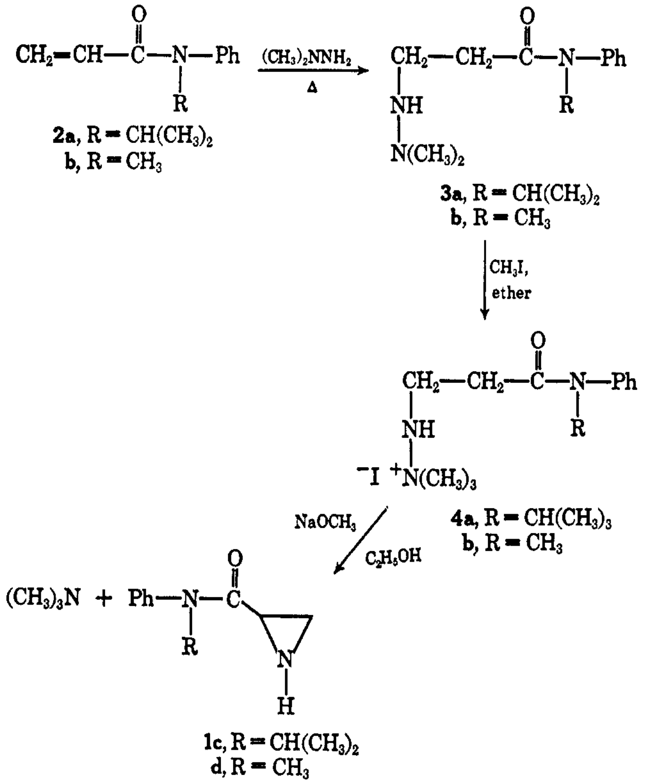
Scheme I



2(-[2-Isopropylphenylcarbamoyl)ethyl]-1,1,1-trimethylhydrazonium Iodide (4a).—N-Phenyl-N-isopropylacrylamide (1 equiv) and 1,1-dimethylhydrazine (2 equiv) was refluxed overnight and concentrated *in vacuo*. Treatment with 1 equiv of methyl iodide in ether gave 1 equiv (100%) of the methiodide. Recrystallization of the methiodide from ethanol–methylcyclohexane (1:3) gave white granules, mp 175–178°. The nmr spectrum showed isopropyl signals at δ 1.1 (6 H doublet) and the nine N-methyl protons as a sharp spike at 3.35.

Anal. Calcd for $C_{15}H_{26}N_3OI$: C, 46.00; H, 6.71; I, 32.40. Found: C, 45.74; H, 6.71; I, 32.41.

N-Phenyl-N-isopropyl-2-aziridinecarboxamide (1c).—Methiodide **4a** (260 g, 0.66 mole) and sodium methoxide (1.36 moles) were refluxed in 1500 ml of ethanol for 18 hr. The solution was poured into 3000 ml of water and extracted with methylene chloride. The extracts were washed with water, dried, and concentrated to 105 g of an oil. Distillation of this oil separated 76 g (57%) of aziridine **1a**, bp 110° (0.35 mm). The nmr spectrum showed isopropyl signals at δ 1.1 (6 H) and 4.9 (1 H). The ring protons showed the expected 12 lines of an ABC spectrum at δ 1.4 (1 H), 1.75 (1 H), and 2.0 (1 H).[11] The trimethylamine evolved was identified as its picrate, mp 215° (lit.[12] mp 216°).

Anal. Calcd for $C_{12}H_{16}N_2O$: C, 70.60; H, 7.89. Found: C, 70.75; H, 7.98.

N-Phenyl-N-methyl-2-aziridinecarboxamide (1d).—N-Phenyl-N-methylacrylamide[13] (1 equiv) and 1,1-dimethylhydrazine (2 equiv) were refluxed for 5 hr and concentrated *in vacuo*. Treatment with 1 equiv of methyl iodide in ether furnished 284 g (0.78 mole) of the methiodide **4b**. Recrystallization from ethanol–methylcyclohexane (1:3) gave white granules, mp 147–150°. The nmr spectrum exhibited the amide methyl spike at δ 3.15 (3 H) and the nine-proton trimethylamino spike at δ 3.35.

Anal. Calcd for $C_{13}H_{22}N_3IO$: I, 35.00. Found: I, 35.56.

