fraction, 6.2 g. of a yellow oil, b.p. 106–132°/3–4 mm., was obtained. The oil was dissolved in 125 cc. of acetic acid and then treated with 3 l. of a 5% potassium permanganate solution. After 1 hr. standing at room temperature, the mixture was treated with sulfur dioxide until the excess permanganate had been destroyed and it was then filtered. The solid collected on the filter melted at 69–91°. The solid was fractionally crystallized from ethanol. The early fractions consisted of grey plates of m.p. 115 ± 1°, but later fractions had much lower melting points and were therefore treated again with potassium permanganate. The resulting solid was fractionally crystallized, first from ethanol and then from an ethanol-ether mixture. The first fractions from ethanol were grey plates of m.p. 115 ± 1°, and the later fractions from ethanol-ether were tan crystals of m.p. about 99°. On recrystallization from ethanol, the lower-melting crystals yielded 2.2 g. of tan crystalline 1-naphthyl phenyl sulfone, m.p. 100.5–101.5° (lit.[13] 99.5–100.5°), and the higher-melting material furnished 4.2 g. of grey 2-naphthyl phenyl sulfone, m.p. 116.5–117.5° (lit.[13] 115–116°). Each sulfone gave a positive qualitative test for sulfur and a negative test for nitrogen, and a mixture of equal parts of the two sulfones melted at 77–111°. The final product composition was 34% 1-naphthyl phenyl sulfone and 66% 2-naphthyl phenyl sulfone, and the combined yield was 27%.

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Carbamates. I. From Monohydric Alcohols and Toluene-2,4-diisocyanate[1]

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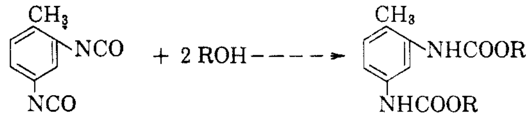
The reaction between an isocyanate and an alcohol to give the carbamate (urethan) is well known.[2] The early application of the reaction to the identification of alcohols was suggested by A. W. Hoffman[3,4] in 1885. The use of various isocyanates has appeared over the years, and a review was presented by Witten and Reid[5] in 1947. The formation of the dicarbamates from toluene-2,4-diisocyanate (or, 4-methyl-*m*-phenylene diisocyanate) has been reported for several of the monohydric alcohols.[6–9] This paper confirms compounds already presented and gives data for fifteen new ones.

Toluene-2,4-diisocyanate(I) reacts readily with monohydric alcohols to form the corresponding dialkyltoluene-2,4-dicarbamates(II).



I II

The reaction proceeds readily at room temperature for the lower, normal, primary alcohols with a definite evolution of heat. The higher, normal, primary alcohols (above eight carbon atoms) react less vigorously. Triethylamine in dry ether was employed as the catalyst for the higher alcohols, together with a heating process of 100° for a period of 4–6 hr. Tertiary butyl and tertiary amyl alcohols failed to give satisfactory derivatives.

The dialkyl toluene-2,4-dicarbamates are colorless, crystalline solids which are readily purified by crystallization from ethyl alcohol. The derivatives above ten carbon atoms show greater solubility in petroleum ether and can be crystallized from this medium.

The application of the dialkyl toluene-2,4 dicarbamates to the qualitative identification of monohydric alcohols offers a good spread of melting points when compared with the various series of carbamates.[5] The total data for the dicarbamates of the monohydric alcohols are presented in Table I.

EXPERIMENTAL

Materials. The toluene-2,4-diisocyanate was obtained from both Monsanto and Du Pont, and was fractionated *in vacuo*. A cut of not over 2° in range was used. Typical boiling ranges: 104–105° (5 mm.); 110–110.5°C. (9.5 mm.). The material was freshly distilled as used, and was stored and handled in a "dry box." The alcohols were obtained from Eastman, or Matheson, and were distilled after drying over Drierite; a cut of not over 0.5° was taken. The solid alcohols were recrystallized from petroleum ether or ethyl alcohol.

Preparation. Two and one-half milliliters (2.5 ml., 0.017 mole) of the diisocyanate were transferred to a test tube (dry box) which contained 0.035 mole of the given alcohol, and 2–3 drops of triethylamine in dry ether. The test tube carried a drying tube of calcium chloride for protection against moisture. The test tube and contents were heated in an oil bath from 4–6 hr. (higher alcohols were heated from 8–10 hr.) at 100°. (For purposes of qualitative identification, 2 ml. of the alcohol are heated on the boiling water bath for 1 hr. with 0.5 ml. of the diisocyanate.) The reaction mixture sets to a crystalline mass upon cooling. The lower members were recrystallized from ethyl alcohol (95%). The higher members were recrystallized from petroleum ether (35–60°). Usually, a highly crystalline product with a sharp melting point resulted after 4–5 recrystallizations. Each sample was dried under reduced pressure in a drying pistol prior to the analysis for nitrogen.

