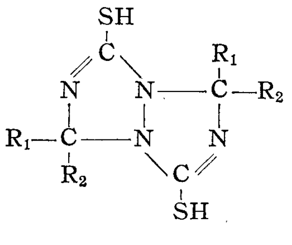
(Received October 5, 1957)

UDC 547.792.9.07

14. Kiyoshi Futaki and Senji Tosa: Syntheses of *s*–Triazolidino–[1,2–*a*]–*s*–triazolidine–3,7–dithione Derivatives.

(*Research Section, Kyoto Factory, Mitsubishi Paper Mills Ltd.**)

Bailey and McPherson[1] reported the synthesis of 3,5′–dimercapto–5,3′–diphenyl dihydrotriazolotriazole by the reaction of benzalazine with sodium thiocyanate in glacial acetic acid. Later, Sunner[2] studied reactions between hydrazine thiocyanate and aldehydes, and he assumed the chemical structure of the product of this reaction as *s*–triazolino[1,2–*a*]–*s*–triazolines.



In 1953, Miyatake[3] studied the reaction between several azines and sodium thiocyanate according to the procedure of Bailey and McPherson[1] and obtained several compounds which he also assumed as *s*–triazolino[1,2–*a*]–*s*–triazolines.

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* Nagaoka-cho, Otokuni-gun, Kyoto-fu (二木　清，土佐宣治).

[1] J.R. Bailey, A.T. McPherson: J. Am. Chem. Soc., **39**, 1322(1917).

[2] S. Sunner: Svensk Kem. Tidskr., **64**, 121(1952).

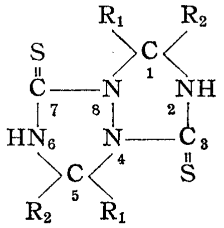
[3] K. Miyatake: Yakugaku Zasshi, **73**, 460(1953).

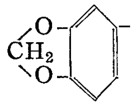
In spite of researches by many chemists the chemical structure of these compounds had only been presumed and lacked sufficient evidences on which it should be based. The authors also studied the reaction between sodium thiocyanate and several other aldazines or ketazines to obtain a series of compounds which have not been reported.

Starting with azines, such as acetaldazine, hexanaldazine, *m*-nitrobenzaldazine, piperonaldazine, and ethyl acetoacetate ketazine, homologs of the assumed *s*-triazolidino[1,2-*a*]-*s*-triazolidines were easily obtained, but when cinnamaldazine, salicylaldazine, and anisaldazine were used as the starting materials, anticipated products were not obtained. The product obtained from anisaldazine was so labile that it decomposed partially during recrystallization or even in a dessicator under a reduced pressure and its analytical data showed deviation from the expected or calculated ones.

It was further found that homologs of *s*-triazolidino[1,2-*a*]-*s*-triazolidines were directly prepared when aliphatic aldehydes (such as acetaldehyde, propionaldehyde, butyraldehyde, caproic aldehyde, caprylic aldehyde, lauryl aldehyde) were added dropwise into a mixture of aqueous solution of hydrazine dihydrochloride and sodium thiocyanate. The melting points and analytical data of these compounds which were prepared by the authors are listed in Table I.

