Seliwanoff's reaction was positive. One hundred grams of powdered root was treated in the way described for *Allium nuttallii.* The inulin obtained was redissolved in water and reprecipitated with alcohol. The yield was 3.2 g. The specific rotation was −27.7°. The product was soluble in water, but less soluble in dilute alcohol than the inulin from camas or wild onions; 40% alcohol dissolved 5% of inulin.

Summary

1. Three new sources of inulin are described, two plants of the family of *Liliaceae* and one of the *Compositae.*
2. The specific rotation of inulin from these sources ranged from −28 to −33°. All products were soluble in water and dilute alcohol.
3. In the light of this work and that of Chevastelon, it appears that there is no correlation between the specific rotation and the solubility of inulin.
4. No claim is made that any of the products described was a definite chemical individual.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ILLINOIS]

IDENTIFICATION OF ALCOHOLS. PARA-NITROPHENYL URETHANS

BY R. L. SHRINER AND RICHARD F. B. COX

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The common reagents used for the preparation of solid derivatives of the alcohols are 3,5-dinitrobenzoyl chloride, phenyl isocyanate and α-naphthyl isocyanate. Since the melting points of many of these derivatives of the common aliphatic alcohols are rather low, which makes them difficult to purify, and since the differences in the melting points of certain pairs of compounds are rather small, it was thought that a series of higher-melting derivatives would be of value. The present communication presents the data obtained on *p*-nitrophenyl urethans of the common aliphatic alcohols. Table I summarizes the properties of the new derivatives and also lists the melting points of the 3,5-dinitrobenzoates, phenyl urethans and α-naphthyl urethans for comparison.

From the above table it is evident that the *p*-nitrophenyl urethans possess a few advantages over the other derivatives. The general melting point range is higher, which makes them easier to recrystallize. In two instances the melting point difference does not permit absolute identification, namely, *n*-propyl and isopropyl alcohols and hexyl and heptyl alcohols.

Para-nitrophenyl urethans may be prepared by the reaction between an alcohol and either *p*-nitrophenyl isocyanate or *p*-nitrophenylcarbamyl

TABLE I

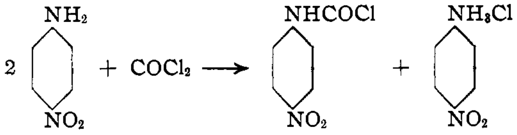
MELTING POINTS OF ALCOHOL DERIVATIVES

Alcohol	3,5-Dinitrobenzoate[1]	Phenyl urethan[2]	α-Naphthyl urethan[3]	*p*-Nitrophenyl urethan
Methyl	107.8	47	124	179.5
Ethyl	92.7	52	79	129
n-Propyl	73.0	58	105	115
Isopropyl	122.1	90	78	116
n-Butyl	62.5	Oil	71	95.5
Sec.-butyl	75.6	..	97	75
Isobutyl	86.5	80	104	80
n-Amyl	46.4	..	68	86
Isoamyl	61	55	67	97.5
Hexyl	58	..	59	103
Heptyl	46.9	68	62	102
Octanol-2	32.2	114	63	Oil
Ethylene glycol	..	157	176	135.5

chloride. Swartz[4] prepared *p*-nitrophenyl isocyanate by heating *p*-nitrophenylcarbamyl chloride which was obtained by the action of phosphorus pentachloride on ethyl *p*-nitrophenylcarbamate. The latter was made by the rearrangement of N-bromo-*p*-nitrobenzamide with sodium ethylate.[5]

Vittenet[6] prepared these reagents by the action of phosgene on *p*-nitraniline. Since the latter method makes use of readily available and inexpensive starting materials, a study was made of this procedure. Also, *p*-nitrophenylcarbamyl chloride was easier to prepare than the isocyanate and hence its preparation and use were studied.

When phosgene was passed into fused *p*-nitraniline similarly to the procedure used for phenyl isocyanate,[7] considerable charring and tar formation took place. Vittenet[6] refluxed together a toluene solution of *p*-nitraniline and a benzene solution of phosgene and succeeded in preparing *p*-nitrophenyl isocyanate in small amounts. As soon as phosgene is run into a solution of *p*-nitraniline in toluene, a precipitate of *p*-nitraniline hydrochloride separates.



Malone and Reid, THIS JOURNAL, 51, 3426 (1929). Students have difficulty in obtaining these melting points. The values for these dinitrobenzoates usually obtained are one to two degrees lower.

[2] Clarke, "Organic Analysis," Arnold and Co., London, 1928.

[3] French, Bickel and Wirtel, THIS JOURNAL, 48, 747, 1736 (1926).

