[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Alpha-Naphthyl Isothiocyanate as a Reagent for Primary and Secondary Aliphatic Amines

BY C. M. SUTER AND EUGENE W. MOFFETT[1]

It has been shown recently[2] that phenyl and o-tolyl isothiocyanates are useful in preparing solid derivatives of primary aromatic amines. For the aliphatic primary and secondary amines α-naphthyl isothiocyanate gives derivatives melting above 65° in all cases thus far investigated. The melting points are not far different, where comparison is possible, from those of the corresponding substituted ureas[3] obtained from α-naphthyl isocyanate and the amines, but the isothiocyanate has the advantage of reacting less readily with water and alcohol. A few of the lower melting thioureas have a tendency to separate from their solutions in 80% alcohol as oils which crystallize only after standing so their purification is occasionally rather difficult. Several pairs of the derivatives have practically identical melting points but mixtures of these pairs melt from 10–20° below the melting point of the pure compounds.

Several of the sym-alkyl-α-naphthylthioureas have been prepared before by Dyson and co-workers[4] incidental to other work, but the melting points recorded by these authors are for the most part not in good agreement with those obtained in the present investigation. Recently,[5] however, there has appeared a partial revision of the values previously given with the explanation that the compounds were more easily obtained pure from the aliphatic amine and α-naphthyl isothiocyanate than by the first method employed, in which the aliphatic isothiocyanate and α-naphthylamine were used. In the present work the n-propyl and n-hexyl derivatives were made by both methods and no difference could be noted in the purity of the products obtained by the two reactions when pure starting materials were used. For purposes of comparison the most recent values of the melting points reported by Dyson and co-workers are included in Table I in the experimental part.

Experimental

Materials Used.—Except for the methyl- and ethylamines, which were Eastman products, the amines were prepared by reduction of cyanides and oximes with sodium and n-butyl alcohol[6] or from alkyl bromides and alcoholic ammonia. The n-propyl[7]

(1) Eastman Kodak Company Fellow, 1931–1932.

(2) Otterbacher and Whitmore, THIS JOURNAL, 51, 1908 (1929).

(3) French and Wirtel, ibid., 48, 1736 (1926).

(4) Dyson and Hunter, Rec. trav. chim., 45, 421 (1926); Dyson, Hunter and Soyka, J. Chem. Soc., 2964 (1927); Dyson and Hunter, Chem. News, 134, 4 (1927).

(5) Dyson, Hunter and Morris, J. Chem. Soc., 2282 (1932).

(6) A more detailed report of the use of n-butyl alcohol in sodium reductions will be published shortly.

(7) Hecht, Ber., 23, 282 (1890).

and n-hexyl[8] isothiocyanates were made in good yields according to the procedure of Delépine.[9] The α-naphthyl isothiocyanate[10] was made by a modification of the method described in "Organic Syntheses"[11] for the preparation of phenyl isothiocyanate. Instead of separating the α-naphthyl isothiocyanate from the lead sulfide by steam distillation the reaction mixture was extracted several times with hot alcohol. After recrystallization from alcohol (95%) the product melted at 55–56°.

Preparation of Sym-alkyl-α-naphthylthioureas.—A mixture of 0.02 mole of an amine and the same amount of α-naphthyl isothiocyanate, either alone or with a small quantity of 95% alcohol as a solvent, was heated for thirty minutes on the steam-bath. The product was recrystallized from hot dilute alcohol (80% in most cases) until the melting point remained unchanged. The yield of pure thiourea was generally above 50% of the theoretical amount. A similar procedure was employed for condensing n-propyl and n-hexyl isothiocyanate with α-naphthylamine. The results are summarized in Table I. The nitrogen analyses are averages of two closely agreeing determinations