The methiodide (284 g, 0.78 mole) was dissolved in 500 ml of ethanol containing 49 g (0.9 mole) of sodium methoxide. The solution was refluxed for 16 hr, poured into water, and extracted with methylene chloride. The extract was washed with water, dried, and concentrated. Distillation separated 48 g (35%) of aziridine **5b**, bp 108° (0.5 mm). The nmr spectrum showed the N-methyl signal at δ 3.25 and the ring protons showed the same ABC spectrum as **5a**.[11]

Anal. Calcd for $C_{10}H_{12}N_2O$: C, 68.25; H, 6.88; N, 15.90. Found: C, 67.91; H, 7.06; N, 15.97.

Registry No.—**1c**, 15315-36-3; **1d**, 15315-37-4; **2a**, 51315-38-5; **4a**, 15315-39-6; **4b**, 15315-40-9.

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[11] G. Szeimies and R. Huisgen, *Chem. Ber.*, **99**, 491 (1966).

[12] A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., Ltd., New York, N. Y., 1956, p 661.

[13] E. H. Specht, A. Neuman, and H. T. Neher, U. S. Patent 2,773,063 (1956); *Chem. Abstr.*, **51**, 8778 (1956).

Heterocyclic Systems with a Bridgehead Nitrogen. I. 2-Alkyl-3,4-dihydro-*as*-triazino[3,4-*b*]benzothiazol-3-ones

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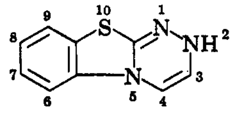
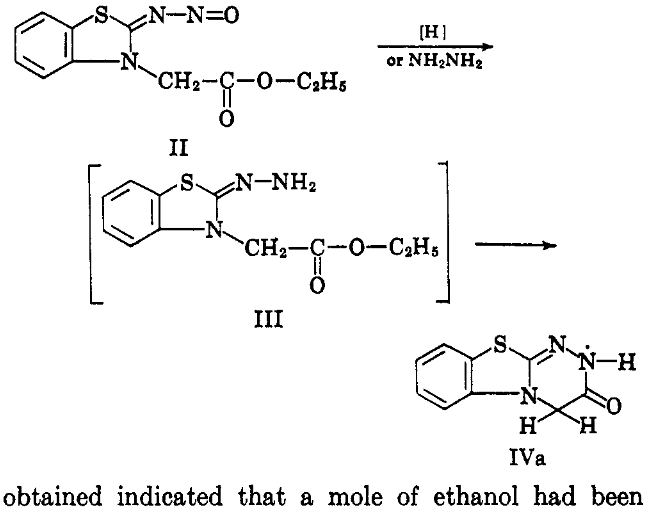
Received September 26, 1967

The only previous report of the 2H-*as*-triazino[3,4-*b*]benzothiazole system (I)[1] is that of Allen and Van Allan.[2] These investigators treated 3-carbethoxymethyl-2-nitrosiminobenzothiazoline (II) with zinc and acetic acid, hoping to obtain the hydrazone III. The nitrogen analysis of the compound which they obtained indicated that a mole of ethanol had been lost, resulting in the product, 2H-3,4-dihydro-*as*-triazino[3,4-*b*]benzothiazol-3-one to which they assigned structure IVa. This structure was confirmed in our laboratory by an apparently unequivocal synthesis which was effected by the reaction of 2-hydrazinobenzothiazole (V) and ethyl bromoacetate. The compound so obtained was identical (infrared spectrum and mixture melting point) with that obtained by following the procedure of Allen and VanAllan. Additional support for this structure was obtained by several other synthetic approaches to this compound (IVa). Hydro-



I



II

III

IVa

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[1] This ring system does not appear in the Ring Index or in its supplements I, II, and III. Compound IVa is not listed in the formula index of Chemical Abstracts. The molecular formula reported for IVa in the experimental section of ref 2, is that of the hydrazone and not IVa.

[2] C. F. H. Allen and J. A. VanAllan, *J. Org. Chem.*, **13**, 603 (1948).

