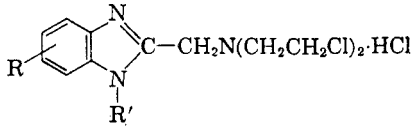
TABLE I

SUBSTITUTED 2-[BIS(2-CHLOROETHYL)AMINOMETHYL]BENZIMIDAZOLE HYDROCHLORIDES



R	R′	Yield, %	M.P., °C.	Analyses							
				Calculated				Found			
				C	H	N	Cl	C	H	N	Cl
5(or 6)-Chloro	H	45	146–147	41.97	4.37	12.24	41.40	41.86	4.23	12.07	41.52
5,6-Dichloro	H	49	171–173	38.17	3.73	11.13	46.95	38.24	3.85	11.26	47.01
5,6-Dimethyl	H	70	180–182	49.93	5.98	12.48	31.59	49.97	6.06	12.53	31.62
H	CH_3	61	137–138.5	48.37	5.58	13.03	33.03	48.47	5.60	13.12	32.8

2-[Bis(2-chloroethyl)aminomethyl]benzimidazole hydrochloride. This substance ("benzimidazole mustard") was obtained from the corresponding 2-hydroxyethyl compound by means of thionyl chloride, as had been described previously.[1] In order to obtain a pure product, several recrystallizations from ethanol are necessary in order to remove a lower melting by-product, which apparently is the dihydrochloride. It is less soluble in ethanol than the monohydrochloride and could be isolated from the first fractions of the ethanol recrystallization as a white crystalline substance, melting at 142–143° (after recrystallization from a small amount of ethanol).

Anal. Calcd. for $C_{12}H_{17}Cl_4N_3$: Cl, 41.2. Found: Cl, 41.4.

The substituted 2-[bis(2-chloroethyl)aminomethyl]benzimidazole hydrochlorides were prepared by the same general procedure from the alcohols and thionyl chloride. The crude products were twice recrystallized from absolute ethanol; usually, ether was added to the alcoholic solutions until cloudiness appeared.

The yields, physical properties, and analyses of the compounds are presented in Table I.

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Methyl 2-Nitro-3-ethoxyacrylate and Related Compounds

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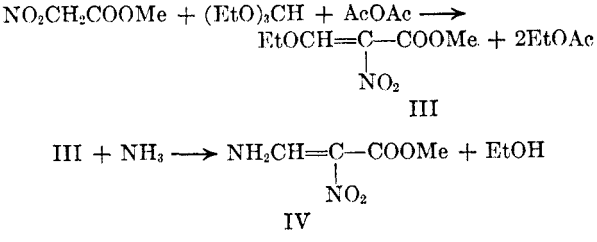
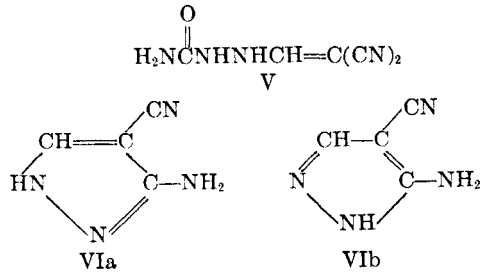
Active methylene compounds react with acetic anhydride and alkyl orthoformates to form alkoxymethylene derivatives.[1] The latter, in turn, readily undergo addition-elimination reactions with displacement of the alkoxyl group by nucleophilic agents. Thus, with ammonia ethoxymethylenemalononitrile, I, yields aminomethylenemalononitrile, II.[2] This note will serve to record the analogous synthesis of methyl 2-nitro-3-ethoxyacrylate, III, and methyl 2-nitro-3-aminoacrylate, IV, from methyl nitroacetate. Also described are methods of preparation and spectral data for several new derivatives of I.



The structure of the compound derived from I with semicarbazide was assigned by comparison of its ultraviolet spectrum with those of I, II, and the product of I with hydrazine. I, II, and the semicarbazide product, V, all showed high intensity maxima between 248 and 267 mμ with minima below 215 mμ. The product of I with hydrazine which has been shown[3] to be the cyclized 3 (or 5)-amino-4-cyanopyrazole, IVa or b, exhibited only inflections at 214 and 240 mμ superimposed on a high intensity shorter wave length band. On this basis V was uncyclized semicarbazidomethylenemalononitrile.



