2-Carboxymethylthio- and 2-Hydrazino-1, 3-diazaazulenes

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2-Mercapto-1, 3-diazaazulene[1] (I) easily undergoes condensation with monochloroacetic acid to form 2-carboxymethylthio-1, 3-diazaazulene[2] (II), as has already been reported, and various properties of II, and 2-hydrazino-1, 3-diazaazulene[3] derived from I and II, are described in this paper.

II forms a pale yellow, crystalline powder only sparingly soluble in water and organic solvents, and has a melting point exceeding 300°C. Its esterification by the Fischer method affords methyl ester IV of m. p. 118~118.5°C and the ethyl ester V of m. p. 89°C. V is also obtained upon reaction of ethyl monochloroacetate on the sodium salt of I. These esters easily undergo hydrolysis to regenerate II and are converted into an amide (VI) of m. p. 207~208°C by the action of 40% ammonia water.

It is known, that pyridines[4] and quinolines[5] possessing a carboxymethylthio group in the α-position generally form a cyclized product, called meso-ionic compound, on heating with acetic anhydride. On refluxing II in acetic anhydride, it is converted into an extremely sparingly soluble substance* of violet color. The analytical values of this substance suggest an intermolecular dehydrated product but no detailed examination has been made on it.

* A part of this work was presented as a paper at the 10th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1957.

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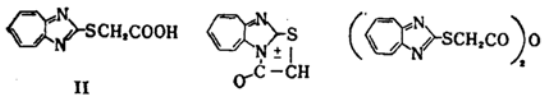
* Duffin and Kendall[4] reported that the use of phosphorus pentoxide or thionyl chloride in place of acetic anhydride as the dehydration agent afforded structurally unkonwn substance as a brown powder.

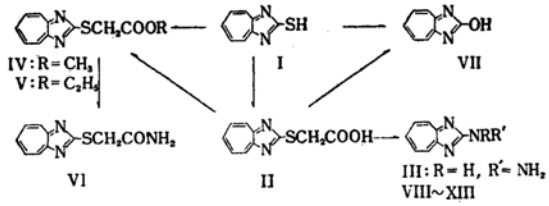


II

Refluxing of II in concentrated hydrochloric acid results in its conversion to 2-hydroxy-1, 3-diazaazulene (VII) in good yield. Such comparatively facile hydrolysis of II suggests the possibility of I being desulfurized by the action of monochloroacetic acid.

Desulfurization of heterocyclic compounds with a mercapto group by the action of monochloroacetic acid has been reported by numerous workers on thiopyrimidines[6], thioquinoline[7], thiohydantoin[8], thiouracil[9] and thiooxazole and thiothiazole[10]. On heating I in aqueous solution of excess of monochloroacetic acid, II is first formed after 15~20 min. When this mixture is heated for a longer period, such as further 25 hr., without isolation of II, the separated II dissolves gradually and changes almost quantitatively into VII.

Oxidation of the ethyl ester V with hydrogen peroxide in glacial acetic acid, in an attempt to obtain the ethoxycarbonylsulfonyl derivative, invariably gives VII as the product, whether the reaction is carried out at 60~70°C with an excess of the reagent or at room temperature with an equivalent amount of the reagent, and the sulfone is not isolated. Ohta[10] obtained the sulfone by oxidation of carboxymethylthio derivatives of thiazole and thiadiazole under the same conditions but found that the same oxidation of oxadiazole had changed it into the hydroxy derivatives and the sulfone was not obtained. II also undergoes oxidation by hydrogen peroxide to form VII.



IV: R = CH_3
V: R = C_2H_5

VI II III: R = H, R' = NH_2
VIII~XIII

The carboxymethylthio group present in 2-position of pyrimidine is known to be substituted by amino and benzylamino groups[11]. II also reacts comparatively easily with various amines to form derivatives listed in Table I.

In the foregoing reaction, II reacts most readily with hydrazine and III is formed in a good yield only by letting stand their mixture at room temperature.

III has already been obtained by the application of hydrazine to 2-chloro-1, 3-diazaazulene but its properties are almost unknown. As has already been mentioned, III can now be prepared easily from II but it can also be obtained easily from I by refluxing it with hydrazine hydrate in butanol, generating hydrogen sulfide gas.

III easily undergoes condensation with various ketones and aldehydes in alcohol to form the corresponding hydrazones (Table II). The ultraviolet absorption maxima of these hydrazones are indicated in Table III.

