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Degradation of 2,4,6-Trialkyltetrahydro-1,3,5-thiadiazines during Storage

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Degradation of 2,4,6-trialkyltetrahydro-1,3,5-thiadiazines (alkyl = methyl, III; alkyl = ethyl, IV) during storage was investigated. Both thiadiazines synthesized from aldehydes, ammonia, and hydrogen sulfide decomposed largely to 2,4,6-trialkyldihydro-1,3,5-dithiazines (alkyl = methyl, I; alkyl = ethyl, II) and *N,N'*-dialkylidene-1,1-diaminoalkanes (alkyl = ethyl, VII; alkyl = propyl, VIII) during storage. Some other compounds which simultaneously occurred were identified as *N*-ethylidene-1-aminoethene (X), *N*-ethylidene-1,1'-diaminoethane (XI), and *N*-propylidene-1-amino-1-propene (XII) by GC–MS. Diaminoalkanes VII and VIII were thermally decomposed further to XI and XII, respectively. A pathway was proposed for the degradation of III and IV to these compounds as well as to I and II. Odor profiles of I–IV were described in relation to pH alteration.

Ethanal, propanal, ammonia, and hydrogen sulfide are known as degradation products of lipids and amino acids during cooking and also as natural precursors of heated flavor components (Forss, 1967; Fujimaki et al., 1969).

A flavor substance, 2,4,6-trimethyldihydro-1,3,5-dithiazine (I) is generally formed from a mixture of ethanal, ammonia, and H_2S; the reaction to form I occurs almost spontaneously (Brinkman, et al., 1972; Kubota et al., 1982a,b). Wöhler and von Liebig (1847) first isolated I from the mixture of H_2S and 2,4,6-trimethylhexahydro-1,3,5-triazine (V). Later, I was known to occur as a major component in heated beef broth (Brinkman et al., 1972). The substance has so far been detected in beef (Wilson et al., 1973, 1976; MacLeod and Coppock, 1977), lamb fat (Buttery et al., 1977), mutton (Nixon et al., 1979), antarctic krill (Kubota et al., 1980), small shrimp (Kubota et al., 1982a), and soya bean (Sugawara et al., 1983). In red bean (Buttery et al., 1975) and small shrimp (Choi et al., 1983), I is also a major component of the volatile oil. In a reaction mixture of cysteine with xylose (Ledl and Severin, 1973, 1974), I was detected, and similarly in a thermally decomposed product of cysteine or cystine alone (Ledl, 1976).

2,4,6-Trimethyltetrahydro-1,3,5-thiadiazine (III), together with I, has been produced from a mixture of ammonia and bis(1-mercaptoethyl) sulfide prepared from ethanal and H_2S, as reported by Boelens et al. (1974). They also described that III decomposed rapidly when it was applied to GC. Ledl (1975) isolated 2,4,6-triethyldihydro-1,3,5-dithiazine (II) from a mixture of propanal, ammonia, and H_2S. No report on the isolation of 2,4,6-triethyltetrahydro-1,3,5-thiadiazine (IV) has been available yet.

The present paper reports synthetic pathways of I and II via III and IV. We also propose decomposition pathways of III and IV to I, II, and *N,N'*-dialkylidene-1,1-diaminoalkanes (alkyl = ethyl, VII; alkyl = propyl, VIII). Brief descriptions on some organoleptic characteristics of I and II have been known as heated meat or beef odor (Ledl, 1975; Kubota et al., 1980) and onion odor (Ledl, 1975); we report here some characteristics of III and IV together with I and II in more detail.

