166° C.), 150 ml. of methanol, and 15 ml. of concentrated hydrochloric acid was refluxed for 20 minutes under a stream of nitrogen. Evaporation of the light-yellow solution under diminished pressure gave a light-colored solid. Trituration of this solid with cold ether (10 ml.) gave crude benzenepentol; pale-yellow crystals, weight 1.00–1.05 grams (77–81%).

For recrystallization, 0.5 gram was dissolved in warm *p*-dioxane (18 ml.) and quickly filtered (molecular sieves), and the filtrate was kept at 15° for 30 minutes. The crystals were filtered off, washed with cold 1-to-1 (v./v.) *p*-dioxane–pentane (5 ml.), and while still containing solvent (to avoid oxidation by air), were dried in a vacuum desiccator, giving white to pinkish crystals of benzenepentol, 0.3 gram. Saturation of the filtrate with pentane and cooling, gave an additional crop (0.15 gram); total 0.45 gram (90%). The compound does not melt, but decomposes at 264–269° C.; it was identical to an authentic sample (*3, 5*).

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New Alkylsulfenyl *N,N*-Dialkyldithiocarbamates

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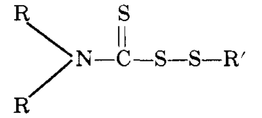
Twelve alkylsulfenyl *N,N*-dialkyldithiocarbamates have been prepared by the reaction of sodium *N,N*-dialkyldithiocarbamates with alkylsulfenyl chlorides. The alkylsulfenyl chlorides were prepared by the reaction of chlorine with alkyl disulfides.

THREE METHODS have been reported for the preparation of alkylsulfenyl *N,N*-dialkyldithiocarbamates. Watson (*8*) used *N,N*-dialkyldithiocarbamate ions as nucleophiles for the displacement of the sulfite ion in alkylthiosulfuric acids. Hunt (*5*) used a similar method which consists of an *in situ* reaction of an alkyl mercaptan with thiocyanogen to form a reactive sulfur-sulfur bond which is cleaved by the *N,N*-dialkyldithiocarbamate ion. A recent review by Kice (*6*) discusses mechanisms of sulfur-sulfur bond cleavage.

The compounds reported in this paper (Table I) were prepared by the reaction of sodium *N,N*-dialkyldithiocar-

Table I. Alkylsulfenyl *N,N*-Dialkyldithiocarbamates



							Analysis, %[a]							
							C		H		N		S	
Compound	R′	R	B.P., ° C./Mm.	η_D^T	λ_{max}^{EtOH} Mμ	10^3	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
I	$t\text{-}C_4H_9$	C_2H_5	114–15/0.12–0.15	1.5768^{25}	284	7.55	45.52	45.75	8.07	8.20	5.90	6.09	40.51	40.45
					243	7.6								
II	$t\text{-}C_4H_9$	CH_3	110–18/0.28–0.47[b]		281	6.7	40.15	40.38	7.22	7.21	6.69	6.53	45.94	46.07
			(m.p. 70–72.5°)		240	7.6								
III	$t\text{-}C_4H_9$	$n\text{-}C_4H_9$	140–4/0.08–0.12[c]	$1.5487^{26.5}$	284	7.4	53.19	53.22	9.27	9.15	4.77	5.00	32.77	33.00
					246	7.12								
IV	$n\text{-}C_4H_9$	$n\text{-}C_3H_7$	132–7/0.07	$1.5578^{26.5}$	282	7.43	49.76	49.91	8.73	8.82	5.28	5.26	36.23	36.02
V	$n\text{-}C_4H_9$	CH_3	113–16/0.05[d]	1.5933^{25}	278	8.35	40.15	40.28	7.22	7.26	6.69	6.49	45.94	45.98
VI	C_2H_5	C_2H_5	101–7/0.015–0.07	1.5945^{24}	281	8.71	40.15	40.05	7.22	7.39	6.69	6.53	45.94	45.72
VII	C_2H_5	CH_3	99–101/0.05[e]	1.6272^{25}	281	7.25	33.12	33.30	6.11	6.01	7.72	7.90	53.04	52.94
VIII	C_2H_5	$n\text{-}C_3H_7$	99–101.5/0.05–0.06	1.5740^{25}	282	8.15	45.52	45.64	8.07	8.15	5.90	6.03	40.51	40.29
IX	$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	160–2/0.37	1.5477^{27}	282	7.16	53.19	53.05	9.27	9.29	4.77	4.63	32.77	32.64
X	$n\text{-}C_4H_9$	C_2H_5	113.5–17/0.19	1.5708^{27}	281	8.17	45.52	45.36	8.07	8.11	5.90	5.74	40.51	40.36
XI	C_2H_5	$n\text{-}C_4H_9$	133–6/0.11–0.17	1.5596^{27}	282	8.15	49.76	49.85	8.73	8.91	5.28	5.34	36.23	36.36
XII	$t\text{-}C_4H_9$	$n\text{-}C_3H_7$	128.5–35/0.04–0.06[f]	1.5613^{26}	284	7.43	49.76	49.62	8.73	8.62	5.28	5.41	36.23	36.01
					243	7.19								

[a] Performed by Galbraith Laboratories, Knoxville, Tenn. [b] Reported b.p. 125° C./0.7 mm. (*7*) and m.p. 69–70° C. (*4*). [c] Reported 173–77°/1.0 mm. Hg (*7*). [d] Reported b.p. 170–75°/2.0 mm. (*5*). [e] Reported b.p. 100–02°/0.005 mm., n_D^{20} 1.6119 (*8*). [f] Reported m.p. 61° C. (*4*).

