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]

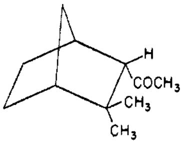
BY WYMAN R. VAUGHAN AND RANDOLPH PERRY, JR.

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).

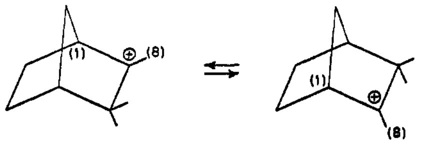
(5) W. R. Vaughan and R. Perry, Jr., *ibid.*, **74**, 5355 (1952).

(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).

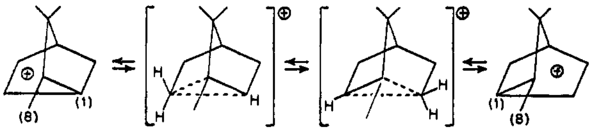
(7) H. Meerwein and F. Montfort, *Ann.*, **435**, 207 (1923).

of optical activity was followed until the solution became too dark to permit further observations. After 163 min. there was 16.6% residual rotation; thus to assure complete racemization the solution was allowed to stand for 10.75 hr. and then was worked up to give racemic isobornyl chloride which was reconverted to camphene by treatment with sodium ethoxide.[7] The resulting camphene was purified and proved to be fully racemic.

Two reasonable paths for racemization would seem to be available: the first was proposed as a consequence of Nametkin's study of the behavior of 1-substituted camphenes.[8] It is pictured (without regard for the concerted nature of rearrangements) most simply as a shift of the *endo* methyl of the "camphenehydro" ion



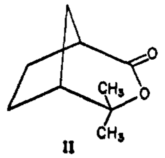
The second path embodies a hydride shift in the rearrangement stage or subsequent to it (again without regard for the concerted nature of rearrangements).



Evidence in favor of the latter is adducible from the work of Ritter and Vlases,[9] who report the inactivation of 8-substituted camphenes. Nametkin's findings taken with those of Ritter and Vlases suggest the possibility of concurrent modes of rearrangement, since the two inactivations are individually incompatible.

By labeling carbon-8 it becomes possible to consider the two paths without recourse to camphene derivatives, which it might be argued can behave differently from camphene itself. The Nametkin hypothesis predicts formation of a camphene which will retain a portion of its initial radioactivity in the isopropylidene bridge: 50% if one methyl is involved, as demanded by the stereospecificity[10] of the general Wagner–Meerwein rearrangement. The alternative hydride shift will not affect the status of the original methylene group, which will retain 100% of the radioactivity at the 8-position, if the Nametkin racemization is not involved. Thus ozonolysis will afford a radioactive dimethylnorcampholide (and camphenilone) only if the methyl shift mechanism is involved, and retention of more than 50% of the initial radioactivity would imply concurrent involvement of the alternative hydride shift mechanism.

In the ozonolysis reaction camphenilone and the lactone, dimethylnorcampholide (II), are produced in about equal quantities.[11]

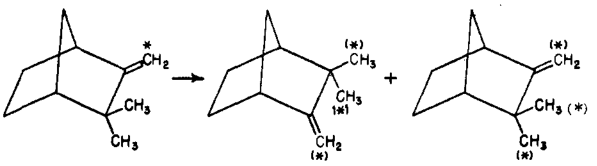


II

The notoriously high cryoscopic constant of camphenilone coupled with its relatively low melting point and high volatility render it a difficult substance for small-scale study. Consequently it was decided to isolate and purify the more tractable II as the major fragment from the ozonolysis, since it, like camphenilone, contains the two methyl groups of camphene into which the C^{14} may have become distributed. The operations and results duplicate the literature[11] findings exactly, and thus it was possible to obtain a suitably pure sample of II for combustion.

Making suitable correction for the "dilution" of the labeled sample as described above the following data are obtained: Total radioactivity of original sample ("standard" run on methylcamphenilol) 2.34 $\times 10^8$ c./min./mole; radioactivity of dimethylnorcampholide (prepared from racemized camphene, itself obtained from active camphene prepared from the standard sample of methylcamphenilol) 1.55 $\times 10^8$ c./min./mole; % radioactivity retained in dimethylnorcampholide 1.55/2.34 $\times$ 100 = 66.3%.

