(67%, based on the silicon tetrachloride) of tetra-*n*-hendecylsilane distilling at 248–251° (0.15 mm.), $n^{25}D$ 1.4608.

Anal. Calcd. for $C_{44}H_{92}Si$: C, 81.39; H, 14.28; Si, 4.32. Found: C, 81.60, 81.69; H, 14.30, 14.40; Si, 4.14, 4.20.

The *n*-docosane was recrystallized from absolute ethanol to give 1.3 g. (37%) of platelets melting at 43–44°.[8]

Di-*n*-octadecyldiphenylsilane, di-*n*-hendecyldiphenylsilane and di-10-hendecenyldiphenylsilane (see Table I) were prepared by a similar procedure.

Tetra-(*m*-fluorobenzyl)-silane.—To 0.076 mole of *m*-fluorobenzylmagnesium chloride (prepared in 76% yield from the corresponding chloride and magnesium) in 195 ml. of ether was added 2.4 g. (0.014 mole) of silicon tetrachloride in 50 ml. of ether. After refluxing, hydrolysis and separation as before, vacuum distillation of the residue gave 1.1 g. (50%) of 3,3′-difluorobibenzyl distilling at 60–63.5° (0.2 mm.) and 4.6 g. (71%) of tetra-(*m*-fluorobenzyl)-silane distilling at 238–240° (0.2 mm.). The 3,3′-difluorobibenzyl solidified on standing and melted at 33–34°.[9]

The tetra-(*m*-fluorobenzyl)-silane solidified on standing; recrystallization from petroleum ether (b.p. 60–70°) gave 4.0 g. (62%) of colorless rhombic crystals melting at 62–63°.

Anal.[10] Calcd. for $C_{28}H_{24}F_4Si$: C, 72.39; H, 5.21; F, 16.36. Found: C, 72.38, 72.34; H, 5.25, 5.22; F, 16.21, 16.44.

(8) The reported m.p. for *n*-docosane is 43.5–44.5°; see G. Egloff, "Physical Constants of Hydrocarbons," Vol. V, Reinhold Publ. Corp., New York, N. Y., 1953, p. 242.

(9) The reported m.p. for 3,3′-difluorobibenzyl is 34–35°; see M. Szwarc and J. S. Roberts, THIS JOURNAL, **70**, 2831 (1948).

(10) The silicon analyses of this compound were erratically low possibly due to loss of silicon as SiF_4. A similar difficulty in the analysis of fluorine-containing organosilicon compounds has been reported; see H. Gilman, A. G. Brook and L. S. Miller, *ibid.*, **75**, 3757 (1953).

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The Synthesis of Propanediol Phosphate-2-C^{14} from Pyruvamide-2-C^{14} and the Purification of Labeled Pyruvic Acid[1]

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Recently evidence[4,5] has been obtained in this Laboratory that 1,2-propanediol-1-phosphate (PDP) is formed from pyruvate in appreciable amounts by glycolyzing rat tissue homogenates under anaerobic conditions. The synthesis and purification of PDP-2-C^{14} was undertaken in order to test the significance of PDP in the metabolism of normal and neoplastic tissues. A procedure for preparing PDP-2-C^{14} for use as a biological tracer is presented, and a chromatographic procedure for the purification of C^{14}-labeled pyruvic acid is included.

Experimental and Results

Synthesis of PDP-2-C^{14}.—Pyruvamide-2-C^{14} [6] was used as the starting material because of its commercial availability. The purity of the pyruvamide-2-C^{14} was determined by carrier crystallization with unlabeled pyruvamide since contamination with non-pyruvamide-C^{14} is usually present. This permitted a calculation of the true specific activity of the pyruvamide-2-C^{14}, a figure used to determine purity of the PDP-2-C^{14}. The procedure routinely used was as follows: 22 mg. of pyruvamide-2-C^{14} was stirred with 10 ml. of anhydrous diethyl ether and added to 3 ml. of an approximately 0.5 *M* solution of $LiAlH_4$ (Metal Hydrides Co., Beverly, Mass.) at a rate just necessary to produce gentle reflux.[7] The mixture of pyruvamide-2-C^{14} and $LiAlH_4$ was refluxed for four hours, and allowed to stand overnight at room temperature. The ether was removed by evaporation of the mixture to 3–5 ml.; 10 ml. of anhydrous $CHCl_3$ was added and the evaporation repeated. Then 0.6–0.7 ml. of $POCl_3$ (Eastman Technical grade) in 10 ml. of anhydrous $CHCl_3$ was introduced. The mixture was refluxed for 4–5 hours, and allowed to stand overnight at room temperature. Fifteen ml. of water was added, and the $CHCl_3$ removed by evaporation on a steam-bath. The water solution was approximately 1.3–1.5 *M* with respect to HCl, which was liberated from the $POCl_3$ used. In order to hydrolyze possible contaminating phosphate esters in the PDP-2-C^{14} preparation, the water solution was heated for two hours at 100°. PDP is insensitive to hydrolysis under these conditions.[8] The solution was cooled, and neutralized to *p*H 7 with small additions of 10 *M* KOH. Then 12–14 ml. of 1 *M* barium acetate was added to precipitate inorganic phosphate as the barium salt. PDP is not precipitated.[8] The milky suspension of barium phosphate was heated for 5 minutes at 100° with constant stirring. The barium phosphate was removed by centrifuging, and washed five times with 25-ml. portions of water, resuspending the barium phosphate and heating for five minutes at 100° with each wash. The combined supernatant solutions were allowed to percolate through a 2 × 20 cm. column of Dowex-50 (H form). The column was washed with five successive 10-ml. portions of water. The combined eluates were evaporated *in vacuo* at room temperature to approximately 5 ml. Organic phosphorus was measured as an estimate of PDP-2-C^{14} present.[9] The yields ranged from 65–70% in several test runs.

