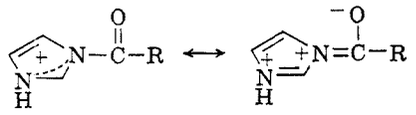
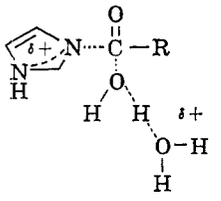
tonated to afford a good leaving group,[19] resonance between the ring and the carbonyl would necessitate the importance of resonance structures having more than one positive charge residing on the imidazole ring which should not be favorable in comparison to the resonance structures that can be written for the neutral species. Thus, if inhibition of resonance was



the principle cause of the observed abnormal order of reactivity in reactions of the neutral species then it would be expected that a more nearly normal order would be obtained in the hydrolysis of N-acylimidazolium ions which, of course, is not the case. Also, ground-state effects such as steric inhibition of resonance between the ring and the carbonyl would not explain why a normal steric order is obtained in the aminolysis reaction with diethylamine.[7] Thus, there is apparently a feature of the hydrolysis transition state which allows the accelerating effect due to acyl group branching to become important.

A transition state for the hydrolysis of N-acylimidazolium ions in which the carbon–nitrogen bond is breaking in concert with nucleophilic attack by a water



molecule, so that relief of strain would occur, is consistent with all of the data presently available. This mechanism is exactly analogous to that proposed previously[1] for the imidazole-catalyzed hydrolysis of the neutral species.

All of the compounds hydrolyze more slowly in acidic D_2O, k_H/k_D being equal to or greater than 2.26 in each case. These values are in accord with proton transfer in the rate-determining step[20] as shown, although neither the actual number of water molecules involved nor their mode of action can be specified with certainty. Jencks and Carriuolo[21] have previously suggested that in the hydrolysis of N-acetylimidazolium ion more than one molecule of water is involved, arriving at this conclusion on the basis of the D_2O solvent isotope effect, large negative ΔS^*, and salt and acid effects.

A concerted type of mechanism, such as shown, in which the leaving group departs as the nucleophile attacks, would not involve a kinetically significant tetrahedral intermediate in which the oxygen atoms can become equivalent and, therefore, it would be predicted that O^{18} exchange into the amide carbonyl would not occur when the reaction was run in water enriched with O^{18}. This is consistent with the results obtained by Bunton[6] in a study of the hydrolysis of N-acetylimidazolium ion where little O^{18} exchange was found.

Acknowledgment.—This work was supported by grants from the National Institutes of Health and the American Cancer Society. We also wish to acknowledge tuition support for J. A. F. from the National Institutes of Health Research Training Grant GM 197. The program for the calculation of the rate constants was written by Mr. Laszlo Engelman of the University of Southern California Computer Sciences Laboratory.

(19) This assumption is supported by the finding of Wolfenden and Jencks[4] that the hydrolysis of 1-acetyl-3-methylimidazolium ion serves as a model for the hydrolysis of N-acetylimidazolium ion.

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(21) W. P. Jencks and J. Carriuolo, *J. Am. Chem. Soc.*, **83**, 1743 (1961).

Benzo[c]quinolizinium Salts *via* Intramolecular Cylization[1,2]

ALAN FOZARD AND C. K. BRADSHER

Department of Chemistry, Duke University, Durham, North Carolina

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cis-2′-Chloro-2-stilbazoles, obtained by irradiation of the *trans* form with ultraviolet light, cyclize intramolecularly at suitable temperatures affording benzo[*c*]quinolizinium salts. A direct formation of benzo[*c*]quinolizinium salts is achieved by treating *trans*-2′-chloro-2-stilbazoles with iodine at high temperatures. Certain 5-substituted benzo[*c*]quinolizinium salts are obtained directly in the initial condensation between an α-substituted picoline and 2-chlorobenzaldehyde.

Earlier work carried out in this laboratory has afforded convenient methods for the synthesis of the benzo[*a*]-[3–5] (phenanthridizinium) and the benzo[*b*]-quinolizinium[6–7] (acridizinium) ions. A convenient method has now been found for the synthesis of the hitherto difficulty accessible[8–9] benzo[*c*]quinolizinium ion III.

