

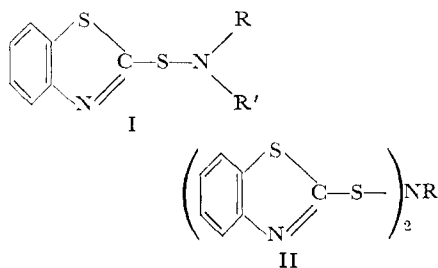
Delayed Action Accelerators for Vulcanizing Rubber . . .

Preparing *N*-Alkyl- and *N*-Cycloalkylbis-(2-benzothiazolesulfen)amides

Purer accelerators which have more effective delayed action can be obtained by improving conditions for their preparation

OF THE DELAYED action accelerators used to prevent scorch when rubber is vulcanized, *N*-substituted derivatives (I) of 2-benzothiazolesulfenamide are the most useful.

Messer (2) has shown that *N*-alkyl- and *N*-cycloalkylbis(2-benzothiazolesulfen)amides (II) are also excellent accelerators.



His products, prepared by adding 1 mole of 2-benzothiazolesulfenyl chloride to about 2 moles of primary amine, were quite impure. Recent work in these laboratories has shown that a pure bis(2-benzothiazolesulfen)amide has considerably more delayed action than the pure mono-2-benzothiazolesulfenamide derived from the same primary amine. Therefore, a study was initiated to improve the Messer reaction as a source of the bis compounds, using 2 moles of 2-benzothiazolesulfenyl chloride and 3 moles of amine.

Experimental

Examples of the two best procedures for preparing bis(2-benzothiazolesulfen)amides and procedures for demonstration of a side reaction are given. All melting points are uncorrected.

***N*-Isopropylbis(2-benzothiazolesulfen)amide by Direct (Amine to Sulfenyl Chloride) Addition at -10°C .** Technical 2-benzothiazolyl disulfide was crystallized once from ethylene chloride to give material melting at $177-179^{\circ}\text{C}$.

A solution of 0.40 mole of 2-benzothiazolesulfenyl chloride was prepared by the method of Messer (7); chlorine (14.2 grams, 0.20 mole) was added above the surface of a stirred suspension of 66.4 grams (0.20 mole) of the disulfide in 500 ml. of anhydrous ethylene chloride at room temperature. Since the sulfenyl chloride is extremely sensitive to moisture, its contact with the atmosphere was kept to a minimum.

A solution of 35.4 grams (0.60 mole) of isopropylamine in 100 ml. of anhydrous ethylene chloride was added to the stirred sulfenyl chloride solution at -11° to -9°C . during a 2-hour period. Stirring was continued for $1/2$ hour at this temperature, and then the mixture was permitted to come to room temperature. The mixture was filtered and the isopropylamine hydrochloride was washed with two 100-ml. portions of ethylene chloride.

The washings were added to the filtrate, and the ethylene chloride was removed by steam distillation. The residue consisted of 75.7 grams (97%) of pale pink solid melting at 97° to 101°C . Recrystallization from ligroin (boiling point, 60° to 90°C .) with Norit-A treatment gave 42 grams (54%) of colorless crystals melting at $106-107^{\circ}\text{C}$. (Table I).

The methyl, ethyl, *tert*-butyl, and cyclohexyl derivatives were prepared by this procedure at -20°C . Methylamine and ethylamine were added as a gas below the surface of the sulfenyl chloride solution.

***N*-Isopropylbis(2-benzothiazolesulfen)amide by Concurrent Addition at 25°C .** A solution of 0.40 mole of 2-benzothiazolesulfenyl chloride in 500 ml. of anhydrous benzene and a solution of 35.4 grams (0.60 mole) of isopropylamine in 100 ml. of anhydrous benzene were added concurrently to a flask equipped with a stirrer, two dropping funnels, and a thermometer. The addi-

Table I. *N*-Substituted Bis(2-benzothiazolesulfen)amides

Substituent	M.P., ^a $^{\circ}\text{C}$.	Nitrogen, %	
		Calcd.	Found
CH_3	110	11.63	11.38
CH_2CH_3	92	11.20	10.92
$\text{CH}(\text{CH}_3)_2$	106-107	10.80	10.67
$\text{C}(\text{CH}_3)_3$	143-144	10.42	10.20
C_6H_{11}	133-134	9.79	9.68

^a Recrystallized from ligroin (b.p. $60-90^{\circ}\text{C}$.) or *n*-hexane.

tion rates were adjusted so that both solutions were added during a 2-hour period; the rates were kept as constant as possible, and the temperature was kept at 23° to 26°C . during the mixing.

