acetate, b.p. 135–138° (25 mm.) was obtained by the general procedure previously described.[3]

Anal. Calcd. for $C_7H_{13}OSCl$: C, 46.52; H, 7.23. Found: C, 46.61, 46.54; H, 6.69, 6.87.

Thiacyclohexane. Starting with 34 g. (0.19 mole) of 5-chloropentyl thiolacetate, 16.52 g. (87%) of thiocyclohexane, b.p. 140–141° was obtained. Whitehead, Dean, and Fidler[8] reported the b.p. to be 141.6°.

2-Chloropropyl thiolacetate. Starting with 153 g. (2 moles) of 2-chloropropene (Shell Chemical Co.) and 114.2 g. (1.5 moles) of freshly distilled thiolacetic acid, 216 g. (94.2%) of 2-chloropropyl thiolacetate, b.p. 71° (10 mm.), was obtained by the general method previously described.[3,4] It was necessary to employ an ice water bath to control the exothermic reaction on a run of this size. Culvenor, Davies, and Heater[9] reported the b.p. to be 70–71° (9 mm.).

Thiacyclopropane (propylene sulfide). A. Starting with 68 g. (0.45 mole) of 2-chloropropyl thiolacetate, the above procedure was carried out with the exception that sodium carbonate was substituted for sodium hydroxide, which caused polymerization. Distillation of the combined extracts through a three-plate Vigreux column yielded 8.5 g. (25%) of thiacyclopropane, b.p. 72–75°, and 11 g. (16% recovery) of the starting material. The reaction flask continued a considerable amount of polymeric material.

B. Forty-five grams (0.29 mole) of 2-chloropropyl thiolacetate was stirred overnight with 500 ml. of methanol containing 5 ml. of concentrated hydrochloric acid. The reaction mixture was then neutralized to a *p*H of 7 (indicator paper) with a dilute sodium hydroxide solution. The reaction mixture was stirred at room temperature for an additional hour, and then extracted 4 times with 50-ml. portions of pentane. Distillation through a 3-plate Vigreux column yielded 7 g. (30.5%) of thiacyclopropane, b.p. 72–75°. Considerable polymeric material remained in the distillation flask.

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Synthesis of DL-Norleucine-2-C^{14}

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Since DL-norleucine-2-C^{14} was desired for metabolic studies but had not previously been synthesized, the following synthesis was undertaken:[2–7]

$$R = CH_3CH_2CH_2CH_2$$

$$RBr \xrightarrow[\text{Ether}]{Mg^\circ} RMgBr \xrightarrow[H_2SO_4]{C^{14}O_2} R{-}C^{14}OOH \xrightarrow[\text{Ether}]{LiAlH_4}$$

$$RC^{14}H_2OH \xrightarrow{PBr_3} RC^{14}H_2Br \xrightarrow[\text{Ether}]{Mg^\circ} RC^{14}H_2MgBr \xrightarrow[H_2SO_4]{CO_2}$$

$$RC^{14}H_2COOH \xrightarrow[PCl_3]{Br_2} R{-}C^{14}HCOOH \xrightarrow{\text{concd. } NH_3}$$

(Br)

$$R{-}C^{14}H{-}COOH$$

(NH_2)

EXPERIMENTAL

Valeric acid-1-C^{14}. *n*-Butylmagnesium bromide (0.203 mole) was prepared according to standard procedures and carbonated with $C^{14}O_2$ in a vacuum manifold at 2-mm. pressure.[3] The acid was recovered from the reaction flask by steam distillation over silver sulfate. The product was separated, washed with ether, dried several hours over anhydrous magnesium sulfate, and redistilled to yield 7.1–9.1 ml. (77–83%), b.p. 170–190°.

n-Amyl alcohol-1-C^{14}. Valeric-acid-1-C^{14} was reduced to *n*-amyl alcohol-1-C^{14} with $LiAlH_4$ using anhydrous ether as a solvent.[4] The product was recovered by separation of the ether phase, removal of the ether and distillation of the fraction boiling between 128–140°. The yield was 76–78% (6.4–7.0 ml.).

Caproic-acid-2-C^{14}. *n*-Amyl bromide-1-C^{14} was prepared by the bromination of *n*-amyl-alcohol-1-C^{14} with PBr_3.[5] The reaction mixture was allowed to stand for 2 hr. The product was recovered by distillation and washed successively with water, concd. H_2SO_4 and 10% Na_2CO_3. The product was dried over anhydrous Na_2SO_4 and redistilled, collecting the fraction boiling between 125–128°. The yield was 70–72% (5.5–5.1 ml.). *n*-Amylmagnesium bromide-1-C^{14} was then prepared and carbonated at −20° by passing inactive CO_2 gas through the solution. Caproic-acid-2-C^{14} was recovered by the method used for valeric acid-1-C^{14} and yielded 55–66% (5.5–7.3 ml.).

