tassio-salt, and treatment with methyl iodide in portions until the mixture was neutral to phenolphthalein, yielded, after saponification and decarboxylation at 160°, 115 mg. (18% from the mesylate, XI) of **α-methyl-γ-(6-methoxy-8-methyl-1-naphthyl)-butyric acid (XII)** as a yellow solid. The analytical sample was recrystallized from an ether–petroleum ether mixture as slightly yellow microcrystals, m.p. 116–118°.

Anal. Calcd. for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40. Found: C, 75.03; H, 7.86.

(b) **By a Methyl γ-Bromotiglate Reformatsky Reaction with the Ketone (VIII).**—The crude Reformatsky ester, obtained from 2 g. of the ketone VIII and 4 g. of methyl γ-bromotiglate[14] in a 3:1 ether–benzene mixture, was dehydrated with 1.5 g. of potassium acid sulfate, isomerized with 0.5 g. of 5% palladized charcoal by the method of Stork[17] and saponified to yield 50 mg. (1.8%; based on unrecovered ketone, 5%) of α-methyl-γ-(6-methoxy-8-methyl-1-naphthyl)-butyric acid (XII), m.p. 115–117°, undepressed on admixture with the substance obtained from method (a). The amount of starting ketone recovered was 1.31 g. (65%).

1-Keto-2,5-dimethyl-7-methoxy-1,2,3,4-tetrahydrophenanthrene (XIII).—The butyric acid (XII, 66 mg.) was converted to the acid chloride with 1 ml. of oxalyl chloride in benzene solution and then cyclized with stannic chloride exactly as described by Bachmann, Cole and Wilds[18] for the corresponding intermediate in their equilenin synthesis; yield of **1-keto-2,5-dimethyl-7-methoxy-1,2,3,4-tetrahydrophenanthrene (XIII)** was 36 mg. (59%), m.p. 175–176.5°, after recrystallization from an ether–petroleum ether mixture.

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.14. Found: C, 80.52; H, 7.51.

1-Ethyl-2,5-dimethyl-7-methoxyphenanthrene (IV).—A solution of a Grignard reagent, prepared from 1 g. of magnesium turnings and 5 g. of ethyl iodide in 20 ml. of anhydrous ether under an atmosphere of nitrogen was added to 36 mg. of the ketone XIII in 10 ml. of dry ether and refluxed for one hour. After decomposition of the excess reagent with water and addition of dilute acid, the organic layer was separated and washed well with dilute acid, dried and evaporated. The oily residue was covered with methanol when the oil solidified, weight 33 mg. (87%), m.p. 104–114°. Recrystallization from methanol gave the **1-ethyl-2,5-dimethyl-7-methoxy-3,4-dihydrophenanthrene** as colorless microcrystals, m.p. 114.5–116°.

Dehydrogenation of 23 mg. of the dihydro derivative with 23 mg. of palladized charcoal at 250–260° for seven minutes gave 14 mg. (61%) of **1-ethyl-2,5-dimethyl-7-methoxyphenanthrene (IV)**, which melted at 115–116.5° after recrystallization from methanol as colorless plates. When this sample was mixed with compound B (m.p. 115–116.7°) the melting point was 115–116.5°. The infrared absorption spectrum exhibited the following peaks: $\lambda_{max}^{mineral\ oil}$ 6.12(s), 6.35(w), 7.11(w), 7.43(m), 7.73(w), 7.86(s), 8.18(m), 8.31(m). 8.57(s), 9.12(m-s), 9.38(m-s), 9.43(m-s), 9.72(m), 10.50(m), 11.28(m-s), 11.66(s), 11.86(w), 12.14(m), 12.80(m), 13.75 (m-s) μ.

The *sym*-trinitrobenzene complex melted at 134–135°. When it was mixed with this derivative of compound B (m.p. 133–135°) the melting point was 133–135°. The picrate melted at 116–118° alone and when mixed with this derivative of compound B (m.p. 118–119°).

DETROIT, MICHIGAN

(17) G. Stork, THIS JOURNAL, **69**, 2937 (1947).