TABLE I. *s*-Triazolidino[1,2-*a*]-*s*-triazolidine-3,7-dithiones



No.	R_1	R_2	m.p.(°C)	Formula	Analyses (%) Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
(III)	CH_3	H	178(decomp.)	$C_6H_{10}N_4S_2$	35.64	4.99	27.72	35.83	4.91	—
(IV)	C_2H_5	H	176.5~177.5	$C_8H_{14}N_4S_2$	41.73	6.13	24.34	41.90	6.15	—
(V)	C_3H_7	H	165~166	$C_{10}H_{18}N_4S_2$	46.50	7.00	21.7	46.76	7.00	—
(VI)	C_5H_{11}	H	168	$C_{14}H_{26}N_4S_2$	53.48	8.34	17.82	53.83	8.25	17.38
(VII)	C_7H_{15}	H	168.5~169.5	$C_{18}H_{34}N_4S_2$	58.35	9.25	15.12	58.49	9.27	15.06
(VIII)	$C_{11}H_{23}$	H	153.5~154	$C_{26}H_{50}N_4S_2$	64.69	10.44	11.61	64.79	10.20	—
(IX)	CH_3	$CH_2CO_2C_2H_5$	132~133 (decomp.)	$C_{14}H_{22}O_4N_4S_2$	44.90	5.91	14.90	44.90	5.95	—
(X)	*m*-NO_2-C_6H_4	H	187~188	$C_{16}H_{12}O_4N_6S_2$	46.16	2.91	20.19	45.80	2.96	—
(XI)		H	185~186 (decomp.)	$C_{18}H_{14}O_4N_4S_2$	52.18	3.41	13.52	51.94	3.23	—

In order to determine the chemical structure of these homologs, four possible structures which might be obtained by possible reaction mechanism illustrated in Chart 1 were formulated.

Coinciding with Bailey and McPherson's report, the compound (I), m.p. 186~187°, was obtained when a mixture of benzalazine and sodium thiocyanate was allowed to stand at room temperature. This compound, $C_{16}H_{14}N_4S_2$, was soluble in diluted solution of sodium hydroxide, showed positive reaction with iodo-azide reagent and blue-green color by Grote's reagent.[4] When it was refluxed in dilute ethanol, benzaldehyde thiosemicarbazone was obtained. In addition, it was easily oxidized by hydrogen

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[4] Merck Index 5th ed.

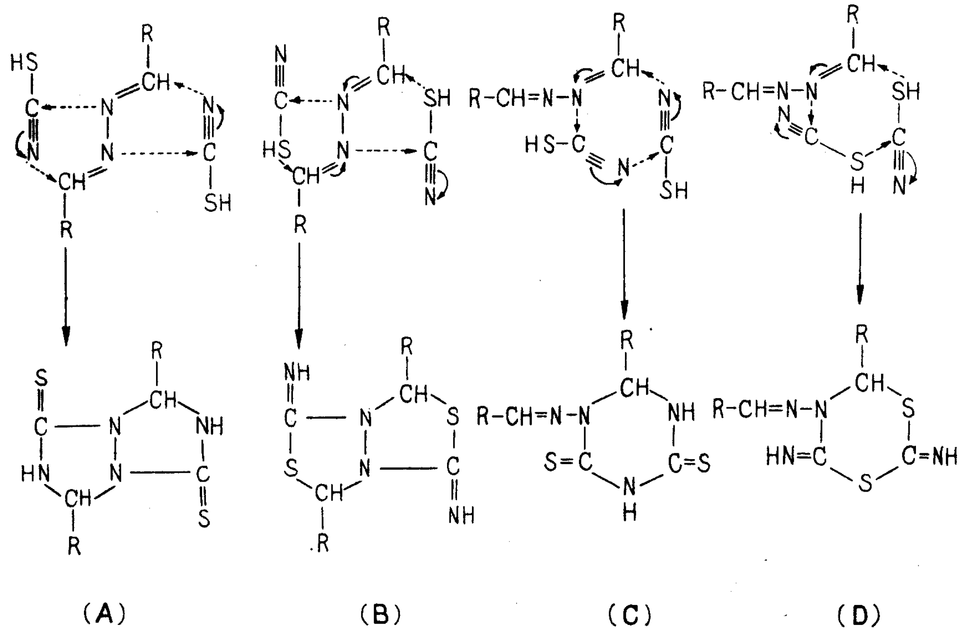

Chart 1.

