0.269 g. of starting material, (±)-IV (12% yield), m.p. 129–131°. The sodium carbonate solution was acidified with hydrochloric acid, and, after complete precipitation, 0.322 g. of crude (±)-V (20% yield), m.p. 227–230°, was collected by filtration. On sublimation of this solid at 130–160° (0.02 mm.) pure (±)-V was obtained, m.p. 234–235°, lit.[26] m.p. 234°.

Anal. Calcd. for $C_8H_{15}NO_3$: C, 55.73; H, 8.73; N, 8.09; neut. equiv., 173. Found: C, 55.60; H, 8.74; N, 8.04; neut. equiv., 175.

D-(+)-α-Acetamido-β,β-dimethylbutyric Acid [D-(+)-V].—Ozonolysis of 0.781 g. of (*R*)-(+)-N-acetyl-α-phenylneopentylamine [(*R*)-(+)-IV, 3.81 mmoles] in 35 ml. of glacial acetic acid was accomplished as outlined above except that the reaction time was reduced to 35 hr. No unreacted starting material was isolated, and the crude product, D-(+)-V (13% yield), sublimed without melting at 190° (sealed tube), was sublimed at 140–150° (0.02 mm.). Pure D-(+)-V had $[\alpha]^{26}D$ +4° (*c* 2.06) and an infrared spectrum identical with that of (±)-V.

Anal. Calcd. for $C_8H_{15}NO_3$: C, 55.73; H, 8.73; N, 8.09; neut. equiv., 173. Found: C, 55.61; H, 8.80; N, 8.30; neut. equiv., 170.

(±)-α-Benzamido-β,β-dimethylbutyric Acid [(±)-VI].—A suspension of 0.739 g. of (±)-α-acetamido-β,β-dimethylbutyric acid [(±)-V, 4.27 mmoles] in 20 ml. of 10% hydrochloric acid was boiled for 4 hr. The solvent was then removed at reduced pressure leaving 0.638 g. of a pale yellow solid. To 0.108 g. of this solid (0.647 mmole) in 4 equiv. of 1 *N* sodium hydroxide was added 0.083 g. of benzoyl chloride (0.54 mmole) over a period of 30 min. while stirring and cooling in an ice bath. The mixture was stirred for an additional 30 min. at room temperature and then washed with ether. The aqueous solution was acidified with hydrochloric acid and the precipitate was collected by filtration. Recrystallization of this material from ethanol–water gave 0.061 g. of pure (±)-VI [40% yield based on (±)-V], white plates, m.p. 164–165° (ethanol–water), lit.[12] m.p. 165°. The infrared spectrum of the derivative was identical with that of an authentic sample, m.p. 164–165°, prepared from racemic α-amino-β,β-dimethylbutyric acid, sublimed without melting at 240° (sealed tube), obtained from Nutritional Biochemical Co., Cleveland, Ohio.

Anal. Calcd. for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.11; H, 7.30; N, 5.79.

D-(−)-α-Benzamido-β,β-dimethylbutyric Acid [D-(−)-VI].—D-(+)-α-acetamido-β,β-dimethylbutyric acid [D-(+)-V] was hydrolyzed and the N-benzoyl derivative was prepared as outlined above. The pure product, D-(−)-VI (33% yield), crystallized with 1 mole of water, m.p. 103–105° (ethanol–water), lit.[12] m.p. 105° for the L isomer. After drying at 78° (1 mm.) for 15 hr. the sample lost the water of crystallization and had m.p. 150–151°, $[\alpha]^{27}D$ −30° (*c* 1.98), and an infrared spectrum identical with that of (±)-VI; lit.[12] m.p. 151°, $[\alpha]^{25}D$ +26.2° (*c* 3) for the L isomer.

Anal. Calcd. for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.40; H, 7.16; N, 5.97.

Acknowledgment.—This work was supported in part by a grant (G-14524) from the National Science Foundation.

(26) F. Knoop and N. Okada, *Arch. ges. Physiol.*, **201**, 3 (1923).

