or by saponification of the methyl ester. The acid (3 g.) suspended in 18 ml. of benzene and 12 ml. of purified thionyl chloride was refluxed for 1.5 hours. The solvent and excess thionyl chloride were removed *in vacuo* leaving a reddish crystalline solid. The crude pyrazinoyl chloride was purified by vacuum sublimation (2.0 mm.) at a bath temperature of 50–60° to give colorless crystals that weighed 2.9 g. (84% yield) and had m.p. 59–61°.[9] Attempts to distil the acid chloride as described by Dalmer and Walter[8] resulted in extensive decomposition.

When pyrazinoyl chloride is stored, it rapidly turns red with concurrent decomposition. Consequently, it was prepared and used immediately.

Acid Chloride of Methyl Pyrazine-2,3-dicarboxylate.—Methyl acid pyrazine-2,3-dicarboxylate (2.0 g.) was refluxed in 6 ml. of benzene and 3.3 ml. of thionyl chloride for one hour. The solvent and excess thionyl chloride were removed under vacuum and the amber residue (weight 2.2 g.) was fractionally distilled. The three fractions of methyl acid chloride all boiled at 94–96° (0.2 mm.); the center cut (1.4 g., n^{25}D 1.5301) was analyzed.

Anal. Calcd. for $C_7H_5O_3N_2Cl$: C, 41.91; H, 2.51; N, 13.96. Found: C, 42.25; H, 2.41; N, 14.29.

A portion of the acid chloride (1.0 g.) reacted exothermally with 1 ml. of methanol. The methanol was evaporated and the residue in 15 ml. of ether was washed with excess sodium bicarbonate in 20% sodium chloride solution. The ether phase was dried over anhydrous sodium sulfate and evaporated to give the crystalline dimethyl ester, weight 0.95 g., m.p. 59–62°. The m.p. was raised to 62–63° by low temperature recrystallization from ether. The reported[6] m.p. is 47–50°.

Anal. Calcd. for $C_8H_8O_4N_2$: C, 48.91; H, 4.11; N, 14.28. Found: C, 49.07; H, 4.18; N, 14.33.

β-Dimethylaminoethyl Pyrazinoate Hydrochloride.—Freshly prepared pyrazinoyl chloride (2.7 g., 0.019 mole) dissolved in 25 ml. of dry benzene was treated with 1.7 g. (0.019 mole) of β-dimethylaminoethanol. The ester hydrochloride precipitated immediately as a semi-crystalline, colorless solid and after one hour at 5° was filtered; weight 3.7 g. Recrystallization from *n*-propanol–isopropyl alcohol gave needles, m.p. 184–185°. By comparable methods the β-diethylaminoethyl and β-dibutylaminoethyl ester hydrochlorides were prepared (see Table I).

Methyl β-Diethylaminoethyl Pyrazine-2,3-dicarboxylate Hydrochloride.—A solution of 6.4 g. of the acid chloride of methyl pyrazine-2,3-dicarboxylate in 8 ml. of benzene was treated with an equimolar quantity (3.42 g.) of β-diethylaminoethanol. The precipitated ester hydrochloride was filtered, washed with benzene and dried; weight 9.6 g., m.p. 98–110°. Two recrystallizations from acetone gave colorless crystals, m.p. 113–115°. Reaction of the acid chloride with β-dimethylaminoethanol or β-dibutylaminoethanol gave the respective ester hydrochlorides (see Table I).

β-Dibutylaminoethyl Acid Pyrazine-2,3-dicarboxylate.—To 10.9 g. (0.072 mole) of pyrazine-2,3-dicarboxylic anhydride in refluxing benzene, 12.5 g. (0.072 mole) of β-dibutylaminoethanol was added in small portions over a period of four hours. The mixture was heated for an additional hour and then the tan crystals were filtered and dried *in vacuo;* weight 22.2 g. Two recrystallizations from *n*-butanol–acetone afforded colorless crystals, m.p. 151–152°. In a similar manner the β-dimethylaminoethyl and β-diethylaminoethyl esters were prepared with the appropriate amino alcohol.

BROOKLYN 2, N. Y.

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[9] B. Meltsner, Thesis, Polytechnic Institute of Brooklyn, 1950.

[CONTRIBUTION FROM THE ORGANIC CHEMICALS DIVISION, NITRO RESEARCH DEPARTMENT, MONSANTO CHEMICAL COMPANY]

Chloro-substituted Unsaturated Alkylmercapto Thiazoles

BY JOHN J. D'AMICO

RECEIVED AUGUST 4, 1952

The following nine compounds have been synthesized and characterized: 2-(3-chloro-2-butenylmercapto)-benzothiazole, 2-(2-chloroallylmercapto)-benzothiazole, 2-(*trans*-2,3-dichloro-2-butenylmercapto)-benzothiazole, 2-(3-chloroallylmercapto)-benzothiazole, 2-(2-chloroallylmercapto)-4-methylthiazole, 2-(3-chloro-2-butenylmercapto)-4-methylthiazole, 2,2′-bis-(2-butenylmercapto)-benzothiazole, 2-(4-chloro-2-butenylmercapto)-benzothiazole and 2-(2-butynylmercapto)-benzothiazole.