(18) W. E. Bachmann, W. Cole and A. L. Wilds, *ibid.*, **62**, 824 (1940).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR SCIENCE AND ENGINEERING, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Mechanisms of Racemization of Camphene-8-C^{14} [1]

BY JOHN D. ROBERTS[*] AND JOEL A. YANCEY

RECEIVED JANUARY 3, 1953

It has been shown by C^{14}-tracer studies that optically-active camphene racemizes by at least two different mechanisms in the presence of hydrated titanium dioxide, pyruvic acid or aniline hydrochloride. One of these mechanisms does not cause isotope-position rearrangement of camphene-8-C^{14} and probably involves successive hydride and Wagner rearrangements. This mechanism predominates with hydrated titanium dioxide and aniline hydrochloride. Racemization of camphene-8-C^{14} with pyruvic acid is accompanied by extensive isotope-position rearrangement and is well formulated by assuming interconversion of enantiomorphic "camphenonium" (camphene-hydro) cations through methyl group shifts (Nametkin rearrangements).

Camphene (I) is racemized more or less readily by a variety of acidic reagents.[2-4] Two types of mechanisms have been suggested for these processes which may be illustrated (and experimentally distinguished) with optically active camphene-8-C^{14} (Ia).

Both mechanisms involve formation of the "camphenonium" (camphene-hydro) cation (IIa) by addition of a proton to Ia. Mechanism A then proceeds by 2,6-hydride migration to yield the isomeric non-classical cation III,[5] or possibly the symmetrical tricyclonium ion IV,[5b] either of which would yield Ia and Ib thus giving racemic camphene. Mechanism A stems from an early suggestion of Meerwein[6] regarding the mode of racemization of isobornyl chloride and is given substantial support by the findings that: (1) 2,6-hydrogen migrations occur readily in cationic reactions of norbornyl[5b,7] and fenchyl[8] derivatives and (2) 8-substituted camphenes appear to racemize without substantial rearrangement.[3,9]

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[*] Crellin Laboratory, California Institute of Technology, Pasadena 4, Calif.

(1) Supported in part by the program of research of the U. S. Atomic Energy Commission.

(2) (a) P. Lipp and G. Stutzinger, *Ber.*, **65**, 241 (1932); (b) S. Yamada, *Bull. Chem. Soc. Japan*, **16**, 336 (1941).

(3) J. J. Ritter and G. Vlases, Jr., THIS JOURNAL, **64**, 583 (1942).

(4) For refs. to related reactions and discussion see J. L. Simonsen and L. N. Owen, "The Terpenes," Vol. II, 2nd Ed., University Press, Cambridge (1949), Chap. V, particularly pp. 290–293.

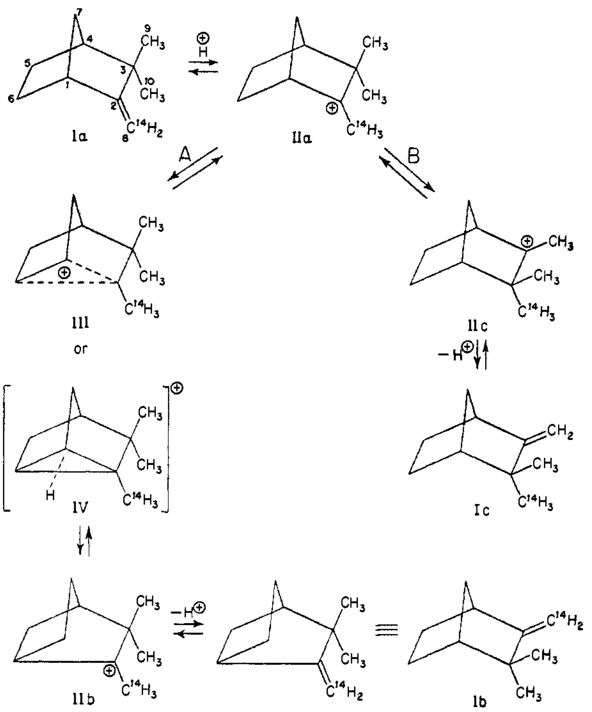
(5) For extensive studies of intermediates of this type in other reactions see (a) S. Winstein and D. S. Trifan, THIS JOURNAL, **71**, 2953 (1949); **74**, 1147, 1154 (1952); (b) J. D. Roberts and C. C. Lee, *ibid.*, **73**, 5009 (1951); (c) S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan and H. Marshall, *ibid.*, **74**, 1127 (1952.)