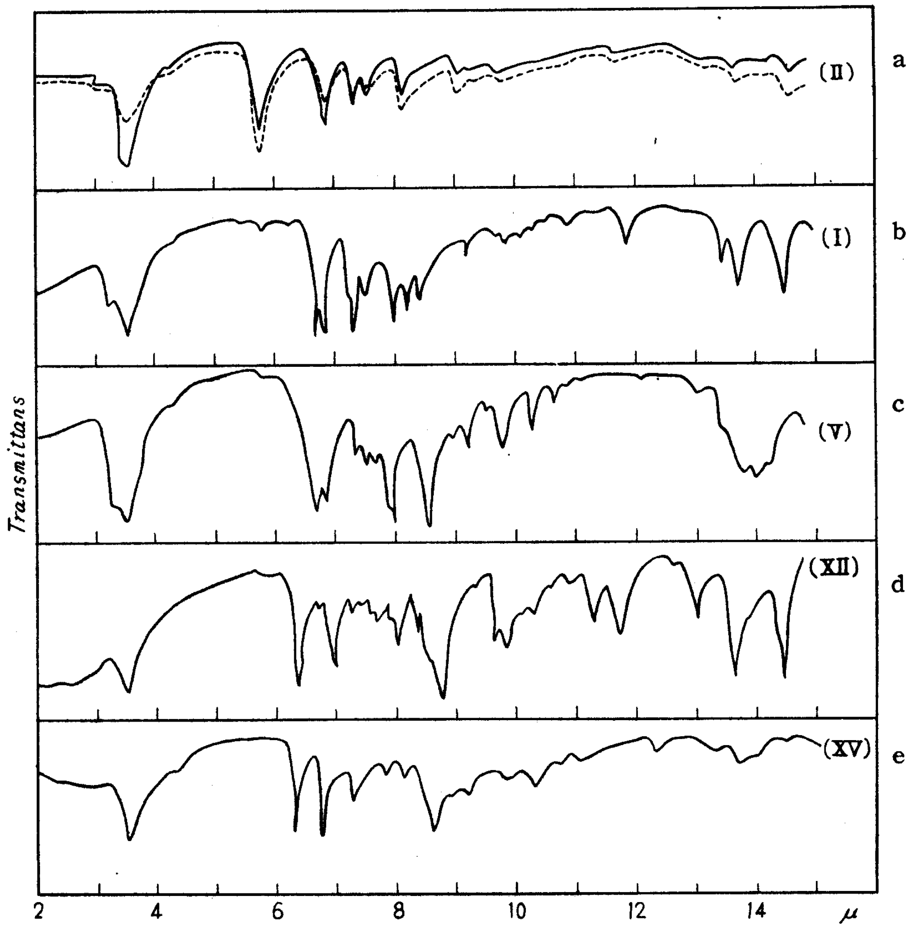

Fig. 1. Infrared Absorption Spectra of Compounds (II), (I), (V), (XII), and (XV) (in Nujol)

peroxide in diluted potassium hydroxide solution (Kitamura's reaction),[5] giving a compound (II), $C_{16}H_{14}O_2N_4$, which melted at 205.5°. Although this melting point was lower by 5° than that (210.5°C) of the compound which was directly prepared from benzalazine and potassium cyanate in acetic acid by Bailey and Moore's procedure,[6] the melting point on admixture of these two compounds showed no depression. In addition, infrared absorption spectroscopic data showed that the wave length of all absorption peaks of these two compounds agreed (Fig. 1-a). Therefore, these two are believed to be identical substance.

