Summary

Benzhydrylmagnesium chloride can be prepared in very low yields by adding benzhydryl chloride to magnesium in ether. It reacts normally with dimethyl sulfate to give *unsym.*diphenylethane.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MISSOURI]

ALPHA-NAPHTHYLISOCYANATE AS A REAGENT FOR PHENOLS AND ALIPHATIC AMINES[1]

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This investigation of α-naphthylisocyanate as a reagent for phenols and aliphatic primary and secondary amines is a continuation of a similar study of that substance as a reagent for alcohols.[2]

On the whole, α-naphthylisocyanate proved to be a satisfactory reagent for phenols and aliphatic amines. The procedure used in the preparation of derivatives was very simple. In the cases of the phenols it consisted essentially in heating the two substances together for a few minutes. In the cases of the amines the application of heat was unnecessary, the reaction going at room temperature. The reaction was found to be a general one; of the thirty-two substances tried, only the polyhydroxy phenols failed to react. The derivatives were in all cases found to be easily purified. At the fairly high temperatures used, the α-naphthylisocyanate reacted readily with moisture, so that certain amounts of dinaphthyl-urea were always formed with the urethan. The dinaphthyl-urea, however, is very insoluble in boiling ligroin (b. p., 100–120°) while the urethans are in general, readily soluble so that the separation is easily accomplished. In this respect the α-naphthylisocyanate possesses certain advantages over the analogous phenylisocyanate. In the latter case the separation of the urethan from the diphenyl-urea is sometimes a matter of some difficulty, due to the solubility of the urea in organic solvents. The naphthylurethans crystallized well from ligroin and had sharp melting points. In general, very good yields of the urethans were obtained, so that from three to five drops of the phenol were usually found sufficient for identification purposes.

The reaction is catalyzed by trimethylamine or triethylamine dissolved in dry ether. The catalytic effect of the amine is shown by the following facts. *o*-Nitrophenol, heated repeatedly with α-naphthylisocyanate failed to produce a urethan. When this procedure was followed by the

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[1] This paper is an abstract of a thesis submitted by A. F. Wirtel in partial fulfilment of the requirements for the Professional degree in Chemical Engineering at the University of Missouri.

[2] Bickel with French. THIS JOURNAL, **48,** 747 (1926).

addition of the ether solution of the amine, the desired derivative immediately separated. Addition of dry ether alone had no effect. Similarly, *o*-chlorophenol did not react when heated with the reagent, while the addition of the amine to a reaction mixture of those two substances which had not been previously heated caused reaction to take place at once. Here again, the addition of dry ether alone was without effect.

o-Aminophenol reacted readily with the reagent at room temperature. Analysis showed that only one molecule of the isocyanate had reacted. The product was soluble in alkali; from the solution it was precipitated by acidification, indicating that the amino group alone had been attacked. Boiling the reaction mixture failed to get reaction to take place on the hydroxyl group also.

In addition to the phenols and amines, a few miscellaneous compounds containing hydroxyl and imino groups were tested. Addition of the α-naphthylisocyanate to the oximes of acetone, benzophenone and benzaldehyde caused reaction to take place at once, with the evolution of considerable heat. The reagent reacted with acetamide and acetanilide when the mixtures were heated for one or two minutes. The derivatives in all cases were readily soluble in hot ligroin, from which they crystallized well.

Experimental Part[3]

The reaction was usually carried out in a test-tube. This was dried by heating in a Bunsen flame, then closed with a stopper carrying a calcium chloride tube, and allowed to cool. The phenol with a slight excess of the α-naphthylisocyanate was placed in the test-tube and heated by a small flame. In the majority of cases from 3 to 10 drops of the phenol were used. The solutions usually became dark red as the reaction took place, although in a few cases no color was developed. After gentle boiling for a minute or two, the reaction mixture was allowed to cool. When the material did not solidify, even when the wall of the tube had been vigorously rubbed with a glass rod, the heating was repeated, two or three times if necessary. When repeated trials failed to cause a precipitation, a single drop of a dry ether solution of trimethyl- or triethylamine was added. In practically every case this caused the reaction mixture to solidify. The contents of the test-tube were then extracted with boiling ligroin (b. p., 100–120°), the solution was filtered and the material separating

TABLE I

	Urethan		N. %		
Substance	M. p., °C.	Formula	Calcd.	Found	Catalyst
Phenol	132–133	$C_{17}H_{13}O_2N$	5.32	5.28	no
o-Cresol	141–142	$C_{18}H_{15}O_2N$	5.05	5.00	no

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[3] The α-naphthylisocyanate derivatives of the amino acids have been prepared. Neuberg and Manasse, *Ber.*, **38**, 2359 (1905). Neuberg and Rosenberg. *Biochem. Z.*, **5**, 456 (1907).

TABLE I (*Concluded*)