(6) H. Meerwein and F. Montfort, *Ann.*, **435**, 207 (1924).

(7) J. D. Roberts, paper presented at the 75th Anniversary Meeting of the American Chemical Society, Sept. 7, 1951.

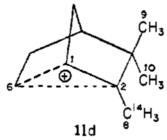
(8) W. v. E. Doering and A. P. Wolf, Abstracts of the XIIth International Congress of Pure and Applied Chemistry, New York, N. Y., Sept. 11, 1951, p. 437.

(9) The argument here is not rigorous since as Ritter and Vlases[3] point out the structures of the racemization products were not confirmed by chemical means. Furthermore, even if racemization occurred by mechanism B (above), the 8-substituted camphenes may be more thermodynamically stable than their 9- or 10-substituted isomers and hence no apparent rearrangement need accompany racemization.



Mechanism B involves a conventional methyl shift common to many terpene reactions[4] and generally known as a Nametkin rearrangement.[4]

A and B may be experimentally distinguished by the C^{14}-distributions resulting from the operation of each starting with labeled camphene (Ia). With mechanism A, no change in the C^{14}-distribution would occur, while with B, the C^{14} would become distributed among the side chain carbon atoms. If the structure of the cation IIa is taken as written, either the *exo*(9)- or *endo*(10)-methyl group could migrate and, at equilibrium, the C^{14} would be expected to be distributed equally among the three methyl groups. If IIa is considered best formulated as the non-classical bridged cation IId, one would anticipate that the *exo*(9)-methyl group would migrate preferentially since the bonding between carbons 2 and 6 should tend to shield position 2 from *endo*-attack. In this circumstance, the C^{14}-distribution in the racemized camphene would have 50% at position 8 and 50% at positions 9 and 10, provided that the difference in rates of migration of methyls 9 and 10 was large.



IId

In the present research, the racemization and rearrangement of camphene-8-C^{14} (Ia) have been investigated. The starting material Ia was prepared by addition of methyl-C^{14}-magnesium iodide to camphenilone and dehydration of the resulting 2-methyl-C^{14}-camphenilol. Direct dehydration with pyruvic acid[10] at 140–150° was unsatisfactory since it resulted with extensive isotope-position rearrangement (*cf.* Table I). Formation and pyrolysis of 2-methyl-C^{14}-camphenilyl benzoate gave Ia with 2–6% rearrangement.

The amount of C^{14} in the 8-position of the labeled camphene samples was determined by degradation. Ozonization yielded the 8-carbon as formaldehyde which was isolated as the dimethone derivative and oxidation with nitrogen dioxide gave the other carbons as camphenilone which was isolated and purified as the semicarbazone.[11]

The experimental results from a number of racemization and rearrangement experiments are given in Table I. It is quite clear that, in none of our experiments, does either mechanism A or B operate exclusively. With hydrated titanium dioxide (employed as a commercial pinene isomerization catalyst)[12] and aniline hydrochloride, mechanism A predominates while, with pyruvic acid in acetonitrile, mechanism B is of comparable importance. With each catalyst, it is evident that, on attainment of equilibrium, the C^{14} will be distributed statistically among the three side-chain groups. This distribution would result from simultaneous operation of A and B irrespective of the stereochemistry of methyl group rearrangements of IIa or IId. At present, we have no satisfying explanation for the differences between pyruvic acid and the other catalysts in inducing racemization by the different mechanisms.

Acknowledgment.—We are pleased to acknowledge the aid of Mrs. Clare M. Regan with the C^{14}-analyses.