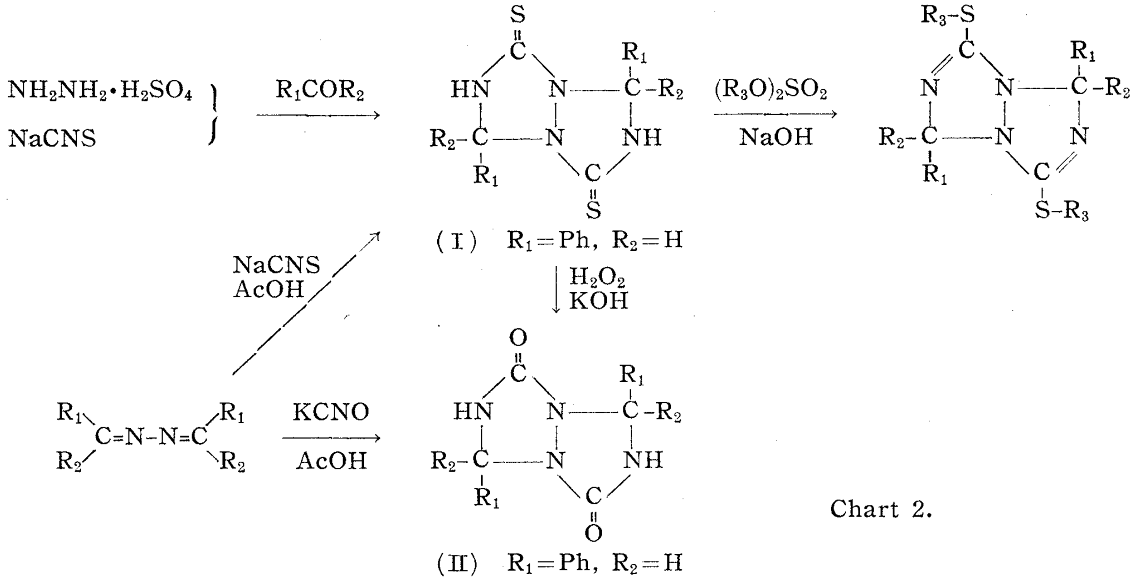

Chart 2.

These evidences indicated that the structure (B) and (D) are to be rejected. The infrared spectra of three compounds, obtained as mull, are shown in Fig. 1 a, b, and c. Compound (I) showed a strong absorption at 1500 cm^{-1} (-N-C=S) and compound (II) at 1740 cm^{-1} which indicated a lactam linkage of a five-membered ring.

The ultraviolet absorption spectrum of compound (I) showed absorption maximum at 265 mμ which was strongly deviated from that of benzaldehyde thiosemicarbazone (Fig. 2). If compound (I) had structure (C), it would be anticipated that its ultraviolet absorption spectrum would not deviate markedly from that of benzaldehyde thiosemicarbazone.

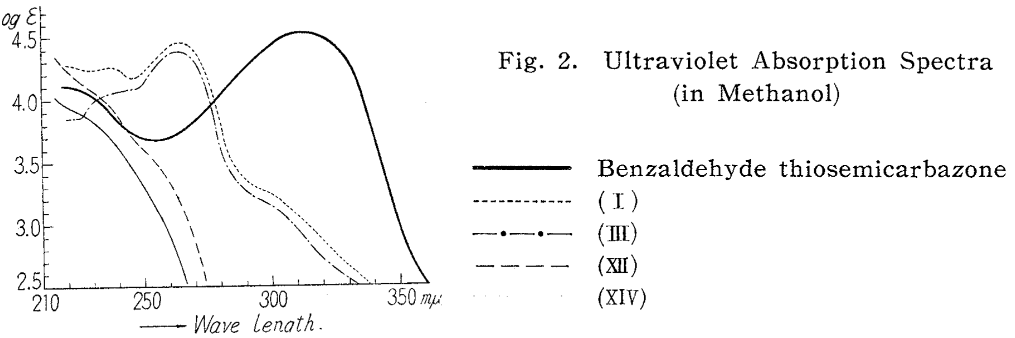

Fig. 2. Ultraviolet Absorption Spectra (in Methanol)

Considering from these spectral findings, structure (A) should be assigned to compound (I) as the most possible one; in other words, the structure of (I) would be 1,5-diphenyl-*s*-triazolidino[1,2-*a*]-*s*-triazolidine-3,7-dithione.