The spectra of III and IV did not bear the expected resemblance to those of the corresponding dinitriles. IV exhibited medium-low intensity maxima at 235 and 312 mμ while III showed only a low intensity inflection at 252 mμ. Elemental analyses, the formation of a phenylurea from IV and

(1) For leading references see R. G. Jones, *J. Am. Chem. Soc.*, **73**, 3684 (1951). A discussion of the mechanism is given by R. G. Jones, *J. Am. Chem. Soc.*, **74**, 4889 (1952).

(2) O. Diels, H. Gartner, and R. Kaack, *Ber.*, **55**, 3429 (1922).

(3) R. K. Robins, *J. Am. Chem. Soc.*, **78**, 784 (1956).

phenylisocyanate, and the conversion of III to a bis-hydrazine derivative, probably 2-nitro-3-hydrazinoacrylyl hydrazide, however, indicated that the assigned structures were probably correct.

EXPERIMENTAL[4]

Materials. Ethoxymethylenemalononitrile, I, is commercially available from Kay-Fries Chemicals, Inc., New York. With aqueous ammonia it gave aminomethylenemalononitrile, II, m.p. 143–145° (lit.[2] 146°). Methyl nitroacetate, b.p. 95–96° (18 mm.) was prepared in 32% over-all yield from nitromethane via dipotassium nitroacetate. The procedure has been described by Feuer, Hass, and Warren.[5]

Methyl 2-nitro-3-ethoxyacrylate, III. Two tenths mole (24.0 g.) methyl nitroacetate, heated overnight on the steam bath with 0.3 mole (44.4 g.) ethyl orthoformate and 0.5 mole (51.0 g.) acetic anhydride and the reaction mixture fractionated *in vacuo*, gave as a high boiling main cut 23.1 g. (66%) of III, a mobile yellow liquid, b.p. 119–121° (1.0 mm.).

Anal. Calcd. for $C_6H_9NO_5$: C, 41.11; H, 5.16; N, 8.00. Found: C, 41.04, 41.30; H, 4.99, 5.26; N, 7.62, 7.94.

Methyl 2-nitro-3-aminoacrylate, IV. Addition of 5.0 g. III to 20 ml. cold, stirred 28% ammonium hydroxide, filtration of the pale green solid which immediately precipitated, and washing the filter cake with cold ethyl acetate gave 3.85 g. (95%) crude IV, m.p. 154–156°. A single recrystallization from 200 ml. ethyl acetate furnished 2.75 g. (66%) of an analytical sample as clusters of cream colored needles, m.p. 163.2–163.6°.

Anal. Calcd. for $C_4H_6N_2O_4$: C, 32.89; H, 4.11; N, 19.16. Found: C, 33.03, 33.09; H, 4.16, 4.29; N, 18.53, 18.23, 18.98.

Methyl 2-nitro-3-(N'-phenylureido)acrylate. One half gram of IV, 1 g. phenylisocyanate, and 2 drops pyridine, heated 90 min. on the steam bath, taken up in hot chloroform, filtered, and cooled to crystallize, and the product recrystallized from ether-chloroform, yielded 250 mg. (28%) of chartreuse crystals, m.p. 180.2–182.2°.

Anal. Calcd. for $C_{11}H_{11}N_3O_5$: C, 49.81; H, 4.15; N, 15.84. Found: C, 49.59, 49.76; H, 4.39, 4.45; N, 15.60, 15.61.

2-Nitro-3-hydrazinoacrylyl hydrazide. Dropwise addition of 4.0 g. III in 4.0 ml. methanol to a cooled, swirled solution of 10 ml. 85% hydrazine hydrate in 10 ml. methanol caused immediate formation of a thick yellow slurry. The mixture, diluted with 25 ml. methanol, cooled, and filtered, and the product washed with methanol, and air dried yielded 3.20 g. (88%) of the hydrazino hydrazide, m.p. 232–234° (dec.). Recrystallization from a large quantity of methanol gave an analytical sample, m.p. 235–236° (dec.).

Anal. Calcd. for $C_3H_7N_5O_3$: C, 22.36; H, 4.35; N, 42.50. Found: C, 22.66, 22.68; H, 4.47, 4.57; N, 42.79, 42.57.