It seemed logical to expect that the benzo[*c*]quinolizinium system might be prepared by the intramolecular quaternization of a *cis*-2′-chloro-2-stilbazole. For the initial attempt it was decided to prepare *cis*-2′-chloro-4′-nitro-2-stilbazole (II, $R_4 = NO_2$; X = Cl) in which the chlorine atom is activated by a *p*-nitro group. *trans*-2′-Chloro-4′-nitro-2-stilbazole (Ib) was

(1) This work was described in a preliminary communication by A. Fozard and C. K. Bradsher, *Chem. Commun.*, 288 (1965).

(2) This research was supported by a grant (CA-05509) from the National Cancer Institute of the National Institutes of Health.

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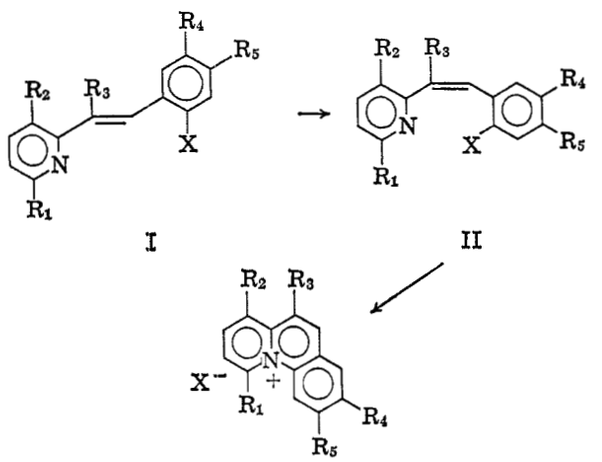
(9) *Cf.* O. Westphal, K. Jann and W. Heffe, *Arch. Pharm.*, **294**, 37 (1961).

TABLE I

trans-2′-HALO-2-STILBAZOLES

Compd I	R_1	R_2	R_3	R_4	R_5	X	Yield, %	Mp or bp, °C (mm)	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
a	H	H	H	H	H	Cl	62	75–76.5[a–c]	$C_{13}H_{10}ClN$	72.38	4.67	6.49	...	...	...
b	H	H	H	NO_2	H	Cl	73	122–122.5[d,e]	$C_{13}H_9ClN_2O_2$	59.90	3.48	10.74	59.67	3.55	10.63
c	H	CH_3	H	NO_2	H	Cl	80	141–142.5[d,e]	$C_{14}H_{11}ClN_2O_2$	61.19	4.04	10.19	61.09	4.15	10.17
d	H	CH_3	H	H	H	Cl	70	100–102[a,f]	$C_{14}H_{12}ClN$	73.20	5.27	6.09	73.40	5.29	6.16
e	H	H	H	H	Cl	Cl	62	75–76[a,f]	$C_{13}H_9Cl_2N$	62.40	3.63	5.59	62.32	3.59	5.50
f	H	CH_3	H	H	Cl	Cl	69	116–118[a,f]	$C_{14}H_{11}Cl_2N$	63.65	4.21	5.30	63.55	4.18	5.19
g	H	H	CH_3	H	H	Cl	69	163 (3)[g]	$C_{14}H_{12}ClN$	73.20	5.27	6.09	73.18	5.28	5.97
h	H	H	C_6H_5	H	H	Cl	57	80.5–82[a,h]	$C_{19}H_{14}ClN$	78.20	4.83	4.80	78.26	5.00	5.10
i	CH_3	H	H	H	H	Cl	50	154 (1)[g]	$C_{14}H_{12}ClN$	73.20	5.27	6.09	73.18	5.56	5.98
j	H	H	H	H	H	I	50	63–64[a,f]	$C_{13}H_{10}IN$	50.84	3.29	4.56	51.35	3.46	4.56

[a] Recrystallized from 60–90° ligroin. [b] Colorless blunt needles. [c] Lit.[10] mp 76–77°. [d] Recrystallized frome thanol. [e] Pale yellow needles. [f] Colorless needles. [g] Colorless liquid. [h] Colorless rhombs.