In general, six-membered, heterocyclic aromatic compounds of nitrogen possessing a hydrazino group in the α-position undergoes cyclization between the ring nitrogen and the hydrazino group by the action of formic acid, ethyl orthoformate, or acetic anhydride and form triazole derivatives. They also undergo

TABLE I. 2-SUBSTITUTED DERIVATIVES OBTAINED FROM 2-CARBOXYMETHYLTHIO COMPOUND

Compd. No.	R	R'	Cryst. form*	m. p., °C	Yield %	N Analysis Calcd.	N Analysis Found	Ref.
III	H	NH_2	y. N.	189	89	—	—	3
VIII	H	H	y. N.	295(d.)	43	—	—	12
IX	H	CH_3	y. P.	172~173	90	—	—	3
X	CH_3	CH_3	y. P.	133~134	92	—	—	3
XI	H	C_6H_5	o. P.	239~240	80	—	—	2
XII	H	$CH_2C_6H_5$	y. P.	173	75	17.86	17.92	—
XIII	H	NHC_6H_5	y. P.	222	30	23.72	23.40	—

* y, yellow; o, orange; N, needles; P, prisms.

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TABLE II. REACTION PRODUCTS OF III WITH VARIOUS KETONES AND ALDEHYDES

R_1	R_2	Cryst. form*	m.p. °C	Mol. form	Analysis Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
CH_3	CH_3	y. N.	201(d.)	$C_{11}H_{12}N_4$	65.98	6.04	27.98	67.05	5.72	27.67
H	C_6H_5	y. N.	235(d.)	$C_{15}H_{12}N_4$	72.56	4.89	22.57	72.51	4.59	22.56
H	C_6H_4Br	y. N.	274(d.)	$C_{15}H_{11}N_4Br$	55.06	3.38	17.12	55.63	3.48	17.11
H	$C_6H_4N(CH_3)_2$	r. P.	247(d.)	$C_{17}H_{17}N_5\cdot H_2O$	66.00	6.19	22.64	66.18	6.21	22.81
H	$C_6H_4OCH_3$	o. P.	241(d.)	$C_{16}H_{14}ON_4\cdot 1/2H_2O$	66.88	5.26	19.50	66.80	4.78	19.52
H	$C_6H_4NO_2$	y. N.	290	$C_{15}H_{11}O_2N_5\cdot 3/2H_2O$	56.24	4.45	21.86	55.87	4.39	21.86
H	$C_6H_4O_2CH_2$	o. P.	262(d.)	$C_{16}H_{12}O_2N_4\cdot H_2O$	61.93	4.55	18.06	62.12	4.05	18.55

* y, yellow; r, red; o, orange; N, needles; P, prisms.

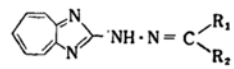

TABLE III. ULTRAVIOLET MAXIMA OF 1,3-DIAZAAZULENYL-2-HYDRAZONES

R_1	R_2	λ_{max}^{MeOH} mμ (log ε)				
CH_3	CH_3	—	248(4.46)	264(4.46)	295(*)	370(4.35)
H	C_6H_5	—	243(4.46)	285(4.38)	305(*)	389(4.50)
H	C_6H_4Br-*p*	—	242(4.48)	286(4.37)	305(*)	391(4.55)
H	$C_6H_3O_2CH_2$-3,4	219(4.33)	245(4.46)	287(4.30)	312(4.22)	400(4.46)
H	$C_6H_4OCH_3$-*p*	—	245(4.46)	289(4.26)	310(4.21)	408(4.41)
H	$C_6H_4NO_2$-*p*	—	240(4.42)	268(*)	300(*)	410(4.57)
H	$C_6H_4N(CH_3)_2$-*p*	—	242(4.43)	265(*)	317(4.35)	428(4.47)

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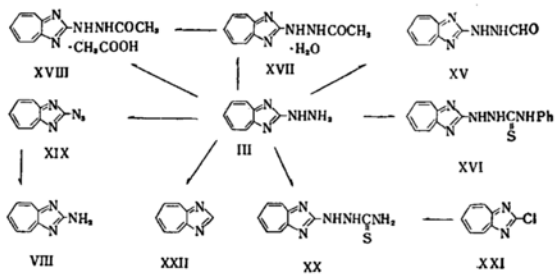
cyclization by the action of nitrous acid to form tetrazole derivatives[13].

III does not cyclize by the reaction of these reagents, even under a rather drastic conditions. The reaction of III with formic acid gives the formate XV of m. p. 249°C (decomp.) and that with phenyl-mustard oil gives the phenylthiosemicarbazide compound XVI. Application of acetic anhydride to III affords two kinds of crystals, m. p. 248°C (decomp.) (XVII) and m. p. 189°C (decomp.) (XVIII). Further application of acetic anhydride to XVII converts it to XVIII. It is therefore known that XVII is an acetylhydrazino compound with one molecule of water of crystallization while XVIII is an acetate of the acetylhydrazino compound.