Substance	Urethan		N, %		Catalyst
	M. p., °C.	Formula	Calcd.	Found	
m-Cresol	127–128	$C_{18}H_{15}O_2N$	5.05	5.06	no
p-Cresol	146	$C_{18}H_{15}O_2N$	5.05	5.02	no
Thymol	160	$C_{21}H_{21}O_2N$	4.38	4.35	no
Carvacrol	116	$C_{21}H_{21}O_2N$	4.38	4.37	no
o-Nitrophenol	112–113	$C_{17}H_{12}O_4N_2$	9.09	8.97	yes
m-Nitrophenol	167	$C_{17}H_{12}O_4N_2$	9.09	9.16	no
p-Nitrophenol	150–151	$C_{17}H_{12}O_4N_2$	9.09	9.04	no
o-Chlorophenol	120	$C_{17}H_{12}O_2NCl$	4.70	4.50	yes
m-Chlorophenol	157–158	$C_{17}H_{12}O_2NCl$	4.70	4.72	yes
p-Chlorophenol	165–166	$C_{17}H_{12}O_2NCl$	4.70	4.70	no
o-Bromophenol	128–129	$C_{17}H_{12}O_2NBr$	4.09	4.06	yes
p-Bromophenol	168–169	$C_{17}H_{12}O_2NBr$	4.09	4.07	yes
2,4,6-Tribromophenol	153	$C_{17}H_{10}O_2NBr_3$	2.80	2.79	yes
2-Chloro-5-hydroxytoluene	153–154	$C_{18}H_{14}O_2NCl$	4.49	4.48	yes
4-Hydroxy-1,2-dimethylbenzene	141–142	$C_{29}H_{17}O_2N$	4.81	4.81	yes
4-Hydroxy-1,3-dimethylbenzene	134–135	$C_{19}H_{17}O_2N$	4.81	4.77	yes
2-Hydroxy-1,4-dimethylbenzene	172–173	$C_{19}H_{17}O_2N$	4.81	4.75	yes
Resorcinol-monomethyl ether	128–129	$C_{18}H_{15}O_3N$	4.77	4.54	yes
Guiacol	118	$C_{18}H_{15}O_3N$	4.77	4.84	no
Eugenol	122	$C_{21}H_{19}O_3N$	4.20	4.15	no
*iso*Eugenol	149–150	$C_{21}H_{19}O_3N$	4.20	4.23	yes
Orcinol	160	$C_{29}H_{22}O_4N_2$	6.06	5.93	yes
Resorcinol	No reaction				
Hydroquinol	No reaction				
Catechol	No reaction				
Pyrogallol	No reaction				
α-Naphthol	152	$C_{21}H_{15}O_2N$	4.47	4.44	yes
β-Naphthol	156–157	$C_{21}H_{15}O_2N$	4.47	4.39	yes
1-Nitro-2-naphthol	128–129	$C_{21}H_{14}O_4N_2$	7.82	7.69	yes
o-Aminophenol	201	$C_{17}H_{14}O_2N_2$	10.07	9.91	no
Methylamine	196–197	$C_{12}H_{12}ON_2$	14.00	13.96	
Ethylamine	199–200	$C_{13}H_{14}ON_2$	13.08	13.07	
Dimethylamine	158–159	$C_{13}H_{14}ON_2$	13.08	12.97	
Diethylamine	127–128	$C_{15}H_{18}ON_2$	11.57	11.44	
Benzylamine	202–203	$C_{18}H_{16}ON_2$	10.14	10.08	
*iso*Amylamine	131–132	$C_{16}H_{20}ON_2$	10.93	10.85	
Di-*iso*-amylamine	94–95	$C_{21}H_{30}ON_2$	8.58	8.66	
Di-*iso*butylamine	118–119	$C_{19}H_{26}ON_2$	9.39	9.47	
Di-*n*-propylamine	92–93	$C_{17}H_{22}ON_2$	10.37	10.40	
Acetone-oxime	68–69	$C_{14}H_{14}O_2N_2$	11.57	11.39	no
Benzald-oxime	149	$C_{18}H_{14}O_2N_2$	9.65	9.66	no
Benzophenone-oxime	154–155	$C_{24}H_{18}O_2N_2$	7.65	7.69	no
Acetamide	211–212	$C_{13}H_{12}O_2N_2$	12.28	12.23	no
Acetanilide	116–117	$C_{19}H_{16}O_2N_2$	9.21	9.10	no

from the filtrate recrystallized from ligroin. Table I gives a summary of this work.

Orcinol and 1-nitro-2-naphthol reacted with great difficulty with the isocyanate and gave small yields of the urethans. The derivatives from *o*-aminophenol and methylamine were crystallized from alcohol, being too insoluble in hot ligroin. The derivatives from methylamine, ethylamine, dimethylamine and diethylamine were obtained from approximately 30% water solutions. The derivative from benzylamine was obtained from a 10% water solution. Nitrogen was determined by the Kjeldahl method.

Summary

1. α-Naphthylisocyanate proved to be a satisfactory reagent for phenols and primary and secondary aliphatic amines, forming well-crystallizing and sharply melting urethans. Polyhydroxy phenols do not react under the conditions used.

2. The reaction is catalyzed by tertiary aliphatic amines.

3. The reagent apparently can be used satisfactorily with oximes, as well as for acetamide and acetanilide.

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[Contribution from the Chemical Laboratories of Columbia University, No. 513]

THE UNSATURATED FATTY ACIDS ASSOCIATED WITH CORN STARCH

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After the extraneous fat occurring in corn starch is removed completely by common fat-solvents and the whole starch subsequently hydrolyzed, 0.5 to 0.6% of fatty acids are liberated.[1] This fatty material has been shown to contain a saturated portion consisting almost wholly of palmitic acid[1] and an unsaturated portion of unknown composition. The fatty acids in this latter portion now have been identified and the amount to which they occur established. Further, it has been shown that sterols and other substances occurring with the natural fats are absent.

Recently in this Laboratory it was shown that corn starch could be separated conveniently into two parts, namely, α- and β-amylose, by either electrophoresis or ultrafiltration.[2] When these respective amyloses are hydrolyzed, only the alpha[3] portion yields fatty acids,[3] indicating that the source of the fatty acids in whole corn starch is in one definite component of it. With the data made available by this investigation and the knowledge that only one part of the corn starch carries these acids, it will be

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[1] Taylor and Nelson, This Journal, **42,** 1726 (1920).

[2] H. A. Iddles, *Dissertation*, Columbia, **1925**.

[3] Meyer, "Untersüchungen uber die Stärkekörner," Gustav Fischer, Jena, **1895**.