Experimental

2-Methyl-C^{14}-camphenilol.—The following procedure was designed to take advantage of the high yields of 2-methylcamphenilol associated with the action of a large excess of methyl Grignard reagent on camphenilone[13] without undue waste of methyl-C^{14}-magnesium halide. To a solution of methyl-C^{14}-magnesium iodide prepared from 30.8 g. of methyl-C^{14} iodide (containing 0.5 mc. of C^{14}) and 6.2 g. of magnesium in 100 ml. of anhydrous ether was added 29.2 g. of camphenilone[14] dissolved in 60 ml. of ether over 2 hours. The mixture was refluxed for 3 hours and then a solution of non-isotopic methylmagnesium iodide prepared from 30.8 g. of methyl iodide in 70 ml. of ether was added from a dropping funnel over 0.5 hour. The final mixture was heated under reflux for 15 hours and then hydrolyzed by shaking with ice and saturated ammonium chloride solution in a separatory funnel. The aqueous layer was removed and extracted with fresh ether. The combined ethereal extracts were dried over magnesium sulfate, the ether evaporated and the residue sublimed to give 32.6 g. (99%) of 2-methyl-C^{14}-camphenilol, m.p. 113.8–115.6° (lit.[13] 118–119°). The material was identified as the N-phenylcarbamate, m.p. 125.6–126.6° (lit.[15] 126°), and the *p*-nitrobenzoate, m.p. 143.4–144.4° (lit.[13] 143°).

2-Methyl-C^{14}-camphenilyl Benzoate.—Potassium metal (1.93 g.) was converted to fine sand under 100 ml. of benzene. The mixture was cooled and stirred and 7.61 g. of 2-methyl-

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[10] L. Bouveault and G. Blanc, *Compt. rend.*, **140**, 93 (1905).

[11] Ozonization of camphene gives rather poor yields of camphenilone[4] and the separate nitrogen dioxide oxidation was found preferable to isolation of the ketone from the ozonization products.

[12] (a) G. Etzel, U. S. Patent 2,551,795 (1951). (b) We are indebted to Dr. H. E. Schroeder of the E. I. du Pont Co. for a sample of this material.

[13] W. Hückel, W. Doll, S. Eskola and H. Weidner, *Ann.*, **549**, 186 1941).

[14] The camphenilone was prepared by nitrogen dioxide oxidation of camphene, *cf.* P. Lipp, *ibid.*, **399**, 241 (1913). The crude product was distilled and then purified through the semicarbazone. The purified camphenilone had b.p. 80.0–80.5° (60 mm.), m.p. 39.4–41.3° (cor.).

[15] O. Aschan, *ibid.*, **410**, 222 (1915).

TABLE I

CAMPHENE-8-C^{14} RACEMIZATION AND REARRANGEMENT EXPERIMENTS

			$[\alpha]_D$[a]		Camphene[b]		Formaldehyde[e]		Camphenilone[f]				
Catalyst	Temp., °C.	Time, min.	Start	Finish	Meas. act.[b,c]	Cor. act.[d]	Meas. act.[b,c]	Cor. act.[d]	Meas. act.[b,c]	Cor. act.[d]	Re-arr.,[g] %	Racem.,[h] %	k_A/k_B[i]
None[j]	.....	...	.....	......	441	1521	231[k]	1520	6[k]	20	~2[l]	...	....
CH_3COCO_2H[m]	140–150	4	......	......	510	1760	149	872	277	957	52	...	....
$TiO_2.xH_2O$	100 ± 3	210	−21.9°	−8.96°	448	1540	239	1400	4.6	160	4(10)	59	~12
$TiO_2.xH_2O$	160[n]	1.3	−10.1	−2.3	0.1685[o]	...	0.1261[o]	..	0.0375[o]	...	20(22)	77	2
$C_6H_5NH_3Cl$ + $C_6H_5NH_2$	180[n]	13	−18.1	−8.54	0.1689[o]	...	0.1492[o]	..	0.0231[o]	...	12(14)	53	3
CH_3COCO_2H	150–160	10	−22.0	0.00	440	1520	127	592	270	932	61(61)	100	....
CH_3COCO_2H + CH_3CN	156 ± 2	330	−21.6	−11.0	480[p]	1120[p]	176	1030	106	364	22(26)	49	0.7