I II III

R groups not otherwise designated are hydrogen

prepared by the well-known condensation reaction[10] between 2-picoline and an aromatic aldehyde (2-chloro-5-nitrobenzaldehyde, in this case) in boiling acetic anhydride. A benzene solution of the new stilbazole I (R_4 = NO_2, X = Cl) when irradiated with ultraviolet light[11] gave not the expected isomer, but a salt which precipitated in 70% yield over a period of 48 hr. Elemental analysis of the salt and comparison of its ultraviolet spectrum with that of the unsubstituted benzo[*c*]quinolizinium cation III[8] indicated that the new product was 8-nitrobenzo[*c*]quinolizinium chloride (IIIb, X = Cl).

When the method was extended to *trans*-2′-chloro-2-stilbazole (Ia) no precipitation occurred during irradiation, but the ultraviolet spectra of samples taken at intervals during the irradiation showed a shift in absorption to shorter wavelengths which was complete after 48 hr. The product was almost exclusively *cis*-2′-chloro-2-stilbazole (II, X = Cl). On heating this *cis* isomer at 170° for 1 hr, cycloquaternization occurred to give pure benzo[*c*]quinolizinium chloride IIIa (X = Cl) in 55% yield. The only by-product was the *trans*-stilbazole Ia. Purification of the *cis*-stilbazole II (X = Cl) was subsequently found to be unnecessary, the crude material giving a 50% yield of the quinolizinium salt IIIa (X = Cl) when heated.

Attempts were then made to eliminate the irradiation step by heating *trans*-2′-chloro-2-stilbazole (Ia) at higher temperatures in the presence of iodine. When heated at 240° for 6 hr, an 80% yield of very impure benzo[*c*]quinolizinium perchlorate IIIa (X = ClO_4) could be isolated though purification reduced this yield to 54%. At lower temperatures the yield was appreciably reduced while the use of higher temperatures caused considerable decomposition.

The *trans*-2′-iodo-2-stilbazole (Ij) was of interest as it was hoped that after isomerization to the *cis* isomer II (X = I) the better leaving properties of the iodine atom would permit cycloquaternization to occur at a much lower temperature than the analogous *cis*-chlorostilbazole IIa. However, no change occurred on irradiation of the *trans* form Ij and it is assumed that steric hindrance is the dominant factor preventing formation of the *cis* isomer.

Several substituted 2′-chloro-2-stilbazoles (Table I) were prepared; benzo[*c*]quinolizinium derivatives were successfully prepared from them by the methods described (Table II). It was generally found that electron-attracting groups in the benzene ring of the stilbazole or electron-donating groups in the pyridine ring tended to increase the yield of cyclized products and often allowed the use of lower cyclization temperatures. On irradiation, *trans*-2′-chloro-6-methyl-2-stilbazole (Ii) gave the *cis* isomer II (R_1 = CH_3, X = Cl) which failed to cyclize even under extreme conditions of temperature. This unreactivity is presumably due to steric hindrance analogous to the steric strain reported[12] to make 4,6-dimethylquinolizinium salts difficult to prepare.

From steric considerations it might be predicted that α-substituted stilbazoles would form the *cis* isomer to some extent in the initial condensation between an α-substituted picoline and an aromatic aldehyde, but the ultraviolet spectra of the α-methyl- and α-phenyl-2′-chloro-2-stilbazoles (Ig and Ih) indicated that very little, if any, of the *cis* form was present. Heating the *trans*-α-phenylstilbazole (Ih) failed to effect cyclization although the phenylquinolizinium salt IIIh (X = Cl)

(10) *Cf.* L. Horwitz, *J. Org. Chem.*, **21**, 1039 (1956). The great majority of stilbazoles prepared in this manner are obtained in the *trans* form. *cis* and *trans* isomers are readily distinguished by their ultraviolet absorption spectra, the *cis* isomer showing a characteristic shift to shorter wavelengths.

(11) J. L. R. Williams, S. K. Webster, and J. A. Van Allan, *ibid.*, **26**, 4893 (1961).