Chemistry of Dichloromaleimides. I. The Reaction of Dichloromaleimides with Tertiary Amines in Hydroxylic Solvents

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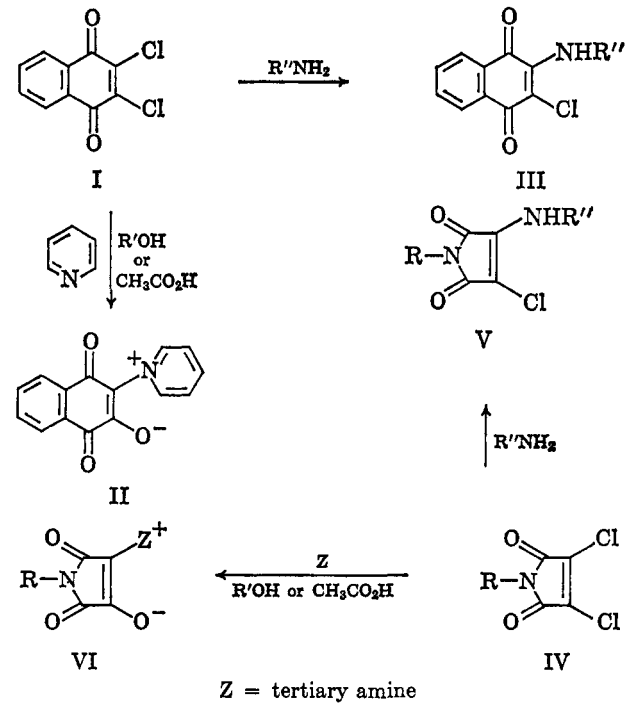
The reaction of N-substituted 2,3-dichloromaleimides with tertiary amines in hydroxylic solvents has been found to give N-(N-substituted 2-oxy-3-maleimidyl)ammonium betaines. A reaction path is postulated.

The reaction of 2,3-dichloro-1,4-naphthoquinone (I) with amines has received considerable study. Compound I reacts with primary amines to give 2-amino-3-chloro-1,4-naphthoquinones[2] (III) (see Scheme I). Of further interest is the interaction of I with pyridine in an alcohol or acetic acid, discovered by Ullmann and Ettisch[3] and later extended by Truitt,[4] to give the pyridinium compound II. The reaction of the structurally related dihalomaleimides with amines, on the other hand, has received little study. Dichloromaleimides (IV) react with primary amines to give 2-amino-3-chloromaleimides (V)[5] and with tertiary arylamines, in the presence of sodium cyanide, to give 4-(2-cyano-3-maleimidyl)arylamines.[6]

It was of interest to determine whether dichloromaleimides (IV) would react with a tertiary heteroaromatic amine, such as pyridine, in a fashion analogous to I, to give VI. Treatment of IV (R = H, $C_6H_5CH_2$, and $C_6H_5CH_2CH_2$) with pyridine in methanol or acetic acid gave yellow solids whose analyses corresponded to compounds **2**, **3**, and **4**, respectively, in Table I. The absence of halogen was confirmed by a

SCHEME I

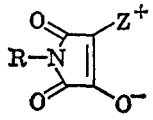


Z = tertiary amine

(1) (a) Author to whom inquires should be addressed. (b) Deceased.
(2) A. Plagemann, *Chem. Ber.*, **15**, 484 (1882).
(3) F. Ullmann and M. Ettisch, *ibid.*, **54B**, 259 (1921).
(4) P. Truitt, F. Mahon, O. Platas, R. L. Hall, and T. Eris, *J. Org. Chem.*, **25**, 962 (1960).
(5) G. Ciamician and P. Silber, *Chem. Ber.*, **22**, 33, 2490 (1889).
(6) E. L. Martin, C. L. Dickinson, and J. R. Roland, *J. Org. Chem.*, **26**, 2032 (1961).