EXPERIMENTAL SECTION

Preparation of Substances. Dithiazine I was synthesized from ethanal, ammonia, and H_2S. H_2S gas was bubbled moderately through the mixture of 2.7 mol of ethanal (132 g, assay ca. 90%) and 2.7 mol of concentrated (25–28%) aqueous ammonium hydroxide (360 mL) with stirring, having kept the temperature of the mixture in a range of −5 to −10 °C until the reaction temperature ceased rising. The reaction consumed approximately two times as much as the theoretical weight of H_2S. After being left overnight at room temperature, the mixture was heated to 64 °C. The organic layer was separated, washed four times with hot water, dried over sodium sulfate, filtered, and stored at −20 °C. Recrystallization was performed

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Table I. Spectral Data and R_f Values of Dithiazines (I, II) and Thiadiazines (III, IV)

compd	spectral data and R_f values
I	MS;[a] NMR;[a] IR;[b] R_f(A) 0.81, R_f(C) 0.78
II	MS;[c] NMR δ 0.3–0.8 (br, 1), 1.04 (t, 6), 1.08 (t, 3), 1.4–2.1 (m, 6), 3.6–4.5 (m, 2), 4.19 (t, 1, J = 6 Hz); IR[d] (liquid) vs. (760, 815, 1460, 2880, 2940, 2980 cm^{-1}), s (1060, 1160, 1180, 1380 cm^{-1}), m (1090, 1140, 1215, 1285, 3290 cm^{-1}); R_f(A) 0.78, R_f(B) 0.82, R_f(C) 0.72
III	MS 146 (M^+, 1), 129 (0.5), 103 (2), 71 (8), 70 (100), 69 (17), 60 (17), 59 (14), 54 (13), 45 (12), 44 (10), 43 (21), 42 (42), 41 (12); NMR[e] δ 0.0–0.7 (br, 2), 1.27 (d, 3, J = 6 Hz), 1.38 (d, 6, J = 6.5 Hz), 3.66 (q, 1, J = 6 Hz), 4.19 (q, 2, J = 6.5 Hz); IR (KBr) vs (740, 1145, 1165, 2970, 3260), s (780, 1015, 1055, 1105, 1220, 1440, 2900, 3420) m, (930, 1370); R_f(A) 0.61, R_f(C) 0.58
IV	MS 188 (M^+, 0), 171 (1), 142 (1), 131 (2), 98 (100), 82 (6), 74 (12), 68 (18), 56 (27), 41 (40); NMR δ 0.0–0.6 (br, 2), 0.96 (t, 3), 0.98 (t, 6), 1.2–2.0 (m, 6), 3.0–3.6 (m, 1), 3.95 (t, 2, J = 6 Hz); IR (liquid) s (750, 815, 1080, 1155, 1460, 2880, 2940, 2980), m (1005, 1050, 1115, 1175, 1210, 1280, 1380, 3280); R_f(A) 0.74, R_f(B) 0.63, R_f(C) 0.69

[a] Brinkman et al., 1972; Kubota et al., 1980. [b] Brinkman et al., 1972. [c] Ledl, 1975. [d] Intensity of absorption: vs = very strong, s = strong, m = medium. [e] Boelens et al. (1974) report δ 0.0 (br, 2), 1.20 (d, 3, J = 6 Hz), 1.34 (d, 6, J = 6.5 Hz), 4.08 (q, 2, J = 6.5 Hz).

three times from dichloromethane: 133 g (90% yield). Anal. Calcd for $C_6H_{13}NS_2$: C, 44.13; H, 8.02; N, 8.58; S, 39.27. Found: C, 44.2; H, 8.0; N, 8.6; S, 39.7.

Dithiazine II was obtained from the mixture of rectified propanal (2.7 mol, 157 g), ammonium hydroxide, and H_2S in the same manner as that of I. Purification was carried out by distillation: 88 g (47%); bp 114.5–115 °C (3 mm); d^{20}_{20} = 1.0373; n^{20}_D = 1.5292. Anal. Calcd for $C_9H_{19}NS_2$: C, 52.63; H, 9.32; N, 6.82; S, 31.22. Found: C, 51.6; H, 9.4; N, 6.8; S, 31.4.

Thiadiazine III was synthesized in the same manner as that of I but by using a half amount of H_2S. White crystalline masses were gradually formed during gas introduction and filtered at reduced pressure. The resultant white powder (130 g) was dissolved in 80 g of methanol and stored at −20 °C. The precipitate was recrystallized five times from a mixed solvent of methanol and CH_2Cl_2 (15:85, w/w): 98 g (59%). Anal. Calcd for $C_6H_{14}N_2S + 2H_2O$: C, 39.54; H, 9.95; N, 15.37; S, 17.59; O; 17.55. Found: C, 38.5; H, 10.1; N, 15.4; S, 18.2; O, 17.8.