(12) V. Boekelheide, H. Fritz, J. M. Ross, and H. X. Kaempfur, *Tetrahedron*, **20**, 33 (1964). See also H. V. Hansen and E. D. Amstutz, *J. Org. Chem.*, **28**, 393 (1963).

TABLE II
BENZO[c]QUINOLIZINIUM SALTS

Compd III	R_1	R_2	R_3	R_4	R_5	X	Method	Cyclization temp, °C	Time, hr.	Yield,[a] %	Mp, °C	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
a	H	H	H	H	H	Cl	A	170	1	50[b,c]	247–249	$C_{13}H_{10}ClN \cdot 0.5H_2O$	69.50	4.94	6.23	69.71	5.16	6.45
	H	H	H	H	H	ClO_4	B	240	6	54[d]	187–189[e]	$C_{13}H_{10}ClNO_4$	55.82	3.61	5.09	...	...	...
	H	H	H	H	H	Br	B	240	6	50[c,f]	241–243	$C_{13}H_{10}BrN$	60.00	3.88	5.38	59.66	3.96	5.11
b	H	H	H	NO_2	H	Cl	A	25	48	80[b,i,g]	306 dec	$C_{13}H_9ClN_2O_2 \cdot H_2O$	56.15	3.95	9.93	55.83	3.95	10.08
	H	H	H	NO_2	H	ClO_4[h]	...	...	...	d	245–247	$C_{13}H_9ClN_2O_6$	48.09	2.79	8.63	47.64	2.64	8.63
c	H	CH_3	H	NO_2	H	Cl	A	25	48	80[b,i,g]	318 dec	$C_{14}H_{11}ClN_2O_2$	61.19	4.04	10.19	61.23	4.19	9.99
d	H	CH_2	H	H	H	Cl	A	165	1	69[b,c]	300–302	$C_{14}H_{12}ClN$	73.20	5.27	6.09	73.01	5.41	5.82
e	H	H	H	H	Cl	Cl	A	170	1	70[b,c]	355 dec	$C_{13}H_9Cl_2N$	62.40	3.63	5.59	62.41	3.65	5.67
	H	H	H	H	Cl	ClO_4	B	240	6	60[d]	260–262	$C_{13}H_9Cl_2NO_4$	49.68	2.87	4.46	49.56	2.87	4.34
f	H	CH_2	H	H	Cl	Cl	A	155	1	77[b]	274–276	$C_{14}H_{11}Cl_2N \cdot 0.5H_2O$	61.53	4.43	5.12	61.76	4.29	4.95
g	H	H	CH_3	H	H	Cl	A	210	1	55[b,j]	273	$C_{14}H_{11}ClN \cdot 0.25H_2O$	72.11	5.40	6.01	72.04	5.34	6.37
	H	H	CH_3	H	H	ClO_4[h]	...	...	...	g	217–218	$C_{14}H_{11}ClNO_4$	57.23	4.12	4.76	56.89	4.10	4.76
h	H	H	C_6H_5	H	H	Cl	A	200	2	50[b,c]	286–287	$C_{19}H_{14}ClN$	78.20	4.83	4.80	77.77	4.88	4.83
	H	H	C_6H_5	H	H	ClO_4	C	140	15	2[d]	264–265	$C_{19}H_{14}ClNO_4$	64.13	3.96	3.94	64.14	4.01	3.84
i	H	H	$COOC_2H_5$	H	H	ClO_4	C	140	15	20[j]	213.5–215	$C_{16}H_{14}ClNO_6$	54.64	4.01	3.98	54.49	4.02	3.89

[a] Based on *trans*-stilbazole initially used. [b] Cyclization carried out on unpurified *cis–trans* mixture from irradiation. [c] Tan irregular clusters from ethanol–ethyl acetate. [d] Tan needles from ethanol. [e] Lit.[8] mp 188–189°. [f] Prepared *via* the perbromide. [g] Small tan needles from ethanol. [h] Prepared by addition of 25% perchloric acid to the chloride. [i] Allowed to stand for 48 hr after irradiation. [j] Tan needles from acetonitrile–ethyl acetate.

could be prepared in good yield by the isomerization procedure described. However, the reaction product from the condensation between 2-benzylpyridine and α-chlorobenzaldehyde in acetic anhydride contained a small amount of 5-phenylbenzo[*c*]quinolizinium chloride (IIIh, X = Cl) isolated as the perchlorate, indicating that some *cis*-stilbazole II ($R_3 = C_6H_5$; X = Cl) must have formed during the course of the reaction. In a similar reaction between ethyl 2-pyridylacetate and *o*-chlorobenzaldehyde, a 20% yield of pure 5-carboethoxybenzo[*c*]quinolizinium perchlorate (IIIi, X = ClO_4) was obtained directly. The actual yield was probably greater as no stilbazole could be isolated from the reaction mixture.

