with anhydrous hydrogen chloride gas. Palladium-charcoal, 1 g., was added *cautiously* (to prevent spontaneous ignition!) and the mixture evaporated under vacuum. While maintaining a constant pressure of nitrogen over the mixture of solids, it was heated at 295–305° for 20 min. The cooled mixture was extracted continuously for 18 hr. with anhydrous methanol, to which a few milliliters of glacial acetic acid had been added. The yellow fluorescing solution was evaporated under vacuum and the residue partitioned between 10% sodium hydroxide solution and chloroform. The aqueous solution was extracted repeatedly with chloroform until no more color transferred. The combined chloroform extracts were washed once with water, dried over anhydrous sodium sulfate, and filtered. After addition of enough glacial acetic acid to discharge the bright orange color, the solution was evaporated under vacuum on the steam bath. The residual yellow mixture of gum and crystals was dissolved in a minimum quantity of chloroform and transferred onto a chromatography column whose contents had been prepared from 33 g. of cellulose and 11 ml. of 1% (by volume) of aqueous acetic acid mixed intimately in dry chloroform. Fifty milliliter eluates were collected and treated with a few milliliters of dilute aqueous hydrochloric acid to prevent possible air oxidation of the desired products.

Desethylflavopereirine (IVa) and Its Tetrahydro Product (Va).—Elution of the chromatogram of the reaction mixture from the dehydrogenation of compound IIIa with wet chloroform removed all tars. Elution with 2.5:1 wet chloroform–*n*-butyl alcohol gave solid products. The first three fractions were combined and the solvent evaporated. Dissolution of the residue in a minimum amount of water and addition of a few drops of glacial acetic acid and 10% aqueous sodium perchlorate solution yielded a precipitate. Crystallization of the latter from aqueous ethanol gave 48 mg. of cream-colored crystals of Va perchlorate, m.p. 242–246°, mixed m.p. 241–246°. Its ultraviolet and infrared spectra were identical with those of an authentic sample, m.p. 242–247°, prepared by dissolving crystalline Va hydrobromide, m.p. 278–281° (lit.,[8] m.p. 280° dec.), in 10% sodium hydroxide solution extracting exhaustively with chloroform, adding glacial acetic acid to the organic extract, evaporating the solvent, and converting the residue to a perchlorate in the above manner.

Anal. Calcd. for $C_{15}H_{14}N_2 \cdot HClO_4$: C, 55.82; H, 4.69; N, 8.68. Found: C, 55.74; H, 4.78; N, 8.75.

The last twenty chromatographic fractions from the chloroform–butanol elution were combined, concentrated to a small volume, and divided into two parts. One was treated with a saturated methanol solution of picric acid. Crystallization of the resulting solid from absolute ethanol yielded 21 mg. of crystalline IVa picrate, m.p. and mixed m.p. 250–252° (lit.,[7f] m.p. 252–253°). The other part was concentrated and ether added. This led to 11 mg. of long needles of IVa chloride, m.p. 291–296° dec. (lit.,[7f] m.p. 295° dec.) infrared spectrum identical with that recorded in the literature.[7f]

Flavopereirine (IVb) and the Tetrahydro Products Vb and Vc.—Elution of the chromatogram of the reaction mixture from the dehydrogenation of compound IIIb,[6] m.p. 112–113.5°, with wet chloroform removed all tars, while elution with 5:1 wet chloroform–*n*-butyl alcohol yielded solid products. The first three fractions were combined and evaporated and the residue dissolved in a minimum amount of hot water and a trace of acetic acid. Dropwise addition of 10% sodium perchlorate led to a precipitate which on crystallization from absolute ethanol yielded 31 mg. of tetrahydroflavopereirine (Vb), m.p. and mixed m.p. 219–222°. Its infrared and ultraviolet spectra were identical with those of an authentic sample.[7c,9]

Since the later fractions of the chromatogram yielded a mixture of products, all eluates were combined, the salts reconverted to their organic bases, the latter transformed to acetic acid salts and chromatographed on cellulose as above. Elution with 9:1 wet chloroform–*n*-butyl alcohol yielded at first a solid which on crystallization from isopropyl alcohol-isopropyl ether afforded 9 mg. of Vc perchlorate, m.p. and mixed m.p. 246–252°. Its infrared and ultraviolet spectra were identical with those of an authentic sample.[6] The later chromatographic fractions were combined and concentrated. Crystallization of the precipitate from isopropyl alcohol and from water gave crystals, m.p. 320–325°. Recrystallization of this substance, 3 mg., from water and drying at 80° and 1 mm. pressure for 18 hr., and a similar treatment of an authentic sample[9] of IVb perchlorate yielded crystalline flavopereirine perchlorate, m.p. and mixed m.p. 323–327°. The ultraviolet and infrared spectra of the two specimens were identical.