Purification of PDP-2-C^{14}.—The PDP-2-C^{14} was subjected to two-dimensional paper chromatography for purification. The eluate from the Dowex-50 column (above) was streaked along the top edge of a $22\frac{1}{2}$ × 18 inch sheet of Schleicher and Schüll #589 filter paper and allowed to dry at room temperature. Approximately 30 micromoles of organic phosphorus was used on each sheet. The paper was developed in a tank designed for descending paper chromatography. The following solvent system was employed: 6 parts isopropyl alcohol, 2 parts concentrated ammonia, 2 parts water saturated Versene solution.[5] The PDP-2-C^{14} was located by placing the dried paper in contact with sensitive X-ray film. The labeled material corresponded in migration rate to samples of known unlabelled PDP used as standard. The region of the paper containing the PDP-2-C^{14} was cut out and eluted by percolating water down the strip of filter paper. The solution was then streaked upon a second sheet of S. and S. #589 paper and developed using the following solvent system: 7 parts isopropyl alcohol–2 parts H_2O saturated with Versene–1 part 2 *M* monochloroacetic acid.[5] Upon isolation as above, the PDP-2-C^{14} had a specific activity (counts per minute per micromole phosphorus) which was equal to the specific activity of the original pyruvamide-2-C^{14} used in the synthesis. The yields from the purification of the PDP-2-C^{14} by the filter paper chromatographic procedure were as follows: isopropyl alcohol–ammonia–Versene system 77–92%; isopropyl alcohol–monochloroacetic acid–Versene system 50–61%. The total over-all yields of highly purified PDP-2-C^{14} (based upon the pyruvamide-2-C^{14}) were 25–39%.

The Purification of C^{14}-Labeled Pyruvic Acid.—In the course of investigations upon the anaerobic metabolism of pyruvate,[8] it was observed that pyruvamide-2-C^{14} and py-

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(3) The studies reported here were used as partial fulfillment of the requirements for the degree of Doctor of Philosophy, University of Wisconsin, June, 1954.

(4) D. P. Groth and G. A. LePage, *Proc. Amer. Assoc. Cancer Res.*, **1**, 17 (1954).

(5) D. P. Groth and G. A. LePage, *Cancer Res.*, in press.

(6) Obtained from Tracerlab, Inc., Boston, Mass., on allocation from the Atomic Energy Commission.

(7) W. G. Brown, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951.

(8) D. P. Groth, G. A. LePage, C. Heidelberger and P. A. Stoesz, *Cancer Res.*, **12**, 529 (1952).

(9) W. W. Umbreit, R. H. Burris and J. F. Stauffer, "Manometric Techniques and Tissue Metabolism, Burgess Publishing Co., Minneapolis, Minnesota, 1945, p. 190.

ruvamide-1-C^{14}, as prepared by the method of Anker,[10] were often seriously contaminated with labeled impurities. A chromatographic procedure for the purification of labeled pyruvic acid was devised to facilitate the use of this compound.

After hydrolysis of the labeled pyruvamide to pyruvic acid by heating in 1 *N* HCl for 1 hour at 100°, the material was absorbed on a column of Dowex-1 chloride. The labeled pyruvic acid was chromatographically eluted with gradually increasing concentrations of HCl in an apparatus of the type described by Busch, *et al.*[11] Each successive fraction of the chromatogram was analyzed for pyruvic acid.[12] In these studies with the chromatographic purification of labeled pyruvic acid, approximately 10–40% of the C^{14} in the total sample, depending upon the purity of the pyruvamide used, was eluted with water only from the column of Dowex-1 Cl, 50–85% was recovered in the pyruvic acid peak (5-ml. fractions 25–33), and 5% in the fractions (35–42) following pyruvic acid. At least two other minor C^{14} fractions, preceding and following the pyruvic acid peak, were observed. The fractions containing the labeled pyruvic acid were combined, evaporated at reduced pressure to a small volume and stored in the frozen state. The purified preparations were essentially free of labeled impurities (less than 1%) as shown by volatility studies. Per mole of labeled pyruvic acid, the stored solutions contained approximately ten moles of HCl. When the final acid concentration was adjusted to 1 molar, the preparations were stable over a period of 6 months.