Semicarbazidomethylenemalononitrile, V. A solution of 4.88 g. (0.04 mole) I, 9.0 g. (0.08 mole) semicarbazide hydrochloride, and 8.2 g. (0.06 mole) sodium acetate trihydrate in 100 ml. 50% aqueous ethanol, allowed to stand overnight at room temperature, concentrated to 40 ml., and cooled, deposited 3.35 g. (56%) of a light tan solid, m.p. >360°. An analytical sample was obtained as clusters of fine white needles on recrystallization from ethanol.

Anal. Calcd. for $C_5H_5N_5O$: C, 39.72; H, 3.31; N, 46.34. Found: C, 39.61, 39.86; H, 3.46, 3.56; N, 46.97, 46.69.

Ultraviolet spectra. Solvent methanol. λ_{max} (log ϵ): *I*, 248 (4.11); *II*, 267 (4.17), 344 (3.11); *III*, 252[s] (3.18); *IV*, 235 (3.20), 312 (3.11); *V*, 249 (3.87); *VI*, 214[s] (4.03), 240[s] (3.81). Superscript s = shoulder or inflection.

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(4) All melting points are corrected. Microanalyses by Professor Katherine Gerdeman, Department of Chemistry, University of Maryland. Ultraviolet spectra were determined with a Cary Model 14 spectrophotometer using 1-cm. silica cells.

(5) H. Feuer, H. B. Hass, and K. S. Warren, *J. Am. Chem. Soc.*, **71**, 3078 (1949).

Studies of Configuration. V. The Preparation and Configuration of *cis*-3-Methoxycyclopentanecarboxylic Acid

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In continuing the investigation of the ether–acid chloride rearrangement[1] we have undertaken the preparation of 3-methoxycyclopentanecarboxylic acid and have characterized the *cis* isomer.

The preparation of 3-oxocyclopentanecarboxylic acid has been previously described by Hope,[2] by Ingold, Shoppee, and Thorpe,[3] by Vaughn,[4] and more recently by Shemyakin and co-workers.[5] The addition of diethyl malonate to diethyl itaconate using a molar excess of diethyl malonate afforded tetraethyl 1,1,3,4-butanetetracarboxylate (I) in 93% yield. Sodium ethoxide in toluene converted I to triethyl 3-oxo-1,2,4-cyclopentanecarboxylate (II) in 66% yield. Hydrolysis and decarboxylation afforded 3-oxocyclopentanecarboxylic acid (III) in nearly quantitative yield. The procedure of Vaughn[4] in which the intermediates I and II are not isolated afforded 3-oxocyclopentanecarboxylic acid in 54% yield from diethyl itaconate.

Of several methods of reduction investigated, hydrogenation over Raney nickel of either the sodium salt of III or the methyl ester afforded the most tractable mixtures of *cis*- and *trans*-3-hydroxycyclopentanecarboxylic acid (IV). Crystallization from ether-pentane at low temperatures afforded 60% of a crystalline isomer, m.p. 50.4–51.8°. Evidence is presented below to show that this is the *cis*-isomer.

Conversion of 3-hydroxycyclopentanecarboxylic acid to its lactone was attended with some difficulty. Direct heating of crude IV resulted in polymerization and no lactone was obtained. Heating a dilute solution of the mixed isomers of IV in

(1) D. S. Noyce and H. I. Weingarten, *J. Am. Chem. Soc.*, **79**, 3093, 3098 (1957).

(2) E. Hope, *J. Chem. Soc.*, **101**, 892 (1912).

(3) C. K. Ingold, C. W. Shoppee, and J. F. Thorpe, *J. Chem. Soc.*, 1477 (1926).

(4) H. A. Vaughn, Jr., Dissertation, Columbia University; *Chem. Abstr.*, **51**, 16314 (1957).

(5) M. M. Shemyakin, L. A. Shchukina, E. I. Vinogradova, M. N. Kolosov, R. G. Vdovina, M. G. Karapetyan, V. Ya. Rodionox, G. A. Ravdel, Yu. B. Shvetsov, E. M. Bamdan, E. S. Shaman, K. M. Ermolaev, and E. P. Semkin, *Zhur. Obshchet Khim.*, **27**, 742 (1957); *Chem. Abstr.*, **51**, 16313 (1957).