TABLE I

N-α-NAPHTHYL-N'-ALKYLTHIOUREA

			N, %	
Amine	M. p. (corr.), °C.	Formula	Calcd.	Found
Methylamine	191–192 (198)[a]	$C_{12}H_{12}N_2S$	12.96	12.96
Ethylamine	120–121 (121)	$C_{13}H_{14}N_2S$	12.17	12.10
n-Propylamine	102–103 (101–102)	$C_{14}H_{16}N_2S$	11.47	11.26
n-Butylamine	108–109 (100)	$C_{15}H_{18}N_2S$	10.85	10.85
n-Amylamine	102–103 (104)	$C_{16}H_{20}N_2S$	10.29	10.23
n-Hexylamine	78–79	$C_{17}H_{22}N_2S$	9.79	9.72
n-Heptylamine	68–69 (65–66)	$C_{18}H_{24}N_2S$	9.33	9.37
n-Octylamine	71.5–72.2	$C_{19}H_{26}N_2S$	8.95	8.89
i-Propylamine	142–143	$C_{14}H_{16}N_2S$	11.47	11.42
i-Amylamine	96.5–97.5 (95)	$C_{16}H_{20}N_2S$	10.29	10.23
i-Hexylamine	78.5–79.5	$C_{17}H_{22}N_2S$	9.79	9.81
2-Aminobutane	136–137	$C_{15}H_{18}N_2S$	10.85	10.72
2-Aminoheptane	101–102	$C_{18}H_{24}N_2S$	9.33	9.27
2-Aminooctane	82–83	$C_{19}H_{26}N_2S$	8.95	8.89
2-Amino-3-methylbutane	133–134	$C_{16}H_{20}N_2S$	10.29	10.18
Cyclohexylamine	141–142	$C_{17}H_{20}N_2S$	9.86	9.81
Benzylamine	171–172	$C_{18}H_{16}N_2S$	9.59	9.55
Dimethylamine	167–168	$C_{13}H_{14}N_2S$	12.17	12.28
Diethylamine	107–108	$C_{15}H_{18}N_2S$	10.85	10.75
Di-n-propylamine	160–161	$C_{17}H_{22}N_2S$	9.79	9.62
Di-n-butylamine	122–123	$C_{19}H_{26}N_2S$	8.95	9.01
Di-i-amylamine	117–118	$C_{21}H_{30}N_2S$	8.18	8.13
Dibenzylamine	130–131	$C_{25}H_{22}N_2S$	7.33	7.20

[a] The melting point of the methyl derivative depends to a marked extent upon the rate at which the temperature of the sample is raised. The value given here was obtained by a rise of approximately 1° per minute. At several times this rate the value given by Dyson, Hunter and Morris was checked. The compound will melt at 189° if the temperature is held at this point for two or three minutes.

(8) Frentzel, *Ber.*, **16**, 746 (1883).

(9) Delépine, *Compt. rend.*, **144**, 1126 (1907); *Bull. soc. chim.*, [4] **3**, 642 (1908).

(10) Hofmann, *Ber.*, **15**, 986 (1882); Mainzer, *ibid.*, **15**, 1414 (1882); Heller and Bauer. *J. prakt. Chem.*, [2] **65**, 380 (1902); Dyson and Hunter, *Chem. News*, **134**, 4 (1927).

(11) "Organic Syntheses," John Wiley and Sons, New York, 1926, Vol. VI, p. 72

made by the Kjeldahl method. The melting points recorded in parentheses are those listed by Dyson, Hunter and Morris.[5]

Summary

A number of substituted thioureas have been made by the action of α-naphthyl isothiocyanate upon primary and secondary aliphatic amines. These compounds are solids which may be used in identification of the amines.

The Structure of the Acids Obtained by the Oxidation of Tri-isobutylene

BY JAMES B. CONANT AND GEORGE W. WHELAND

Butlerow[1] obtained an acid by the oxidation of triisobutylene to which he assigned the empirical formula $C_{11}H_{22}O_2$. He suggested that the acid was probably di-*tert*-butylmethylacetic acid. Spiegler[2] many years later reported the formation of the same acid by the oxidation of a pigment from black wool, but in view of the results of the present investigation, his identification seems very doubtful.

We have investigated Butlerow's acid using rather large amounts of material and have found that it is in reality a mixture of two acids. The material described by Butlerow and prepared according to his directions melts at 66–70°; the two component acids into which it can be separated melt at 88–89° and 129–129.5°, respectively. The two components were present in approximately equal amounts. A mixture of the two acids appears to be identical with Butlerow's material in all particulars. The separation may be effected either by a fractional extraction of an ethereal solution with sodium carbonate or by taking advantage of the difference in the mode of reaction of the two acid chlorides with aqueous ammonia. The acid chloride of the alpha acid (the lower melting) is converted into the amide while the beta acid chloride regenerates the free acid. The latter is easily separated from the amide of the alpha acid by virtue of its solubility in dilute alkali.

Both the alpha and beta acids have the empirical formula $C_{12}H_{24}O_2$ and not $C_{11}H_{22}O_2$ which Butlerow assigned to his material. The empirical formula was established by the analyses of the free acids, the methyl esters, and the p-chloroanilides. Because of the well-known difficulties of burning compounds with highly branched chains, the carbon analyses

(1) Butlerow, *Ber.*, **12**, 1482 (1879); *J. Russ. Phys.-Chem. Soc.*, **11**, 203 (1879).
(2) Spiegler, *Beitr. Chem. Physiol. Pathol.*, **4**, 40–50 (1903); *Chem. Zentr.*, **2**, 128 (1903).