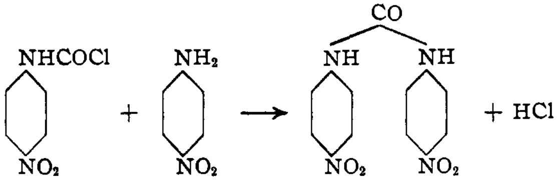
[4] Swartz, *Am. Chem. J.*, 19, 318 (1897).

[5] Swartz, *ibid.*, 19, 301 (1897).

[6] Vittenet, *Bull. soc. chim.*, [3] 21, 587 (1899).

[7] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1928, Vol. VIII, p. 10.

This reaction consumes half the *p*-nitraniline and also makes the reaction difficult to carry out because the undissolved *p*-nitraniline hydrochloride does not react with the phosgene. If a large amount of *p*-nitraniline is present in excess, a second reaction occurs as follows



The reaction mixture therefore contains all these substances and makes it difficult to obtain a pure reagent. Hence the best conditions call for a constant excess of phosgene to prevent the formation of substituted ureas, a temperature sufficiently high to prevent the precipitation of *p*-nitraniline hydrochloride and a good solvent for *p*-nitraniline. It was found that ethyl acetate was not only a good solvent for phosgene[8] but also a much better solvent for *p*-nitraniline than benzene or toluene, and therefore more suitable for the preparation of larger amounts of the reagent.

Although Swartz[4,5] reports that *p*-nitrophenylcarbamyl chloride decomposes at 56° to the isocyanate, the material obtained by the above procedure was always the acid chloride. Evidently the dissociation did not occur in ethyl acetate solution in the presence of phosgene and the hydrogen chloride produced in the reaction.

Experimental Part

Preparation of *p*-Nitrophenylcarbamyl Chloride.—The apparatus was set up as shown in Fig. 1. This arrangement permits the phosgene reaction to be carried out conveniently and without danger providing a good hood and exhaust fan are available.

Five hundred cubic centimeters of ethyl acetate was placed in the 5-liter round-bottomed Pyrex flask. Phosgene was bubbled slowly through the ethyl acetate until it was saturated. A solution of 150 g. of *p*-nitraniline in 1500 cc. of ethyl acetate was run in slowly from the tap funnel over a period of from two and one-half to three hours. The addition of *p*-nitraniline must be at such a rate that the precipitate of *p*-nitraniline hydrochloride which is formed at first is allowed to dissolve and not accumulate. The mixture may be warmed if necessary. A steady stream of phosgene must be kept passing through the solution, and toward the end of the reaction the solution must be boiled gently to break up the *p*-nitraniline hydrochloride, as it dissolves quite slowly.

After the addition of the last of the *p*-nitraniline the stream of phosgene was continued for five minutes and then shut off. The flame under the flask was then turned up and the ethyl acetate distilled. The brown residue was treated with 800 cc. of hot carbon tetrachloride and the insoluble residue (the disubstituted urea) removed by filtration. About two-thirds of the carbon tetrachloride was distilled and the solution cooled. The *p*-nitrophenylcarbamyl chloride crystallizes and is filtered. By concentration of the mother liquor a further crop may be obtained. The product may be re-

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[8] Baskerville and Cohen, *Ind. Eng. Chem.*, 13, 333 (1921).

crystallized again from carbon tetrachloride and yields light yellow needles, melting at 57°. The yield of crude product after one recrystallization was 210 g. (96.5% of the theoretical).

Anal. Subs., 0.2001: 20.0 cc. of 0.10 *N* HCl. Calcd. for $C_7H_5O_3N_2Cl$: N, 13.97. Found: N, 14.00.

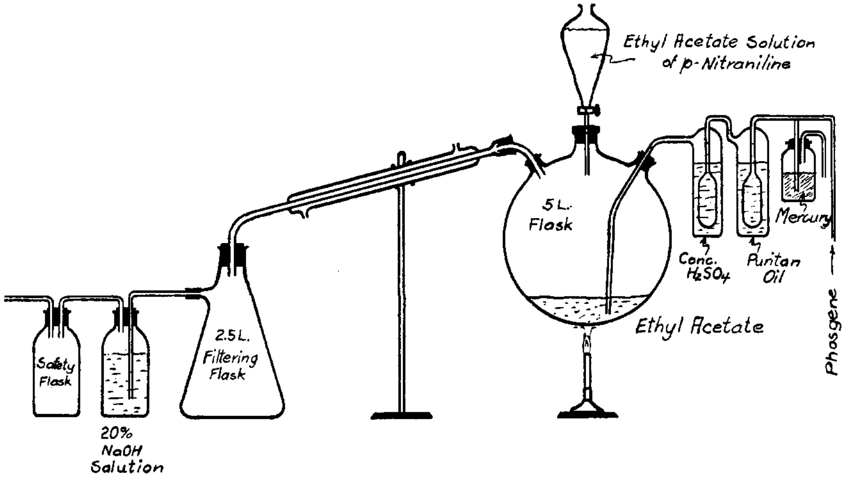

Fig. 1.