1,5-Diphenyl-, 1,5-dimethyl-, and 1,5-dipropyl-*s*-triazolidino[1,2-*a*]-*s*-triazolidine-

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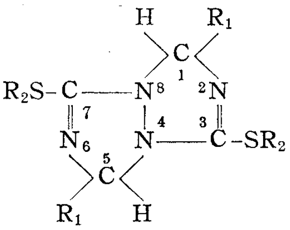
5) R. Kitamura: Yakugaku Zasshi, **58**, 676, 816(1938).

6) J. R. Bailey, N. H. Moore: J. Am. Chem. Soc., **39**, 279(1917).

3,7-dithione easily reacted with dialkyl sulfate in diluted sodium hydroxide solution to afford dialkyl-substituted compounds. The ultraviolet absorption spectra of these products showed that absorption maxima had shifted to a shorter wave length than that of the starting materials (Fig. 2). The infrared spectra of these compounds are shown in Fig. 1 d and e, where absorption band of 1500 cm^{-1} in the starting materials had disappeared and a new absorption band appeared at 1577 cm^{-1}, which would result from an azomethine linkage. It is concluded on these bases that products of alkylation reaction were S-alkylated compounds rather than N-alkylated ones. The physical and analytical data of these compounds are shown in Table II.

TABLE II. 3,7-Bis(alkylthio)-*s*-triazolino[1,2-*a*]-*s*-triazolines



No.	R_1	R_2	m.p. (°C)	Formula	Analyses (%)					
					Calcd.			Found		
					C	H	N	C	H	N
(XII)	C_6H_5	CH_3	117.5~118	$C_{16}H_{18}N_4S_2$	61.01	5.12	15.81	60.84	5.20	—
(XIII)	C_6H_5	C_2H_5	102~103	$C_{20}H_{22}N_4S_2$	62.81	5.80	14.65	62.62	5.69	—
(XIV)	CH_3	CH_3	88~89	$C_8H_{14}N_4S_2$	41.73	6.13	24.34	41.70	6.10	—
(XV)	C_3H_7	CH_3	51~52	$C_{12}H_{22}N_4S_2$	50.33	7.74	19.57	50.31	7.64	19.26

The authors are indebted to Prof. S. Uyeo of the University of Osaka for his kind guidance, to Dr. Y. Kashida of the University of Tokyo for valuable advices, to Dr. Y. Ohyama, the chief of the Research Section of their Factory, and to Mr. S. Takagi of the University of Osaka, for giving them many facilities. Thanks are also due to Mr. M. Fukuda of the University of Osaka for microanalytical data.

Experimental

1,5-Dimethyl-*s*-triazolidino[1,2-*a*]-*s*-triazolidine-3,7-dithione (III)—(i) A solution of 3.5 g. of NaSCN in 20 cc. of glacial AcOH was added dropwise into stirred solution of 1 g. of acetaldazine in 10 cc. of AcOH which was cooled in an ice bath. After all of the NaSCN solution was added, stirring was continued further for 1 hr. in an ice bath and then for 1 hr. at room temperature. Precipitated crystals were collected and recrystallized from EtOH. Yield, 0.8 g., m.p. 178°(decomp.) (cf. Table I).

(ii) 165 g. of 43.7% aq. solution of acetaldehyde was added dropwise into a vigorously stirred mixture of 78 g. of $NH_2{\cdot}NH_2{\cdot}2HCl$ and 122 g. of NaSCN in 120 cc. of water during which time the reaction temperature was kept at 5~10°. After all of the solution of acetaldehyde was added, stirring was further continued for 1 hr. at 5~10° and then 3 hrs. at 20°. The reaction mixture was allowed to stand over night and precipitated crystals were collected, washed with water, and recrystallized from EtOH. Yield, 86.3 g. of white crystals, m.p. 178°(decomp.), undepressed on admixture with the sample obtained by the method (i) (cf. Table I).