Thus 2/3 of the original radioactivity is retained in II after the racemization. Accordingly the C^{14} originally at position 8 must have become statistically distributed among positions 8, 9 and 10.



Distribution of C^{14} among these *three* positions abundantly indicates the necessity of involving both racemization processes, since the *trans* migration principle in the Wagner–Meerwein rearrangement admits only of migration of the *endo* methyl of the isopropylidene bridge in camphene hydrochloride.

The question of configuration in camphene hydrochloride is not of serious moment inasmuch as the rearrangement to isobornyl chloride requires the chlorine to be *exo*; and even were there appreciable quantities of the *endo* isomer present, it would be converted to the more stable *exo* form, since both methylcamphenilol (*exo*) and camphene hydrate (*endo*) afford the same camphene hydrochloride with hydrogen chloride.[12]

Without examination of partially racemized camphenes it is not possible to determine to what extent methyl and hydrogen migration contribute; however, the near-statistical distribution suggests both are appreciably involved, which is in keeping with Nametkin's results on the one hand and

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[8] For a brief discussion and leading references see Sir John Simonsen, "The Terpenes." Vol. II, 2nd ed., Cambridge University Press, Cambridge, 1949, pp. 290–293.

[9] J. J. Ritter and G. Vlases, Jr., THIS JOURNAL, **64**, 583 (1942); *cf.* L. A. Subluskey and L. C. King, *ibid.*, **73**, 2647 (1951).

[10] For extensive discussion of the mechanism of 1,2-shifts, *cf.* G. W. Wheland, "Advanced Organic Chemistry," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1949, Ch. 12, esp. pp. 529–534.

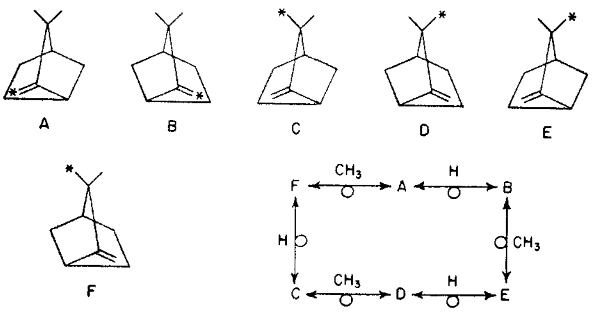
[11] C. Harries and Baron J. Palmén, *Ber.*, **43**, 1432 (1910).

[12] O. Aschan, *Ann.*, **383**, 65 (1911); **410**, 272 (1915).

Ritter's and Vlases' on the other, both investigations affording ample quantities of product resulting from the particular process being established.

The various isotopic antipodes and the relationships between them are illustrated in Chart I where (+)-A is arbitrarily taken to be the initial camphene-8-C^{14}.

CHART I



It is apparent that until at least one methyl migration (*e.g.*, A → F or B → E) has occurred, no change in the distribution of C^{14} is possible although racemization can occur (*e.g.*, A → B).

Acknowledgment.—The senior author wishes to express his thanks to the Board of Governors of the Horace H. Rackham School of Graduate Studies of the University of Michigan for the award of a Summer Faculty Research Fellowship which enabled him to initiate this study and to the Michigan Memorial Phoenix Project for a grant to purchase counting equipment.

Experimental[13]

