1,1-Dimethylbutyl-*N*-Phenyl Urethan

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THE PHENYLURETHAN of 2-methyl-2-pentanol has been prepared. The original investigator (*1*) of 2-methyl-2-pentanol erroneously reported having prepared this urethan. In that method, one which is not applicable to tertiary alcohols, the carbinol was boiled with the phenyl isocyanate for a few minutes and the product was recrystallized from alcohol and acetone. The resulting product was the diphenyl urea.

Since the Tables for Identification of Organic Compounds (*4*) list only three derivatives for the alcohol: the 3,5-dinitrobenzoate; the benzoate; and allophanate; the phenylurethan should be a useful addition to the list. A slight modification of the method of McElvain (*3*) for preparing the phenylurethan of a tertiary alcohol was used.

EXPERIMENTAL

Into a 100 ml. round bottom flask, connected to a reflux condenser by a ground glass joint, was placed 1.5 grams of 2-methyl-2-pentanol which is commercially available (*2*). Two grams of phenyl isocyanate and 0.1 gram of sodium acetate were added. A calcium chloride drying tube was fitted to the top of the condenser. The flask was placed in a boiling water bath, where it was kept for four hours. A white precipitate appeared shortly after the beginning of the reaction and slowly increased throughout the heating period. Octane, boiling 124° C., was added to the reaction mixture to dissolve the phenylurethan and separate it from the insoluble diphenyl urea formed by dehydration of some of the tertiary alcohol. The octane solution was allowed to come to a boil and filtered. The solution was evaporated down to 5 ml., and allowed to cool. The phenylurethan separated as needles. These were filtered, washed carefully with a small portion of ice cold octane, and recrystallized three times from octane. The final product was filtered with suction and air dried for two days until a constant melting point of 52° C. was obtained. The final yield of a dense silvery mass of very fine needles was 0.73 gram (22.4% of theoretical). *Anal.* Calcd. for $C_{13}H_{19}O_2N$: C, 70.55%; H, 8.65%. Found: C, 70.49%; H, 8.62%.

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Some Butanediol Derivatives

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A number of butanediol derivatives such as 2-(*p*-chlorophenyl)-3-methyl-2,3-butanediol(phenaglycodol) were found to possess anticonvulsant effects and, as a further investigation five new analogs of phenaglycodol have been prepared. These analogs are:

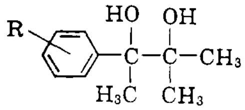
2-(*p*-xenyl)-3-methyl-2,3-butanediol,
2-(*p*-methylmercaptophenyl)-3-methyl-2,3-butanediol,
2-(*p*-phenylmercaptophenyl)-3-methyl-2,3-butanediol,
2-(*m*-trifluoromethylphenyl)-3-methyl-2,3-butanediol,

and

2-(*p*-trifluoromethylphenyl)-3-methyl-2,3-butanediol.

IN VIEW OF the fact that some butanediol derivatives have an anticonvulsant effect, we have prepared a number of phenaglycodol (I) analogs, the medicinal effects of which will be the subject of another publication.

In five new synthesized analogs (Table I), we have replaced the *p*-chlorophenyl group in I by xenyl (II), *p*-methylmercaptophenyl (III), *p*-phenylmercaptophenyl (IV), *m*-trifluoromethylphenyl (V) and *p*-trifluoromethylphenyl (VI).



I, R = *p*-Cl
II, R = *p*-C_6H_5
III, R = *p*-SCH_3
IV, R = *p*-SC_6H_5
V, R = *m*-CF_3
VI, R = *p*-CF_3

The syntheses of II, III, and IV commenced with Friedel-Crafts reaction of the appropriate aromatic hydrocarbon with ethyl α-oxo-chloroacetate followed by reaction of the products with methylmagnesium iodide (*2*).

In the Friedel-Crafts reaction some of the ester obtained (the amount depended on the R group) was hydrolyzed to the corresponding acids, which had to be re-esterified.

The products V and VI were prepared via Grignard reaction; the *m*-or *p*-bromotrifluoromethylbenzene was converted to the magnesium derivative, and after reaction with pyruvic acid, the acid obtained was esterified and treated with methylmagnesium iodide (*2*).

The new intermediates prepared to effect the syntheses of the analogs listed in Table I appear in Table II.