Application of sodium nitrite in 2 N hydrochloric acid or in acetic acid to III gives extremely labile yellow needles (XIX) of m. p. 135°C (decomp.). The ultraviolet absorption maxima of XIX appear at 228 mμ (log ε 4.03), 262 (4.41), and 337 (4.15), and this makes it impossible to assume any skeletal change in 1,3-diazaazulene molecule. The infrared spectrum of XIX shows distinct absorption of an azide at 2150 cm^{-1} [14] and XIX should therefore be 2-azido-1,3-diazaazulene and not the anticipated tetrazole compound. Actually, reduction of XIX with hydrogen sulfide results in quantitative formation of 2-amino-1,3-diazaazulene[12] and this also endorses above assumption.

Reaction of potassium thiocyanate on III in the presence of hydrochloric acid affords reddish brown prisms XX, m. p. 179.5°C, which is also obtained upon reaction of thiosemicarbazide on 2-chloro-1,3-diazaazulene (XXI), and this shows that XX is 2-thiosemicarbazido-1,3-diazaazulene.

III was decomposed by the Stephens-McFadyen method[15] to 1,3-diazaazulene (XXII).



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Experimental

2-Carboxymethylthio-1, 3-diazaazulene (II). — Prepared by the method given in the literature[2].

2-Methoxycarbonylmethylthio-1, 3-diazaazulene (IV). — A mixture of II (100 mg.) suspended in methanol (2 ml.) and added with concentrated hydrochloric acid (0.05 ml.) was refluxed on a water bath for 45 min. This mixture was diluted with water and extracted with chloroform. The chloroform extract was washed with water, dried, and the solvent was evaporated. The residue was dissolved in benzene and the solution was purified by passage through an alumina layer. The yellow crystals (100 mg.), m. p. 120~122°C, was recrystallized from benzenepetroleum ether mixture to pale yellow needles (IV), m. p. 121~122°C.

Found: C, 56.71; H, 4.08; N, 12.12. Calcd. for $C_{11}H_{10}O_2N_2S$: C, 56.41; H, 4.30; N, 11.96%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 238(4.35), 269(4.28), 355(4.19).

2-Ethoxycarbonylmethylthio-1, 3-diazaazulene (V).—a) Obtained by a method similar to that for IV, as pale yellow needles, m. p. 89~89.5°C.

b) A solution of the sodium salt (200 mg.) of I dissolved in ethanol (2 ml.) and added with ethyl monochloroacetate (150 mg.) was refluxed on a water bath for 50 min. Sodium chloride formed by the reaction was filtered off, ethanol was evaporated from the filtrate and benzene soluble portion of the residue afforded 230 mg. of V, m. p. 89~89.5°C.

Found: C, 58.11; H, 4.39; N, 11.56. Calcd. for $C_{12}H_{12}O_2N_2S$: C, 58.06; H, 4.87; N, 11.29%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 238(4.46), 269(4.37), 355(4.29).

2-Carbamoylmethylthio-1, 3-diazaazulene (VI).— A mixture of V (70 mg.) and 40% ammonia water (2 ml.) was stirred for 10 hr. at room temperature. After allowing this to stand over night, the crystals (60 mg.) of m. p. 202~205°C (decomp.) were collected and recrystallized from ethanol to pale yellow needles (VI), m. p. 207~208°C (decomp.).

Found: C, 55.15; H, 3.82; N, 19.57. Calcd. for $C_{10}H_9ON_3S$: C, 54.79; H, 4.14; N, 19.17%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 239(4.49), 270(4.36), 355(4.29).

Action of Acetic Anhydride on II.—A suspension of II (40 mg.) in acetic anhydride (1 ml.) was refluxed for 10 min. in an oil bath. The cooled reaction mixture was thoroughly washed with water and ethanol, and brownish violet powder (30 mg.) which turns black from around 220°C, was obtained.

Found: N, 12.83. Calcd. for $C_{20}H_{14}O_3N_4S_2$: N, 12.54%.

Hydrolysis of II. — A solution of II (50 mg.) dissolved in concentrated hydrochloric acid (0.5 ml.) was refluxed for 2 hr. in an oil bath, hydrochloric acid was evaporated to dryness, and the residue was neutralized with sodium hydrogen carbonate, and crystals (30 mg.) melting at 225~228°C were obtained. Recrystallization from ethanol after treatment with activated carbon afforded crystals of m. p. 244~245°C, undepressed on admixture with VII.