Preparation of *p*-Nitrophenyl Urethans.—It was found that the best method for making the urethans was to prepare a benzene solution of *p*-nitrophenylcarbamyl chloride and add a slight excess of the pure alcohol. The reaction usually takes place spontaneously with evolution of heat and is over in about five minutes. The benzene is distilled and an excess of cold carbon tetrachloride added together with a little norit. The solution is then filtered. This procedure removed any *sym.*-di-[*p*-nitrophenyl]-urea which may be formed by traces of water in the alcohol. Evaporation of the carbon tetrachloride to a small volume and cooling yields crystals of the urethan. The *p*-nitrophenyl urethans with their melting points and analyses are given in Table II.

TABLE II

PARA-NITROPHENYL URETHANS

Alcohol	M. p., °C.	Formula	Nitrogen analyses, % Calcd.	Found
Methyl	179.5	$C_8H_8O_4N_2$	14.28	14.10
Ethyl	129	$C_9H_{10}O_4N_2$	13.33	13.33
Propyl	115	$C_{10}H_{12}O_4N_2$	12.50	12.36
Isopropyl	116	$C_{10}H_{12}O_4N_2$	12.50	12.31
Butyl	95.5	$C_{11}H_{14}O_4N_2$	11.76	11.59
Sec.-butyl	75	$C_{11}H_{14}O_4N_2$	11.76	11.61
Isobutyl	80	$C_{11}H_{12}O_4N_2$	11.76	11.51
Amyl	86	$C_{12}H_{16}O_4N_2$	11.11	11.06
Isoamyl	97.5	$C_{12}H_{16}O_4N_2$	11.11	11.03
Hexyl	103	$C_{13}H_{18}O_4N_2$	10.53	10.09
Heptyl	102	$C_{14}H_{20}O_4N_2$	10.00	9.94
Ethylene glycol	135.5	$C_{16}H_{14}O_8N_4$	14.36	14.00

Summary

1. A procedure for the preparation of *p*-nitrophenylcarbamyl chloride has been worked out.

2. The *p*-nitrophenyl urethans of the common aliphatic alcohols are described.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, NO. 643]

THE SYNTHESIS OF SIMPLE AND OF SUBSTITUTED 2-ALKYLCINNAMIC ALCOHOLS, INCLUDING A MONOMOLECULAR CUBEBIN

BY MARSTON TAYLOR BOGERT AND GARFIELD POWELL[1]

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Introductory

The appearance of the recent articles by Gomberg and Bachmann[2] and by Shankland and Gomberg,[3] lead us to publish some closely related work, carried out in 1929, reported at the Annual Convention of the American Manufacturers of Toilet Articles, New York, last April, and published last spring as part of the Dissertation submitted by the junior author for the Ph.D. degree at Columbia University.

The problem of reducing unsaturated aldehydes to the corresponding unsaturated alcohols has occupied the attention of organic chemists for many years and is a subject of considerable practical importance to the perfume industry.

Iron and acetic acid have been used on aldehydes[4] or on their diacetates,[5] but the methods are tedious and the yields unsatisfactory.

The reducing action of aliphatic Grignard reagents on aldehydes and ketones has been known for many years. Marshall's experiments,[6] supported by the work of Meisenheimer[7] and of Shankland and Gomberg,[3]

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[1] Fritzsche Fellow for 1928–1929 at Columbia University. This investigation could not have been undertaken without the generous assistance of Mr. F. E. Watermeyer, President of Fritzsche Brothers, Inc., of New York, the donor of the Fellowship.—[M. T. B.]

[2] Gomberg and Bachmann, THIS JOURNAL, **52,** 4967 (1930).

[3] Shankland and Gomberg, *ibid.*, **52,** 4973 (1930).

[4] (a) Herzig, *Monatsh.*, **3,** 123 (1882); (b) Lieben and Zeisel, *ibid.*, **4,** 28 (1883); (c) *ibid.*, **7,** 55 (1886).

[5] (a) Barbier and Leser, *Bull. soc. chim.*, [3] **33,** 858 (1905); (b) Hill and Nason, THIS JOURNAL, **46,** 2236 (1924); (c) Pauly, Schmidt and Böhme, *Ber.*, **57B,** 1329 (1924).

[6] (a) Marshall, *J. Chem. Soc.*, **105,** 527 (1914); (b) **107,** 509 (1915); (c) **127,** 2184 (1925).

[7] Meisenheimer, *Ann.*, **446,** 76 (1926).