Experimental Section

All analyses were carried out by Janssen Pharmaceutica, Beerse, Belgium. The melting points were determined in capillary tubes using the Laboratory Devices Mel-Temp apparatus and are uncorrected. The ultraviolet absorption spectra (Table III) were measured in 95% ethanol using a Cary Model 14 spectrometer. Photochemical irradiations were carried out in Pyrex vessels using a 250-w Type ME/D box lamp operating on a dc 110-v supply and placed 6 in. from the sample.

Preparation of the *trans*-Stilbazoles. *trans*-2′-**Chloro-2-stilbazole.**—2-Chlorobenzaldehyde (14.0 g, 0.1 *M*) and 2-picoline (9.3 g, 0.1 *M*) in acetic anhydride (15 ml) were heated under reflux for 16 hr. The excess reagents were stripped off under reduced pressure [100° (2 mm)], and the residue was dissolved in benzene and chromatographed through a column of neutral alumina. Evaporation of the eluent and cooling caused the stilbazole Ia to crystallize. The crystalline solid was suspended in ligroin (bp 60–90°), filtered, and then recrystallized from ligroin to yield 14.0 g (62%) of colorless blunt needles, mp 75–76.6°.

cis-2′-**Chloro-2-stilbazole (II, X = Cl).**—*trans*-2′-Chloro-2-stilbazole (5.0 g) was dissolved in dry thiophene-free benzene (400 ml) in a 600-ml Pyrex beaker and the stirred solution was irradiated. Continuous cooling (to 25°) was provided by a cold finger condenser immersed in the benzene solution. During the course of the reaction, samples were taken and the ultraviolet spectra of the stilbazole was determined. As the reaction proceeded, a shift of the long wavelength maximum from 309 of the *trans* isomer to 285 mμ of the *cis* form occurred. The shift was complete after 48 hr. The benzene was then evaporated on a water bath and the residue was distilled under reduced pressure, giving 3.05 g (61%) of a colorless liquid: bp 130° (0.8 mm); λ_{max} 285 mμ (log ε 4.03).

Anal. Calcd for $C_{13}H_9ClN$: C, 72.40; H, 4.67; N, 6.49. Found: C, 72.27; H, 4.51; N, 6.57.

The **methiodide** crystallized from ethanol as colorless blunt needles, mp 207–208°.

Anal. Calcd for $C_{14}H_{13}ClIN$: C, 46.86; H, 3.65; N, 3.90. Found: C, 46.98; H, 3.68; N, 3.87.

cis-2′-**Chloro-6-methyl-2-stilbazole (II, $R_1 = CH_3$; X = Cl).**—Prepared as above from the *trans* isomer Ih in 55% yield, the *cis*-stilbazole had bp 123–125° (0.2 mm), λ_{max} 290 mμ (log ε 4.07).

Anal. Calcd for $C_{14}H_{11}ClN$: C, 73.20; H, 5.27; N, 6.09. Found: C, 72.87; H, 5.32; N, 5.96.

The **methiodide** crystallized from ethanol as blunt yellow needles, mp 196–198°.

Anal. Calcd for $C_{15}H_{14}ClIN$: C, 48.47; H, 4.06; N, 3.77. Found: C, 48.65; H, 4.17; N, 3.70.

The *trans*-**methiodide** prepared from the *trans*-stilbazole Ih crystallized from ethanol as yellow needles, mp 229.5–230°.

Anal. Calcd for $C_{15}H_{14}ClIN$: C, 48.47; H, 4.06; N, 3.77. Found: C, 48.33; H, 4.04; N, 3.62.