Thiadiazine IV was prepared with propanal instead of ethanal. White round masses appeared during gas bubbling, but they changed rapidly to liquid at room temperature. Recrystallization was performed three times at −20 °C from CH_2Cl_2: 75 g (44%); d^{20}_{20} = 0.9676; n^{20}_D = 1.4971. Anal. Calcd for $C_9H_{20}N_2S$: C, 57.40; H, 10.70; N, 14.87; S, 17.02. Found: C, 55.7; H, 10.5; N, 14.4; S, 16.9. These compounds had been stored at −20 °C until they were used.

Triazine V (trihydrate, mp 91 °C), 2,4,6-triethylhexahydro-1,3,5-triazine (VI), VII, and VIII were prepared by the procedures described by Nielsen et al. (1973). *N*-Propylidene-1-amino-2-propene (IX) was synthesized from allylamine with palladium by the method of Moritani et al. (1975). The compounds VII–IX were immediately submitted to analysis before they were polymerized.

Odor Profile Evaluation. Odor profiles were evaluated by five trained flavorists. They were asked to describe the odors of the compounds I–IV by open discussion.

Apparatus. Gas chromatography–mass spectra (GC–MS) were recorded on a Hitachi Model M-52 mass spectrometer combined with a Hitachi Model 163 gas chromatograph, which was equipped with a 0.28 mm (i.d.) × 40 m glass capillary column coated with OV-101. The temperature of the injection port was maintained at 190 °C. The oven temperture was held at 70 °C for 5 min, and programmed to increase 3 °C/min from 70 to 220 °C. The ionization energy was 20 eV. Most peaks were identified by comparison of their MS spectra and retention times with those of the the corresponding compounds synthesized as described above.

Preparative scale gas chromatographic separation was performed in a Varian Aerograph 2700 equipped with a 3 mm × 2 m glass column packed with 20% Apieson L on Chromosorb W (60–80 mesh). Helium was used as a carrier gas.

Infrared (IR) and nuclear magnetic resonance (NMR) spectra were recorded on a Jasco IRA-1 and on a Hitachi Model R-24B (60 MHz) instrument respectively. In the latter, the solvent was $CDCl_3$ and tetramethylsilane was used as an internal standard.

Thin-layer chromatography (TLC) was performed on a silica gel F plate by using solvent systems of A (methanol–ethyl acetate = 2:1, w/w), B (ethyl acetate), and C (methanol). Spots were visualized in iodine vapor.

RESULTS AND DISCUSSION

Chemical Properties of Dithiazines (I, II) and Thiadiazines (III, IV). Dithiazine I was colorless crystals with mp 47.3 °C [lit. mp 43 °C (Wöhler and von Liebig, 1847), mp 45 °C (Kubota et al., 1980), and mp 46 °C (McClure, 1944)]. It gave one spot on TLC and one peak on GC, indicating that the preparation contained little impurity. Dithiazine II was a colorless liquid at room temperature, and became crystalline below 5 °C. It exhibited the same behavior on TLC and GC as I did. Both I and II were thermally stable under the gas chromatographic conditions.

Thiadiazine III was colorless crystals with mp 69.4 °C and had two hydrates in its form. It showed a property of high sublimation under reduced pressure (ca. 30–40 °C (6–60 mm)). An attempt to obtain anhydrous crystals failed, because of their unstable nature. Thiadiazine IV had a similar appearance to that of II. This compound was able to be distilled, bp 102–102.5 °C (6 mm), but with decomposition to yield a little amount of impurity which could not be assayed in the NMR spectrum. Spectral data and R_f values of these compounds are listed in Table I.

