vious communication[1] except that benzene was substituted for toluene as solvent. In a few cases products were purified by recrystallization without prior distillation (Method B-1).

Lithium Amide Condensation. One-step Reaction. Method C.—A mixture consisting of 0.1 mole of a heterocyclic amine, 0.1 mole of an alkyl halide and 0.1 mole of lithium amide[6] in 100 ml. of benzene was refluxed for 10–20 hours. (When a dialkylaminoalkyl chloride hydrochloride was one of the reactants, the amount of lithium amide was doubled.) The reaction mixture was filtered hot and the residue washed well with benzene. After removing the solvent, the residue which remained was distilled *in vacuo*.

In this manner there was obtained 24.4 g. (96%) of N,N-dimethyl-N'-benzyl-N'-(2-pyridyl)-ethylenediamine, b.p. 121–122° (0.02 mm.) by refluxing a mixture of 18.4 g. (0.10 mole) of 2-benzylaminopyridine, 5.4 g. (0.24 mole of 98% purity) of lithium amide, 17.3 g. (0.12 mole) of dimethylaminoethyl chloride hydrochloride and 200 ml. of benzene for 20 hours. When prepared on the same scale by the two-step reaction (Method B), the yield was 24.7 g. (97%).[3]

Acknowledgment.—The authors are indebted to Endo Products, Inc., for financial support of part of this investigation, and to Mr. David Regenbogen for bringing the procedure of Wohl and Lange[2] to their attention.

(6) The product obtained from Metalloy Corp. is of 98% purity. In the course of handling, the lithium amide content decreases considerably. The practice in our laboratory is to transfer the contents of the one- or two-pound tins to six-ounce amber bottles (narrow-neck and screw-cap) which are kept tightly stoppered and sealed with paraffin. If left open for a minimum of time during the weighing of the compound, the titer remains fairly constant.

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The Phase System BaO–$BaCO_3$

BY J. J. LANDER

In the system BaO–$BaCO_3$ Finkelstein[1] assumes the existence of a basic carbonate in the solid phase and assigns to it the composition $BaO{\cdot}BaCO_3$. But Hackspill and Wolfe[2] assign the composition $2BaCO_3{\cdot}BaO$ to the eutectic and report that they found no evidence for the existence of a basic carbonate in the solid phase. This note reports the results of a thermal analysis investigation of the system which agree with the conclusions of Hackspill and Wolfe.

A modification of the thermal analysis apparatus described by Smith[3] was used. An essential feature is an arrangement for obtaining a constant rate of heat flow into or out of the specimen by maintaining a constant temperature difference across a thermal insulator which surrounds the specimen. Materials were used which could be heated to temperatures as high as 1300°. The ceramic containers were made of alundum and the thermocouples were Pt, Pt + 10% Rh. Two other modifications were made. Heating elements were provided above and below the specimen in order to reduce the size of the equipment, and a number of series junctions were used in the differential thermocouple circuit in order to obtain increased sensitivity. Regulation was by automatic in-out switching of a resistance in the heater circuit.

In a typical run a measured amount of CO_2 was pumped from a known amount of $BaCO_3$ at a temperature of about 1000° in the early stages of decomposition, but as high as 1200° in the final stages. Temperature–time curves for heating and cooling in a closed system between 1100 and 600° were then obtained. Three arrests were usually observed, and these were due to the following transitions: (1) the orthorhombic to hexagonal transition of $BaCO_3$ at 806°; (2) the hexagonal to cubic transition at 968°; (3) the melting of the eutectic at 1030°.

The first two temperatures differ by a few degrees from those given in an earlier report,[4] and are considered more reliable. A typical set of results is shown in Fig. 1.

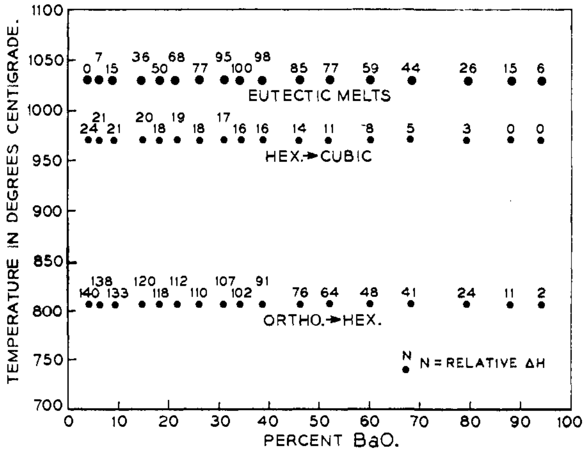

Fig. 1.—Observed relative heats of transitions as a function of temperature and composition.

The following phenomena were observed in a series of three separate sets of runs each started with fresh material: (1) The heat of transition at 806° decreased linearly with increasing BaO content and the temperature of transition remained unchanged (±1°). It is concluded that at 806° and throughout the composition range the separate phases $BaCO_3$ and BaO coexist. (2) The heat of the transition at 968° decreased linearly with increasing BaO content and the temperature of transition remained unchanged (±3°). Therefore, at 968° and throughout the composition range the separate phases $BaCO_3$ and BaO coexist. (3) The eutectic arrest did not appear until about 4% (±1%) decomposition was reached. The heat released increased linearly to a maximum at 33% (±1%) decomposition and decreased linearly to zero at about 98% (±2%) decomposition. The eutectic temperature remained constant at 1030° (±3°).

Quantitative thermal data may be obtained from Fig. 1 and known heats of transition for the reactions $BaCO_3$(ortho) → $BaCO_3$(hex.) and $BaCO_3$ (hex.) → $BaCO_3$(cubic).[5] In Fig. 1 the symbol N = relative ΔH is the heat evolved relative to the heat evolved at the eutectic point, which heat has been arbitrarily assigned the value 100.

The eutectic composition observed, 33% BaO,

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(1) A. Finkelstein, *Ber.*, **39**, 1585 (1906).

(2) L. Hackspill and G. Wolfe, *Compt. rend.*, **204**, 1820 (1937).

(3) C. S. Smith, *AIME*, **137**, 236 (1940).

(4) J. J. Lander, *J. Chem. Phys.*, **17**, 892 (1949).

(5) See J. J. Lander, THIS JOURNAL, **73**, 5794 (1951).

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

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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.), $n^{25}\text{D}$ 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.	Nitrogen, % 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

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(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.

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-

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(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).