Thiazolethiols and some of their derivatives are known to be excellent accelerators for the vulcanization of rubber with sulfur. The purpose of this investigation was the synthesis of chloro-substituted unsaturated alkylmercapto thiazoles and determination of the effect of unsaturation and chloro-substituents on the properties of the rubber vulcanizates. The results and comparison of the activity of these compounds as accelerators for rubber will be reported in another paper.

The new compounds were prepared by treating the sodium salt of either 2-mercaptobenzothiazole or 4-methyl-2-thiazolethiol in an aqueous solution with the following unsaturated chloro compounds: *trans*-1,2,3-trichloro-2-butene, 1,3-dichloro-2-butene, 2,3-dichloro-1-propene, 1,4-dichloro-2-butene, 1,3-dichloropropene and 1-chloro-2-butyne. The reaction may be represented as follows: RSNa + R′Cl → RSR′ + NaCl where R is a thiazolyl group and R′ is either chloro-substituted alkenyl or alkinyl group. In the reaction of the sodium salt of 2-mercaptobenzothiazole with 1,4-dichloro-2-butene, two products were obtained and identified. Physical data are listed in Table I.

Experimental[1]

2-(3-Chloro-2-butenylmercapto)-benzothiazole (I).—A solution containing 1.5 moles of 2-mercaptobenzothiazole was prepared by dissolving 258 g. of 97% 2-mercaptobenzothiazole in 240 g. (1.5 moles) of 25% sodium hydroxide and 1500 g. of water. This solution was filtered and to the stirred filtrate was added 169 g. (1.35 moles) of 1,3-dichloro-2-butene.[2] An exothermic reaction set in, the temperature rising from 27 to 38° within 20 minutes. The reaction mixture was stirred for five hours and the organic layer separated. The unreacted sodium 2-mercaptobenzothiazole was recovered from the aqueous layer by acidification with concentrated hydrochloric acid. The amber oily organic layer was dissolved in 400 ml. of ethyl ether, washed repeatedly with 2% sodium hydroxide, then with water until the wash water was neutral to litmus, and the solvent was removed by distillation. The residue was dried over Attapulgus clay and a yield of 322 g. of an amber oily product was obtained.

2-(2-Chloroallylmercapto)-benzothiazole (II).—This procedure was similar to compound I except 190 g. (1.1 moles) of 97% 2-mercaptobenzothiazole, 176 g. (1.1 moles) of 25% aqueous sodium hydroxide, 1100 g. of water and 111 g.

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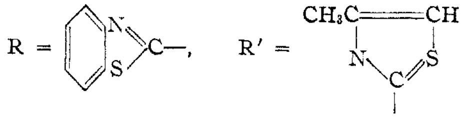
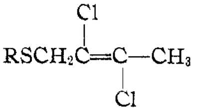
[1] All melting points were taken upon a Fisher-Johns block and are uncorrected.

[2] Kindly supplied by E. I. du Pont de Nemours and Company, Wilmington, Delaware.

TABLE I

DERIVATIVES OF UNSATURATED ALKYLMERCAPTOTHIAZOLES



No.	Derivatives	Yield, % crude	B.p., °C. 1 mm., analytical sample	n^{25}D	Empirical formula	Nitrogen, % Calcd.	Nitrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found	Chlorine, % Calcd.	Chlorine, % Found
I	$RSCH_2CH{=}CClCH_3$	93.5	148–150	1.6552	$C_{11}H_{10}ClNS_2$	5.48	5.73	25.07	25.42	13.86	13.43
II	$RSCH_2CCl{=}CH_2$	95.0	140–142	1.6591	$C_{10}H_8ClNS_2$	5.79	5.92	26.53	26.00	14.66	14.47
III	 $RSCH_2C(Cl){=}C(Cl){-}CH_3$	78.2	43[a]	....	$C_{11}H_9Cl_2NS_2$	4.83	4.87	22.09	22.10	24.43	24.13
IV	$RSCH_2CH{=}CHCl$	91.4	163–165	1.6678	$C_{10}H_8ClNS_2$	5.79	5.87	26.53	26.28	14.66	15.06
V	$R'SCH_2CCl{=}CH_2$	81.5	91–93	1.5849	$C_7H_8ClNS_2$	6.81	7.01	31.17	31.12	17.23	17.17
VI	$R'SCH_2CH{=}CClCH_3$	91.9	112–114	1.5840	$C_8H_{10}ClNS_2$	6.37	6.66	29.18	29.08	16.13	16.06
VII	$RSCH_2CH{=}CHCH_2SR$	34.7	153–155[b]	....	$C_{18}H_{14}N_2S_4$	7.25	7.32	33.18	33.00	..	...
VIII	$RSCH_2CH{=}CHCH_2Cl$	64.9	Dec.	....	$C_{11}H_{10}ClNS_2$	5.48	5.75	25.07	25.08	13.86	13.43
IX	$RSCH_2C{\equiv}CCH_3$	82.4	72–73[a]	....	$C_{11}H_9NS_2$	6.39	6.35	29.24	29.57	...	...