Reaction of I and Monochloroacetic Acid.—a) A suspension of I (100 mg.) in a mixture of monochloroacetic acid (100 mg.) and water (10 ml.) was refluxed for 20 min. in an oil bath, cooled, and the crystals that separated out were collected by filtration to 80 mg. of II, m. p. over 300°C.

b) The reaction was carried out as above but the refluxing was continued for 25 hr. by which the crystals of II dissolved completely. The reaction mixture was evaporated to dryness, ethanol was added to the residue, and this was filtered. The crystals (100 mg.) of m. p. over 300°C so obtained were neutralized with sodium hydrogen carbonate and recrystallized from ethanol to VII, m. p. 244~245°C.

Oxidation of II with Hydrogen Peroxide. — To a suspension of II (80 mg.) in glacial acetic acid (0.5 ml.), 30% hydrogen peroxide (0.2 ml.) was added and the mixture was heated with stirring at 75~80°C for 2 hr. The pale yellow solution so obtained was concentrated under a reduced pressure and neutralized with saturated solution of sodium hydrogen carbonate. The crude crystals (40 mg.) of m. p. 229°C were recrystallized from ethanol to VII, m. p. 244~245°C.

Reaction of II and Ammonia or Amines.—a) A solution of II (100 mg.) dissolved in 40% ammonia water (1.5 ml.) was sealed in a tube and heated at 100°C for 6 hr. The reaction mixture was allowed to stand over night and the crystals (30 mg.) of m. p. 270°C (decomp.) were collected and recrystallized from water to pale yellow needles (VIII), m. p. 294°C (decomp.). The mother liquor left after separation of VIII afforded the recovered II (55 mg.).

b) A solution of II (150 mg.) dissolved in 40% aqueous solution (2 ml.) of methylamine or dimethylamine was sealed in a tube and heated at 100°C for 20 hr. The reaction mixture was evaporated to dryness over sulfuric acid in a vacuum desiccator and the benzene soluble portion of this residue afforded IX, m. p. 173~174°C, and X, m. p. 133~134°C.

c) A mixture of II (150 mg.) in ethanol (2 ml.) and aniline or benzylamine (1 ml.) was heated in a sealed tube at 165~170°C for 7 hr., cooled over night, and crystals that separated out were collected, afforded 120 mg. of XI, m. p. 239°C, and XII, m. p. 173°C.

2-Phenylhydrazino-1, 3-diazaazulene (VIII).—A mixture of II (100 mg.) in ethanol (4 ml.) and added with phenylhydrazine (100 mg.) was heated in a sealed tube at 155~160°C for 6 hr. The crystals that separated out on allowing the reaction mixture to cool were collected (30 mg.) melting with decomposition at 200°C. This was recrystallized from dilute ethanol to orange prisms, XIII, m. p. 222°C (decomp.).

Found: C, 70.64; H, 5.25; N, 23.40. Calcd. for $C_{14}H_{12}N_4$: C, 71.16; H, 5.12; N, 23.72%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 238(4.18), 260(4.56), 354(4.22).

2-Hydrazino-1, 3-diazaazulene (III).—a) II (1 g.) was dissolved in hydrazine hydrate (10 ml.) with warming and the solution was allowed to cool to room temperature by which brown needles, m. p.

187°C (decomp.), separated out. This was recrystallized from ethanol to III (650 mg.), m. p. 188～189°C (decomp.).

b) To a suspension of I (250 mg.) in *n*-butanol (6 ml.), 80% hydrazine hydrate (0.5 ml.) was added and the mixture was refluxed in an oil bath for 4 hr., until there was no longer evolution of hydrogen sulfide. The solvent was evaporated under a reduced pressure, ethanol was added to the residue, and filtration afforded III (220 mg.), m. p. 184～185°C (decomp.).

Reaction of III and Carbonyl Compounds.—A mixture of III and a carbonyl compound (1.1 mol. equiv.) in ethanol was heated for 5～10 min., cooled, and the crystals so formed or obtained by evaporation of ethanol was recrystallized from ethanol or a mixed solvent of ethanol and dioxane. The hydrazones listed in Table II were thereby obtained in a quantitative yield.

Reaction of III and Formic Acid.—A solution of III (100 mg.) dissolved in 80% formic acid (1 ml.) was heated at 90°C for 4 hr. Formic acid was then evaporated under a reduced pressure, the residue was washed with ethanol, and crystals (85 mg.) of m. p. 245°C (decomp.) were obtained. Recrystallization from ethanol afforded XV, m. p. 249°C (decomp.).