General Methods of Cyclization. Method A. Benzo[*c*]-quinolizinium Chloride (IIIa, X = Cl).—*trans*-2′-Chloro-2-stilbazole (Ia) (5 g) in dry thiophene-free benzene (400 ml) was irradiated for 48 hr as in the synthesis of *cis*-2′-chloro-2-stilbazole. The benzene solution from the irradiation was decolorized by passage through a neutral alumina column. The benzene was then evaporated and the crude *cis*-stilbazole was heated in an

TABLE III

ULTRAVIOLET ABSORPTION SPECTRA OF BENZO[c]QUINOLIZINIUM SALTS[a]

Compd III	Substituent	Anion	Maximum, mμ (log ε)
a	...	Cl	229 (4.27), 255 (4.42), 280 (3.98), 295[b] (3.62), 332[b] (3.68), 349 (4.03), 365 (4.16)
b	8-NO_2	Cl	255 (4.54), 288 (4.10), 310[b] (3.94), 342[b] (3.66), 357 (4.01), 374 (4.06)
c	4-CH_3, 8-NO_2	Cl	255 (4.57), 291 (4.02), 305[b] (3.92), 320 (3.79), 346 (3.72), 361 (4.06), 379 (4.12)
d	4-CH_3	Cl	231 (4.02), 256 (4.40), 285 (3.83), 305[b] (3.46), 333[b] (3.62), 354 (4.02), 371 (4.16)
e	9-Cl	Cl	234 (4.26), 260 (4.45), 300[b] (3.64), 340[b] (3.72), 357 (4.08), 374 (4.19)
f	4-CH_3, 9-Cl	Cl	234 (4.17), 258 (4.46), 303[b] (3.59), 313 (3.65), 345[b] (3.65), 361 (4.09), 379 (4.22)
g	5-CH_3	Cl	230 (4.13), 258 (4.36), 284 (3.88), 304[b] (3.46), 340[b] (3.46), 358 (3.88), 374 (3.98)
h	5-C_6H_5	Cl	236 (4.27), 258 (4.47), 310[b] (3.70), 361 (3.92), 375 (4.00)
i	5-$COOC_2H_5$	ClO_4	233 (4.32), 262 (4.62), 310[b] (3.82), 335 (3.82), 350 (4.12), 367 (4.23)

[a] Determined in 95% ethanol. [b] Infraction.

erlenmeyer flask (oil bath) for 1 hr at 170°. During this heating the product was slowly precipitated as a tan crystalline solid. The reaction mixture which was almost completely solid was cooled and then treated with boiling ethyl acetate. Filtration gave 2.5 g (50%) of pure benzo[c]quinolizinium chloride IIIa (X = Cl), mp 247–249°. Recrystallization from 95% ethanol–ethyl acetate produced no change in melting point. Evaporation of the ethyl acetate filtrate gave *trans*-2′-chloro-2-stilbazole (Ia) which recrystallized from ligroin (bp 60–90°) to yield 2.0 g (40%).

When the purified *cis* isomer IIa (X = Cl) was cyclized by heating at 170° for 1 hr, a 55% yield of the quinolizinium salt IIIa (X = Cl), based on *cis* isomer initially used, was obtained.

Method B. Benzo[c]quinolizinium Perchlorate (IIIa, X = ClO_4).—*trans*-2′-Chloro-2-stilbazole (2.0 g) and iodine (0.2 g) were heated at 240° for 6 hr. The semisolid mass was cooled, triturated several times with boiling ethyl acetate; and, the insoluble residue was dissolved in water and filtered. The aqueous solution was decolorized with charcoal and 25% perchloric acid was added. On filtration there was obtained 1.7 g of crude product which, after three recrystallizations from ethanol, was reduced to 1.2 g (55%) of tan needles, mp 187–189°.

The **bromide IIIa** (X = Br) was obtained from the aqueous solution by addition of 10% bromine in 50% aqueous hydrobromic acid to precipitate the perbromide IIIa (X = Br_3). Boiling this for 30 min in 50% aqueous acetone and evaporating to dryness gave the bromide IIIa (X = Br). Recrystallization from ethyl alcohol–ethyl acetate gave 1.2 g of tan irregular crystals, mp 241–243°.

