New Acyl Derivatives of the Hexasulfur Diimides and Heptasulfur Imide

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Diacetyl derivatives of the three hexasulfur diimides, and dibenzoyl derivatives of the 1,4- and 1,5-diimides, all made by acylation of the diimides, are described. Reaction of heptasulfur imide with succinyl chloride gives succinyl bis-(heptasulfurimide).

FROM the reaction of the recently characterized separate isomers (*1, 3*) of hexasulfur diimide with excess acetyl or benzoyl chloride and pyridine, in chloroform solution, all of the possible diacetyl and dibenzoyl derivatives except dibenzoyl-1,3-hexasulfur diimide have been isolated in 40 to 70% yield. In the case of dibenzoyl-1,3-hexasulfur diimide, the reaction gave an unstable sirup which gradually deposited polymeric matter. The stable derivatives were purified by column chromatography on silica gel using benzene as eluent. They are colorless, crystalline solids, readily soluble in carbon disulfide or benzene, and insoluble in hexane.

Table I. Properties of Derivatives

	Derivative	Melting Point, ° C.	Analysis[a] %C	%H	%N	%S	Mol. Wt.[a]	R_f	Infrared Spectrum, Wavelengths in μ: Acyl group	S-N stretch
1-3	Diacetyl	130	15.8	2.0	9.3	63.7	286	0.20	5.7s, 7.3m, 8.3s, 8.5m, 9.6w, 9.9m, 10.7m.	11.9m 12.2m
1-4	Hexasulfur	77	16.2	2.0	9.0	61.6	298	0.16	5.8s, 7.3m, 8.5s, 9.7w, 10.0m, 10.8m	11.9m 12.1w
1-5	Diimide	158	16.3	2.3	9.1	61.9	289	0.17	5.8s, 7.4m, 8.5s, 9.7w, 10.0m, 10.8m	11.9m
1-3	Dibenzoyl	unstable								
1-4	Hexasulfur	156	38.7	2.5	6.4	44.5	436	0.69	5.9s, 8.2s, 8.5w, 9.3w, 9.6s, 9.8s, 10.9w, 14.1m, 14.4w	13.0m 13.1w
1-5	Diimide	183	39.2	2.4	6.5	42.7	392	0.51	5.9s, 8.2s, 8.5w, 9.3w, 9.6s, 9.9s, 11.0w, 14.1m, 14.4w	13.0m
	Succinyl bis-(heptasulfurimide)	195	8.7	0.73	5.3	80.0	...	...	5.8s, 7.4w, 8.3m, 9.1s, 10.2w	12.0–12.5w (poorly characterized)

[a] Calcd. for $(CH_3CO)_2S_6N_2$: C, 15.7; H, 2.0; N, 9.1; S, 62.8; mol. wt. 306.5. Calcd. for $(C_6H_5CO)_2S_6N_2$: C, 39.1; H, 2.3; N, 6.5; S, 44.7; mol. wt. 430.7. Calcd. for $(S_7N)_2(COCH_2)_2$: C, 8.6; H, 0.72; N, 5.0; S, 80.0.

When succinyl chloride was added to a solution of heptasulfur imide in pyridine, hard colorless platelets of succinyl bis-(heptasulfurimide), $S_7N \cdot CO(CH_2)_2CO \cdot NS_7$, were precipitated. This compound is soluble to the extent of about 1% by weight in carbon disulfide at 20° C., and nearly insoluble in benzene or acetic acid. Melting at 195° C., it is the most thermally stable compound known containing eight-membered sulfur-nitrogen rings. Thus, polymers made by coupling the sulfur diimides, triimides (*2*), or tetraimide with succinyl chloride might well have useful properties.

Numerical data on all of these compounds are given in Table I. Melting points (uncorrected) were measured with an ordinary manual apparatus. Molecular weights were determined cryoscopically in benzene with a semi-micro thermistor device. The R_f values refer to thin-layer chromatograms on Merck Kieselgel G, with benzene as developing solvent. For the IR spectra, solutions in carbon disulfide, 1% by weight, were measured in 0.2-mm. thickness on a Perkin-Elmer Infracord machine scanning from 2.5 to 15 μ. The bands listed in the last column are attributed to S-N stretching vibrations because they resemble, in position and structure, bands in the spectra of the corresponding unsubstituted diimides which can only be due to the S-N stretch.

The protons of the succinyl group in succinyl bis-(heptasulfurimide) gave one NMR signal 3.08 p.p.m. downfield from tetramethylsilane (Varian HR 100 spectrometer; 1% solution of compound in carbon disulfide).

LITERATURE CITED

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2-Chloro-1,2,3,4-tetrabromobutane

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THE synthesis of 2-chloro-1,2,3,4-tetrabromobutane has been accomplished by photochemical addition of bromine to 2-chloro-butadiene-1,3. The substance forms colorless crystals, m.p. 32–33°, b.p. 142–143° (4 mm.), d_4^{25} 2.619, n_D^{25} 1.6126.

Anal. Calcd. for $C_4H_5ClBr_4$: C, 11.76; H, 1.23; halogen, 87.0. Found: C, 11.82; H, 1.27; halogen 86.8.

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