N-Camphenilylacetamide.—The Schmidt reaction[14] was carried out on camphenilyl methyl ketone (I), 7.48 g. (0.045 mole) of which was dissolved in 150 ml. of absolute methanol previously saturated at room temperature with dry hydrogen chloride. To this solution was added 4.0 g. (0.06 mole) of sodium azide in small portions over a period of 6 hr. at room temperature. After standing overnight there was added excess 10% aqueous alkali and the mixture was steam distilled. The distillate contained some unchanged ketone and some camphenilylamine (from 6 to 12%) which was recovered by ether extraction. The amine was isolated from the ethereal solution, after drying over magnesium sulfate, by addition of dry hydrogen chloride which caused the amine hydrochloride to precipitate. The major portion of the rearrangement, however, afforded N-camphenilylacetamide which was recovered from the basic distillant by cooling and filtering. Recrystallization from aqueous methanol yielded 5.22 g. (64%), m.p. 140.2–141.2°. An alternative procedure in which 55 ml. of ordinary concentrated hydrochloric acid is used as the reaction medium for 0.05 mole of ketone afforded a somewhat lower yield of N-camphenilylacetamide, m.p. 143.0–143.5°. Both melting points are rather higher than the previously reported value of 135–136°.[15] The microanalysis was carried out on the higher melting sample inasmuch as recrystallization failed to raise the melting point.

Anal. Calcd. for $C_{11}H_{19}NO$: C, 72.88; H, 10.81; N, 7.73. Found[16]: C, 72.70; H, 10.46; N, 7.72.

Hydrolysis of N-Camphenilylacetamide.—The amide is particularly resistant to all forms of acid-induced hydrolysis. A solution of 29.78 g. of the amide (0.164 mole) and 120 g. (1.83 moles) of potassium hydroxide in 220 ml. of ethylene glycol was heated to 150–160° whereupon a vigorous reaction occurred. The volatile product was then slowly distilled into 10% hydrochloric acid until the temperature of the reaction mixture reached 198°. Steam distillation into fresh hydrochloric acid then removed all traces of the amine. The hydrochloric acid solutions were combined and extracted with ether, made alkaline with sodium hydroxide and the liberated amine was extracted into ether (87% yield by assay of an aliquot). The amine is strongly basic, as previously reported,[15] and it absorbs carbon dioxide from the atmosphere rapidly. Thus it is best stored as the hydrochloride which can be precipitated from the dried ethereal solution as indicated in the preceding experiment. If resolution by means of (+)-tartaric acid is desired, the ethereal solution of the racemate may be converted into the diastereomeric tartrates by careful addition of the ether solution to an alcoholic solution of (+)-tartaric acid.

Several derivatives were prepared. The benzamide, m.p. 153.0–154.0° cor., melted somewhat higher than previously reported[15,17] and a mixed melting point with a sample (m.p. 148.5–152.0°)[17] very kindly furnished by Dr. Noyce melted at 150.0–151.0°. However, infrared absorption curves for the present product and for Dr. Noyce's sample are identical. The picrate was prepared: m.p. 215.5–216.0° dec. Previously the value was reported as 205–207° for a picrate prepared from a mixture of the present *endo* with the *exo* form of the amine.[18]

Anal. Calcd. for $C_{15}H_{20}N_4O_7$: C, 48.91; H, 5.47; N, 15.12. Found[16]: C, 48.87; H, 5.28; N, 15.03.

Resolution of Camphenilylamine.—An ether solution of 36.1 g. (0.259 mole) of camphenilylamine was added slowly and with good stirring to a dilute solution of 45 g. (0.30 mole) of (+)-tartaric acid in 90% ethanol. The white solid (dec. 200–202°) which separated immediately was removed by filtration and dissolved in the minimum amount of water at 80°. After standing for 2 to 3 hours at room temperature, the needle-like crystals were filtered off and recrystallized from fresh water as before. The so-called triangular scheme[19] was carried out, and whenever the specific rotation of a given crop was found to be $\leqq +3°$, it was removed from the pattern and consolidated with all other material meeting this specification.

A sample of partially resolved tartrate, 13.94 g. (0.0482 mole), was converted into the (+)-hydrogen camphorate and the same method was then followed for further resolving the mixture, dioxane being used as the solvent. The specific rotation was found to approach a minimum close to 0°, and consequently the camphorate offered no advantage over the tartrate. Figures are given in Table I for comparative purposes.