After stirring for $1/2$ hour the mixture was worked up as above. The product consisted of 76.1 grams (98%) of pale pink solid melting at 97° to 102°C . Recrystallization from ligroin (boiling point 60° to 90°C .) with Norit-A treatment gave 48 grams (62%) of colorless crystals melting at 106° to 107°C . The four other examples were also prepared by this procedure. Methylamine and ethylamine were added as a gas, concurrently with the sulfenyl chloride, to 200 ml. of stirred anhydrous benzene.

Reaction of 2-Benzothiazolesulfenyl Chloride with *N*-Isopropylbis(2-benzothiazolesulfen)amide. A solution of 19.45 grams (0.050 mole) of *N*-isopropylbis(2-benzothiazolesulfen)amide in 100 ml. of anhydrous ethylene chloride was added during 30 minutes to a stirred solution of 0.10 mole of 2-benzothiazolesulfenyl chloride in 125 ml. of anhydrous ethylene chloride. The temperature of the mixture rose from 23° to 30°C . and a solid began to separate during the addition. After 22 hours the mixture was filtered, and the brown residue was

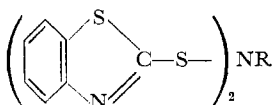
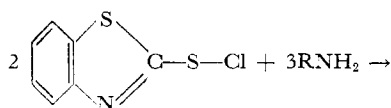
washed with two 25-ml. portions of ethylene chloride. It was dried, slurried in water, again dried, and crystallized once from ethylene chloride to give 19 grams (57%) of crystals melting at 179–180.5° C. A mixture melting point with 2-benzothiazolyl disulfide was not depressed.

Reaction of 2-Benzothiazolesulfenyl Chloride with *N*-Cyclohexyl-2-benzothiazolesulfenamide. The procedure was the same as the preceding one except that *N*-isopropylbis(2-benzothiazolesulfen)amide was replaced with 26.4 grams (0.10 mole) of *N*-cyclohexyl-2-benzothiazolesulfenamide. The yield of crystalline material melting at 179–180° C. was 21 grams (63%). A mixture melting point with 2-benzothiazolyl disulfide was not depressed.

The Mooney scorch times of unpurified products and pure bis(2-benzothiazolesulfen)amides were determined in a typical truck tread stock using a modification of ASTM Method D 1077–55T. The scorch time was taken as the time required for the viscosity to increase 23 units above the minimum at 250° F. using the small rotor.

Results and Discussion

Mooney Rating and Melting Range as Measure of Product Purity. The two known impurities in the products obtained from Reaction 1 are the mono-2-benzothiazolesulfenamide and 2-benzo-



thiazolyl disulfide. Both have much less effective delayed action than the bis(2-benzothiazolesulfen)amide; hence their presence causes reduced delayed action. The greater the proportion of the two impurities present, the shorter the Mooney scorch time. This has been used as a criterion for the purity of the products and is represented by the Mooney rating, which is defined as the scorch time of the product expressed as a percentage of the scorch time of the corresponding pure compound. It has been useful in determining the effects of changes in reaction conditions. It should not be construed as per cent purity because the impurities have ratings of about 50%.

The product melting ranges are in good agreement with the ratings: products having narrow melting ranges have high ratings, while those having wide ranges have low ratings. The presence of considerable amounts of the disulfide results in a wide melting

Table II. Lower Reaction Temperatures or Shorter Addition Times Give Purer *N*-Substituted Bis(2-benzothiazolesulfen)amides^a

Substituent	Temp., ° C.	Melting Range, ^b ° C.	Mooney Rating, %
	2-Hr. Direct Addition		
CH(CH ₃) ₂	25	65–152	67
CH(CH ₃) ₂	10	90–142	76
CH(CH ₃) ₂	0	95–126	87
CH(CH ₃) ₂	–10	97–101	99
CH(CH ₃) ₂	–20	97–102	99
CH(CH ₃) ₂	–30	99–107	98
CH ₃	–20	97–102	92
CH ₂ CH ₃	–20	87–91	95
C ₆ H ₁₁	–20	123–128	96

Direct Addition at 25° C.
Time Min.

