100 ml of methanol was added with stirring 2.0 g (0.05 mole) of sodium hydroxide in 100 ml of methanol and 2.4 g (0.055 mole) of sodium cyanide in 100 ml of methanol. Sodium sulfite precipitated almost instantaneously from the mixture which was then permitted to stand overnight. The sodium sulfite was filtered from the reaction mixture and the filtrate was evaporated to dryness *in vacuo* giving a heavy oil. The product was treated in a benzene solution with anhydrous hydrogen chloride and the solvent was evaporated. The resulting semicrystalline mass was treated with ether and recrystallized from 2-propanol–ether to give 9.78 g (70%) of 3-decyl-2-iminothiazolidine hydrochloride, mp 105–107°.

Anal. Calcd for $C_{13}H_{27}ClN_2S$: C, 55.98; H, 9.76; N, 10.04; S, 11.50. Found: C, 56.08; H, 9.72; N, 9.73; S, 11.72.

2-Methylamino-2-thiazoline.—To a solution of 104.4 g (0.4 mole) of 2-(methylthio)-2-thiazoline hydriodide in 800 ml of ethanol was added 27.0 g (0.4 mole) of methylamine hydrochloride and 16.0 g (0.4 mole) of sodium hydroxide in 80 ml of water. The reaction mixture was heated at reflux for 16 hr. After cooling the mixture to room temperature, a solution of 16.0 g (0.4 mole) of sodium hydroxide in 80 ml water was added. The resultant solution was heated on a steam bath to remove the methyl mercaptan formed in the reaction and the solution was then evaporated to dryness *in vacuo*. The residue was extracted with five 200-ml portions of boiling hexane and the hexane was cooled to yield 24.6 g (53%) of 2-methylamino-2-thiazoline as colorless needles. The product after recrystallization from hexane melted at 88.5–90° (lit.[10] mp 90°).

2-Decylamino-2-thiazoline.—A solution of 13.0 g (0.05 mole) of 2-(methylthio)-2-thiazoline hydriodide and 7.8 g (0.05 mole) of decylamine in 125 ml of ethanol was heated at reflux for 17 hr and cooled to room temperature. Sodium hydroxide (2.0 g, 0.05 mole) was added and the resultant solution was evaporated to dryness *in vacuo*. The residue was extracted with three 250-ml portions of boiling chloroform and the combined chloroform extracts were dried over anhydrous magnesium sulfate and evaporated to dryness *in vacuo* giving an oil which crystallized on cooling. The 2-decylamino-2-thiazoline, 11.8 g (95%), was recrystallized from acetonitrile, mp 60–62°.

Anal. Calcd for $C_{13}H_{26}N_2S$: C, 64.40; H, 10.81; N, 11.55; S, 13.23. Found: C, 64.55; H, 11.04; N, 11.53; S, 13.11.

Registry No.—I, 1779-81-3; 2-amino-2-selenazoline, 15267-04-6; H_2S, 7783-06-4; V, 15267-06-8; VI, 15267-03-5; VII, 15267-07-9; X, 15267-08-0; 3-decyl-2-iminothiazolidine hydrochloride, 15267-09-1; 2-methylamino-2-thiazoline, 10416-51-0; 2-decylamino-2-thiazoline, 15267-11-5.

Acknowledgment.—The authors thank Dr. Thomas R. Sweeney for helpful discussions in the course of this work.

Synthesis of 1H-Aziridine-2-carboxanilides

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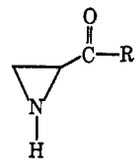
In the course of some other studies we required a facile synthesis of a series of 1H-aziridine-2-carboxanilides (**1c**). The problem of synthesis of aziridines[1] having the gross structure **1** is complicated by several factors. Most of the versatile 1H-aziridine syntheses involve as a first step the initial addition of some electrophile to an olefin, *e.g.*, iodoisocyanate,[2] nitrosyl



1a, R = alkyl, aryl
b, R = O-alkyl
c, R = N-alkyl
aryl

chloride,[3] and carbethoxynitrene.[4] However, the olefin precursor of **1** is an electrophile itself and reaction with the above-mentioned reagents does not occur.[5] There are indeed three known syntheses of compounds such as **1**: (a) reaction of a 2,3-dibromo ester with liquid ammonia,[6] (b) Michael addition of O-methylhydroxylamine followed by base,[7] and (c) reaction of an iodine–ammonia mixture with an unsaturated ketone.[8] Unfortunately, each reaction has severe limitations. Method a works only with liquid esters soluble in liquid ammonia.[5] Sequence b is hampered by the high cost, volatility, toxicity, and weak nucleophilicity of the reagent. Method c is successful only with very electrophilic olefins, *e.g.*, chalcones.[5,8] None of these procedures has been capable of generating aziridine-2-carboxanilides (**1c**).[5] We have devised a synthesis of these compounds that is related to an azirine synthesis.[9]

Addition of 1,1-dimethylhydrazine to N-isopropylacrylanilide (**2a**) occurs quantitatively (see Scheme I). Quaternization of this hydrazine **3a** with methyl iodide is quite facile producing **4a**. When methiodide **4a** is refluxed with sodium methoxide in ethanol, trimethylamine is evolved and aziridine **1c** is generated in 57% yield. When the sequence is applied to **2b** the corresponding aziridine is formed in 27% over-all yield.

We feel that this aziridine synthesis fully complements existing procedures and will be quite useful when older methods fail. The full scope of the reaction has yet to be realized.