Camphenilone.—(The following procedure was used for preparation of optically active samples of camphenilone from the salts used in resolution. Where the racemic compound was used for study of conditions, the hydrochloride was neutralized directly.) Camphenilylamine was liberated from 13.0 g. (0.045 mole) of the tartrate by the addition of excess alkali. It was taken up in ether from which it was extracted by a threefold excess of 10% hydrochloric acid in three equal portions. The acidic extracts were combined and neutralized to phenolphthalein with concd. alkali. After the addition of 5–10 drops of glacial acetic acid and 5.15 g. (0.060 mole) of 37% aqueous formaldehyde[6] the mixture was chilled well in ice and shaken vigorously for 10–15 min. during which time a white solid separated. To the resulting slurry there was added 40 g. (0.029 mole) of hexamine and glacial acetic acid sufficient to bring the acetic acid concentration to about 50%. The mixture was then refluxed for *ca.* 1 hr., after which the flask was chilled and the contents made alkaline with concd. sodium hydroxide. After three extractions with ether the ethereal extracts were combined and washed successively with 5% hydrochloric acid, water and 5% sodium bicarbonate solution. After drying over magnesium sulfate the ethereal solution was distilled through an efficient column yielding 4.65 g. (75%) of camphenilone, b.p. 188–191° (atm.) uncor. The infrared spectrum is identical with that of camphenilone prepared in the conventional manner.[3] The semicarbazone melted at 221–223° and gave no depression with an authentic

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[13] Melting points are uncorrected unless otherwise noted.

[14] We are indebted to Dr. P. A. S. Smith for several helpful suggestions regarding conditions for carrying out this reaction.

[15] W. Hückel, *Ber.*, **69B**, 2769 (1936).

[16] Clark Microanalytical Laboratory, Urbana, Illinois.

[17] D. S. Noyce, THIS JOURNAL, **73**, 20 (1951).

[18] G. Komppa, *Ann.*, **366**, 71 (1909).

[19] *Cf.* A. Weissberger, "Technique of Organic Chemistry," Vol. III, Interscience Publishers, Inc., New York, N. Y., 1950, p. 424.

TABLE I

Source Salt	$[\alpha]^{25}\text{D}^a$	Camphenilone[b,c] M.p., °C.	Camphenilone[b,c] $[\alpha]^{26}\text{D}$	Methylcamphenilol[b,d] M.p., °C.	Methylcamphenilol[b,d] $[\alpha]^{26.6}\text{D}$	Camphene[b,e] M.p., °C.	Camphene[b,e] $[\alpha]^{26}\text{D}$
Hydrochloride	......	39.2–40.8	.....	118–119	.....	50.0–52.5	......
Camphorate	+ 1.36°	41.0–42.8	+76.1°	110–115	+29.1°	47–51	+109.0°
Camphorate	− 2.13	37–40	+62.4	.....	.....	48.0–52.8	+103.5
Camphorate	+10.16	38–40	−30.5				
Tartrate	+19.9	38–40	−30.5				
Residues from tartrate resolutions	......	35–40	−20.6	.....	.....	49.2–51.5	− 27.1

[a] Rotations taken in absolute ethanol, 1.5–2.0% solutions, 1 dm. tube. [b] Rotations taken in benzene, 1.5–2.5% solutions, 1 dm. tube. [c] Reported[3] values: m.p. 38–39°, $[\alpha]^{20}\text{D}$ 66.7° (benzene). [d] Reported[3] values: m.p. 112.0–113.5°, $[\alpha]^{20}\text{D}$ 32.1°. [e] Reported values: m.p. 51–52°; $[\alpha]^{20}\text{D}$ 107.7° (benzene)[3]; m.p. 47°, $[\alpha]^{25}\text{D}$ −113.5° (ether). ···117.5° (toluene.[4])

TABLE II

COUNTING DATA

Compound	No.	Wt., mg.	Total $BaCO_3$, mg.	Plate $BaCO_3$, mg.	Sp. act. $BaCO_3$, ct./min./mg.	Weighted averages, %	Molar sp. act. pdct., ct./min./mol.
Methylcamphenilol (≈active camphene)	1	67.8	922.0	a 13.7	111.2 ± 0.6	111.7 ± 1.5	2.34 × 10^8 ± 1.5%
				b 19.1	112.1 ± 1.2		
	2	59.9	809.6	a 8.8	112.4 ± 1.2	112.3 ± 2.0	2.34 × 10^8 ± 2.0%
				b 17.6	112.2 ± 1.2		
Dimethylnorcampholide (from racemized camphene)		72.8	885.8	a 4.85	21.2 ± 0.3	21.5 ± 4.5	1.55 × 10^8 ± 4.5%
				b 5.7	22.7 ± 0.5		Corrected for dilution
				c 13.85	21.2 ± 0.3		by factor 4.338/
				d 10.0	21.6 ± 0.5		1.126

sample. Rotational and melting point data are given in Table I.