Table I. Analogs of Phenaglycodol

M.P., °C.	Formula	Analyses[a] % Carbon Calcd.	Analyses[a] % Carbon Found	Analyses[a] % Hydrogen Calcd.	Analyses[a] % Hydrogen Found
II. 2-(*p*-Xenyl)-3-methyl-2,3-butanediol					
97-9	$C_{17}H_{20}O_2$	79.6	79.16	7.81	7.78
III. 2-(*p*-Methylmercaptophenyl)-3-methyl-2,3-butanediol					
65-8	$C_{12}H_{18}O_2S$	63.7	62.94	7.96	7.86
IV. 2-(*p*-Phenylmercaptophenyl)-3-methyl-2,3-butanediol					
62	$C_{17}H_{20}O_2S$	70.8	70.58	6.94	6.72
V. 2-(*m*-Trifluoromethylphenyl)-3-methyl-2,3-butanediol					
74-6	$C_{12}H_{15}F_3O_2$	58	58.61	6.04	5.59
VI. 2-(*p*-Trifluoromethylphenyl)-3-methyl-2,3-butanediol					
97	$C_{12}H_{15}F_3O_2$	58	58.90	6.04	5.58

[a] Microanalyses were performed by F. Pascher, Microanalitiches Laboratorium, Bonn, W. Germany. Melting points were corrected.

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Table II. Intermediary Products for Syntheses of Compounds Listed in Table I.

Compound	Lit.	B.P., (Mm. of Hg) °C.	% Yield	Formula	Analyses % Carbon Calcd.	Analyses % Carbon Found	Analyses % Hydrogen Calcd.	Analyses % Hydrogen Found
p-Methylmercaptophenylglyoxylic acid[a]	(*1*)	105-8[b]	42	$C_9H_8O_3S$	55.1	54.96	4.08	4.02
p-Phenylmercaptophenylglyoxylic acid	(*1*)	. . .	16	$C_{14}H_{10}O_3S$	65.11	64.93	3.87	3.76
Ethyl(*p*-methylmercaptophenyl)-glyoxalate	(*2*)	. . .	83	$C_{11}H_{12}O_3S$	58.92	59.13	5.35	5.34
Ethyl(*p*-phenylmercaptophenyl)-glyoxalate[c]	(*2*)	218-24(3)	22	$C_{16}H_{14}O_3S$	67.13	66.82	4.89	4.77
α-(*p*-Xenyl)-α-hydroxypropionic acid	(*1*)	162-3[b]	75	$C_{15}H_{14}O_3$	74.38	74.33	5.78	5.75
α-(*p*-Methylmercaptophenyl)-α-hydropropionic acid[d]		164-7[b]	. . .	$C_{10}H_{12}O_3S$	56.60	56.46	5.66	5.66
α-(*p*-Phenylmercaptophenyl)-α-hydroxypropionic acid[d]		94-7[b]	. . .	$C_{15}H_{14}O_3S$	65.69	65.86	5.10	4.99
Ethyl α-(*p*-methylmercaptophenyl)-α-hydroxypropionate[e]	(*4*)	176-80(5)	78	$C_{12}H_{16}O_3S$	60.0	58.71	6.6	6.41
Ethyl α-(*p*-phenylmercaptophenyl)-α-hydroxypropionate[e]	(*4*)	130-2(3)	74	$C_{17}H_{18}O_3S$	67.54	67.54	5.9	5.76
α-(*m*-Trifluoromethylphenyl)-α-hydroxypropionic acid	(*5*)	101-3[b]	60	$C_{10}H_9F_3O_3$	51.2	50.77	3.84	3.82
α-(*p*-Trifluoromethylphenyl)-hydroxypropionic acid	(*5*)	116-8[b]	68	$C_{10}H_9F_3O_3$	51.2	51.63	3.84	3.73
Ethyl α-(*m*-trifluoromethylphenyl)-α-hydroxypropionate	(*2*)	124-9(6)	83	$C_{12}H_{13}F_3O_3$	54.9	55.11	4.96	5.12
Ethyl α-(*p*-trifluoromethylphenyl)-α-hydroxypropionate	(*2*)	150-2(10)	83	$C_{12}H_{13}F_3O_3$	54.9	54.72	4.96	5.02

[a] Semicarbazone m.p. 269°. [b] Melting point. [c] Dinitrophenylhydrazone m.p. 115°.
[d] Hydrolysis of ester. [e] The literature cited gives the standard method for the preparation of the ketone. We obtained the ester.