Methylpentachlorophenylcarbinol.—1-Pentachlorophenyl-1-acetoxyethane was refluxed for four hours in 150 cc. of acetone and 25 cc. of water containing 1 g. of potassium hydroxide. Most of the acetone was removed with a water pump and water wast hen added. The crude product was filtered off and crystallized from methanol–water to yield 1.5 g. of the carbinol melting at 124–125°. A mixed melting point with an authentic sample of the carbinol showed no depression.

Dehydrohalogenation of 1-Pentachlorophenyl-1-bromoethane, I.—The α-bromide (35.8 g., 0.1 mole) was refluxed for four hours with 300 cc. of absolute ethanol containing potassium hydroxide (11.2 g., 0.2 mole). The mixture was stirred mechanically during the refluxing. The reaction mixture was poured into 2 liters of water. The crude product was filtered off and crystallized from ethanol to give two crops of crystals. The first weighed 12.5 g. and melted at 109–112°. Recrystallization raised the melting point to 113–114.5° and a mixed melting point with pentachlorostyrene showed no depression. The second crop weighing 7 g. and melting from 63–70° was purified by crystallizing successively from acetone, methanol, ethanol and three times from glacial acetic acid. After this treatment the compound melted at 88–89° and analysis indicates that it is 1-pentachlorophenyl-1-ethoxyethane.

Anal. Calcd. for $C_{10}H_9Cl_5O$: C, 37.24; H, 2.79. Found: C, 37.30, 37.48; H, 2.80, 2.72.

1-Pentachlorophenyl-1,2-dibromoethane, IV.—Pentachlorostyrene (5 g., 0.018 mole) and bromine (2.9 g., 0.018 mole) in 150 cc. of carbon tetrachloride were left standing for seven days at room temperature. Removal of the solvent gave a white crystalline solid melting from 88–90° with some previous softening. Crystallization from acetic acid gave 4.5 g. (57%) of IV melting at 95–96°. A mixed melting point with the dibromide isolated from the bromination of pentachlorophenylethane showed no depression.

Summary

Methods of preparation and structural proofs for 1-pentachlorophenyl-1-bromoethane, 1-pentachlorophenyl-2-bromoethane and 1-pentachlorophenyl-1,2-dibromoethane are described.

It is suggested that the difference in the direction of substitution on chlorination and bromination of ethylpentachlorobenzene is ascribable to a difference in the reactivities of chlorine and bromine atoms.

NORTH ADAMS, MASS. RECEIVED APRIL 30, 1947

[CONTRIBUTION FROM THE CHEMICAL CORPS TECHNICAL COMMAND, ARMY CHEMICAL CENTER]

p-Triphenylmethylphenyl and 2-Fluorenyl Isocyanates as Reagents for Alcohols

BY BENJAMIN WITTEN AND E. EMMET REID

Phenyl (I)[1] and α-naphthyl (II)[2] isocyanates are useful for the identification of alcohols, but most of their derivatives have rather low melting points. *p*-Xenyl (III)[3] and 4-iodobiphenyl (IV)[4] iso-

TABLE I

MELTING POINTS OF CARBAMATES

Alcohol	Carbamate							
	p-Triphenylmethylphenyl (V) M. p., °C. (cor.)	2-Fluorenyl (VI) M. p., °C. (cor.)	*p*-Xenyl (3) (III) M. p., °C.	Phenyl (1) (I) M. p., °C.[a]	α-Naphthyl (2) (II) M. p., °C.	*p*-Nitrophenyl (5,6) M. p., °C.	3,5-Dinitrophenyl (6) M. p., °C.	4-Iodobiphenyl (4) IV M. p., °C.
Methyl	214	120	126	47	124	178	127	191.1
Ethyl	216	120	121	52	79	130	83	200.5
n-Propyl	177	114	130	57	80	110	97	188.7
n-Butyl	140	112	109	61	71	96	70	174
n-Amyl	85	93	95	46	68	91	58	165.5
n-Hexyl	81	98	93	42	59	104	75	156.3
n-Heptyl	55	97	105	65	62	105	61	150.9
n-Octyl	61	119	109	74	66	111	69	149.2
n-Nonyl	62	110	115	60	65.5	104	66	149.2
n-Decyl	64	100	112	59.5	72	117	70	147
n-Undecyl	68	109	112	52	73[b]	99.5	62	146.5
n-Dodecyl	70	112	113	74	80	117	81	145.7
n-Tridecyl	74	107	114[b]	70[b]	80[b]			144.5
n-Tetradecyl	76	106	113[b]	71	81[b]			143
n-Pentadecyl	77	108	113[b]	72	85			141.5
Cetyl	79	108	113[b]	73	82.3	118	86	138.5
n-Heptadecyl	79	108	113[b]	79[b]	88.5			138.5
n-Octadecyl	79	107	114[b]	79	89[b]	115	88	137.2