Methylcamphenilol.—This was prepared according to the procedure given by Hückel, *et al.*,[3] by means of large excess of methyl Grignard reagent acting upon camphenilone: yield (based upon 2.00 g. (0.0145 mole) of camphenilone) 1.94 g. (86.6%), m.p. 118–119°, as previously reported,[3] for racemic sample after repeated sublimation. Rotational and melting point data are recorded in Table I. The methylcamphenilol-8-C^{14} used as counting standard and for conversion to labeled camphene was prepared in the same manner using methyl iodide-C^{14}: specific activity 111.7 ct./min./mg. $BaCO_3$; molar specific activity 2.34 × 10^8 ct./min./mole methylcamphenilol.

Camphene. (A) By Xanthate Ester Dehydration of Methylcamphenilol.—A solution of 2.0 g. (0.013 mole) of methylcamphenilol in 5 to 10 ml. of dry benzene was refluxed with excess clean potassium for at least 6 but preferably 12 hr., after which interval gas bubbles were no longer formed on the surface of the molten potassium. The mixture was cooled and the hardened lump of potassium was removed from the yellow-orange solution in which large clear crystals were sometimes observed. After warming slightly 5 ml. (a large excess) of carbon disulfide was added causing immediate separation of a cream to orange colored solid. Lumps were broken up by vigorous shaking and the mixture was then refluxed for 2 hr. There was then added 5 ml. (a large excess) of methyl iodide, and the refluxing was continued for 10 to 12 hr. longer. The mixture was then filtered and the solvent was distilled from the filtrate. The dark, unpleasant smelling oil remaining after removal of the solvent was refluxed for 1 hr. with a solution of 7 pellets of potassium hydroxide in 5 ml. of 95% ethanol, after which it was poured into cold water. The resulting mixture was extracted with ether, the extract treated with Norit, dried over magnesium sulfate, filtered and distilled yielding 1.26 g. (71.5%) of camphene, b.p. 150–154° (atm.). The infrared spectrum was identical with that of authentic camphene.

(B) By Conversion of the Grignard Product.—With 25 ml. of *n*-butyl ether as solvent the Grignard reagent was prepared in the usual manner from 0.0618 mole of methyl iodide. The mixture was heated on the steam-bath for 5 hr. to ensure complete reaction; then 4.25 g. (0.0308 mole) of camphenilone in 10 ml. of *n*-butyl ether was added slowly and the heating was continued for 2 hr. During this period a white solid separated. To this slurry was added 5 g. (0.0658 mole) of carbon disulfide, and heating was continued for an additional 4 to 5 hr. The mixture was at first yellowish in color but gradually became almost black. Next there was added 9.0 g. (a large excess) of methyl iodide, and the mixture was heated on the steam-bath overnight (11 hr.). At the end of this time the mixture was black with a dark greenish cast to it. The flask was cooled and aqueous methanol was added very slowly and with good stirring, the reaction being quite vigorous. Much solid separated at this stage. The mixture was then steam distilled and the distillate separated, the organic layer being dried, filtered and distilled through an efficient column. At 138–148° a fraction which contained appreciable unsaturated material distilled, while at 148–152° there was obtained 1.38 g. (33%) of camphene, m.p. 49–52°, whose infrared spectrum was identical with that of authentic camphene.

Optically Active Camphene-8-C^{14}.—This was prepared from optically active camphenilone (2.757 g. (0.020 mole), m.p. 37–40°, $[\alpha]^{26}\text{D}$ +62.4° (benzene)). The product was purified by distillation and repeated sublimation: m.p. 49.0–52.8°, $[\alpha]^{26}\text{D}$ +103.5° (benzene, molar specific activity 2.34 × 10^8 ct./min./mole (see methylcamphenilol)). This material was used in the racemization studies. The methylcamphenilol taken as standard was removed from the reaction series and suitably purified, whereas the methylcamphenilol for xanthate preparation was used directly without purification.