TABLE I

N-(N-SUBSTITUTED 2-OXY-3-MALEIMIDYL)AMMONIUM BETAINES

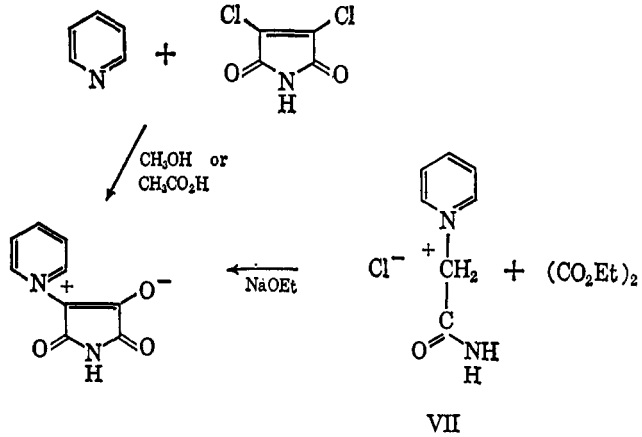


No.	R	Z[a]	M.p., °C.	Recrystn. solvent[b]	Method[c]	Yield, %	Formula	Calcd., % C	Calcd., % H	Calcd., % N	Found, % C	Found, % H	Found, % N
1	$C_6H_5CH_2CH_2$	1	268–270	A	3	32	$C_{15}H_{13}N_3O_3$	63.59	4.63	14.83	63.67	4.84	14.80
2	H	2	309–310[d]	C	2	8	$C_9H_6N_2O_3$	56.84	3.18	14.73	56.64	3.39	14.80
3	$C_6H_5CH_2$	2	208–209	C	2	36	$C_{16}H_{12}N_2O_3$	68.56	4.32	10.00	68.70	4.55	10.02
4	$C_6H_5CH_2CH_2$	2	170–171	A	2	43	$C_{17}H_{14}N_2O_3$	69.37	4.80	9.52	69.04	4.36	9.20
5	$C_6H_5CH_2CH_2$	3	199–201	A	3	99	$C_{18}H_{16}N_2O_3$	70.11	5.23	9.09	69.95	5.08	9.24
6	$C_6H_5CH_2CH_2$	4	296–298	B	1	85	$C_{17}H_{14}N_2O_4$	65.80	4.55	9.03	66.09	4.74	9.04
7	$C_6H_5CH_2CH_2$	5	284–285	B	1	86	$C_{18}H_{15}N_3O_4$	64.09	4.48	12.46	64.44	4.53	12.09
8	$C_6H_5CH_2CH_2$	6	>300	B	4	28	$C_{16}H_{13}N_3O_3$	65.08	4.44	14.23	65.02	4.51	14.35
9	$C_6H_5CH_2CH_2$	7	189–190	A	4	74	$C_{16}H_{13}N_3O_3$	65.08	4.44	14.23	64.85	4.51	14.20
10	$(C_6H_5)_2CH$	8	>300	B	3	94	$C_{26}H_{18}N_2O_3$	76.83	4.46	6.89	76.49	4.30	7.07
11	3-ClC_6H_4	9	210–211	A	1	34	$C_{15}H_{15}ClN_2O_4$	55.81	4.68	8.68	56.07	4.95	8.90
12	4-IC_6H_4	10	180	B	1	30	$C_{19}H_{17}IN_2O_3$	50.91	3.82	6.25	50.60	3.78	6.08

[a] Z^+ is derived from the following amines (Z): 1, imidazole; 2, pyridine; 3, 4-picoline; 4, 3-hydroxypyridine; 5, nicotinamide; 6, pyrazine; 7, pyridazine; 8, isoquinoline; 9, N-methylmorpholine; 10, N,N-dimethylbenzylamine. [b] A = ethanol, B = Methyl Cellosolve, C = water. [c] See Experimental section. [d] Lit.[8] m.p. 309–312°.

negative Beilstein test. The infrared spectra indicated that the maleimide ring was still intact.

Only three compounds of the type VI (R = H, Z = C_5H_5N; R = H, Z = $(CH_3)_3N$; R = $HOCH_2$, Z = C_5H_5N) have previously been described in the literature.[7,8] These had been prepared by the condensation of oxalate esters with appropriately 2-substituted acetamides. The product from the reaction of N-carbamoylmethylpyridinium chloride (VII) with sodium methoxide and diethyl oxalate[8] was shown to be identical in its ultraviolet and infrared spectra with that obtained from the reaction of dichloromaleimide with pyridine. The elemental analysis and melting point also substantiated the identity.