Conversion of Thiadiazines (III, IV) to Dithiazines (I, II) during Storage. A solution of III (50% in methanol), which showed one spot on TLC, gradually became yellowish at room temperature with increasing odor intensity of ammonia and H_2S. The colored solution gave two spots on TLC; one of them exhibited the same R_f value as that of I. When the fresh solution was applied to GC, some peaks (a–e) appeared, as given in Figure 1 part A, where peak d was a major peak. As time elapsed, peak height of d decreased, and instead, that of e increased 7 days after the beginning of storage at room temperature (Figure 1 part B). After 2 months, peak e mainly survived (Figure 1 part C), being identical with that of I as determined by the retention time of GC, MS spectrum, and R_f value of TLC.

The NMR spectrum and R_f value of the compound in peak d isolated by a preparative GC separation procedure were completely the same as those of III as presented in Table I. Therefore, the compound in peak d was identified as III which was a survivor on GC. Thus isolated III was

Table II. MS Fragments and Identification of Decomposition Products of Thiadiazines (III, IV)

peak	compd	MS spectral data
a	X	69 (M^+, 100), 68 (18), 54 (88), 42 (75), 41 (30)
b	XI	86 (M^+, 5), 70 (24), 59 (100), 54 (10), 42 (16)
c	VII	112 (M^+, 1), 85 (1), 70 (100), 56 (6), 54 (8), 44 (5), 42 (22)
c′	(probably an isomer of c)	112 (M^+, 30), 85 (67), 70 (100), 56 (27), 54 (24), 44 (80), 42 (64)
f	XII	97 (M^+, 56), 82 (27), 68 (96), 56 (21), 54 (16), 41 (100)
g	unknown	154 (M^+, 1), 137 (1), 122 (2), 98 (100), 82 (6), 70 (8), 68 (11), 58 (6), 56 (11), 43 (14), 41 (27)
h	VIII	154 (M^+, 5), 127 (21), 125 (11), 98 (24), 82 (8), 70 (13), 68 (9), 58 (100), 56 (9), 55 (10), 41 (10)

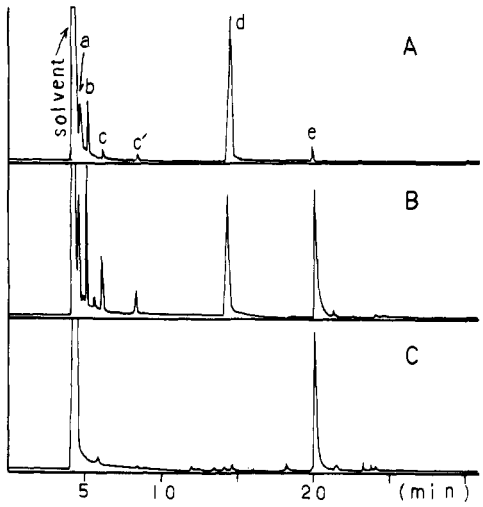


Figure 1. Degradation of thiadiazine III and formation of the related compounds during storage at room temperature: A, fresh solution; B, stored for 7 days; C, stored for 2 months (concentration 50% in methanol).

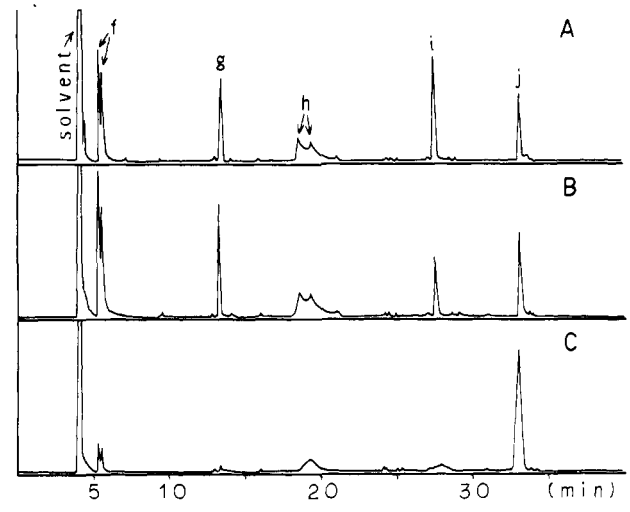


Figure 2. Degradation of thiadiazine IV and formation of the related compounds during storage at room temperature: A, fresh solution; B, stored for 7 days; C, stored for 2 months (concentration 50% in methanol).

repeatedly decomposed on GC, representing the same pattern as shown in Figure 1 part A.