(10) H. S. Anker, *J. Biol. Chem.*, **176**, 1333 (1948).

(11) H. Busch, R. B. Hurlbert and V. R. Potter, *ibid.*, **196**, 717 (1952).

(12) T. E. Friedman and G. E. Haugen, *ibid.*, **147**, 415 (1943).

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cis–trans Isomerization of 1-Bromo-1-propene and Related Compounds

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Chavanne[2] prepared both *cis*- and *trans*-1-bromo-1-propene in 1914. The configuration of the isomers was assigned on the basis of the lower boiling isomer (*cis*) dehydrobrominating seven times faster at 70° than the higher boiling isomer. Chavanne also noted that on standing at room temperature the density of each isomer approached a common, intermediate value after five days and this action was correctly interpretated as a *cis–trans* isomerization. The observation that the 1-bromo-1-propenes isomerize at room temperature was largely ignored in subsequent investigations of these compounds.[3] Some very precise work has been reported on what may have been a mixture of the two isomers.

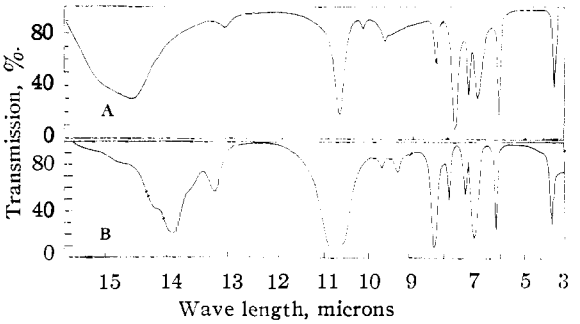

Fig. 1.—Infrared spectra: A, *cis*-1-bromo-1-propene; B, *trans*-1-bromo-1-propene.

(1) Jefferson Chemical Co., Austin, Texas.

(2) G. Chavanne, *Compt. rend.*, **158**, 1698 (1914).

It became necessary to learn more about the isomerization of the 1-bromo-1-propenes when it was planned to use them in the synthesis of a number of related compounds which also exhibit *cis–trans* isomerization.[4] The 1-bromo-1-propenes were prepared along with 2-bromopropene by the dehydrobromination of 1,2-dibromopropane using sodium phenolate. The *cis* and *trans* isomers were separated by low temperature (−18°, −13°) distillation and were stored at temperatures below zero. At these temperatures isomerization in the dark is negligible over a period of a few days.

The characterization and purity of the 1-bromo-1-propenes and the various other *cis–trans* isomers studied were determined by their infrared spectra.[5] All of the *trans* isomers (of 1-bromo-1-propene, 1,3-dibromopropene, 3-bromo-2-propen-1-ol, 1-bromo-3-chloro-1-propene and 1-chloro-1-propene) showed the hydrogen out-of-plane bending band at 10.75 μ which is characteristic of compounds having a halogen and an alkyl or haloalkyl group attached to the carbon–carbon double bond.[6] The *cis* isomers showed a moderately strong, broad hydrogen out-of-plane bending band between 13 and 15 μ which is characteristic of the *cis* configuration. This band was absent in the corresponding *trans* isomers.

The isomeric compounds also showed a consistent shift in the in-plane bending band of the ethylenic hydrogens between the *cis* and *trans* isomers. These bonds are all strong and rather sharp in shape.

	cis	*trans*
1-Bromo-1-propene	7.78	8.32
1,3-Dibromopropene	7.74	8.05
3-Bromo-2-propen-1-ol	7.77	8.10
1-Bromo-3-chloro-1-propene	7.77	8.10
1-Chloro-1-propene	7.65	8.13

Infrared spectra provided an excellent method of analysis for the *cis* and *trans* isomers. The infrared spectra of *cis*- and *trans*-1-bromo-1-propene are shown in Fig. 1 and these show a small amount of cross-contamination. The wave lengths used for analysis were 7.78, 7.87, 8.32 and 8.70 μ. The 2-bromopropene which sometimes occurred in these mixtures was determined from its absorption at 8.70 and 11.2 μ. Analytical standards were selected distillation fractions showing no detectable absorption from other compounds.

To determine the effect of temperature on the rate of isomerization, samples were taken immediately from the distillation column, sealed in glass ampoules, wrapped in metal foil to protect them from light, and placed in a constant temperature bath. Samples were taken from the bath periodically and analyzed immediately by their infrared spectra. Runs were made starting with the *cis*

(3) M. S. Kharasch, H. Engelman and F. R. Mayo, *J. Org. Chem.*, **2**, 288 (1938).

(4) L. F. Hatch and K. E. Harwell, This Journal, **75**, 6004 (1953).

(5) We are indebted to Robert E. Kitson of E. I. du Pont de Nemours & Co., Kinston, North Carolina, for the interpretation of the spectra.

(6) R. E. Kitson, *Anal. Chem.*, **25**, 1470 (1953).