VII

The scope and limitations of the reaction of dichloromaleimides with tertiary amines were studied. The reaction was generally carried out using an excess of the tertiary amine. In most cases, acetic acid was found to be a better reaction solvent than methanol or ethanol for the preparation of the betaines. Pivalic acid could also be employed as a solvent. These results are summarized in Table I.

Pyridine compounds, 3- and 4-substituted, readily gave betaine products while 2- and 2,6-substituted pyridines, such as 2-picoline or 2,6-lutidine, having a sterically hindered azine nitrogen, did not react. Other tertiary heteroaromatic amines such as imidazole, pyrazine, pyridazine, and isoquinoline formed VI, while quinoline failed to do so.

Tertiary amines, such as N,N-dimethylbenzylamine and N-methylmorpholine, reacted with N-substituted dichloromaleimides to form the betaine while the more sterically hindered aliphatic amines, such as triethylamine, did not react. In fact, triethylamine (or 2-picoline or 2,6-lutidine) could be employed along with equimolar quantities of reactive tertiary amines and the appropriate dichloromaleimides to give good yields of the betaine. The omission of the triethylamine gave only 29% of VI when equimolar quantities of pyridine and N-(2-phenylethyl)dichloromaleimide were employed, compared with 78% when triethylamine was included. Aromatic tertiary amines, such as N,N-dimethylaniline did not afford the desired product.

The compounds in Table I were usually obtained as crystals ranging in color from pale yellow to orange-red. They dissolve in concentrated hydrochloric acid to give faintly yellow solutions and are usually reprecipitated upon dilution with water.

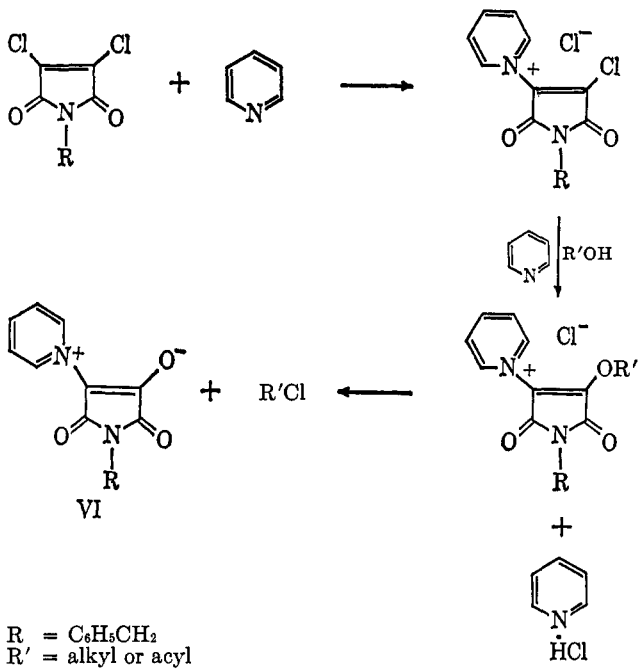
The course of the reaction of dichloromaleimides with tertiary amines in hydroxylic solvents may be postulated using a hetero aromatic amine, such as pyridine, as an example and is shown in Scheme II.

If this scheme is correct, then it should be possible to recover from the reaction mixture an alkyl or an acyl halide (perhaps, more likely, an acid anhydride) depending on the solvent employed. To test this hypothesis, 1 mole of N-benzyldichloromaleimide was heated with 3 moles of pyridine in *n*-butyl alcohol (R′ = *n*-C_4H_9) at 110–120°; *n*-butyl chloride was obtained by distillation from the reaction and VI was isolated in 89% yield. Presumably, the reaction path in acetic

(7) E. G. Howard, U. S. Patent 2,786,060 (1956).

(8) E. G. Howard, A. Kotch, R. V. Lindsey, Jr., and R. E. Putnam, *J. Am. Chem. Soc.*, **80**, 3924 (1958).