1,5-Diethyl-*s*-triazolidino[1,2-*a*)-*s*-triazolidine-3,7-dithione (IV)—12.2 g. of propionaldehyde was added dropwise into a stirred mixture of 10.4 g. of $NH_2{\cdot}NH_2{\cdot}2HCl$ and 16.2 g. of NaSCN in 30 cc. of water at 5~10°. After all of the aldehyde was added, stirring was further continued for 2 hrs. The reaction mixture was allowed to stand over night and precipitated crystals were collected and recrystallized from MeOH. Yield, 11 g., m.p. 176.5~177.5°(cf. Table I).

1,5-Dipropyl-*s*-triazolidino[1,2-*a*]-*s*-triazolidine-3,7-dithione (V)—30.2 g. of butyraldehyde diluted with 30 cc. of MeOH was added dropwise at 5~10° into a stirred mixture of 20.8 g. of $NH_2{\cdot}NH_2{\cdot}2HCl$ and 32.4 g. of NaSCN in 40 cc. of water. After all of the aldehyde was added, stirring was further continued for 1 hr. at 5~10° and then for 4 hrs. at room temperature. The reaction mixture was allowed to stand over night and precipitated crystals were collected, washed with water, and recrystallized twice from MeOH. Yield, 17.8 g. of m.p. 165~166°(cf. Table I).

1,5-Diamyl-*s*-triazolidino[1,2-*a*]-*s*-triazolidine-3,7-dithione (VI)—(i) A solution of 2 g. of hexanal in 10 cc. of MeOH was added at 4~6° into a mixture of 1.6 g. of NaSCN and 1 g. of $NH_2{\cdot}NH_2{\cdot}HCl$ in 20 cc. of 50% (v/v) MeOH. The reaction mixture was then stirred for 30 mins. at the same temperature and further for 2 hrs. at room temperature. The precipitate was collected and washed with MeOH and water. Yield, 3.2 g. Recrystallized from MeOH, it melted at 168°(cf. Table I).

(ii) 1.8 g. of NaSCN in 10 cc. of AcOH was added into a hot solution of 1 g. of hexanaldazine in 5% AcOH and heated for 1.5 hrs. on a water bath. After cool the precipitate was collected. The melting point of these crystals was not depressed on admixture with the sample obtained by the above method (i).

1,5-Diheptyl-*s*-triazolidino[1,2-*a*]-*s*-triazolidine-3,7-dithione (VII)—A solution of 1.00 g. of octanal in 5 cc. of MeOH was added dropwise at 4° into stirred mixture of 0.34 g. $NH_2 \cdot NH_2 \cdot 2HCl$ and 0.60 g. NaSCN in 15 cc. of 50% MeOH. The reaction mixture was kept at the same temperature for 1 hr. and shaken for 2 hrs. at room temperature. The precipitate was then collected, washed with 50% MeOH, dissolved in 2*N* KOH, washed with ether, and acidified with 2*N* HCl. Precipitate was collected and recrystallized from MeOH. Yield, 0.18 g. of m.p. 168.5~169.5°(cf. Table I).

1,5-Diundecyl-*s*-triazolidino[1,2-*a*]-*s*-triazolidine-3,7-dithione (VIII)—A solution of 4.03 g. of laurylaldehyde in 10 cc. of MeOH was added dropwise into a mixture of 1.09 g. of $NH_2 \cdot NH_2 \cdot 2HCl$, 1.70 g. of NaSCN, and 30 cc. of 50% MeOH. The reaction mixture was stirred for 4 hrs., the precipitate was collected, and recrystallized twice from MeOH. Yield, 0.85 g. of m.p. 153~154.5°(cf. Table I).