The similar decomposition occurred in IV as visualized on TLC and GC during storage (Figure 2 parts A–C; peak i, IV; peak j, II). Also the compound in peak i was decomposed on GC, showing the similar pattern as that in Figure 2 part A.

Conversion of Thiadiazines (III, IV) to Diaminoalkanes (VII, VIII) during Storage. During storage of IV in a methanol solution, there was an increase in a characteristic odor of leaves of monocotyl plants, which resembled the odor of VI and VIII. On the other hand, the distillate of IV exhibited medium intensity absorption in the IR spectrum (1650 cm^{-1}, C=N band) and a small proton signal in the NMR spectrum (δ 7.4–7.7, br, N=CH band), whereas both of these did not appear in the spectra of IV before distillation. The two spectral characteristics were considered to be those of a product containing an N=CH bond formed by the elimination of H_2S from IV, most probably due to the formation of VIII. Both fresh VII and VIII showed the strong intensity of absorption and comparable signals. VII: 1655 cm^{-1}; δ 7.6–7.9 (br) [lit. 1660 cm^{-1} δ 7.6 (q, J = 4.5 Hz) (Caprio et al., 1968)] VIII: 1650 cm^{-1}; δ 7.65 (t, J = 4.5 Hz) [lit. 1650 cm^{-1}; δ 7.72 (t, J = 4.5 Hz) (Nielsen et al., 1973)].

When H_2S was bubbled slowly into VIII (colorless liquid, 1.5 g, 0.01 mol, 90% purity by NMR assay) at −10 °C, the intensity of absorption in the IR spectrum of the mixture decreased, followed by the increase in the crystalline mass of IV (0.3 g). This suggests that IV (and III) was converted to VIII (VII) in addition to II (I) as shown in Scheme I.

Other Products from Thiadiazines (III, IV). In order to identify other products from III (IV), VII (ca. 80% purity, 20% of V by NMR assay) was loaded on GC under the same conditions as tested for the behavior of III. Some peaks appeared whose MS spectra and GC retention times were completely the same as those of peaks a–c′ shown in

Scheme I

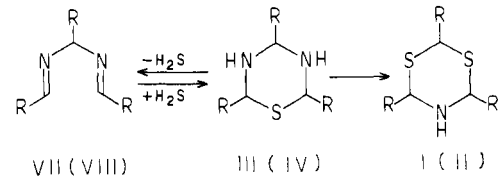
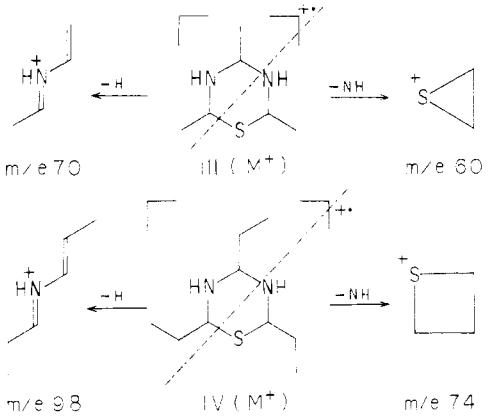


Figure 1 part A. Also, peaks derived from VIII corresponded to peaks f–h in Figure 2 part A. The compounds in the peaks were identified as decomposition products of III and IV by fragment analysis of the MS spectra (Table II). Among them, the compound in peak a was identified as *N*-ethylidene-1-aminoethene (X, CH_2=CHN=$CHCH_3$) according to the fragmentation pattern in the MS spectrum of *N*-propylidene-1-amino-1-propene (XII, CH_3CH=CHN=$CHCH_2CH_3$), which was identified by comparison with the fragmentation of IX (CH_2=CH-H_2N=$CHCH_2CH_3$) and with that of saturated *N*-alkylidene-1-amino-alkanes (RN=R′) as reported by Fischer and Djerassi (1966).