Experimental Section[10]

N-Phenyl-N-isopropylacrylamide (2a).—To 73 g (0.81 mole) of acryloyl chloride in 1.5 l. of ether cooled in a Dry Ice–acetone bath was added slowly with stirring 135 g (1.62 mole) of N-isopropylaniline. The mixture was warmed to 25° and filtered. The filtrate was concentrated an triturated with pentane to induce crystallization. Recrystallization of the product from pentane gave 150 g (98%) of white needles, mp 33–34°. The nmr spectrum showed absorption at δ 1.1 (6 H doublet, isopropyl), 4.9 (1 H multiplet, isopropyl), 5.2–6.4 (3 H, ABX multiplet, olefinic), and 7.2 (5 H aromatic multiplet).

Anal. Calcd for $C_{12}H_{15}NO$: C, 76.25; H, 7.99. Found: C, 76.15; H, 7.84.

(1) For a general survey of aziridine syntheses, see P. A. Fanta in "Heterocyclic Compounds," Vol. 19, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1965, p 524.

(2) A. Hassner and C. Heathcock, *Tetrahedron*, **20**, 1037 (1963).

(3) G. L. Closs and S. J. Brois, *J. Am. Chem. Soc.*, **82**, 6068 (1960).

(4) W. Lwowski and T. W. Mattingly, Jr., *ibid.*, **87**, 1947 (1965).

(5) Unpublished work from these laboratories.

(6) British Patent No. 847,205 (to F. Hoffman-La Roche and Co.); *Chem. Abstr.*, **55**, 7433e (1961).

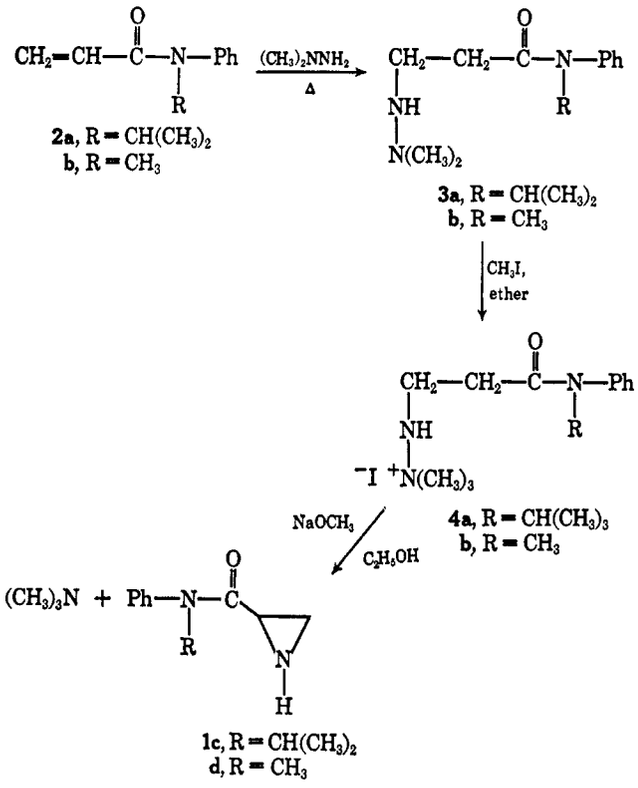
(7) A. H. Blatt, *J. Am. Chem. Soc.*, **61**, 3494 (1939). This reaction was rediscovered by N. H. Cromwell and H. Hoeksema [*ibid.*, **71**, 708 (1949)].

(8) P. L. Southwick and D. R. Christman, *ibid.*, **74**, 1886 (1952). We have applied this reaction to many substituted chalcones with excellent results.

(9) (a) R. F. Parcell, *Chem. Ind.* (London), 1936 (1963). (b) P. A. S. Smith and E. E. Most, Jr., *J. Org. Chem.*, **22**, 358 (1957). (c) D. F. Morrow, M. E. Butler, and E. C. Y. Huang, *ibid.*, **30**, 579 (1965).

(10) Melting points are corrected; boiling points are uncorrected. The nmr spectra were recorded on a Varian A-60 spectrometer using deuteriochloroform as solvent and tetramethylsilane as an internal standard. Chemical shifts are reported in parts per million downfield from the standard. Magnesium sulfate was used for drying.

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.

(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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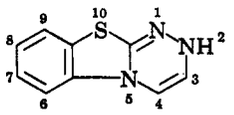
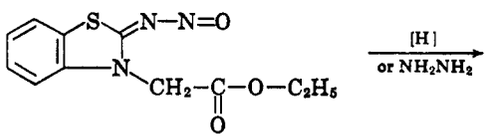
The only previous report of the 2H-*as*-triazino-[3,4-*b*]benzothiazole system (I)[1] is that of Allen and

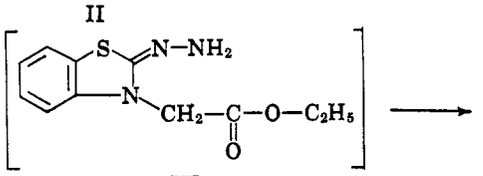


I

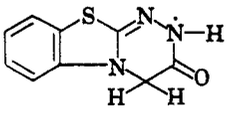
Van Allan.[2] These investigators treated 3-carbethoxymethyl-2-nitrosiminobenzothiazoline (II) with zinc and acetic acid, hoping to obtain the hydrazone III. The nitrogen analysis of the compound which they



II



III



IVa

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-

(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).