SCHEME II



R = $C_6H_5CH_2$
R′ = alkyl or acyl

acid (R′ = CH_3CO) would be analogous. Similar results have been obtained with 2,3-dichloro-1,4-naphthoquinone.[9]

The infrared spectra of the compounds in Table I were examined. Three bands appeared consistently at 5.7–5.73, 5.9–5.95, and 6.1–6.25 μ. The bands at 5.7–5.73 and 5.9–5.95 μ were sharp, of medium to strong intensity, with the latter usually being the stronger band. The band at 6.1–6.25 μ was usually broad and always the strongest band in the spectrum. These bands can be assigned to two carbonyl stretching frequencies (5.7–5.73 and 5.9–5.95 μ) and a carbon–carbon double-bond stretching or ring vibration (6.1–6.25 μ). These bands, then, appear to be the characteristic feature of the maleimide structure.[10]

Ultraviolet absorption data for representative examples of the betaines in Table I were obtained in ethanol. Dichloromaleimide absorbs at 234 mμ (log ϵ 4.23). N-(2-Phenylethyl)dichloromaleimide absorbs at 233 mμ (log ϵ 4.15). The betaines show this peak with reasonable uniformity as to location and intensity in the range 219–247 mμ (log ϵ 3.79–4.27), in addition to absorption in the 300–400-mμ region. The pyridinium betaines (**2**, **4**, **6**, **7**, **8**, and **9**) show two bands in the 300–400-mμ region in the ranges 328–360 (log ϵ 3.69–4.02) and 350–413 (3.71–4.07), while the imidazolium and trialkylammonium betaines (**1** and **11**) show only one band in this region at 377 mμ (log ϵ 3.32) and 350 (3.24), respectively. No. **2** shows a slight solvent shift absorbing at 227, 328, and 350–370 mμ in water and 232, 340, and 373 mμ in ethanol.

Experimental[11]

Infrared spectra were obtained using a Beckman IR8 infrared spectrophotometer with filter-grating monochromator. The materials were examined as potassium bromide pellets or liquid films. Ultraviolet spectra were obtained with a Beckman DK recording spectrophotometer, using 1-cm. quartz cells. Dichloromaleimide was prepared from dichloromaleic anhydride and urea.[12] The N-substituted dichloromaleimides were prepared by treatment of dichloromaleic anhydride with the appropriate primary amine in glacial acetic acid at 100–120°.[6,13,14] The preparation of N-(2-phenylethyl)dichloromaleimide is typical.

N-(2-Phenylethyl)dichloromaleimide.—To a solution of 157 g. (0.80 mole) of dichloromaleic anhydride in 180 g. of glacial acetic acid was slowly added 92 g. (0.76 mole) of 2-phenylethylamine. The reaction mixture was heated at 115° for 1 hr. and cooled to precipitate the product; the product was filtered, washed with ethanol, and dried to give 181 g. (88%) of solid, m.p. 129–130°. Recrystallization from ethanol yielded 163 g., m.p. 130.5–132.0°.

Anal. Calcd. for $C_{12}H_9Cl_2NO_2$: C, 53.36; H, 3.36; N, 5.19. Found: C, 53.18; H, 3.56; N, 5.00.

The following methods were employed to prepare the maleimidylbetaines listed in Table I.

1. **Treatment of an N-Substituted Dichloromaleimide with an Excess of a Tertiary Amine in Refluxing Methanol. 4-[N-(3-Chlorophenyl)-2-oxy-3-maleimidyl]-4-methylmorpholinium Betaine[14] (11, Table I).**—A suspension of 2.76 g. (0.01 mole) of N-(3-chlorophenyl)dichloromaleimide in 20 ml. of methanol was treated with 6.06 g. (0.06 mole) of N-methylmorpholine, refluxed for 16 hr., poured into 10 ml. of water, and refrigerated. The yellow solid which precipitated was filtered, washed with ethanol and diethyl ether, and dried to give 1.1 g. (34%) of product, m.p. 204–205°. Recrystallization from ethanol yielded 0.93 g., m.p. 210–211°.

2. **Reaction of Dichloromaleic Anhydride with Methanol and a Primary Amine, Followed by Treatment with a Tertiary Amine. 1-(N-Benzyl-2-oxy-3-maleimidyl)pyridinium Betaine[14] (3, Table I).**—A mixture of 8.35 g. (0.05 mole) of dichloromaleic anhydride and 15 ml. of methanol was refluxed for 0.5 hr., the solution was cooled, and 9.8 g. (0.12 mole) of pyridine and 5.3 g. (0.05 mole) of benzylamine were added. The reaction mixture was then heated at 90–100° for 0.5 hr., cooled to precipitate the product, and filtered. The greenish yellow solid obtained from both the filter cake and the filtrate were combined, washed with acetone, and dried to give 5.0 g. (36%) of product, m.p. 208–209°. Recrystallization of a 2.0-g. sample from 1 l. of water yielded 1.3 g., m.p. 208–209°.