[a] Melting points reported by van Gelderen, *Rec. trav. chim.*, **52**, 969–975 (1933), methyl 124°, ethyl 119°, *n*-propyl 130°, *n*-butyl 109°, *n*-amyl 102°, *n*-hexyl 98°, *n*-heptyl 105°, *n*-octyl 110°, *n*-nonyl 115°, *n*-decyl 111°, *n*-undecyl 106°, *n*-dodecyl 113°. Melting points reported by Morgan and Pettet, *J. Chem. Soc.* 1124–1126 (1931); methyl 127°, ethyl 119°, *n*-propyl 129°, *n*-butyl 109°, *n*-amyl 99°. [b] New compound (m. p. cor.).

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[1] Huntress and Mulliken, "Identification of Pure Organic Compounds, Tables of Data on Selected Compounds of Order I," John Wiley and Sons, Inc., New York, N. Y., 1941.

[2] Huntress and Mulliken, ref. 1; Tischer, *Ber.*, **72B**, 291–297 (1939).

[3] Morgan and Pettet, *J. Chem. Soc.*, 1124–1126 (1931); M. J. van Gelderen, *Rec. trav. chim.*, **52**, 969–975 (1933).

[4] Siniti Kawai and Kunisaburo Tamura, *C. A.*, **24**, 4256; *Proc. Imp. Acad. (Japan)*, **6**, 198–200 (1930).

cyanates have been advocated since they give higher melting derivatives.

As is evident from Table I and Fig. 1 these reagents are good for certain alcohols but not for others. This is also true for the other isocyanates which have been reported as reagents: *o,m,p*-nitrophenyl,[5,6] 3,5-dinitrophenyl,[6] *p*-methoxyphenyl[7] and 3,4-dimethoxyphenyl.[7] None of these reagents give good differentiation for the higher alcohols. The data for the derivatives of *p*-nitrophenyl and 3,5-dinitrophenyl isocyanates are included in Table I for comparison.

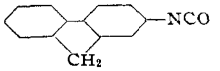
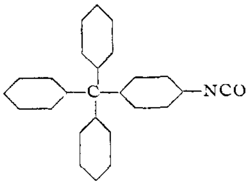
We have prepared two new isocyanates, *p*-triphenylmethylphenyl (V) and 2-fluorenyl (VI), and treated them with the normal alcohols from methyl to octadecyl, and for comparison have supplied the missing derivatives of these alcohols with I, II, III, IV. The melting points, old and new, are given in Table I and are plotted in Fig. 1.

The fact that aminotetraphenylmethane has a high melting point suggested the preparation of its isocyanate. Its high molecular weight is an advantage when only small amounts of alcohol are available.

2-Fluorenyl isocyanate was of interest since the structure of fluorene is so much like that of biphenyl. The melting points of its derivatives are not greatly different from those of *p*-xenyl isocyanate but show greater differences for adjacent alcohols. Of all the derivatives made, those of fluorene are the easiest to recrystallize to constant melting point. This may be due to the rigidity of the fluorene molecule as compared with the biphenyl from which III and IV are derived.