MS Spectra of Thiadiazines (III, IV) and Other Compounds. The principal fragments in the MS spectra of III and IV are presented in Table I. Decomposition of the molecular ion (M^+, m/e 146) of III occurred through elimination of $CH_3CH(S)NH$ to yield the m/e 70 ion. The residue expelled the NH group to give the m/e 60 ion. The similar decomposition also occurred in the MS spectrum of IV (Scheme II).

The fragments for other compounds are shown in Table II. X: The fragments indicated decomposition of M^+ (69) through elimination of the CH_3 group to yield the ion, 54, CH_2=CHN^+≡CH. *N*-Ethylidene-1,1′-diaminoethane (XI, $CH_3CH(NH_2)$N=$CHCH_3$): Decomposition of M^+ (86) occurred through elimination of the NH_2 and C_2H_4 groups to yield the ions 70 (in Scheme II) and 59 (CH_3C(=

Scheme II



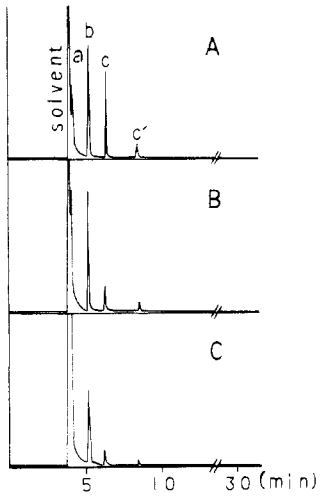


Figure 3. Degradation of triazine V and formation of the related compounds during storage at room temperature: A, fresh solution; B, stored for 7 days; C, stored for 1 month (concentration 25% in methanol).

$N^+H_2)NH_2$). VII: M^+ (112) yielded the ions, 85 (CH_3C-($=N^+H_2)N=CHCH_3$), 70, 56, and 42 ($CH_2=N^+=CH_2$) through stepwise elimination of the C_2H_4, NH_2, and two CH_3 groups. Fragmentation of the 70 ion gave the ion 44 ($CH_3CH=N^+H_2$). XII: Decomposition of M^+ (97) gave the ions 82 ($CH_3CH=CHN^+\equiv CCH_3$) and 68 ($CH_3CH=CHN^+\equiv CH$) through elimination of the CH_3 and C_2H_5 groups. VIII: M^+ (154) yielded the ions 127 ($CH_3CH_2CH(N^+H=CH_2)N=CHCH_2CH_3$), 98 (in Scheme II), 70, and 56 through stepwise elimination of the C_2H_4, CH_2NH_2, C_2H_5, and CH_3 groups. Fragmentation of the ion 98 gave the ion 58 ($CH_3CH_2CH=N^+H_2$).

Degradation of Triazines (V, VI) during Storage. Caprio et al. (1968) reported the production of VII as one of the thermal degradation products from V. The fresh solution of V was applied to GC; some peaks (a–c′) appeared, as given in Figure 3 part A. As time elapsed, the peak height of b and c decreased and that of a increased 1 month after the beginning of storage (Figure 3 parts B and C). Under the present analytical condition, V was not separable from VII; peak c was found to contain only VII by the fragment analysis. This result indicates that V was degraded to X via VII and XI. Nielsen et al. (1973) have showed that V (VI) is readily convertible to VII (VIII) upon elimination of ammonia. Further, on the degradation pathway of V, Meier et al. (1968) have suggested that this compound decomposes to X via VII in a pyrolysis system heated at 250–350 °C. Pathways for the formation of XI and *N*-propylidene-1,1′-diaminopropane (XIII) are unknown; there is only a possibility that XI (XIII) occurs as an intermediate in a pathway for the formation of V (VI) from ethanal (propanal) and ammonia (Nielsen et al., 1973). In this pathway, the presence of XIII, CH_3CH_2C-$H(NH_2)N=CHCH_2CH_3$ can be assumed but was not detected, possibly due to rapid deamination or disproportionation; the occurrence of XII has also been reported by Ripoll et al. (1980). Thus, a possible pathway for the breakdown of V (VI) is summarized as follows. V (VI) → VII (VIII) → XI (XIII) → X (XII) Incidentally, NMR and IR spectral data of VII, VIII, X, and XII have been given hitherto by some workers (Meier et al., 1968; Nielsen et al., 1973; Ripoll et al., 1980), while MS data of these substances have been described little, probably due to their unstable nature.