3. **Treatment of an N-Substituted Dichloromaleimide with an Excess of a Tertiary Amine in Acetic Acid. 2-(N-Benzhydryl-2-oxy-3-maleimidyl)isoquinolium Betaine[14] (10, Table I).**—A solution of 2.9 g. (0.0088 mole) of N-benzhydryldichloromaleimide in 30 ml. of glacial acetic acid was treated with a solution of 5.8 g. (0.045 mole) of isoquinoline in 7 ml. of glacial acetic acid at 100–110° for 1 hr. The yellow solid which precipitated was filtered, washed with acetone and ether, and dried to give 3.3 g. (94%) of product, m.p. >300°. Recrystallization of a 2.3-g. sample from Methyl Cellosolve yielded 2.05 g., m.p. >300°.

4. **Treatment of Equimolar Quantities of an N-Substituted Dichloromaleimide and a Tertiary Amine in Acetic Acid in the Presence of an Excess of Triethylamine. 1-[N-(2-Phenylethyl)-2-oxy-3-maleimidyl]pyridazinium Betaine[14] (9, Table I).**—A solution of 2.7 g. (0.01 mole) of N-(2-phenylethyl)dichloromaleimide in 25 ml. of glacial acetic acid was treated with a solution of 0.8 g. (0.01 mole) of pyridazine and 3.05 g. (0.03 mole) of triethylamine in 7 ml. of glacial acetic acid at 100–110°, for 2 hr., poured into water, and refrigerated. The solid which precipitated was filtered, washed with ether, and dried to give 2.2 g. (74%) of product, m.p. 187–189°. Recrystallization from ethanol yielded 1.6 g., m.p. 189–190°.

Isolation of *n*-Butyl Chloride from the Reaction of N-Benzyldichloromaleimide with Pyridine in *n*-Butyl Alcohol.—A mixture of 25.6 g. (0.10 mole) of N-benzylchloromaleimide, 23.7 g. (0.30 mole) of pyridine, and 100 ml. of *n*-butyl alcohol was heated to 110–120° for 1 hr. during which time the fraction, b.p. 80–100°, was distilled and collected. Redistillation of this fraction gave 3.4 g. of liquid, b.p. 77–78°, $n^{20}D$ 1.4026 (*n*-butyl chloride, lit.[15] b.p. 78°, $n^{20}D$ 1.4022), which gave a positive Beilstein test and an infrared spectrum identical with an authentic sample. The reaction residue solidified upon cooling. It was filtered,

(9) J. A. VanAllan and G. A. Reynolds, *J. Org. Chem.*, **28**, 1019 (1963).

(10) R. H. Wiley and S. C. Slaymaker, *J. Am. Chem. Soc.*, **80**, 1385 (1958).

(11) Melting points were taken on a Fisher-Johns block and corrected to standards. Analyses are by Drs. Weiler and Strauss, Oxford, England.

(12) F. L. Dunlap, *Am. Chem. J.*, **18**, 332 (1896).

(13) G. H. F. Walker and F. R. Bradbury, U. S. Patent 2,962,504 (1960).

(14) S. L. Shapiro, L. Freedman, and M. J. Karten, U. S. Patent 3,129,225 (1964).

(15) "Merck Index," P. G. Stecher, Ed., Merck and Co., Inc., Rahway, N. J., 1960, p. 180.

washed with *n*-butyl alcohol and ether to give 24.9 g. (89%) of product, m.p. 207–209°. This was recrystallized from ethanol to give 19.0 g. of solid, m.p. 208–209°, whose infrared spectrum was identical with that of **3** (Table I).

Acknowledgment.—The authors are grateful to M. Blitz and W. Greenfield for the ultraviolet spectra and to Mrs. O. Kitrey for the infrared spectra.