[a] All rotations measured at 26–28° in a 2.00-dm. tube using concentrations of 6–8 g. per 100 ml. of *n*-hexane and are accurate to ±0.1°. [b] Radioactivity of compound determined by combustion and conversion to barium carbonate. [c] Measured C^{14}-activities using a windowless methane-filled counter ("Nucleometer") of "infinitely thick" barium carbonate samples with cross-sectional area of 2.90 cm.^{2} prepared as described by J. D. Roberts, W. Bennett, E. W. Holroyd and C. H. Fugitt, *Anal. Chem.*, **20**, 904 (1948). The values are corrected for background and have standard deviations of less than 3% or ±5 counts/min. whichever is higher. [d] C^{14}-Activities corrected for self-absorption and dilution by non-labeled carbon atoms as detailed by J. D. Roberts, R. E. McMahon and J. S. Hine, THIS JOURNAL, **72**, 4237 (1950). Values are expressed in dis./min./mg. of barium carbonate. [e] Radioactivity of formaldehyde as the methone derivative. [f] Radioactivity of camphenilone as the semicarbazone. [g] % Isotope-position rearrangement = average of the values calculated from the formaldehyde and camphenilone activities using the camphene activity as a standard. Appropriate corrections were made for the rearrangement in the preparation of the camphene. The values in parentheses are not corrected for the C^{14}-distribution in the starting material. [h] % Racemization under the given conditions. [i] Ratio of the rates of camphene racemization by mechanisms A and B. Using the theory of simultaneous first-order reactions, it can be shown that k_A/k_B = [ln(mole fraction of unracemized camphene/mole fraction of unrearranged camphene)/ln(mole fraction of unrearranged camphene)]. [j] Typical camphene sample prepared by the pyrolysis of 2-methyl-C^{14}-camphenilyl benzoate. [k] Average of two determinations. [l] With other preparations the amount of rearrangement ranged from 2–6% in this reaction. [m] Camphene obtained by dehydration of 2-methyl-C^{14}-camphenilol with pyruvic acid (ref. 10). [n] Run at the reflux temperature. [o] C^{14}-Activities determined by vibrating reed electrometer method as described by O. K. Neville, THIS JOURNAL, **70**, 3499 (1948). [p] The activity of this material was unaccountably low and the % rearrangement was based on the activities of the dimethone and semicarbazone derivatives.

C^{14}-camphenilol dissolved in 60 ml. of benzene added rapidly. The whole was then heated under reflux for 2.5 hours, at the end of which time, the potassium had almost completely dissolved. The mixture was cooled, treated with a solution of 7.0 g. of redistilled benzoyl chloride in 60 ml. of benzene over 10 minutes, and then stirred at room temperature for 17 hours. Water (150 ml.) was added and the benzene layer separated, washed with sodium bicarbonate solution, dried over magnesium sulfate and distilled through a small wire-helix packed column. The yield of 2-methyl-C^{14}-camphenilyl benzoate, b.p. 118.8–122.0° (0.7–0.9 mm.), was 10.8 g. (84%). An analogous preparation of non-isotopic material gave a product of b.p. 133–138° (1.7 mm.), n^{25}_D 1.5318.

Anal. Calcd. for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 78.61; H, 8.55.

Camphene-8-C^{14}.—The following experiment is typical. 2-Methyl-C^{14}-camphenilyl benzoate (1.10 g.) was heated in a small flask equipped with a 4-cm. Vigreux column using a Wood's metal bath. Pyrolysis occurred smoothly at a bath temperature of 300–320° and the fraction boiling below 165° amounted to 0.48 g. (83%) of quite pure camphene. The infrared spectrum showed very slight absorption at 845 cm.$^{-1}$ where tricyclene has a strong band[16] and a small band at 717 cm.$^{-1}$ which may have been due to traces of bornylene. In all other respects, the infrared spectrum was virtually identical with the spectrum of a sample of highly-purified camphene.[12b] The product was diluted with highly purified camphene for degradation, racemization and rearrangement experiments. The carrier camphene was only partially optically active but the rotation was large enough to permit measurement of the racemization rates to better than 5% accuracy.

Dehydration of 1.79 g. of 2-methyl-C^{14}-camphenilol by heating with 1.8 g. of pyruvic acid for 4 minutes at 140–150° gave 0.93 g. (59%) of radioactive camphene which after dilution with ordinary camphene and degradation was found to be very extensively rearranged (*cf.* Table I).