1,5-Bis(ethoxycarbonylmethyl)-1,5-dimethyl-*s*-triazolidino[1,2-*a*]-*s*-triazolidine-3,7-dithione (IX)—A mixture of 5.8 g. of ethyl acetoacetate ketazine[7] and 6.8 g. of NaSCN in 20 cc. of glacial AcOH was allowed to stand at room tempereture for 3 days. Precipitated crystals were collected, washed with water, and recrystallized from MeOH. Yield, 3.0 g. of m.p. 132.5~133.5°(decomp.)(cf. Table I).

1,5-Bis(*m*-nitrophenyl)-*s*-triazolidino[1,2-*a*]-*s*-triazolidine-3,7-dithione (X)—A mixture of 3.0 g. of *m*-nitrobenzaldazine and 3 g. NaSCN in 100 cc. of glacial AcOH was allowed to stand at room temperature for 8 days, precipitated crystals were collected, and dissolved in *N* NaOH. The filtrate of this solution was acidified with AcOH and the precipitated crystals were collected, washed with water, and recrystallized from acetone. Yield, 2.6 g. of m.p. 187~188°(decomp.) (cf. Table I).

1,5-Bis(3′,4′-methylenedioxyphenyl)-*s*-triazolidino[1,2-*a*]-*s*-triazolidine-3,7-dithione (XI)—A mixture of 1.48 g. of piperonaldazine and 1.5 g. of NaSCN in 50 cc. of glacial AcOH was allowed to stand at room temperature over night. Precipitated crystals were collected, washed with water, and recrystallized from MeOH. Yield, 3 g. of m.p. 132.5~133.5°(cf. Table I).

Reaction of 1,5-Diphenyl-*s*-triazolidino[1,2-*a*)-*s*-triazolidine-3,7-dithione (I) with Hydrogen Peroxide (Kitamura's Reaction)—16 cc. of 30% H_2O_2 was added dropwise into a vigorously stirred solution of 1.6 g. of (I) in 10 cc. of 2*N* NaOH. The reaction soon occurred with evolution of heat and temperature of the solution reached 40°, after which the reaction temperature was kept at 40~45°. After H_2O_2 addition was completed, the reaction mixture was further stirred for 15 mins. at the same temperature and then cooled. Precipitated crystals were collected, washed with water, and dissolved in *N* NaOH. The filtrate of this solution was acidified with AcOH, the precipitate was collected, washed with water, and recrystallized from MeOH. Yield, 0.2 g. of m.p. 205.5°(decomp.). Mixed m.p. with the sample of m.p. 210.5°(decomp.), prepared according to Bailey and Moore's method,[6] was 206.5°. *Anal.* Calcd. for $C_{16}H_{14}O_2N_4$: C, 65.29; H, 4.80. Found : C, 65.39; H, 4.76.

3,7-Bismethylthio-1,5-diphenyl-*s*-triazolino[1,2-*a*]-*s*-triazoline (XII)—3.32 g. of Me_2SO_4 was added dropwise at 5~10° into a stirred solution of 4.07 g. of (I) in 10 cc. of 10% NaOH. After all Me_2SO_4 was added, stirring was further continued for 30 mins. at the same temperature and then for 4 hrs. at room temperature. Precipitated crystals were collected, washed with *N* NaOH and water, and recrystallized from MeOH. Yield, 3.9 g. of m.p. 109.5°(corr.). Further recrystallization from ether yielded colorless hexagonal crystals of m.p. 117.7~118°(corr.) (cf. Table II).

3,7-Bisethylthio-1,5-diphenyl-*s*-triazolino[1,2-*a*]-*s*-triazoline (XIII)—3.4 g. of Et_2SO_4 was added dropwise at 5~10° into a stirred solution of 3.26 g. of (I) in 24 cc. of 10% NaOH. After all Et_2SO_4 was added, stirring was further continued for 30 mins. at the same temperature and then for 6 hrs. at room temperature. Precipitated crystals were collected and recrystallized from MeOH. Yield, 2.8 g. of m.p. 102~103°(corr.) (cf. Table II).