3-Isothiazolone–*cis*-3-Thiocyanoacrylamide Equilibria[1,2]

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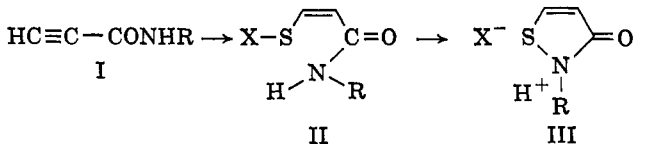
cis-3-Thiocyanoacrylamides (II) were obtained by the addition of hydrogen thiocyanate to the propiolamides. Conversion to the correspondingly substituted 3-isothiazolones (III) was effected readily by treatment with acid or with the stoichiometric quantities of metal salt (Fe^{2+}, Ni^{2+}) and alkali. Cyanide ion rapidly regenerated the *cis*-3-thiocyanoacrylamides from the 3-isothiazolones, and the S–N bond in the latter was also cleaved by treatment with sodium thiophenolate, sodium *t*-butyl mercaptide, hydrogen sulfide, and sulfite ion. Several methods were developed which provide evidence for equilibria between 3-isothiazolones (+HCN) and *cis*-3-thiocyanoacrylamides.

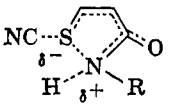
Formation of the 3-isothiazolone nucleus by an unpredicted ring contraction of the 1,4-thiazepine ring system[5] led us to investigate the synthesis of 3-isothiazolones. In a recent communication[6] we introduced a new synthesis which follows the sequence I → III (X = CN or SO_3^-). Since initial experiments with the Bunte salts (II, X = SO_3^-) failed to yield



I II III

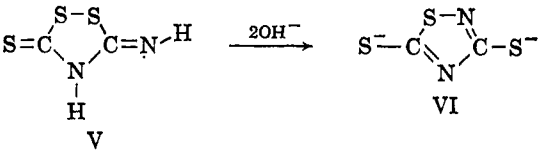
crystalline intermediates, the major part of the investigation was carried out using the *cis*-3-thiocyanoacrylamides (II, X = CN). Detailed consideration of the properties of the 3-thiocyanoacrylamides has revealed very interesting relationships between these compounds and the corresponding 3-isothiazolones.

On the basis of recent developments in the chemistry of isothiazoles,[7] we designed the synthesis of 3-isothiazolones along lines suggested by the isothiazole synthesis of Wille, Capeller, and Steiner.[7g] We reasoned that the proximity of the weakly nucleophilic amide nitrogen to the sulfur attached to two electron-withdrawing groups would facilitate S–N orbital overlap, thus lowering the activation energy for the cyclization process, II → III. Postulation of a range of possible transition states (IV) in which the developing formal charges on S and N could be dispersed not only through the conjugated system but also by stretching of the S–CN and/or N–H bonds suggested potential roles for solvation, for proton removal, and for removal of cyanide ion in effecting the ring closure.



IV

Some support for the projected synthesis was drawn from the work of Hantzsch and Wolvekamp[8] on isoperthiocyanic acid (V) and perthiocyanates (VI). The reaction is complex, involving the formation and



V VI

the redissolution of sulfur.[9] Some similarity of mechanism may exist between this process and the isothiazole synthesis due to Hatchard.[7c] Finally, an example closer to our process is found in the work of Reissert and Manns,[10] who observed the formation of 4,5-benz-3-isothiazolone from 2,2′-dicarboxamidodiphenyl disulfide.

The *cis*-3-thiocyanoacrylamides (II) were obtained readily by the addition of hydrogen thiocyanate to the propiolamides. The stereochemical assignments for the products were made from the n.m.r. coupling constants: $J_{2,3}$ = 9 c.p.s. for *cis* and 14 c.p.s. for *trans*.[11] The *cis* product (*i.e.*, from *trans* addition) was expected to predominate[12–14] and, in fact, constituted about 85% of the product obtained from propiolamide (I, R = H). In the case of the N-alkylpropiolamides (I, R = CH_3 or C_2H_5) the yields of the corresponding 3-thiocyanoacrylamides were lower and no *trans* product was ob-

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