

colorless oil which was dissolved in ether and treated with dry hydrogen chloride. The separated dehydropelletierine hydrochloride was recrystallized from alcohol-ether, m.p. 136–138°.

Anal. Calcd. for $C_8H_{10}NOCl$: N, 8.23. Found: N, 8.22.

The picrate was prepared from the hydrochloride in alcohol.

Anal. Calcd. for $C_{14}H_{12}N_4O_8$: N, 15.38. Found: N, 15.47.

Reduction of II.—A solution of 0.51 g. of dehydropelletierine hydrochloride in 25 ml. of absolute alcohol was stirred in an atmosphere of hydrogen in the presence of 0.05 g. of platinum oxide catalyst. Absorption of three molecular equivalents of hydrogen occurred within 45 minutes and the reduction was stopped even though hydrogen up-take had not ceased. The catalyst was filtered off and the alcohol removed under vacuum. The addition of anhydrous ether caused crystallization of a very hygroscopic hydrochloride, which was dissolved in alcohol and converted into the picrate, m.p. 231–232°. Octahydropyrococline picrate is reported to melt at 232°. ¹

Anal. Calcd. for $C_{14}H_{18}N_4O_7$: N, 15.82. Found: N, 16.13.

The aurochloride was prepared from the hydrochloride in water, m.p. 190°. ⁷

Carrying out the reduction in alcohol at higher concentrations (up to 1.0 g. per 8 ml.) gave identical results. When either the hydrochloride or the free base was reduced in the same manner in glacial acetic acid at high concentrations (1.0 g. of the hydrochloride per 4.0 ml.) the solution began to darken shortly after the reduction was begun. All attempts to obtain a crystalline picrate from the reaction mixture gave only small amounts of octahydropyrococline picrate.

(7) K. Löffler and H. Kaim, *Ber.*, **42**, 94 (1909).

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The Preparation of $NaC^{14}N$ and $NaCN^{15}$

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1. Preparation of $NaC^{14}N$.—Many methods of preparation of $NaC^{14}N$ from $BaC^{14}O_3$ have been described during recent years^{2–10}; however, nearly all of them require special apparatus which is often not immediately available in most laboratories. The original method of Adamson,⁴ in which barium carbonate is heated with sodium azide, has been found by most workers to give erratic results. The essential feature of the following modification of Adamson's method is that only ordinary laboratory apparatus is used, and no special pumping or heating arrangements are necessary. Although the yields are not quite as high as those obtained in some of the methods involving more complicated

(1) This note is based on a portion of a thesis to be submitted by Alan G. MacDiarmid in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the University of Wisconsin.

(2) R. D. Cramer and G. B. Kistiakowsky, *J. Biol. Chem.*, **137**, 549 (1941).

(3) R. B. Loftfield, *Nucleonics*, **1**, No. 3, 54 (1947).

(4) A. W. Adamson, *THIS JOURNAL*, **69**, 2564 (1947).

(5) R. Abrams, *ibid.*, **71**, 3835 (1949).

(6) B. Belleau and R. D. H. Heard, *ibid.*, **72**, 4268 (1950).

(7) G. O. Henneberry and B. E. Baker, *Can. J. Research*, **26B**, 345 (1950).

(8) G. O. Henneberry, W. F. Oliver and B. E. Baker, *ibid.*, **29**, 229 (1951).

(9) J. A. McCarter, *THIS JOURNAL*, **73**, 483 (1951).

(10) J. W. Spyker and A. C. Neish, *Can. J. Chem.*, **30**, 461 (1952).

apparatus, e.g., that of Henneberry and Baker,⁷ the simple procedure below is excellent for the rapid preparation.

The apparatus consists of a length of glass tubing (approximately $2\frac{1}{2}$ by $\frac{1}{4}$ in.) sealed at one end, connected to one arm of a T-joint by rubber tubing. The stem of the T projects down into the first (B) of two vertical test-tubes (about 1×6 in., stoppered). The other arm leads through a right angle to the bottom of the second test-tube (C) from the top of which glass tubing leads to a nitrogen inlet and a 50-ml. reservoir bulb (D). The test-tubes are slipped snugly through 4-in. squares of asbestos.

The $BaC^{14}O_3$ is placed on a small watch glass and sufficient inert barium carbonate is added to it to give a total weight of approximately 0.1 g. This is then mixed into a paste with a little ethyl alcohol, using a small glass rod, and is allowed to dry in a desiccator. It is scraped from the watch glass on to black glazed paper and any lumps are gently broken up by pressing with a spatula. The barium carbonate is then mixed well, while still on the glazed paper, with 1.5 g. of sodium azide which has been finely powdered, in small amounts, in a mortar.