DL-*norleucine-2-C^{14}.* α-Bromocaproic acid-2-C^{14} was prepared by brominating caproic acid-2-C^{14} with Br_2 and PCl.[6] The product was recovered by fractional distillation at 10-mm. Hg pressure collecting the product boiling at 128–131°. Yield: 45–67% (5.14–5.91 g.). α-Bromocaproic acid-2-C^{14} was then added to a flask containing concentrated NH_3, tightly stoppered and heated in a 50–55° water bath for 24 hr. The flask was then cooled to and kept at 4° for 24 hr. The shiny white flakes which crystallized were recovered by filtration, washed with cold methanol, and dried at 105°.[7] The yield was 59–62% (2.16–2.24 g.). The over all yield was 8.2–8.3% based on $BaC^{14}O_3$, and the over all isotopic yield based on the specific activity of $BaC^{14}O_3$, was 6.7–7.2% (3.67–3.97 mc.). The specific activities of the final products were 1.64 μc./mg. and 1.85 μc./mg. for 2 successive syntheses. These specific activities were determined by the oxidation of the product to $C^{14}O_2$ with $K_2S_2O_8$.[8] The $C^{14}O_2$ was then precipitated as $BaC^{14}O_3$ and counted at infinite thickness in a Tracerlab windowless Geiger flow gas counter and autoscaler. The total isotopic yield was increased by 0.2 mc. by the addition of inactive norleucine to the filtrate and subsequent recrystallization. Paper chromatograms developed with butanol–acetic acid–H_2O and phenol-H_2O systems in one and/or two dimensions and sprayed with ninhydrin showed a single spot which coincided with known samples of norleucine. Mixed chromatograms also showed a single spot. Autoradiograms of these papers showed only a single radioactive spot matching the ninhydrin spot showing the radioactive purity of the norleucine.

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Anal.[9] Calcd. for $C_6H_{13}O_2N$; C, 54.94; H, 9.99; N, 10.68. Found: C, 55.00, 55.16; H, 9.81, 9.75; N, 10.56, 10.55.

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Crystallizable Polystyrene. II. Polymerization of Styrene with Triphenylmethyl Potassium and Related Compounds

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In preceding publications[1,2] the preparation of crystallizable polystyrene with Alfin-type catalysts was reported. The present work deals with the extension of the organometallic catalysts for the polymerization of styrene to include alkali metal derivatives of triphenylmethane and related compounds. Triphenylmethylpotassium, diphenylcyclohexylmethylpotassium, and diphenylmethylpotassium have been found to produce crystallizable polystyrene, having the same range of crystallizability as the polymers prepared using the Alfin catalyst. The highest degree of crystallizability comparable to that produced by the Alfin catalysts was obtained by use of triphenylmethylpotassium. 1,1-Diphenylethylpotassium, benzylpotassium, triphenylmethylsodium, sodium hydride, potassium amide, and potassium gave noncrystallizable polystyrene. Table I contrasts the results obtained when styrene was polymerized using the above catalysts.

In accord with previous observations using the Alfin catalysts,[1,2] polymerizations with triphenylmethylpotassium conducted in a benzene medium, produced high yields of noncrystallizable polystyrene. The heterogeneous isotactic polymerization system was thus converted to a homogeneous nonisotactic polymerization since benzene acted as a solvent for triphenylmethylpotassium. A hexane medium, however, provided the required heterogeneous system, facilitating isotactic polymerization.

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EXPERIMENTAL

Polymerizations. The polymerizations and crystallizations were carried out as previously described.[1]

Catalysts. The catalysts were bottled under dry nitrogen with self-sealing caps and were dispensed by means of hypodermic syringes and needles.

Triphenylmethylpotassium. Triphenylmethylpotassium was prepared according to the method of Levine, Baumgarten, and Hauser.[3] The triphenylmethylpotassium was transferred to a hexane suspension by removal of ether by distillation. The hexane suspension was transferred from the reaction flask by nitrogen pressure and was stored in a bottle capped with a self-sealing cap.

Diphenylmethylpotassium. Diphenylmethylpotassium was prepared in ether solution according to the method of Yost and Hauser.[4] The ether was subsequently replaced with hexane.

Benzylpotassium. Benzylpotassium was prepared from chlorobenzene and potassium in a toluene medium, according to the procedure of Gilman, Pacivitz, and Baine.[5]

Potassium amide. Potassium amide was prepared in liquid ammonia.[3] The liquid ammonia was replaced by hexane.

Diphenylcyclohexylmethylpotassium. Diphenylcyclohexylmethylpotassium was prepared according to the directions of Ziegler and Schnell,[6] with some modifications. The potassium compound was prepared using diphenylcyclohexylchloromethane (m.p. 83–84°) which was prepared from the carbinol *via* acetyl chloride. Diphenylcyclohexylchloromethane was treated with potassium amide, according to the directions used for the preparation of diphenylmethylpotassium.[4] Diphenylcyclohexylacetic acid was obtained in 92% crude yield by the carbonation of diphenylmethylcyclohexylpotassium and melted at 202–203° upon recrystallization from acetic acid. This melting point is in agreement with that obtained by Ziegler and Schnell[6] by carbonation of the diphenylcyclohexylmethylpotassium which they obtained by reaction of potassium on diphenylcyclohexylcarbinol methyl ether. The catalyst was transferred to hexane solution as already described.

1,1-Diphenylethylpotassium. 1,1-Diphenylethylene[7] was reduced to 1,1-diphenylethane with sodium ethylate, according to the directions of Klages.[8] 1,1-Diphenylethylpotassium was prepared by essentially the same method as that used for diphenylmethylpotassium. However, in this case, hexane was used in place of ether since 1,1-diphenylethane was soluble in hexane. 1,1-Diphenylpropionic acid obtained by carbonation of the potassium salt was obtained in 94% crude yield and melted at 171–172° on crystallization from benzene. This melting point is in agreement with that obtained by Ziegler and Schnell[6] on carbonation of 1,1-diphenylethylpotassium which they obtained by the action of potassium on 1,1-diphenylethylcarbinol methyl ether.

Potassium. A 0.1-g. piece of freshly cut potassium was used. The polymer grew outward from the surface of the potassium.

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