Physiological and herbicidal testing. Since a number of car-

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[1] This paper was presented before the Organic Chemistry Section at the fall meeting of the American Chemical Society at Chicago, Sept. 6–11, 1953.

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TABLE I

DIALKYL TOLUENE-2,4-DICARBAMATES FROM CERTAIN MONOHYDRIC ALCOHOLS

Alcohol	Dicarbamate M.P. Lit., °C.	Dicarbamate M.P. Obsd., °C. (Uncorr.)	Formula	Nitrogen Calcd.	Nitrogen Found
Methyl	170–171[9]; 171[8]	170	$C_{11}H_{14}N_2O_4$	11.76	11.67
Ethyl	136.5[8]; 137[7]	135	$C_{13}H_{18}N_2O_4$	10.52	10.57[a]
n-Propyl		104	$C_{15}H_{22}N_2O_4$	9.52	9.66
Isopropyl	134[10]; 136[8]	134	$C_{15}H_{22}N_2O_4$	9.52	9.49
n-Butyl	80[9]	81	$C_{17}H_{26}N_2O_4$	8.69	8.66[a]
Isobutyl		120	$C_{17}H_{26}N_2O_4$	8.69	8.53
sec-Butyl	93[8]	89	$C_{17}H_{26}N_2O_4$	8.69	8.68
n-Amyl		89	$C_{19}H_{30}N_2O_4$	7.99	7.87
Isoamyl		76	$C_{19}H_{30}N_2O_4$	7.99	7.84
Neopentyl		132	$C_{19}H_{30}N_2O_4$	7.99	7.98[a]
n-Hexyl		83	$C_{21}H_{34}N_2O_4$	7.40	7.38
n-Heptyl		82	$C_{23}H_{38}N_2O_4$	6.89	7.03
n-Octyl	69[9]	69–70	$C_{25}H_{42}N_2O_4$	6.45	6.57[a]
n-Nonyl		72	$C_{27}H_{46}N_2O_4$	6.06	6.10
n-Decyl		72–73	$C_{29}H_{50}N_2O_4$	5.71	5.71[a]
n-Undecyl		61	$C_{31}H_{54}N_2O_4$	5.40	5.52[a]
n-Dodecyl	86[8]	87	$C_{33}H_{58}N_2O_4$	5.12	5.16
n-Tetradecyl		90	$C_{37}H_{66}N_2O_4$	4.65	4.67[a]
n-Hexadecyl	95–96[9]	93–94	$C_{41}H_{74}N_2O_4$	4.25	4.21[a]
n-Octadecyl		99.5–100	$C_{45}H_{82}N_2O_4$	3.92	3.89[a]
Cyclohexyl		158	$C_{33}H_{30}N_2O_4$	7.48	7.32
Benzyl		101–102	$C_{23}H_{22}N_2O_4$	7.18	7.11
β-Phenylethyl		129.5–130	$C_{25}H_{26}N_2O_4$	—	—

[a] Micro-Dumas by a commercial laboratory, others by macro-Kjeldahl.

bamates have been tested for carcinogenic activity,[11] as well as having been reported to show definite influence on experimental animal tumors,[12] six members of this series of carbamates (the dimethyl, diethyl, di-*n*-butyl, di-*sec*-butyl, di-*n*-decyl, and di-*n*-octadecyl) were submitted through the National Research Council (Chemical-Biological Coordination Center) to the National Cancer Institute for tumor chemotherapy against Sarcoma 37 in CAF1 mice. The results were negative. The herbicidal properties of certain carbamates[13–15] have attracted attention within recent years also. Certain members of the present series of dicarbamates are to be tested for herbicidal properties.

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A Synthesis of Aceanthrene

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Whilst the formation of 9,10-dihydrophenanthrene derivatives by the interaction of phenyllithium and 2,2′-dibromomethylbiphenyls has been fairly extensively studied,[1] the analogous formation of an ethane-bridge between the 1,8-positions of a naphthalene system has only been observed in one case, the synthesis of acenaphthene from 1,8-dibromomethylnaphthalene.[2] It seemed, therefore, worthwhile to add at least one more example.

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