The apparatus is flushed out with dry nitrogen and a slow stream kept up throughout the experiment. The carbonate-azide mixture is introduced into A. Bunsen burners are then placed under the test-tubes so that the inner blue cone of the flame just impinges on the bottom of the test-tubes. The asbestos shields are placed approximately 1.5 inches above the bottoms of the test-tubes, which should now glow with a dull red heat. The tube A is raised and is tapped gently so that its contents are slowly emptied into the test-tube B. This should take about 15 minutes. As the powder reaches the bottom of B minute explosions occur and some of the undecomposed powder is blown over into C where it finally reacts. Metallic sodium collects on the sides of the tubes and remains there throughout the course of the experiment since no air enters the tube after the miniature explosions because of the nitrogen reservoir, D. The asbestos shields are now removed and the base and walls of both test-tubes are heated to a dull red heat for ten minutes by movement of the Bunsen burners. They are then allowed to cool, the nitrogen supply is turned off, and water is carefully added drop by drop to B and C to decompose the sodium. The contents of C are transferred with boiling water to B so that there is approximately 20 ml. of liquid in B. About 5 ml. of 0.1 N barium hydroxide is added to remove any carbonate formed; the solution is brought to boiling and filtered. The filtrate is placed in a distillation apparatus with boiling chips, acidified with 50% sulfuric acid and the $HC^{14}N$ distilled into approximately 10 ml. of 0.1 N sodium hydroxide. The strength, and also the specific activity of the resulting sodium radiocyanide solution, may be adjusted by the addition of inert sodium cyanide.

In the above manner of preparation, many of the experimental variables in Adamson's original method are eliminated. Consistent yields of 70% or more were obtained in blank runs with inert barium carbonate. Using the written directions above, yields of over 70% were obtained in the Department of Biochemistry at this University.¹¹

2. Preparation of $NaCN^{15}$.— $NaCN^{15}$ was prepared from potassium phthalimide¹² containing N^{15} in the following manner.

A small steel "bomb" is made by drilling a hole ($2\frac{1}{2} \times \frac{3}{8}$ inch) in a hexagonal steel bar. This can be sealed by a bolt which screws into the hole for a distance of about half an inch. The joint is made gas tight by means of a soft copper washer. The bomb is then thoroughly washed inside with hot soap and water, rinsed with water and acetone and dried. Traces of rust in the bomb cause the formation of small amounts of hexacyanoferrate(II) impurity in the sodium cyanide.

0.3 g. of potassium phthalimide and 1.5 g. of sodium slices are placed in the bomb which is then heated in a furnace for 20 minutes at 700° in an upright position. After cooling, water is carefully added drop by drop to the contents of the bomb to decompose any remaining sodium. The carbonized mass is then extracted with hot water, and

(11) D. Wilson, Department of Biochemistry, University of Wisconsin, private communication, Nov., 1952.

(12) Potassium phthalimide containing N^{15} obtained from Eastman Kodak Co., Rochester 4, N. Y.

treated with approximately 5 ml. of 0.1 *N* barium hydroxide solution to precipitate any carbonate. The solution is brought to boiling, filtered from carbon and barium carbonate, acidified with 50% sulfuric acid and the HCN¹⁵ distilled over into 20 ml. of 0.1 *N* sodium hydroxide. Ordinary sodium cyanide may then be added to this to obtain a solution of the desired normality or atom per cent. excess N¹⁵.

Four preparations were carried out using ordinary potassium phthalimide, and yields of 97–100% were obtained in each case.

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Terpenes in the Essential Oil of *Haplopappus laricifolius*, Gray¹

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As part of a study of various essential oil plants of southern Arizona, some of the principal terpene constituents in the volatile oil of *Haplopappus laricifolius*, Gray were determined. The oil was obtained by steam distillation of the leaves and small stems of the plant, a resinous, perennial shrub found at 3000 to 6000 feet elevation. The yellow oil comprised about 0.6% of the fresh weight of plant material and had the following constants: d^{32} 0.8631, n^{20}_D 1.4842, α^{34}_D -14.06°, acid no. 3.7, ester no. 7.8, and ester no. after acetylation, 40. The oil was fractionated *in vacuo* into 29 fractions; and by means of their physical constants and crystalline derivatives, certain fractions were shown

hydrous sodium sulfate prior to fractionation through a helix-packed column. The physical constants of the fractions were determined in the usual manner, and those for the fractions concerned are listed in Table I.

Fractions 1b, 2 and 3 were shown to contain α -pinene by preparation of the nitrosochloride, which showed no depression in its melting point³ when mixed with the same derivative of an authentic sample of α -pinene, and by determination of the nitrogen percentage of the nitrosochloride, the preparation of which was carried out according to the method of Wallach.⁴ After recrystallization six times from chloroform-methanol the final product was obtained in the form of colorless plates melting at 106–107°. The melting point of an equal mixture of the nitrosochlorides of fraction 2 and authentic α -pinene was also 106–107°.