Degradation Procedure for C^{14}-Labeled Camphene.—A sample (1.5–2.0 g.) of radioactive camphene was accurately weighed and dissolved in 25.0 ml. of *n*-hexane. After determination of the optical rotation, about 15 ml. of hexane was distilled off and the residue treated with nitrogen dioxide (Matheson) in a test-tube immersed in ice-water. The hexane was evaporated under reduced pressure from the crude nitrogen dioxide addition product which was then refluxed with 30% potassium hydroxide solution for several hours. The resulting camphenilone was steam distilled and extracted from the steam distillate with ether. The crude product was converted to the semicarbazone which was purified by two crystallizations from ethanol–water before C^{14}-assay.

Another portion (0.3–0.5 g.) of the labeled camphene was treated with ozone in 10–15 ml. of chloroform at 0° until slightly more than the calculated amount of ozone had been passed through. The solvent was removed under reduced pressure, 70 ml. of water was added and the mixture refluxed for 30–45 minutes. The insoluble material was removed by filtration, 300 ml. of a saturated solution of methone (dimethyldihydroresorcinol) added and the whole allowed to stand overnight. The crystalline formaldehyde methone was collected and recrystallized twice from methanol–water.

Racemization and Rearrangement Experiments. A. Hydrated Titanium Dioxide.—A sample of 4.6 g. of camphene-8-C^{14} was heated with 0.25 g. of hydrated titanium dioxide[12] at 100 ± 3° in a flask equipped with a magnetic stirrer for 3.5 hours. The reaction mixture was taken up in ether, filtered, the ether distilled and the camphene sublimed. The recovery was 3.8 g. (82%). The rotation and degradation data are given in Table I.

In another experiment, 5.4 g. of camphene was refluxed for 1.3 minutes with 0.24 g. of the titanium dioxide catalyst and recovered as before. The recovery was 4.2 g. (78%). The other data are given in Table I.

B. **Aniline Hydrochloride.**—A sample of 7.1 g. of camphene-8-C^{14} was heated under reflux for 13 minutes with 6.8 g. of aniline hydrochloride and 9.6 ml. of aniline. The mixture was cooled and the aniline hydrochloride washed out with water. Distillation gave a fraction boiling below 170° which was taken up in ether and washed several times with dilute hydrochloric acid and finally with water. Evaporation of the ether and sublimation of the residue afforded 3.7 g. (52%) of partially racemized camphene. The other data are given in Table I.

C. **Pyruvic Acid.**—Camphene-8-C^{14} (7.8 g.) and 8.8 g. of pyruvic acid were heated and shaken in a test-tube equipped with a cold-finger condenser at 150–160° for 10 minutes. The mixture was cooled, diluted with water, neutralized with potassium carbonate and extracted with ether. The extracts were combined, dried over magnesium sulfate and the ether distilled. The residue was sublimed

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(16) G. Swann and F. J. Cripwell, *Ind. Chemist*, **24**, 573 (1948).

at 10 mm. and afforded 2.7 g. (35%) of racemic camphene. The other data are given in Table I.

In another experiment, 7.3 g. of camphene-8-C^{14} was heated with 1.5 ml. of pyruvic acid and 30 ml. of acetonitrile in a sealed tube immersed in refluxing bromobenzene, b.p. 156°, for 5.5 hours. The reaction mixture was treated as above, and afforded 4.1 g. (56%) of sublimed camphene. The other data obtained in this experiment are given in Table I.

CAMBRIDGE 39, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

Racemization in the Camphene Hydrochloride–Isobornyl Chloride Rearrangement[1,2]

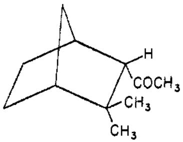
BY WYMAN R. VAUGHAN AND RANDOLPH PERRY, JR.

RECEIVED JANUARY 3, 1953

A new route to optically active camphenilone is described. By means of C^{14}-labeled methyl iodide, the optically active camphenilone is converted into methylcamphenilol and thence by the xanthate dehydration to optically active camphene labeled in the 8-position. Racemization by standard rearrangement procedures affords camphene which is shown by ozonolysis and analysis of the resulting dimethylnorcampholide to have the isotopic carbon statistically distributed among the 8-, 9- and 10-positions. It is concluded that the racemization occurs in part by migration of one of the *gem*-methyl groups in accord with the Nametkin hypothesis and in part by an alternative process not involving methyl migration.