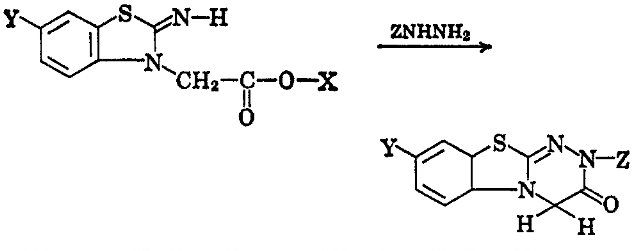
TABLE I

Compd	Method of synthesis	Yield, %	Mp, °C	Crystn solvent	Ir, $\nu_{C=O}$, μ	Uv[a]		Calcd, %			Found, %		
						λ_{max}, mμ	(ϵ_{max})	C	H	N	C	H	N
IVa	C[b]	92.7	260–61	Ethanol	5.99	233 308	17,400 14,400	52.67	3.44	20.47	53.02	3.89	20.12
IVb	C[c]	94.5	181–89 dec	Ethanol	6.02	224 308	17,700 13,500	54.78	4.14	19.16	54.90	4.21	18.94
IVc	C	53.0	<165	2-Propanol	5.99	225 308	19,100 14,100	53.02	4.42	16.86	52.94	4.49	16.86
IVd	C	24.4	182–84	Ethanol	5.98	225 307	20,300 13,400	46.00	2.80	14.63	46.29	2.45	14.55
IVe	G	57.8	191–97	Benzene	6.03	223 229s 308	19,500 18,800 14,100	65.06	4.44	14.23	65.24	4.30	14.22
IVf	D	41.8	196–98	Ethanol	5.98	230 306	19,800 14,600	47.13	3.65	12.69	47.70	3.71	12.86

[a] Taken in methanol. [b] The alternate methods of synthesis gave the following yields: A (31.3%), B (48.9%), D (100%), E (100%), and F (22.9%). [c] Synthesis by method D gave a yield of 63.4%.

genation of the nitrosimino ester (II) using palladium–charcoal catalyst, gave a mixture which was shown by its infrared spectrum to be the hydrazone ester (III) contaminated with a small amount of the triazinone IVa. The infrared spectrum showed, among other bands, an ester carbonyl at 5.78 μ and a lactam carbonyl at 5.99 μ. This hydrazone was characterized no further since it readily underwent ring closure to the triazinone IVa on heating in benzene or ethanol as well as in dilute hydrochloric acid. An alternate synthesis of the triazinone IVa from the nitroso ester II was effected by treatment with hydrazine.

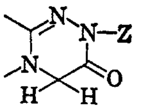
A procedure which appears to be a general synthesis of 2-alkyl-3,4-dihydro-*as*-triazino[3,4-*b*]benzothiazol-3-ones involves treatment of a 3-carboxymethyl-2-iminobenzothiazoline, (VIa and c) or its ethyl ester (VIb), with an alkyl hydrazine. The reaction of a hydrazine with the acid form (VIa and c) was used to make IVa as well as its 2-methyl (IVb) and 2-(2′,2′,2′-trifluoroethyl)-8-ethoxy (IVf) derivatives. The reaction of a hydrazine with the ester VIb was used to synthesize IVa as well as its 2-methyl, 2-(2′-hydroethyl), 2-(2′,2′,2′-trifluoroethyl), and 2-benzyl derivatives (IVb–f).



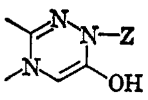
VIa, X = H; Y = H
b, X = C_2H_5; Y = H
c, X = H; Y = OC_2H_5

IVa, Y = H; Z = H
b, Y = H; Z = CH_3
c, Y = H; Z = CH_2CH_2OH
d, Y = H; Z = CH_2CF_3
e, Y = H; Z = $CH_2C_6H_5$
f, Y = OC_2H_5; Z = CH_2CF_3

The infrared spectra (Nujol mulls) of compounds IVb and IVd–f have no peaks in the region of 2.7–3.1 μ. This indicates that there is no OH present. The infrared spectra (KBr) of all of these triazinones (IVa–f) (Table I) have a strong band in the region 5.98–6.03 μ (depending on the substituent at the 2 position), attributable to carbonyl absorption.[3] This evidence favors the lactam VII rather than the lactim VIII form in these compounds.



VII



VIII

Compound VIc was obtained from the reaction of 2-amino-6-ethoxybenzothiazole and sodium chloroacetate.

Experimental Section

Methods of synthesis of 2H- and 2-alkyl-3,4-dihydro-*as*-triazino[3,4-*b*]benzothiazol-3-ones.

A. The method of Allen and VanAllan[2] was used to make 2H-3,4-dihydro-*as*-triazino[3,4-*b*]benzothiazol-3-one (IVa), mp 260–261°. A mixture melting point with the sample prepared by method B was undepressed.