Anal. Calcd. for C₁₀H₁₆ClNO: N, 6.94. Found: N, 6.98.

Fractions 5 and 6 were found to contain β -phellandrene by means of their physical constants and by preparation of the solid nitrosochloride and nitrosite. The former derivative was prepared in the same manner as was pinene nitrosochloride. The product was recrystallized twice from acetone as white prisms, m.p. 101.5–102°. Francesconi and Sernagiotto⁵ reported m.p. 101–102°. The formation of this compound identifies the original constituent as the β -isomer, since, according to West,⁶ the α -isomer does not form a solid nitrosochloride under the conditions employed here. This was also confirmed with an authentic sample of α -phellandrene⁷ in this Laboratory. The presence of phellandrene was confirmed by the immediate formation of the solid nitrosite, prepared according to the test of Wallach and Gildemeister.⁸

l-Phellandral was identified in fractions 18 and 19 by preparation of the 2,4-dinitrophenylhydrazone and by determination of the nitrogen percentage of this derivative. The hydrazone was prepared in the usual manner and, after recrystallization from a 1:1 chloroform-ethanol solution, the product was obtained in the form of reddish-orange prisms which melted at 201–202°. Macbeth and Price⁹ reported m.p. 202–203°.

Anal. Calcd. for C₁₆H₂₀N₄O₄: N, 16.87. Found: N, 17.00.

TABLE I
PHYSICAL CONSTANTS OF CERTAIN FRACTIONS OF OIL OF *Haplopappus laricifolius*

Fract.	Pure compound (literature)	Press., mm.	Distn. temp., °C.	Wt., g.	Wt., %	n^{20}_D	d^{30}_{16}
1b		19	58–60	3.8	2.38	1.4748	0.8542
2		19	60–62	16.9	10.58	1.4768	.8576
		700	157				
3		19	62–64	11.5	7.20	1.4788	.8558
	α -Pinene	20	52 ^a			1.4670 ^b	^b
		760	155–156 ^b				
5		19	66–68	18.4	11.51	1.4817	.8558
6		19	68–70	31.7	19.84	1.4835	.8488
		703	169–170				
	β -Phellandrene	24	78 ^c			1.4826 ^d	^d
		758	178–179 ^c				
18		0.25	64–68	0.7	0.44	1.4920	.9509
19		0.25	68–70	0.3	0.19	1.4929	.9509
	Phellandral	1.5	75 ^e			1.4912 ^f	^f

^a C. von Rechenberg's tables of boiling points at reduced pressures of isolates and synthetics, reproduced by Ernst Guenther, "The Essential Oils," Vol. I, D. Van Nostrand Co., Inc., New York, N. Y., 1948, p. 379. ^b F. H. Thurber and R. C. Thielke, THIS JOURNAL, **53**, 1030 (1931); d^{20} 0.8590. ^c G. E. Smith and T. F. West, *J. Soc. Chem. Ind.*, **56**, 300 (1937). ^d P. A. Berry, *Australian Chem. Inst. J. Proc.*, **14**, 376 (1947); $d^{15}_{15.5}$ 0.843. ^e R. G. Cooke and A. K. Macbeth, *J. Chem. Soc.*, 1408 (1938). ^f A. R. Penfold, *ibid.*, **121**, 266 (1922); d^{20} 0.9412.

to contain *dl*- α -pinene, *l*- β -phellandrene, and *l*-phellandral, making up, respectively, 20, 30 and about 1% of the whole oil. A more complete analysis will be presented in a future publication.

Experimental

The oil obtained by steam distillation was dried over an-

(1) In part from the Ph.D. dissertation of W. F. McCaughey, University of Arizona, May, 1951. Supported by a grant from the Warner-Hudnut Co., Inc., New York, N. Y.

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(3) All melting points uncorrected; determined on a Fisher-Johns block.

(4) O. Wallach, *Ann.*, **245**, 201 (1888), **270**, 181 (1892).

(5) L. Francesconi and E. Sernagiotto, *Gazz. chim. ital.*, **46** (I), 119 (1916).

(6) T. F. West, *J. Soc. Chem. Ind.*, **58**, 122T (1939).

(7) This sample kindly supplied by Fritzsche Brothers, Inc., New York, N. Y.

(8) O. Wallach and E. Gildemeister, *Ann.*, **246**, 282 (1888).

(9) A. K. Macbeth and J. R. Price, *J. Chem. Soc.*, 152 (1935).