Found: C, 57.36; H, 3.90; N, 30.41. Calcd. for $C_9H_8ON_4$: C, 57.44; H, 4.29; N, 29.77%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 257(4.42), 347(4.09).

Reaction of III and Phenyl-mustard Oil.—Phenyl-mustard oil (90 mg.) was added to the solution of III (100 mg.) dissolved in ethanol (6 ml.) and the mixture was refluxed for 15 min. The crystals that separated out on cooling this reaction mixture were collected by filtration and recrystallized from ethanol to XVI (90 mg.) as reddish violet prisms, which does not indicate any definite melting point, gradually turning black by heating.

Found: C, 59.62; H, 4.00; N, 23.28. Calcd. for $C_{15}H_{13}N_5S$: C, 61.01; H, 4.44; N, 23.72%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 257(4.61), 347(4.13), 460 (3.50).

Reaction of III and Acetic Anhydride.—A mixture of III (50 mg.) and acetic anhydride (0.2 ml.) was allowed to stand at room temperature by which III dissolved once and crystals (30 mg.) of m. p. 210°C separated out. These crystals were recrystallized from ethanol to XVII, m. p. 248°C (decomp.).

Found: C, 54.38; H, 5.34; N, 25.22; H_2O, 7.72. Calcd. for $C_{10}H_{10}ON_4 \cdot H_2O$: C, 54.54; H, 5.49; N, 25.44; H_2O, 8.18%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 259(4.48), 350(4.18).

The filtrate left after separation of XVII was concentrated and the crystalline residue was recrystallized from ethanol to XVIII (10 mg.), m. p. 189°C (decomp.).

Found: C, 55.18; H, 5.10; N, 21.34. Calcd. for $C_{10}H_{10}ON_4 \cdot CH_3COOH$: C, 54.95; H, 5.38; N, 21.37%.

Reaction of III and Nitrous Acid.—A solution of sodium nitrite (95 mg.) in water (0.3 ml.) was added dropwise into a solution of III (200 mg.) dissolved in 2 N acetic acid (2 ml.) at room temperature. The mixture was then heated for a few minutes at 80°C, diluted with water, and extracted with benzene. The benzene layer was treated with activated carbon and crystals, m. p. 133～134°C (170 mg.), were obtained. This was recrystallized from benzene-petroleum ether mixture to pale yellow prisms XIX, m. p. 134～135°C (decomp.). Ultraviolet λ_{max}^{MeOH} mμ (log ε): 228(4.03), 262(4.41), 337(4.15), 370(shoulder).

Picrate: Yellow needles from ethanol, m. p. 273～274°C (decomp.).

Found: N, 15.68. Calcd. for $C_8H_5N_5 \cdot C_6H_3O_7N_3$: N, 15.79%.

Hydrogen sulfide gas was passed through a solution of XIX (100 mg.) dissolved in water (8 ml.) by which the solution gradually turbid. After thoroughly saturating hydrogen sulfide, the white precipitate so formed was collected by filtration, the portion of the precipitate soluble in hydrochloric acid was combined with the filtrate, and the solution was evaporated. The residue was neutralized with sodium hydrogen carbonate and yellow crystals (60 mg.), m. p. 289°C (decomp.), were obtained. This was recrystallized from water to yellow needles, m. p. 294°C (decomp.), whose ultraviolet and infrared spectra agreed completely with those of 2-amino-1,3-diazaazulene.

Reaction of III and Potassium Thiocyanate.—To a solution of III (400 mg.) dissolved in water (2.5 ml.) and added with 4 drops of concentrated hydrochloric acid, aqueous solution of potassium thiocyanate (260 mg.) was added and the mixture was heated on a water bath for 15 min. The crystals formed on coolling this solution were collected (460 mg.) and recrystallized from diluted ethanol to brown prisms, XXI, m. p. 179～179.5°C (decomp.).

Found: C, 49.43; H, 3.92; N, 31.45. Calcd. for $C_9H_9N_5S$: C, 49.31; H, 4.14; N, 31.95%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 265(4.50), 300(3.75), 367 (4.34).

Stephens-McFadyen Decomposition of III.—III (50 mg.) was dissolved in 50% acetic acid (4 ml.), to which 10% copper sulfate solution (1.2 ml.) was added. The mixture was then warmed on a water bath, the solution turned yellowish green and nitrogen gas evolved. After 10 min., the reaction mixture was filtered, and the filtrate was neutralized with a solid sodium hydrogen carbonate, extracted with chloroform. The chloroform extracts were evaporated, and the residue was dissolved in benzene and purified through a short column of alumina. The elute gave yellow needles, m. p. 115～118°C, and no depression with authentic 1,3-diazaazulene on mixed fusion.

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