[a] M.p.; recrystallization from ethyl alcohol. [b] M.p.; recrystallization from benzene.

(1.0 mole) of 2,3-dichloro-1-propene[3] were used. A yield of 229 g. of an amber oily product was obtained.

2-(*trans*-2,3-Dichloro-2-butenylmercapto)-benzothiazole (III).—This procedure was similar to compound I except 190 g. (1.1 moles) of 97% 2-mercaptobenzothiazole, 176 g. (1.1 moles) of 25% aqueous sodium hydroxide, 1100 g. of water and 130 g. (0.81 mole) of *trans*-1,2,3-trichloro-2-butene[4] were used. The light yellow solid product was recovered by filtration and washed with water until the wash water was neutral to litmus. A yield of 184 g., m.p. 38–41°, was obtained, which upon crystallization from ethyl alcohol melted at 43°.

2-(3-Chloroallylmercapto)-benzothiazole (IV).—The procedure was similar to compound I except 190 g. (1.1 moles) of 97% 2-mercaptobenzothiazole, 176 g. (1.1 moles) of 25% aqueous sodium hydroxide, 1100 g. of water and 111 g. (1.0 mole) of 1,3-dichloropropene[3] were used. A yield of 220 g. of an amber oily product was obtained.

2-(2-Chloroallylmercapto)-4-methylthiazole (V).—This procedure was similar to compound I except 34 g. (0.26 mole) of 4-methyl-2-thiazolethiol, 41.5 g. (0.26 mole) of 25% aqueous sodium hydroxide, 300 g. of water and 28.5 g. (0.26 mole) of 2,3-dichloro-1-propene were used. A yield of 45 g. of an amber oily product was obtained.

2-(3-Chloro-2-butenylmercapto)-4-methylthiazole (VI).—This procedure was similar to compound I except 29 g. (0.22 mole) of 4-methyl-2-thiazolethiol, 35.2 g. (0.22 mole) of 25% aqueous sodium hydroxide, 300 g. of water and 27.5 g. (0.22 mole) of 1,3-dichloro-2-butene were used. A yield of 44 g. of an amber oily product was obtained.

2,2'-Bis-(2-butenylmercapto)-benzothiazole (VII) **and 2-(4-Chloro-2-butenylmercapto)-benzothiazole** (VIII).—A solution of sodium 2-mercaptobenzothiazole was prepared by mixing 172 g. (1.0 mole) of 97% 2-mercaptobenzothiazole, 160 g. (1 mole) of 25% aqueous sodium hydroxide and 1100 g. of water. The solution was filtered and to the stirred filtrate was gradually added 63 g. (0.5 mole) of 1,4-dichloro-2-butene.[5] An exothermic reaction set in immediately, the temperature rising from 25–35° within 20 minutes. Stirring was continued for 24 hours, the aqueous layer then decanted and the semi-solid residue diluted with 400 g. of acetone. The acetone mixture was stirred thoroughly; the white solids were filtered and when dried at 70° gave 67 g. of a white solid, m.p. 147–151°, which after recrystallization from benzene melted at 153–155°. Analysis confirmed it to be 2,2'-bis-(2-butenylmercapto)-benzothiazole.

The acetone was removed from the filtrate by distillation under reduced pressure and the residue was dried over Attapulgus clay. A yield of 83 g. of an amber oily product was obtained which could not be distilled under 1 mm. pressure without decomposition. Analysis confirmed that this product was the desired 2-(4-chloro-2-butenylmercapto)-benzothiazole.

2-(2-Butynylmercapto)-benzothiazole (IX).—This procedure was similar to compound I except 156 g. (0.85 mole) of 97% 2-mercaptobenzothiazole, 136 g. (0.85 mole) of 25% aqueous sodium hydroxide, 910 g. of water and 73 g. (0.82 mole) of 1-chloro-2-butyne[6] were used. The reaction mixture was stirred for 24 hours. The product was recovered by filtration, washed with water until the washings were neutral to litmus and air-dried at 30°. A yield of 153 g., m.p. 68–70°, was obtained, which upon recrystallization from ethyl alcohol melted at 72–73°.

Acknowledgment.—The author wishes to acknowledge his indebtedness to Mr. M. W. Harman of this Laboratory for assistance rendered during the course of this investigation. Grateful acknowledgment is also made for the analyses rendered by Mr. Edward Null and to the Monsanto Chemical Company for permission to publish this work.

NITRO, WEST VIRGINIA

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[3] Kindly supplied by Shell Chemical Corporation, Emeryville, California.

[4] L. F. Hatch and J. J. D'Amico, THIS JOURNAL, **73**, 4393 (1951).

[5] Kindly furnished by Dow Chemical Company, Midland, Michigan.

[6] L. F. Hatch and V. Chiola, THIS JOURNAL, **73**, 360 (1951).