is in agreement with that reported by Hackspill and Wolfe. The solubility of BaO in $BaCO_3$ is approximately 4%.

MURRAY HILL, NEW JERSEY RECEIVED MAY 18, 1951

o-Toloxypropyl Carbamates

BY B. J. LUDWIG AND E. C. PIECH

In view of the marked anticonvulsant activity exhibited by carbamate esters of certain 2,2-disubstituted 1,3-propanediols,[1] it appeared of interest to prepare some carbamate derivatives of the muscle relaxant drug mephenesin (3-*o*-toloxy-1,2-propanediol) and the closely related *o*-toloxypropanols for pharmacological screening.

Employing the procedure described earlier for the carbamylation of substituted propanediols,[2] we have prepared the compounds described in Table I. While this work was in progress there appeared the publication of Yale, *et al.*,[3] describing a monocarbamate ester of mephenesin. These authors ascribed to their compound the primary ester structure on the basis of greater reactivity of the primary hydroxyl group of mephenesin with phosgene. It was of interest that the monocarbamate prepared by us, by ammonolysis of the cyclic carbonate of mephenesin, proved to be identical to that obtained by Yale, *et al.*

The results of the pharmacological studies carried out on these compounds will be published elsewhere.

Experimental[4]

1-*o*-Toloxy-2-propanol and **3-*o*-toloxy-1-propanol** were prepared by the condensation of *o*-cresol with propylene chlorohydrin and trimethylene chlorohydrin, respectively.

3-*o*-Toloxy-1-isopropoxy-2-propanol.[5]—Thirty-four grams (0.25 mole) of 1-chloro-3-isopropoxy-2-propanol[6] was added with stirring to a solution of 27 g. (0.25 mole) of *o*-cresol and 11.2 g. (0.28 mole) of sodium hydroxide in 100 ml. of water. The solution was heated to boiling and refluxed for two hours. The cooled solution was extracted with chloroform and the chloroform extract washed free of alkali. Upon removal of solvent, the crude ether was obtained as a thick oil. Distillation under reduced pressure gave 39 g. (70%) of 3-*o*-toloxy-1-isopropoxy-2-propanol; b.p. 132–134° (3 mm.), $n^{25}D$ 1.4979.

Anal. Calcd. for $C_{13}H_{20}O_3$: C, 69.61; H, 8.92. Found: C, 69.52; H, 8.91.

Conversion of these toloxy propanols to the corresponding carbamate esters was accomplished using a slight modification of the general procedure described earlier.[2] The phosgene reaction mixture after standing overnight was treated directly with gaseous ammonia until alkaline, and the water soluble components removed by extracting with water. The crude amides obtained by evaporation of the solvent under reduced pressure solidified on cooling, and were purified by recrystallization from benzene–ligroin mixture and finally from water. Over-all yields of 60–80% were obtained.

4-*o*-Toloxymethyl Dioxolone-2.—This compound was prepared by the phosgenation of mephenesin in the presence of antipyrine according to the procedure described earlier for the preparation of cyclic carbonates of 2,2-disubstituted-1,3-propanediols.[2] From 18.2 g. of mephenesin there was obtained 15 g. (72%) of 4-*o*-toloxymethyl dioxolone-2. The product, purified by crystallization from water, melted at 96–97°.

Anal. Calcd. for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81. Found: C, 63.50; H, 5.81.

3-*o*-Toloxy-2-hydroxypropyl carbamate was obtained by ammonolysis of the above cyclic carbonate of mephenesin with an excess of liquid ammonia in a steel vessel at room temperature. Purification was effected by crystallization from water.

3-*o*-Toloxy-1,2-propanediol Dicarbamate.—Using the procedure described earlier for the preparation of 2,2-disubstituted-1,3-propanediol dicarbamates,[2] 36.4 g. (0.2 mole) of mephenesin yielded 32 g. of crude dicarbamate. This product was purified by crystallization first from water, then from ethanol.

The physical constants and analytical data for these compounds are summarized in Table I.

TABLE I

Compound	Yield, %	M.p., °C.	Formula	Nitrogen, % Calcd.	Found
3-*o*-Toloxy-2-propyl carbamate	67	73–73.5	$C_{11}H_{15}NO_3$	6.71	6.59
3-*o*-Toloxy-1-propyl carbamate	78	96–97	$C_{11}H_{15}NO_3$	6.71	6.60
3-*o*-Toloxy-1-isopropoxy-2-propyl carbamate	60	68.5–69	$C_{14}H_{21}NO_4$	5.24	5.28
3-*o*-Toloxy-2-hydroxypropyl carbamate	65	93–94	$C_{11}H_{15}NO_4$	6.22	6.29
3-*o*-Toloxy-1,2-propanediol dicarbamate	55	168–169	$C_{12}H_{16}N_2O_5$	10.45	10.59

RESEARCH DIVISION
WALLACE LABORATORIES, INC.
NEW BRUNSWICK, N. J. RECEIVED JUNE 8, 1951

Synthesis of Butadiene-2,3-C^{14} [1]

BY KINGSLEY M. MANN[2] AND ROBERT F. NYSTROM

In connection with polymerization studies and the preparation of more complex compounds by the Diels–Alder reaction, it was necessary to develop a small-scale preparation for high-purity butadiene-2,3-C^{14}.

The synthesis of tagged butadiene is an eight-step process, furnishing an over-all yield of 49% based on radioactive carbon dioxide. The method briefly outlined is: (a) conversion of $C^{14}O_2$ to methylene-labeled succinic acid (four steps) in an 89% yield by modification of the procedure recently described by Kushner and Weinhouse[3]; (b) esterification of the acid; (c) reduction of the ester to 1,4-butanediol-2,3-C^{14} by lithium aluminum hydride; (d) conversion of the diol to 1,4-dibromobutane-2,3-C^{14}; and (e) reaction between the dibromide and trimethylamine to give the di-

(1) Unpublished data by Dr. F. M. Berger of these laboratories.

(2) B. J. Ludwig and E. C. Piech, THIS JOURNAL, **73**, 5779 (1951).

(3) H. L. Yale, E. J. Pribyl, W. Braker, F. H. Bergeim and W. A. Lott, *ibid.*, **72**, 3710 (1950).

(4) All temperatures reported are uncorrected. Microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Middle Village, Long Island, N. Y.

(5) Some pharmacological properties of this compound have been described by C. H. Hine, H. E. Christensen, F. J. Murphy and H. Davis, *J. Pharmacol. Exptl. Therap.*, **97**, 414 (1949). The preparation and physical constants of this compound were not described by these authors.

(6) Generously supplied by Shell Development Company, Emeryville, California.

(1) This work was performed under Atomic Energy Commission Contract AT-(40-1)-282.

(2) The Upjohn Co., Kalamazoo, Mich.

(3) Kushner and Weinhouse, THIS JOURNAL, **71**, 3558 (1949).