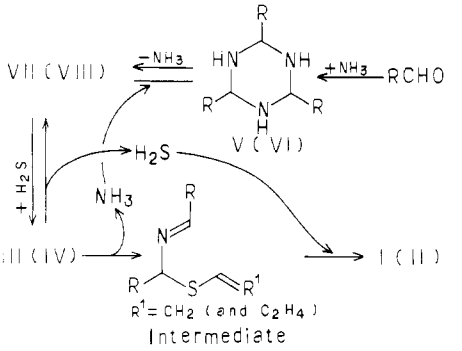


Figure 4. Possible pathways for the formation and decomposition of thiadiazines (III, IV).

Overall Pathways for Degradation of Thiadiazines (III, IV). Thiadiazine III (IV) changed readily to I (II) and also to VII (VIII) and other compounds to which VII (VIII) was further degraded thermally, as described above. When VII (VIII) was formed by the elimination of H_2S from III (IV), the released H_2S probably reacted with an intermediate to produce I (II) (Figure 4). The intermediate was considered to be acyclic alkylidene imine presented as the *m/e* 129 (171) ion in the MS spectrum of III (IV) (Table I). This imine seemed to be produced by the elimination of ammonia from III (IV) ($M - NH_3$), resulting in the formation of I (II) on reaction with the released H_2S. Therefore, the amount of H_2S affects the formation of I (II). When H_2S occurs in small amounts, III (IV) decomposes almost simultaneously to VII (VIII).

Dithiazine I has long been found in various foods (Brinkman et al., 1972; Kubota et al., 1980; Choi et al., 1983). It is likely that the reaction to form I (II) proceeds spontaneously by the route (Figure 4) from ethanal (propanal), ammonia, and H_2S. Other compounds such as III, IV, and acyclic N-containing compounds (VII, VIII, X, XI, and XII) have hardly been detected in natural products yet, possibly because they are thermally unstable.

ODOR ASPECTS

Fresh solutions of I–IV (0.05 mol in 95% ethanol) were titrated with 0.5 and 2.0 N HCl to allow changes in pH of the solutions. The accompanied change in odor profiles was tested with the alteration of pH values. The strength and quality of odors were affected by pH alteration (Table III). Changes in the quality of odors occurred near equivalent points (E_p), indicating that the protonated form has different odors than its dissociated form. For example, an odor of I before addition of the dilute HCl gave the flavorists various images, e.g., roasted shrimp, boiled scallop, heated soya bean, and boiled corn cob. The decrease in pH to 2.7, which in close to the E_p value (2.5), resulted in addition of a little sweet odor. At pH 1.6 below

Table III. Organoleptic Properties of Compounds I–IV at Different pH Values and Equivalent Points (E_p)

compd	E_p	pH	odor profiles
I	2.5[a]	8.1[b]	medium roast shrimp
		3.5	medium roast shrimp
		2.7	medium roast shrimp with slight sweetness
		1.6	weak edible mushroom "shiitake"
II	1.7	7.3[b]	weak raw pumpkin, white part of Allium plants
		5.5	odor added with green note
		4.5	strong leek
		2.1	medium leek, onion
		0.4	weak Allium plants
III	4.0	9.1[b]	strong roast cereal
		5.5	strong roast popcorn
		4.0	medium ammonium sulfide
		1.4	strong ammonium sulfide
IV	6.4	9.0[b]	weak avocado, raw pumpkin, unriped orange
		6.1	odor added with that of green vegetable
		4.9	strong fresh leek, slightly earthy
		3.0	very strong crushed fresh leek
		1.9	weak staled mustard

[a] 2.7 (Collins and Graymore, 1958). [b] Before addition of HCl.

E_p, the solution gave weak edible mushroom odor.

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