

of the catalyst not represented by nickel and aluminum. The spectrographic analysis for sodium is in good agreement with results of chemical analyses; this element may be present as sodium aluminate³ or as sodium hydroxide not removed despite extensive washing.

The data given in Table I show that the maximum alumina formed is 1% rather than 21% as reported by Ipatieff and Pines. Since aluminum (III) oxide is insoluble in hot 60% nitric acid, the small but measurable difference in the quantity of alumina found using concentrated and dilute acid cannot be attributed to solubility. Furthermore it is significant that the decrease in the quantity of alumina found when concentrated nitric acid is used to dissolve the catalyst samples parallels qualitatively the trend in oxidation potential of nitric acid as a function of concentration. This clearly indicates that alumina is not a constituent of W-6 Raney nickel prepared by the method of Adkins and Billica but rather that alumina is formed during dissolution of the samples taken for analysis. This conclusion is further supported by X-ray diffraction studies on Raney nickel carried out both in this laboratory and in connection with work described by Taylor and Weiss.⁸ In both instances, no diffraction maxima attributable to any of the known forms of aluminum(III) oxide or its hydrates were observed. Finally, it should be recognized that the type of specific composition data proposed by Ipatieff and Pines is also unwarranted on the grounds that, even with respect to the two major components, the composition of W-6 Raney nickel catalysts is not rigorously reproducible and varies over an appreciable range owing to unavoidable variation in the conditions that prevail during the leaching of the nickel-aluminum alloy.

(8) A. Taylor and J. Weiss, *Nature*, **141**, 1055 (1938).

DEPARTMENT OF CHEMISTRY
THE UNIVERSITY OF TEXAS
AUSTIN, TEXAS

RECEIVED JULY 19, 1951

Benzylamine as a Reagent for the Characterization of Isothiocyanates^{1,2,3}

BY LOWELL E. WELLER, CHARLES D. BALL AND
HAROLD M. SELL

In an investigation concerning the occurrence of mustard oils in plants it became necessary to identify minute quantities of isothiocyanates. Since a suitable derivative was not available, work was directed toward obtaining solid derivatives of some of the more common isothiocyanates which have been obtained from plants. The substituted benzylthioureas formed by treating benzylamine with the aliphatic and aromatic isothiocyanates herein reported are crystalline compounds with convenient melting points. The reaction of the basic benzylamine with the acidic isothiocyanates proceeds spontaneously without the addition of heat

to give nearly quantitative yields of the substituted benzylthioureas.

Experimental

Materials Used.—Ethyl, allyl and phenyl isothiocyanate as well as benzylamine were commercial products of Eastman Kodak Company. These were distilled under reduced pressure before they were used. Benzyl, 2-methylthioethyl, 2-methoxyethyl and β -phenylethyl isothiocyanate were synthesized by the method described by Slotta, *et al.*⁴ Crotonic isothiocyanate was prepared from the corresponding thiocyanate according to the general procedure of Gerlich.⁵ The remaining isothiocyanates listed were prepared in 50–70% yields according to the method as given by Delépine.⁶

Preparation of Substituted Benzylthioureas.—A mixture of 0.01 mole of the isothiocyanate in 5 ml. of 95% ethanol and an equimolar amount of benzylamine dissolved in the same solvent (5 ml.) was boiled gently for five minutes. Water was added until the hot solution appeared cloudy, then enough ethanol was added to clear the hot solution. If upon cooling an oil separates out it can usually be caused to crystallize readily by scratching the sides of the vessel. However, a better procedure at this point was to redissolve the oil in the hot solvent and then increase the ethanol content of the solution. Upon slow cooling the product will usually crystallize out. Skelly B⁷ was used for the first recrystallization of *n*-butyl, crotonic and isoamyl benzylthiourea since these did not crystallize readily from their aqueous ethanolic solutions. If benzylamine was added to the isothiocyanate in the absence of a solvent the reaction proceeded spontaneously with the evolution of heat. Aqueous ethanol (60–70%) was then added for recrystallizing the product. Usually two recrystallizations were sufficient for purification. The yields of the recrystallized products were approximately 60–70%. The nitrogen values reported were the averages of two Kjeldahl determinations.⁸

TABLE I
DERIVATIVES OF ISOTHIOCYANATES

Isothiocyanate	Formula	Substituted M.p., °C.	benzyl thioureas Nitrogen, %	
			Found	Calcd.
Methyl	C ₉ H ₁₂ N ₂ S	78	15.6	15.5
Ethyl	C ₁₀ H ₁₄ N ₂ S	103	14.2	14.4
Allyl	C ₁₁ H ₁₄ N ₂ S	94.5	13.6	13.6
<i>n</i> -Propyl	C ₁₁ H ₁₆ N ₂ S	88	13.3	13.4
Isopropyl	C ₁₁ H ₁₆ N ₂ S	126	13.4	13.4
<i>n</i> -Butyl	C ₁₂ H ₁₈ N ₂ S	50	12.8	12.6
<i>s</i> -Butyl	C ₁₂ H ₁₈ N ₂ S	78	12.4	12.6
Isobutyl	C ₁₂ H ₁₈ N ₂ S	112	12.7	12.6
Crotonic	C ₁₂ H ₁₆ N ₂ S	49.5	12.7	12.7
<i>n</i> -Amyl	C ₁₃ H ₂₀ N ₂ S	62	12.0	11.8
Isoamyl	C ₁₃ H ₂₀ N ₂ S	54	11.8	11.8
2-Methoxyethyl ^a	C ₁₁ H ₁₆ ON ₂ S	71	12.5	12.5
3-Methoxy propyl ^a	C ₁₂ H ₁₈ ON ₂ S	51	11.7	11.8
2-Methylthioethyl ^a	C ₁₁ H ₁₆ N ₂ S ₂	58	11.7	11.7
Phenyl	C ₁₄ H ₁₄ N ₂ S	153	11.4	11.6
Benzyl	C ₁₅ H ₁₆ N ₂ S	148	11.0	10.9
2-Phenylethyl	C ₁₆ H ₁₈ N ₂ S	118	10.5	10.4
1-Naphthyl	C ₁₈ H ₁₆ N ₂ S	173 ^b	9.7	9.6

^a Preparation and properties not reported in the literature.

^b Previously reported as 171–172°, C. M. Suter and E. W. Moffett, *THIS JOURNAL*, **55**, 2497 (1933).

DEPARTMENTS OF AGRICULTURAL CHEMISTRY AND
CHEMISTRY

MICHIGAN STATE COLLEGE

EAST LANSING, MICHIGAN

RECEIVED OCTOBER 22, 1951

(4) K. H. Slotta and H. Dressler, *Ber.*, **63**, 888 (1930).

(5) G. Gerlich, *Ann.*, **178**, 80 (1875).

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

(7) A petroleum ether, b.p. 62–67°, marketed by the Skelly Oil Company, Chicago, Ill.

(8) J. B. Niederl and V. Niederl, "Organic Quantitative Microanalysis," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1942, p. 72.

(1) Published as Journal Article No. 1276 of the Michigan Agricultural Experiment Station.

(2) From the Master's thesis of Lowell E. Weller, Michigan State College.

(3) This research was supported by the Horace H. Rackham Research Endowment.