TABLE II

PREPARATION OF ISOCYANATES

Compound	Amine used, 10 g. Name	Yield isocyanate, %	M. p., (cor.) °C.	Formula	Carbon, %		Hydrogen, %		Nitrogen, %	
					Found	Calcd.	Found	Calcd.	Found	Calcd.
2-Fluorenyl isocyanate	Aminofluorene[b]	87	69–70		81.2	81.14	4.5	4.38	6.6	6.8
p-Triphenylmethylphenyl isocyanate	*p*-Amino-tetraphenylmethane[c]	93	168–169		86.6	86.40	5.3	5.30	3.42	3.88
p-Xenyl isocyanate	4-Aminobiphenyl	87	59–60[a]						7.18	7.18

[a] van Gelderen, *Rec. trav. chim.*, **52**, 969–975 (1933), reports melting point of 56.5–57°. [b] Kuhn, "Organic Syntheses," **13**, 74–76 (1933). [c] Ullmann and Munzhuber, *Ber.*, **36**, 407 (1903).

Inspection of Fig. 1 shows that no one of these reagents is satisfactory for all of these alcohols. The derivatives of the lower alcohols from phenyl isocyanate, except butyl, are too low melting and those from dodecyl to octadecyl melt over too narrow a range. α-Naphthyl isocyanate is a better reagent but the melting points of adjacent derivatives are sometimes close together. *p*-Xenyl isocyanate serves well up to octyl but is of no use for the rest of the alcohols. The same can be said for 4-iodobiphenyl isocyanate which gives high melting points all the way. It was expected that *p*-triphenylmethylphenyl isocyanate would give high melting derivatives. This proved to be true for the alcohols up to butyl but the

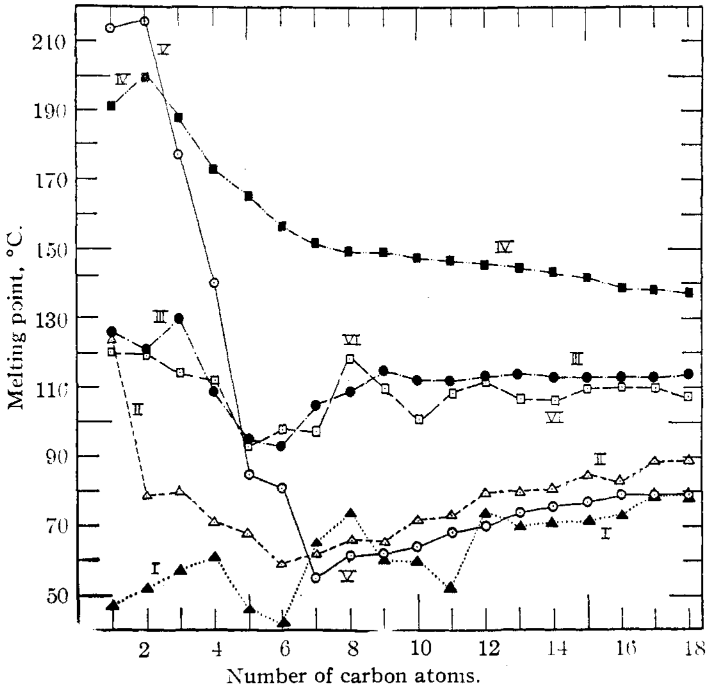


Fig. 1.—Melting points of carbamates.

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[5] C. W. van Hoogstraten, *Rec. trav. chim.*, **51**, 414 (1932).

[6] F. Hoeke, *ibid.*, **54**, 514 (1935).

[7] O. Brunner and R. Wöhrl, *Monatsh.*, **63**, 377 (1933).

melting points of the rest are surprisingly low.

An inspection of Fig. 1 shows which one, or two, of these reagents to use to differentiate between any two alcohols.

Experimental

Preparation of Isocyanates.—The compound *p*-xenyl isocyanate was prepared by treating *p*-xenylamine hydrochloride with phosgene following the method of Hardy.[8] The compounds, 2-fluorenyl isocyanate and *p*-triphenylmethylphenyl isocyanate were prepared similarly from the appropriate amine hydrochloride.

