CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 75.]

NORMAL HEPTYL THIOCYANATE AND SOME NEW ALKYL ESTERS OF DITHIOCARBAMIC ACID.

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Received January 7, 1903.

SEVERAL years ago, in connection with certain investigations then under way, the writer had occasion to prepare the substances described in this paper. As there is but little likelihood of this line of work being resumed, it seems advisable to record the properties of these new compounds for the information of other workers in this field, particularly since J. v. Braun, in his recent article on the dithiourethanes,[1] calls attention to the fact that only two (ethyl and isopropyl) alkyl esters of unsubstituted dithiocarbamic acid are mentioned in the literature.

Normal Heptyl Thiocyanate, $C_7H_{15}SCN$.—Normal heptyl bromide was prepared by the action of bromine and amorphous phosphorus upon normal heptyl alcohol, the bromide being driven out of the crude reaction product by a rapid current of steam. The separated bromide was washed with water, with sodium carbonate solution, with water again, dried with calcium chloride, treated with cold concentrated sulphuric acid to remove unchanged heptyl alcohol, washed, dried again and distilled. As thus prepared, normal heptyl bromide forms a colorless oil, boiling at 175.5°-177.5° (uncorr.) at 765 mm., and volatile with steam. In concentrated alcoholic solution this bromide rapidly transposes with potassium thiocyanate, the reaction being complete in about half an hour, if conducted at the boiling-point of the solution. The separated thiocyanate, washed and dried, distils at 234°-236° (uncorr.). Rectified under diminished pressure, the pure substance is obtained as a colorless mobile oil of peculiar but not unpleasant odor, boiling-point 136° (corr.) at 28 mm.; sp. gr. at 20°, 0.92.

Normal Heptyl Sulphonic Acid, $C_7H_{15}SO_3H$.—The thiocyanate was oxidized by heating with moderately strong nitric acid. After the evaporation of the nitric acid, the syrupy residue was taken up with water, excess of barium carbonate added, the mixture boiled, and filtered hot. The barium salt of the sulphonic acid crystallized from the filtrate, on cooling, in pearly white scales, only moder-

[1] *Ber. d. chem. Ges.*, **35**, 3369 (1902).

ately soluble in cold water or in cold 95 per cent. alcohol, and containing no water of crystallization. Spring and Winssinger,[1] by the action of chlorine upon the normal heptyl sulphoxide, obtained a mixture which they believed contained barium heptyl sulphonate, but they did not separate the mixture or obtain the barium salt in question in a pure state.

Normal Heptyl Dithiocarbamate, $H_2NCSSC_7H_{15}$.—Normal heptyl thiocyanate was treated with hydrogen sulphide at 100°, the hydrogen sulphide being driven in against a pressure of 7 inches of mercury. In the course of six to ten hours, glassy prisms of the dithiocarbamic ester separated. Recrystallized from a mixture of naphtha and carbon bisulphide, large glassy prisms of soapy feel were obtained, melting at 65°, and easily soluble in methyl alcohol, chloroform, benzene, acetone and carbon bisulphide, difficultly soluble in naphtha or kerosene.

Normal Propyl Dithiocarbamate, $H_2NCSSC_3H_7$, prepared from normal propyl thiocyanate and hydrogen sulphide in a similar manner, crystallizes from a mixture of naphtha and carbon bisulphide, in large colorless prisms, melting-point 57°, insoluble in water, very easily soluble in methyl, ethyl or isoamyl alcohols, in benzene, toluene, acetone, chloroform or carbon bisulphide, easily soluble in hot naphtha or kerosene but on cooling tends to separate as an oil. Through the kindness of Dr. Austin F. Rogers, of the Mineralogical Department of this University, the crystals were measured, with the following results:

Crystals—tabular, parallel to basal pinacoid.

Monoclinic—$a : b : c = 0.8536 : 1 : 0.9447$. $\beta = 77° 7'$.

Observed forms—*c* (001), *a* (100), *m* (110), *t* (012), *q* (011).

			Measured.	Calculated.
mm'''	(110 ∧ $1\bar{1}0$)	(7)	100° 28′	.....
cm	(001 ∧ 110)	(6)	80° 8′	.....
cq	(001 ∧ 011)	(6)	43° 38.5′	.....
c'm	($00\bar{1}$ ∧ $1\bar{1}0$)	(3)	99° 53.5′	99° 52′
qq'''	(011 ∧ $0\bar{1}1$)	(4)	94° 44′	94° 43′
ct	(011 ∧ 012)	(3)	24° 45′	24° 43′

Cleavage—perfect, parallel to *c*; imperfect, fibrous parallel to *a*.

Isoamyl Dithiocarbamate, $H_2NCSSC_5H_{11}$, from amyl thiocyanate and hydrogen sulphide, under similar conditions, crystallizes from a mixture of carbon bisulphide and naphtha in glassy

[1] *Bull. Soc. Chim.*, **49**, 72.

micaceous scales, melting-point 51.5°, easily soluble in methyl or ethyl alcohols, in chloroform, carbon bisulphide, benzene, acetone, very difficultly soluble in boiling water, difficultly soluble in cold naphtha or kerosene but easily soluble in these solvents when boiling.

NOTE.—Since writing the above, an article has appeared by Delépine,[1] in which he describes the methyl, ethyl, normal and isopropyl, benzyl and *p*-nitrobenzyl dithiocarbamates, and gives the melting-point of the normal propyl compound as 58°.

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THE FREEZING-POINTS OF DILUTE SOLUTIONS.

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Received January 9, 1903.

THE difficulties which attend the accurate determination of the freezing-points of dilute solutions, according to the ordinary method of procedure, are well known. A brief perusal of the work of Jones,[2] Loomis,[3] Nernst and Abegg,[4] and Raoult[5] is enough to convince even a hasty reader that besides the common errors of thermometry, and of quantitative work in general, the process is especially complicated by the slowness with which the equilibrium is attained. This complication results in either supercooling or superheating, according as the system is being cooled or warmed. Nernst and Abegg performed a valuable service in calling attention to this danger, and the latter of the two, as well as Loomis and Raoult, carried out a few accurate determinations guarding especially against it. Unfortunately, however, their precautions were so elaborate that few experiments were made, and the difficulty seems to have deterred other workers in the same field.

It is easy to see that another method may be used, a method which overcomes the chief difficulty in a simpler manner; and the

[1] *Bull. Soc. Chim.*, **3**, 29-30, 48 (1903).

[2] Jones: *Ztschr. phys. Chem.*, 11, 110 and 529; **12**, 623 (1893).

[3] Loomis: *Wied. Ann.*, **51**, 500 (1894); also *Ztschr. phys. Chem.*, **32**, 578 (1900); **37**, 407 (1901).

[4] Nernst and Abegg: *Ztschr. phys. Chem.*, **15**, 681 (1894); also Abegg: *Ibid.*, **20**, 207 (1898).

[5] Raoul : *Compt. Rend.*, **125**, 751 (1897).