Method C. 5-Carboethoxybenzo[c]quinolizinium Perchlorate (IIIi, X = ClO_4).—Ethyl 2-pyridylacetate (4.1 g), *o*-chlorobenzaldehyde (3.5 g), and acetic anhydride (5 ml) were refluxed for 15 hr. The acetic anhydride was evaporated and the residue was poured into water (150 ml). The aqueous layer was decanted from the black oily solid and treated with aqueous 25% perchloric acid (1 ml) precipitating very impure material which was filtered off and discarded. The filtrate was treated with excess 25% perchloric acid and the precipitate was collected. Crystallization from acetonitrile–ethyl acetate gave 1.4 g (20%) of tan needles, mp 212–215°.

2-Amino-Δ²-thiazolines from Aminoethyl Thiosulfates. The Mass Spectra of 2-Amino-Δ²-thiazolines and Related Compounds

DANIEL L. KLAYMAN AND GEORGE W. A. MILNE

Walter Reed Army Institute of Research, Division of Medicinal Chemistry, Washington, D. C. 20012, and The National Institutes of Health, National Heart Institute, Laboratory of Metabolism, Bethesda, Maryland 20014

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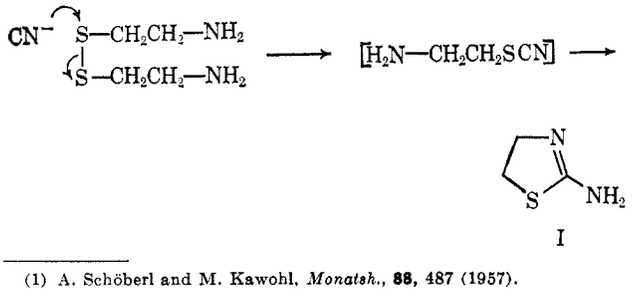
The attack of cyanide ion on primary and secondary aminoethyl thiosulfates yields 2-amino-Δ²-thiazolines. 2-Aminoethyl 2-aminoethanethiolsulfonate and 2-aminoethyl 2-aminoethanethiolsulfinate on treatment with cyanide also yield 2-amino-Δ²-thiazoline (I). The mass spectra of I, three isomeric methyl-2-amino-Δ²-thiazolines, 2-imino-3-amidinothiazolidine, and 2-amino-5,6-dihydro-4H-1,3-thiazine, made from thiosulfates by the above method, as well as 2-methylamino-Δ²-thiazoline and 2-amino-Δ²-selenazoline, have been analyzed and found to support the assigned structures. A previously undescribed variation of the McLafferty rearrangement is reported.

Among the various methods for the preparation of 2-amino-Δ²-thiazoline (I) is the reaction of cyanide ion with cystamine [bis(2-aminoethyl) disulfide].[1] The presumed intermediate, 2-aminoethylthiocyanate, cyclizes rapidly and has not been isolated. Footner and Smiles[2] reported that the action of cyanide ion on alkyl thiosulfates (Bunte salts) gives alkylthiocyanates and sulfite. When this reaction was applied to sodium 2-aminoethyl thiosulfate, a good yield of I was obtained. The cyanide displacement of sulfite from thiosulfate was tried on several other representative primary and secondary aminoethanethiosulfates to give the corresponding 2-amino-Δ²-thiazolines or 2-iminothiazolidines, when N-substituted aminoethanethiosulfates were the starting materials. This reaction was used to prepare 2-imino-3-methylthiazolidine



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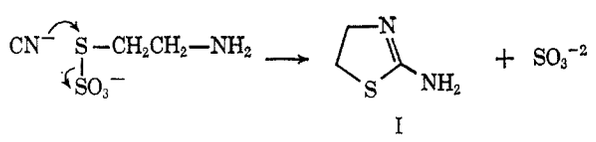

I

(1) A. Schöberl and M. Kawohl, *Monatsh.*, **88**, 487 (1957).

(2) H. B. Footner and S. Smiles, *J. Chem. Soc.*, **127**, 2887 (1925).