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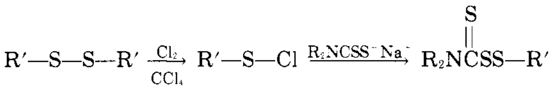
bamates with alkylsulfenyl chlorides. This method has been described by Douglass (*2*), Himel and Edwards (*4*), and Schulze *et al.* (*7*).

Alkylsulfenyl chlorides were prepared by treating carbon tetrachloride solutions of alkyl disulfides with chlorine. The following sequence of reactions illustrates this method:



$$R'{-}S{-}S{-}R' \xrightarrow[CCl_4]{Cl_2} R'{-}S{-}Cl \xrightarrow{R_2NCSS^-Na^+} R_2N\overset{\overset{S}{\|}}{C}SS{-}R'$$

When R′ was normal alkyl, the sulfenyl chloride was prepared at −20° to −25° C. in order to minimize formation of α-chloroalkylsulfenyl chlorides (*1, 3*). When R′ was *tert*-butyl, a reaction temperature of 25° to 32° C. was used. The higher temperature favors sulfur-sulfur bond cleavage in tertiary alkyl disulfides and lower temperatures favor carbon-sulfur bond cleavage (*7*).

EXPERIMENTAL

Sodium *N,N*-Di-*n*-propyldithiocarbamate. To a solution of 50.6 grams (0.5 mole) of di-*n*-propylamine in 150 ml. of water was added 39.6 grams (0.52 mole) of carbon disulfide. The reaction vessel was cooled by an ice bath, and the carbon disulfide was added at a rate sufficient to maintain a temperature of 10° to 15° C. A solution of 20.0 grams (0.5 mole) of sodium hydroxide in 50 ml. of water was then added at a rate sufficient to maintain the temperature below 15° C. The mixture was stirred for 4 hours, left at room temperature for 15 hours, and reduced to about one third the original volume by evaporation of water. This solution was cooled to obtain a solid which was collected by filtration. The solid was washed with ether and dried to obtain 55.8 grams (51.3%) of sodium *N,N*-di-*n*-propyldithiocarbamate monohydrate (m.p. 54–57° C.).

***tert*-Butylsulfenyl *N,N*-Di-*n*-propyldithiocarbamate (XII).** Chlorine(7.1 grams, 0.10 mole) was added just above the surface of a stirred solution of 17.8 grams (0.10 mole) of *tert*-butyl disulfide in 250 ml. of carbon tetrachloride. The temperature of the reaction was maintained at 20° to 30° C. by use of an ice bath. Soon after the chlorine had been added, the solution of sulfenyl chloride was added rapidly to a stirred suspension of 37.2 grams (0.17 mole) of sodium *N,N*-di-*n*-propyldithiocarbamate monohydrate in 500 ml. of carbon tetrachloride. When normal alkylsulfenyl chlorides were used, the suspension of dithiocarbamate was cooled to −25° C. before addition of the sulfenyl chloride. The cloudy solution was warmed slowly and heated under reflux for 2 hours. A suspended solid (probably sodium chloride) was removed by filtration, and the filtrate was washed with water before being dried over magnesium sulfate. Evaporation of the solvent gave a viscous liquid which was distilled through a short-path apparatus. A second distillation gave 16.3 grams (36.3%) of a yellow liquid [b.p. 128.5-35°/0.04–0.06 mm., $\lambda_{\max}^{\text{liquid film}}$ 1475 cm.$^{-1}$ (N=C=S)].

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Vapor Pressures and Heats of Sublimation of Some High Melting Organic Explosives

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A method is described for the determination of vapor pressures in the range of 10^{-5} to 10^{-9} torr. Measurements are reported on six nitro compounds: cyclotrimethylenetrinitramine, RDX; cyclotetramethylenetetranitramine, beta polymorph, β-HMX; 2,4,6-trinitroaniline, TNA; 1,3-diamino-2,4,6-trinitrobenzene, form I polymorph, DATB-I; 1,3,5-triamino-2,4,6-trinitrobenzene, TATB; and 2,2′,4,4′,6,6′-hexanitrostilbene, HNS. Relationships between heats of sublimation and intermolecular hydrogen bonding are discussed.

AS PART of a study at this laboratory directed toward the determination of the physical properties of organic high explosives, it was necessary to measure the vapor pressures of several explosives at elevated temperatures. Experiments of this type have rarely been performed before because of the poor stability of poly-nitro compounds at high temperatures, the difficulty in obtaining pure samples, etc. Recently, the need for explosives to withstand the temperature and pressure regimes imposed by space exploration has provided the impetus necessary to overcome the several experimental difficulties. This paper describes a method for the determination of vapor pressures in the range of 10^{-5} to 10^{-9} torr. Measurements are reported on six nitro compounds: cyclotrimethylenetrinitramine, RDX; cyclotetramethylenetetranitramine, beta polymorph, β-HMX; 2,4,6-trinitroaniline, TNA; 1,3-diamino-2,4,6-trinitrobenzene, form I polymorph, DATB-I; 1,3,5-triamino-2,4,6-trinitrobenzene, TATB; and 2,2′,4,4′6,6′-hexanitrostilbene, HNS.

EXPERIMENTAL

The Langmuir method was used for the determination of vapor pressures from measurements of the rates of sublimation at constant temperature (*4, 9*). Vapor pressures were computed from the observed weight loss of the sample heated in a vacuum. The expression used was:

$$P(\text{torr}) = 17.14 \times G \times (T/M)^{1/2}$$