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%.

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.

Received January 25, 1962

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

---

(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.

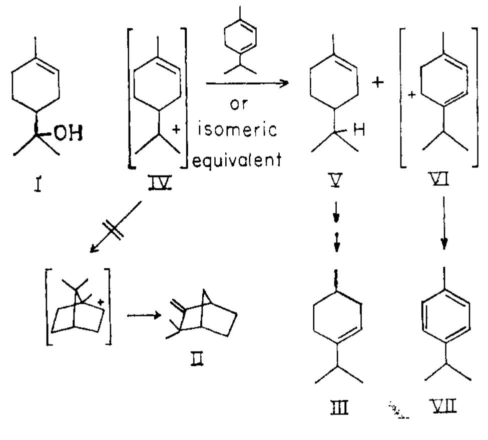
(3) A. I. Vogel, "Practical Organic Chemistry," 3rd ed., Longmans, London, 1956, p. 873.

reported that about 16% of camphene (II) was formed in a refluxing 4:1 ethanol–sulfuric acid mixture.[1] The identification of this particular fraction as camphene was based on (1) its identical retention time on a rape seed oil gas chromatographic column with authentic camphene, (2) its solidification when seeded with authentic camphene, and (3) the lack of melting point depression of the resulting solid when further camphene was added.

This report was surprising since our own attempts to force bicyclic ring closures of this same and related cyclohexenyl systems under nonequilibrium, kinetically controlled conditions were unsuccessful.[2]

The isomerization of α-terpineol was repeated in the manner described[1] to give a mixture of products whose proportions by gas-liquid chromatographic analysis appeared to be the same as those reported previously. However, when the lower boiling fractions were analyzed on a LAC-446 column, the retention time of the "camphene" peak differed very slightly from that of authentic camphene.[3] Moreover, 1:9 and 9:1 mixtures of this peak with camphene gave distinct shoulders which indicated definitely that the peak could not be camphene and was misidentified. Interestingly, a 1:1 mixture gave a single peak which indicates how similar the retention times of the two materials were to each other. We are unable to explain the seeding results of von Rudolph except to note the tendency of bicyclic molecules to form solid solutions with a large variety of molecules.[4]

The unknown "camphene" peak was isolated by preparative gas-liquid chromatography using a LAC-446 column to give a *liquid* of >95% peak purity. This liquid gave an analysis for a structure close to a $C_{10}H_{18}$ hydrocarbon. Another sample of >97% peak purity obtained with a silicone oil column had infrared and NMR spectra which indicated that it was 3-*p*-menthene (III).[5] Authentic 3-*p*-menthene of greater than 99% peak purity[6] gave infrared and NMR spectra essentially superimposable on that of the unknown.



The formation of 3-*p*-menthene can be readily accommodated into the isomerization scheme[1] of α-terpineol. The initially formed α-terpinyl carbonium ion (IV) could accept a hydride ion from one of the menthadienes to give 1-*p*-menthene (V) which would rapidly isomerize under the acidic conditions to give the more stable[7] 3-*p*-menthene, as observed. The other product of the hydride transfer (VI) is simply a protonated *p*-cymene which would lose its proton to become the observed *p*-cymene (VII).

Experimental

To 80 g. of α-terpineol in 320 ml. of 95% ethanol was added 80 ml. of concd. sulfuric acid. The solution was heated under reflux for 1 hr. and then steam distilled into an ice-cooled flask. The organic portion of the distillate was recovered by extraction and solution in ether. This ethereal solution was washed with bicarbonate solution, then with water, and finally dried over anhydrous magnesium sulfate. The dried solution was distilled through a 2-ft. Podbielniak-type[8] distillation column, and the fractions with b.p. 52–58° (17 mm.) and b.p. 58–60° (17 mm.) were collected. The 3-*p*-menthene, 70% of the first fraction, was isolated by preparative gas chromatography on a 6-ft. × 1/2 in. column packed with 10% LAC-446 (Wilkens Instrument and Research) on Chromosorb W using a flow rate of 600 ml./min. and a column temperature of 81°. Reinjection of the collected sample, $n^{23.5}_D$ 1.4519, indicated peak purity >95%.

Anal. Calcd. for $C_{10}H_{18}$: C, 86.88; H, 13.12. Found: C, 87.18; H, 12.98.

Commercial camphene was recovered unaltered by this isolation technique.

Another sample of 3-*p*-menthene of >97% peak purity was isolated using a commercial 5-ft. × 1/2-in. column packed with 20% GE-SF-96 silicone oil on acid-washed Chromosorb W (Wilkens Instrument and Research). The infrared spectrum (neat) was identical with the published spectrum[5] and a spectrum obtained with an authentic sample of pure (>99% peak purity) 3-*p*-menthene.[6] The NMR spectrum, determined on a Varian A-60 using a Varian 12-in. magnet, was complex but the three groups of peaks were in the expected ratio of 1:6:9 (with group centers at τ = 4.52, 8.0, and 9.0, respectively). With the exception of two small peaks at τ = 4.34 and 4.42 the spectrum of the isolated sample was identical with that of authentic 3-*p*-menthene.

Acknowledgment.—We are indebted to the National Science Foundation for support which made the completion of this study possible.

---

(1) E. Von Rudolph, *Can. J. Chem.*, **39**, 1 (1961).

(2) C. F. Wilcox, Jr., and S. S. Chibber, in press.

(3) Greater differences were noted on a silicone oil column.

(4) J. Pirsch, *Angew. Chem.*, **57**, 40 (1944).

(5) American Petroleum Institute Research Project 44 at the National Bureau of Standards; infrared spectral data; Serial No. 1779.

(6) We are indebted to the Hercules Powder Co. for a generous gift of this authentic *p*-3-menthene.

(7) H. Pines and H. E. Eschinazi, *J. Am. Chem. Soc.*, **78**, 1178 (1956).

(8) J. Cason and H. Rapoport, "Laboratory Text in Organic Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1950, p. 232.