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[8] L. H. Groves and G. A. Swan, *J. Chem. Soc.*, 650 (1952).

[9] The authors are indebted to Professor Henry Rapoport for a gift of a sample of this compound.

Synthesis of Toluene-α-D_3-1-C^{14}; Exchange during an Attempted Catalytic Deuteration

JAMES S. CLOVIS[1] AND GEORGE S. HAMMOND

Contribution No. 2809 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, Calif.

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Toluene-α-D_3-1-C^{14} was needed as a precursor of radioactive *p,p'*-ditrideuteromethylhydrazobenzene. The nondeuterated hydrazotoluene had previously been synthesized from radioactive toluene. In order to comparet he yields of the products from the rearrangement of the two compounds, it was desired to have the compounds with equal specific activity. Accordingly toluene-1-C^{14} was used as the initial precursor of toluene-α-D_3-1-C^{14}.

It was reasoned that the most economical method of synthesis would be to reduce methyl benzoate with deuterium gas in the presence of copper chromite

$$C_6H_5\text{—}CH_3 \xrightarrow{KMnO_4} C_6H_5CO_2H \xrightarrow{CH_2N_2}$$
$$C_6H_5CO_2Me \xrightarrow[CuCrO_2]{D_2} C_6H_5CD_3$$

Practice hydrogenations were carried out under different conditions. The experimental data are listed in Table I.

Optimum conditions appeared to involve use of ethanol as a solvent. However, the toluene that was obtained by the reaction of deuterium with radioactive methyl benzoate was shown by infrared analysis to have very little deuterium in the methyl group. Apparently there was a rapid equilibration of the deuterium gas with the hydrogen present in the ethanol, or the ethanol itself was directly responsible for the reduction.

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[1] National Institutes of Health Predoctoral Fellow, 1961–1962.

TABLE I

HYDROGENATION OF METHYL BENZOATE IN THE PRESENCE OF COPPER CHROMITE[a]

No.	Solvent	Grams of Methyl Benzoate	Press.[b] of H_2 in P.S.I.	Temp.	Time	Product Composition[c]		
						CH_3OBz	$C_6H_5CH_2OH$	$C_6H_5CH_3$
1	C_2H_5OH, 195 ml. abs.	25	1450–1500	190[d]	15 hr.	100	...	...
2	C_2H_5OH, 195 ml. abs.	25	1500	250–290	12 hr.	67	27	25
3	C_2H_5OH, 200 ml. abs.	25	1500	250–290	67 hr.	...	30	70
4	C_2H_5OH, 200 ml. abs.	25	1450	320–340	64 hr.	...	<2	>98
5	Methylcyclohexane, 200 ml.	27	1450	320–340	63 hr.	100	...	...
6	...	18[e]	1500	320–340	41 hr.	Lg.	...	Sm.
7	...	27	1500	320–340	140 hr.	60–70	...	30–40
8[f]	C_2H_5OH, 250 ml. abs.	25	1650[f]	320–340	73 hr.	...	Trace	>98

[a] Ten grams of catalyst was used in all runs except No. 6. [b] This refers to the initial pressure of the gas before the bomb was heated. The pressure was never allowed to drop below 1100 p.s.i. Considerable amounts of hydrogen dissolved in ethanol, but very little went into methylcyclohexane or methyl benzoate. It is felt that higher pressures of hydrogen would have significantly shortened the reaction time. The practice runs were, however, governed by the size of the bomb and the supply of deuterium gas. [c] All values are approximate and as no other products were detected by vapor phase chromatography, it was assumed that starting material was completely accounted for by the compounds listed here. [d] It is estimated that 5–6 hr. are required for the contents of the bomb to reach the temperature indicated by the thermocouple. [e] Five grams of catalyst was used. [f] Reaction of radioactive methyl benzoate with deuterium. As toluene and ethanol form an azeotrope, the two were separated by addition of an equal volume of water to the solution followed by extraction of the resulting mixture with pentane. The separated pentane solution was then dried with calcium chloride and the toluene was recovered by distillation. The infrared spectrum of the radioactive toluene obtained from the actual deuteration showed only a trace of possible C—D absorption around 2100 cm.$^{-1}$ and the usual C—H absorption of the methyl group in the 2000–3000-cm.$^{-1}$ region.