Into a 1-liter, 3-necked flask equipped with a mechanical agitator, a gas inlet tube, a thermometer and a reflux condenser, was introduced 10 g. of the appropriate amine dissolved in 200 ml. of toluene. The solution was agitated, heated to 50° and dry hydrogen chloride passed in until the solution was saturated. The solid hydrochloride precipitated from solution. The solution was heated to reflux and dry phosgene was passed in until nearly all of the solid had dissolved (about two hours). The mixture was filtered, and the filtrate, which contained the isocyanate, was evaporated to dryness. The residue was recrystallized from ligroin. The results are summarized in Table II.

Preparation of Carbamates.—A solution of 0.5 g. of *p*-triphenylmethylphenyl, 2-fluorenyl, or *p*-xenyl isocyanate dissolved in 5 ml. of toluene reacted with 50% excess of the *n*-alcohol by heating in a boiling water-bath for three hours. With methyl and ethyl alcohols a larger excess was used (5 moles per mole of isocyanate). With methyl alcohol the solution was heated to reflux for three hours. The solution was evaporated to dryness under reduced pressure and the residue was recrystallized twice from alcohol. There was always present some substituted urea which formed as a result of the action of water on the isocyanate, but this compound was insoluble in the alcohol from which the carbamate was crystallized. The carbamates are colorless crystalline solids and the yields are 60–70%.

The carbamates from phenyl and α-naphthyl isocyanates were prepared in similar manner except that the compounds were recrystallized twice from 90–120° ligroin.

Each compound gave an analysis for nitrogen in good accord with that required by theory.

Acknowledgment.—The authors wish to thank Mr. Cecil A. Rush for the microanalyses of the compounds reported in this paper.

Summary

p-Triphenylmethylphenyl isocyanate and 2-fluorenyl isocyanate have been synthesized and two series of carbamates obtained by the reaction of these reagents with the normal alcohols, from methyl to *n*-octadecyl alcohol, inclusive, have been prepared. The missing members of the carbamates from phenyl, α-naphthyl, *p*-xenyl isocyanates have been synthesized.

Comparisons of the melting points indicate that no one reagent is suitable for the identification of all of the alcohols; the reagent has to be selected for the particular alcohol suspected of being present.

EDGEWOOD ARSENAL, MD. RECEIVED APRIL 23, 1947

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[8] Hardy, *J. Chem. Soc.*, 2011 (1934).

[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XXIX. The Conductance of Some Electrolytes in Nitrobenzene at 25°[1]

BY CHARLES R. WITSCHONKE[2] AND CHARLES A. KRAUS

I. Introduction

In the preceding paper of this series,[3] results were presented which go to show how the properties of electrolytes in nitrobenzene solution are dependent on various constitutional factors. The substances studied were found to fall into three main classes: (1) strong electrolytes whose dissociation constants are in accord with the dielectric constant of the solvent and the dimensions of the constituent ions of the salt; (2) weak electrolytes in which non-coulombic interactions must be considered along with the usual interaction due to coulombic forces; and (3) weak electrolytes in which dissociation into free acid and base takes place to a measurable extent.

In the present paper are presented results of a more detailed study of the phenomena mentioned above, along with some further studies relating to factors not previously considered. This investigation relates to: (A) solutions of stable electrolytes, both inorganic and organic (salts of the alkali metals and of the partially or completely substituted ammonium ions); (B) solutions of salts of weak bases, such as aniline and pyridine, which undergo dissociation into free acid and base; (C) the effect of added bases, such as amines, on the dissociation constant of weak electrolytes, such as partially substituted ammonium salts and trimethylhydroxyammonium salts; and (D) the conductance of solutions of triphenylmethyl halides and of triphenylmethylborofluoride.

The conductance of typical salts of various anions was measured and the influence of the anion on the properties of the electrolyte was studied.

II. Experimental

Apparatus and Procedure.—For the most part, these have been described in earlier papers of this series.[3] Small quantities of the added bases were introduced into the solvent reservoir by

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[1] This paper is based on a portion of a thesis presented by Charles R. Witschonke in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Brown University, May, 1941.

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[3] Taylor and Kraus, THIS JOURNAL, **69**, 1731 (1947).