CH(CH ₃) ₂	120	88–130	74
CH(CH ₃) ₂	60	94–120	95
CH(CH ₃) ₂	25	95–102	99

^a Product yields, 94–98%. ^b See Table I for melting point of pure compound.

range whose clearing point is above the melting point of the pure bis(sulfen)amide.

A Side Reaction: Means for Suppressing It. Addition of 3 moles of isopropylamine to 2 moles of 2-benzothiazolesulfenyl chloride (direct addition) during 2 hours at 25° C. gave a product having a Mooney rating of only 67%. This indicates that the sulfenyl chloride, in excess during direct addition, attacks sulfenamides. That this is true has been shown by the isolation of 2-benzothiazolyl disulfide in yields above 50% from the reaction of the sulfenyl chloride with *N*-cyclohexyl-2-benzothiazolesulfenamide (I; R = C₆H₁₁, R' = H) and with *N*-isopropylbis(2-benzothiazolesulfen)amide [II; R = CH(CH₃)₂].

Conditions which would be expected to suppress this side reaction are lower reaction temperatures during direct (amine to sulfenyl chloride) addition, faster direct addition, concurrent addition, and inverse (sulfenyl chloride to amine) addition.

For 2-hour direct addition, product purity increased as the reaction temperature was decreased. In the –10° to –30° C. range, the products from four amines have melting ranges and Mooney ratings approaching those of the pure compounds (Table II).

Faster direct addition at 25° C. resulted in increased purity (Table II). Addition time decrease from 2 to 1 hour caused considerable improvement; a decrease to 25 minutes gave an even purer product.

The data in Table III show the beneficial effect of concurrent addition, during which neither the amine nor sulfenyl chloride is in excess, in contrast to direct and inverse addition; 2-hour addition times at 25° C. were used.

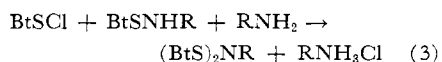
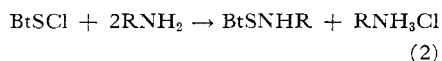
Table III. Concurrent 2-Hour Addition at 25° C. Gives Purer *N*-Substituted Bis(2-benzothiazolesulfen)amides^a

Substituent	Mode of Addition	Melting Range, ^b ° C.	Mooney Rating, %
CH(CH ₃) ₂	Direct	88–130	74
CH(CH ₃) ₂	Inverse	98–145	83
CH(CH ₃) ₂	Concurrent	97–102	96
CH ₃	Concurrent	101–106	94
CH ₂ CH ₃	Concurrent	87–89	97
C(CH ₃) ₃	Concurrent	136–139	97
C ₆ H ₁₁	Concurrent	123–129	95

^a Product yields, 97–99%. ^b See Table I for melting point of pure compound.

Two-hour inverse addition at 25° C. using isopropylamine gave a product having a Mooney rating of only 83%; lowering the temperature to –20° C. had no evident effect. This can be explained as follows:

The first step on adding a small amount of sulfenyl chloride to a large amount of amine is the formation of the monosulfenamide (Reaction 2), which competes with amine for the sulfenyl chloride being added. If the amine is the more reactive, which seems more probable, Reaction 2 will be favored over Reaction 3. Reaction 2, where Bt = 2-Benzothiazolyl, requires 4 moles of amine for 2 moles of sulfenyl



chloride. Since only 3 moles of amine are used for 2 moles of sulfenyl chloride, a point will be reached in the addition when the supply of amine is exhausted, but not all of the sulfenyl chloride has been added. When it is added, it will attack both the bis(sulfen)amide and monosulfenamide with formation of 2-benzothiazolyl disulfide. Infrared examination of the product obtained at 25° C. showed it to contain about 80% bis(sulfen)amide, 10% monosulfenamide, and 10% disulfide.

Acknowledgment

The author is indebted to Robert R. Barnhart for conducting the Mooney scorch tests.

Literature Cited

- (1) Messer, W. E. (to United States Rubber Co.), U. S. Patent 2,257,974 (1941).
- (2) *Ibid.*, 2,321,305 (1943).

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