The following, more standard method of synthesis, was then resorted to:

$$C_6H_5CH_3 \xrightarrow{KMnO_4} C_6H_5CO_2H \xrightarrow{LiAD_4} C_6H_5CD_2OH \xrightarrow{SOCl_2}$$

$$C_6H_5CD_2Cl \xrightarrow{Mg} C_6H_5CD_3$$

This path proved successful and gave an over-all yield of 63%.

Experimental

Benzoic acid-1-C^{14} was prepared by permanganate oxidation[2] of toluene-1-C^{14}. Yields of 90–98% were obtained. The highest yield was obtained when the reaction mixture was kept just below the reflux temperature.

Methyl benzoate-1-C^{14} was prepared in virtually quantitative yield by the reaction of diazomethane with benzoic acid.

Copper chromite was prepared by the method of Vogel.[3]

Attempted Preparation of Toluene-α-D$_3$-1-C^{14}.—All hydrogenation were carried out in a 500-cc. bomb. The product compositions were determined by gas chromatography with an Apiezon-J column.

Benzyl Alcohol-α-D$_2$-1-C^{14}.—A solution of 38 g. (0.316 mole) of benzoic acid-1-C^{14} in several hundred ml. of ether was added with stirring over a period of 1.5 hr. to 20 g. (> 0.45 mole) of $LiAlD_4$ (> 95% purity) in 650–700 ml. of ether. The mixture was stirred for a total of 14 hr. after which time it was worked up by standard techniques. A total of 28.7 g. (83.5% yield) of benzyl alcohol-α-D$_2$-1-C^{14} was isolated (b.p. 95° at 10 mm).

Benzyl Chloride-α-D$_2$-1-C^{14}.—To 50 ml. of thionyl chloride (0.69 mole) in 50 ml. of ether was added the 28.7 g. (0.26 mole) of benzyl alcohol in 45 ml. of ether. The resulting solution was stirred at room temperature for 7 hr. and then distilled. The gas that was evolved during distillation probably came from either the formation and resulting decomposition or from the decomposition of the previously formed benzyl chlorosulfite. Thirty grams (91% yield) of benzyl chloride–α-D$_2$-1-C^{14} was collected at 92–93°, at a pressure of 50 mm.

Toluene-α-D$_3$-1-C^{14}.—To 5.69 g. (0.234 g.-atom) of magnesium turnings in 80 ml. of anhydrous ether was added gradually over a 20-min. period the 30 g. (0.234 mole) of benzyl chloride. It was necessary to apply gentle heat to initiate the reaction which was then controlled by intermittant cooling with an ice water bath. After all of the benzyl chloride had been added, the reaction mixture refluxed spontaneously for 10–15 min.; heat was then applied for another 25 min. to continue the reflux action. After this time 25 g. of deuterium oxide (1.25 moles) was added over a 30-min. period. The magnesium salts soon coagulated and left a clear ether solution. The mixture was stirred for 100 min. under gentle reflux and was then worked up. A total of 19.6 g. (88% yield) of toluene-α-D$_3$-1-C^{14}, which contained a trace of ether, was isolated. Analysis by n.m.r. showed 0.15 atom of deuterium in the ring. No hydrogen could be detected in the methyl group by n.m.r., while the infrared spectrum indicated a possible trace. The over-all yield leased on the 30 g. of starting toluene-1-C^{14} was 63%.

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(2) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed., John Wiley and Sons, New York, 1956, p. 250.

(3) A. I. Vogel, "Practical Organic Chemistry," 3rd ed., Longmans, London, 1956, p. 873.

The Reidentification of "Camphene" from the Acid-Catalyzed Isomerization of α-Terpineol as 3-*p*-Menthene

CHARLES F. WILCOX, JR., MARY F. WILCOX, AND
SHYAM S. CHIBBER

Contribution from the Department of Chemistry, Cornell University, Ithaca, N. Y.

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In a recent study of the isomerization of α-terpineol (I) under various acidic conditions it was