Until comparatively recently "optically pure" camphene has not been available for study and, of the published routes to it,[3,4] neither admits of preparation of the optically pure substance labeled in the 8-position. Inasmuch as it seemed desirable to minimize the operations subsequent to introduction of C^{14}, it was decided to develop an entirely new route to optically active camphenilone which then could be readily converted in one or two steps to the desired optically active labeled camphene.

The preparation of a suitable starting material, 2,2-dimethyl-3,6-*endo*-methanocyclohexyl methyl ketone (I), has already been described.[1,5] Conversion of I into N-camphenilylacetamide was achieved by means of the Schmidt reaction using sodium azide in concentrated hydrochloric acid. Owing to the hygroscopic character of camphenilylamine and its tendency to absorb carbon dioxide rapidly, it was never handled as the free base but was identified by comparison of the infrared spectrum of its N-benzoyl derivative and that of an authentic sample.



I

In exploratory work the racemic amine was converted directly to camphenilone in excellent yield by means of a modification of the Sommelet reaction in which hexamine and formaldehyde are used to convert a primary amine to a carbonyl function.[6]

Subsequently camphenilylamine was resolved using (+)-tartaric acid and (+)-camphoric acid. Since both resolving agents were subject to the same objection (the fully resolved salts are all but optically inactive), the resolution involved recrystallization until the specific rotation of the salt fell below an arbitrary minimum. Conversion to camphenilone of several such samples established the acceptability of this procedure inasmuch as samples of this nature afforded camphenilone comparable with that of the highest reported optical purity and subsequently yielded camphene of correspondingly high optical purity.

In passing from camphenilone, $[\alpha]^{26}\text{D}$ 76.1° (benzene), to camphene, $[\alpha]^{26}\text{D}$ 109.0° (benzene), use was made of the Grignard reaction, using ordinary methyl iodide. The methylcamphenilol thus produced was dehydrated to camphene by means of the xanthate ester procedure which obviates racemization at this critical stage. Slightly less "active" camphenilone, $[\alpha]^{26}\text{D}$ 62.4° (benzene) was used with C^{14} Grignard to give slightly less active camphene, $[\alpha]^{26}\text{D}$ 103.5° (benzene).

It is of interest to record that it may not be necessary to isolate the alcohol from the Grignard reaction when it is intended for subsequent xanthate formation. If a higher boiling ether is employed, the Grignard reaction mixture may be treated with carbon disulfide and excess methyl iodide to give the methyl xanthate directly without isolation of the alcohol and subsequent time-consuming conversion to the potassium alkoxide. Unfortunately time did not permit full exploration of this aspect of the problem, but work is continuing on this modification of the original Chugaev reaction.

Once the optically active 8-labeled camphene was obtained, it was racemized by a procedure worked out by Meerwein and Montfort.[7] To provide bulk in subsequent operations, the labeled camphene was "diluted" with a known quantity of pure racemic camphene and then was dissolved in ether and converted to camphene hydrochloride with dry hydrogen chloride at 0°. The crude hydrochloride was dissolved in cresol, and a portion was placed in a 1-dm. polarimeter tube where the loss

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(1) Presented in part before the Division of Organic Chemistry, 121st Meeting, American Chemical Society, Buffalo, N. Y., March 26, 1952.

(2) Abstracted from a portion of the Ph.D. dissertation of Randolph Perry, Jr., University of Michigan, 1953.

(3) W. Hückel, W. Doll, S. Eskola and H. Weidner, *Ann.*, **549**, 199 (1941).

(4) J. P. Bain, A. H. Best, B. L. Hampton, G. A. Hawkins and L. J. Kitchen, THIS JOURNAL, **72**, 3124 (1950).

(5) W. R. Vaughan and R. Perry, Jr., *ibid.*, **74**, 5355 (1952).

(6) J. Graymore and D. R. Davies, *J. Chem. Soc.*, 293 (1945); S. J. Angyal, P. J. Morris, J. R. Tetaz and J. G. Wilson, *ibid.*, 2141 (1950).

(7) H. Meerwein and F. Montfort, *Ann.*, **435**, 207 (1923).