B. To 10% hydrochloric acid (15 ml) was added 1 g of 3-carbethoxymethylbenzothiazoline-2-hydrazone (III). This solution was heated on a steam bath for 1 hr and the resulting mixture cooled and filtered to give 0.40 g of IVa.

C. A mixture of 3-carbethoxymethyl-2-iminobenzothiazoline hydrobromide (II) (0.05 mole) and hydrazine or an alkyl hydrazine (0.10 mole) in 95% ethanol (200 ml) was heated under reflux for 20 hr. The resulting mixture was cooled and the material filtered off and purified by crystallization.

D. A mixture of 3-carboxymethyl-2-iminobenzothiazoline (0.05 mole) and a hydrazine (0.10 mole) in ethanol (200 ml) was heated under reflux for 5 hr. The resulting mixture was cooled and the product filtered off and purified by crystallization.

E. A mixture of 3-carbethoxymethyl-2-nitrosiminobenzothiazoline (II) (7.5 g) and 95% hydrazine (1 ml) in ethanol (100 ml) was heated under reflux for 30 min during which time the orange mixture became colorless and a white solid formed. This mixture was filtered and 6.0 g of IVa obtained.

F. A mixture of 2-hydrazinobenzothiazole (16.5 g), ethyl bromoacetate (16.7 g), and triethylamine (15 ml) in 2-propanol (150 ml) was heated under reflux for 4 hr. The solvent was then concentrated to one-fourth volume, diluted with water, and filtered. The cake was washed with cold 2-propanol to give 4.7 g of IVa.

G. Potassium carbonate (5.0 g) in water (25 ml) was added to benzylhydrazine dihydrochloride (5.0 g) in ethanol (200 ml). Then 3-carbethoxymethyl-2-iminobenzothiazoline hydrobromide (8.14 g) was added and the mixture was heated under reflux for 20 hr. The mixture was cooled and filtered to give 4.3 g of white solid, mp 191–197°.

3-Carbethoxymethylbenzothiazoline-2-hydrazone (III).—A mixture of 3-carbethoxymethyl-2-nitrosiminobenzothiazoline (II)

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(3) W. G. Overend, L. M. Turton, and L. F. Wiggins, *J. Chem. Soc.*, 3500 (1950).

(7.0 g) and 10% palladium on charcoal (1 g) in tetrahydrofuran (200 ml) was shaken under 45 psig of hydrogen until the calculated quantity (2 equiv) was consumed. The mixture was then filtered through a celite pad and the solvent was removed by evaporation *in vacuo* to give 4.1 g (66.1%) of crude material. This material was purified no further. Infrared bands were ν 3.08 and 3.20 (NH_2) and 5.78 μ (ester C=O).

3-Carboxymethyl-6-ethoxy-2-iminobenzothiazoline (VIc).—To 2-amino-6-ethoxybenzothiazole (15 g) in a boiling water–ethanol mixture (400–150 ml) was added sodium chloroacetate (20 g) in water (125 ml). This mixture was heated under reflux for 2 hr. The ethanol was then boiled off and the aqueous mixture cooled and filtered. The filter cake was dried and stirred with 250 ml of boiling benzene for 10 min and then filtered to give 10.4 g (53.4%). This material crystallized from water. On heating, the material did not melt but decomposed slowly between 160 and 240°.

Anal. Calcd for $C_{11}H_{12}N_2O_3S$: N, 11.10. Found: N, 10.75.

Registry No.—IVa, 15315-41-0; IVb, 15315-42-1; IVc, 15315-43-2; IVd, 15315-44-3; IVe, 15315-45-4; IVf, 15315-46-5; VIc, 15315-47-6; III, 15315-48-7.

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1-Pyrazoledithiocarboxylates

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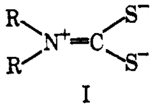
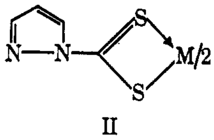
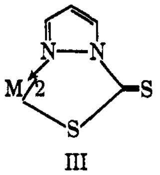
Addition of carbon disulfide to strongly nucleophilic anions yields the anions of dithiocarboxylic acids. Dithiocarbamates, an important class of chelating agents, are produced from secondary amines, base, and carbon disulfide.[1] Much of their stability is attributed to strong ground state contribution of the zwitterionic form, I.