3,7-Bismethylthio-1,5-dimethyl-*s*-triazolino[1,2-*a*]-*s*-triazoline (XIV)—2.65 g. of Me_2SO_4 was added dropwise at 5~10° into a stirred solution of 2.0 g. of (III) in 16 cc. of 10% NaOH. After all Me_2SO_4 was added, stirring was further continued for 30 mins. at the same temperature and then for 4 hrs. at room temperature. Precipitated crystals were collected and recrystallized from MeOH. Yield, 1.4 g. of m.p. 88~89°(cf. Table II).

3,7-Bismethylthio-1,5-dipropyl-*s*-triazolino[1,2-*a*]-*s*-triazoline (XV)—2.65 g. of Me_2SO_4 was added dropwise at 5~10° into a stirred solution of 2.58 g. of (V) in 16 cc. of 10% NaOH. After all Me_2SO_4 was added, stirring was further continued for 30 mins. at the same temperature and then for 4 hrs. at room temperature. Precipitated crystals were collected and recrystallized from MeOH and then from ether, to crystals of m.p. 51~52°(cf. Table II).

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7) L. Wolff : Ber., **37**, 2830(1904).

Summary

Several kinds of 1,5-substituted *s*-triazolidino[1,2-*a*]-*s*-triazolidine-3,7-dithiones and 1,5-substituted 3,7-bisalkylthio-*s*-triazolino[1,2-*a*]-*s*-triazolines (see Tables I and II) were synthesized and their chemical structure was determined from their chemical and spectroscopic properties.

(Received October 7, 1957)

UDC 545.723.1 : 547.233.2

15. **Makoto Yokoo**: Application of Azotometry. XVI.* Quantitative Determination of Secondary Amines.

(*Research Laboratories, Takeda Pharmaceutical Industries, Ltd.***)

There are found many reports on the qualitative determination of secondary amines, but methods for their quantitative determination are very few, such as the polarographic[1] or colorimetric[2] method.

Since Alekseev[3] previously announced that secondary amines can be converted into hydrazine derivatives via nitrosamines and since hydrazines can be readily determined by Iwasaki's azotometry[4] the author attempted utilization of this reaotion for the quantitative determination of secondary amines and succeeded in establishing a new method. The method was carried out after the following scheme.

$$>NH + HNO_2 \longrightarrow >N\cdot NO \xrightarrow{Zn + HCl} >N\cdot NH_2 \xrightarrow[AZM]{K_3Fe(CN)_6} N_2\uparrow$$

Amines determined by this method were various kinds of secondary amines such as dimethylamine, diethylamine, dibenzylamine, diphenylamine, proline, and kainic acid. Of these amines, dimethylamine, diethylamine, and dibenzylamine were used as their hydrochlorides and the others as such after purification by recrystallization.

It was also found that coexistence of a primary and a tertiary amine dose not affect the value.

Method

1) **Reagents:**
   - i) Potassium nitrite solution: ca. 600 mg./cc.
   - ii) Sulfaminic acid solution: 200 mg./cc.
   - iii) Zinc powder
   - iv) Devarda's alloy: Al 45%, Cu 50%, Zn 5%.
   - v) Potassium ferricyanide solution: $K_3Fe(CN)_6$ 5 g, $NaNO_2$ 70 g, H_2O 100 cc.

2) **Procedure:**

About 0.2 or 0.1 m.mole of a sample is weighed exactly and dissolved in a flask or

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* This report constitutes part of a series entitled "Application of Azotometry" by Masaharu Yamagishi.

** Juso-Nishino-cho, Higashiyodogawa-ku, Osaka (横尾 亮).

[1] A. A. Smales: J. Soc. Chem. Ind. (London), **67**, 210(1948).

[2] S. J. Clark: Mikrochim. Acta, **1956**, 967.

[3] N. F. Alekseev: C. A., **50**, 4722(1956).

[4] K. Iwasaki: Seikagaku, **23**, 207(1951).