I


II

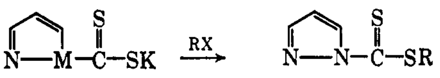

III

It was of interest to prepare 1-pyrazoledithiocarboxylates, since it appeared likely that an analogous structure would be energetically unfavorable[2] and that chelates of structure III rather than II would be formed (with divalent transition metal ions), due to the favorable geometry[3] involved. In a similar case of bis(methylthiohydroxamate)nickel(II), where a question of four *vs.* five-membered ring structure exists, the latter was established by X-ray studies.[4] In fact it should be expected that chelating systems analogous to III will be formed from pyrazolide ion and molecules of general structure A=C=A′ where A,A′ may be for instance, O, S, or NR. Chelates of structure III are also related to those obtained from metal pyrazolides and hexafluoroacetone.[5]

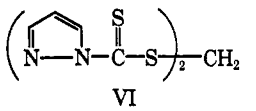
Results and Discussion

Addition of carbon disulfide to a suspension of potassium pyrazolide in benzene or tetrahydrofuran solvent resulted in exothermal formation of a dark yellow solid, soluble in water and alcohols.

This material is moderately stable to storage in a closed container where it develops a pressure of carbon disulfide. The structure IV assigned to it was indicated by the nmr spectrum which was characteristic of 1-substituted pyrazoles. Further support for this structure was obtained by preparing a number of well-characterized derivatives Va–c and VI which were formed in good yields when IV was treated with diverse alkyl halides. Compounds Va–c were bright yellow liquids whereas VI was a bright yellow solid, mp 182–184. They were all indefinitely stable to storage.


IV

Va, R = CH_3
b, R = $CH_2CH{=}CH_2$
c, R = n-C_4H_9


VI

The identity of compounds V and VI was supported, apart from elemental analyses, by their nmr spectra. For instance Va had doublets at τ 1.54 (J = 3.0 cps, further split by 0.75 cps) and 2.33 (J = 1.6 cps, further split by 0.75 cps), a quadruplet made up of two overlapping doublets (J = 3.0 and 1.6 cps) at 3.70, and a singlet at 7.47 with relative areas 1:1:1:3. These were assigned to the 5-H, 3-H, 4-H, and methyl hydrogens, respectively, assuming a correlation between coupling constants similar to that found for other 1-substituted pyrazoles.[6]

Similarly, methylenebis(1-pyrazoledithiocarboxylate) (VI) had doublets at τ 1.39 (J = 2.9 cps) and 2.20 (J = 1.6 cps), a quadruplet made up of two overlapping doublets at 3.52 (J = 2.9, 1.6 cps), and a singlet at 4.78 in 1:1:1:1 ratio, assigned to the 5-H, 3-H, 4-H, and methylene protons, respectively.

Sodium 1-pyrazoledithiocarboxylate was prepared analogously from sodium pyrazolide and carbon disulfide. It was less stable to storage than the potassium salt. Solutions of alkali metal 1-pyrazoledithiocarboxylates are less stable than the solid salts, particularly on the acid side. Here the decomposition by acid is even faster than that of alkali dithiocarbamates

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[1] See, for instance, G. D. Thorn and R. A. Ludwig, "The Dithiocarbamates and Related Compounds," Elsevier Publishing Co., Amsterdam, 1962.

[2] The amount of resonance energy gained by the $N^+{=}C{-}S_2^{-2}$ system would not compensate for the loss of the resonance energy of pyrazole, variously estimated from 27 to 41 cal: H. Zimmerman and H. Geisenfelder, *Z. Electrochem.*, **65**, 368 (1961); A. F. Bedford, P. B. Edmondson, and C. T. Mortimer, *J. Chem. Soc.*, 2927 (1962).

[3] This may be inferred from the formation of a hydrogen-bonded adduct of pyrazole with formaldehyde (R. Hüttel and P. Jochum, *Ber.*, **85**, 820 (1952)) and the facility with which a 1-(2,3-dibromopropyl)pyrazole undergoes cycloquaternization (S. Trofimenko, *J. Am. Chem. Soc.*, **87**, 4393 (1965); T. W. G. Solomons and C. F. Voigt, *ibid.*, **87**, 5256 (1965)).

[4] T. Sato, K. Nagata, Y. Tsukuda, M. Shiro, and H. Koyama, *Chem. Commun.*, 215 (1967).

[5] W. Mahler, U. S. Patent 3,265,705 (1966).

[6] L. G. Tensmeyer and C. Ainsworth, *J. Org. Chem.*, **31**, 1878 (1966), and references cited therein.