Racemization of Optically Active Camphene-8-C^{14}.—The racemization was carried out as described by Meerwein and Montfort.[7] A solution of 1.126 g. (0.00827 mole) of optically active camphene-8-C^{14} and 3.2119 g. (0.0236 mole) of ordinary purified racemic camphene[20] in 35 ml. of dry ether was saturated with dry hydrogen chloride at 0°. After 1 hr. the solvent and excess hydrogen chloride were removed by vacuum distillation leaving a residue of slightly straw colored camphene hydrochloride, m.p. 124–128°, reported 125–127°.[21] This was dissolved in freshly distilled *o*-cresol, and a portion was placed in a polarimeter tube (1 dm.). As time passed the initial pinkish tinge deepened, and the solution became so dark by the time the initial rotation of −1.20° had fallen to −0.20° (16.6%, 163 min.) that further observation was impossible. Since Meerwein had shown that isobornyl chloride may be completely racemized under similar conditions in 190 min., and that camphene hydrochloride rearranges to isobornyl chloride very rapidly under these conditions, it appeared safe to assume complete racemization, based on the relative rate of decrease in optical activity for the present sample as compared with Meerwein's sample, after 10.75 hr. At the end of this time the reaction mixture was poured into 200 ml. of 15% potassium hydroxide, and the resulting mixture was

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(20) Kindly supplied by the Hercules Powder Co.

(21) H. Meerwein and K. van Emster, *Ber.*, **52B**, 1815 (1920).

extracted three times with ether. The combined ethereal extracts were washed twice with 100 ml. of 10% sodium hydroxide solution, and then the organic layer was dried and the ether was distilled using an efficient column leaving crude isobornyl chloride which was reconverted to camphene by refluxing for 2 hr. with excess alcoholic sodium ethoxide. Distillation of the alcoholic solution carried over most of the camphene. To the residue was added 20 ml. of water and the distillation was continued until an oil began to steam distil at about 83°. The alcoholic distillate was drowned with a large quantity of water and then extracted thrice with ether. After drying over magnesium sulfate the ethereal solution was distilled yielding 2.08 g. (0.0153 mole, 48%) of fully racemic camphene, b.p. 146–156° (atm.), m.p. 40–51°. The product was carefully sublimed to give pure camphene, m.p. 49–51°, $[\alpha]^{25}\text{D}$ 0.00° (benzene).

Ozonolysis of Racemized Camphene.—The procedure of Harries and Palmén[11] was followed exactly with similar results. The dimethylnorcampholide was recrystallized thrice from ether, five times from 1:1 ether–petroleum ether (90–100°) and then was sublimed without change in the melting point, 94.0–96.5°, previously 96.0–96.5°[11] and 95–96°[22]; specific activity 21.5 ct./min./mg. $BaCO_3$; sp. molar activity 1.55 × 10^7 ct./min./mole dimethylnorcampholide, corrected for "dilution" of camphene.

Analytical Procedure.—Peroxide fusion in a Parr bomb was used. In each case the conversion to barium carbonate and preparation of plates were carried out as described by Calvin, *et al.*[23] The plates were counted using an N-Wood Model K flow counter and a Nuclear Instrument Chemical Co. model 161 scaler with attached Veeder Root register and Precision Scientific Co. timer. The counter was operated at 1400 v., 125 v. above the threshold, under a constant stream of 3–5 bubbles of "Q" gas per sec. The over-all calculated error for molar specific activity is ±4.5%.[23]

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[22] F. W. Semmler, *Ber.*, **42**, 246 (1909).

[23] M. Calvin, C. Heidelberger, J. C. Reid, B. M. Tolbert and P. F. Yankwich, "Isotopic Carbon," John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 90–92, 118, 283–291.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELAWARE]

The Decomposition of Organic Acids in the Presence of Lead Tetraacetate*

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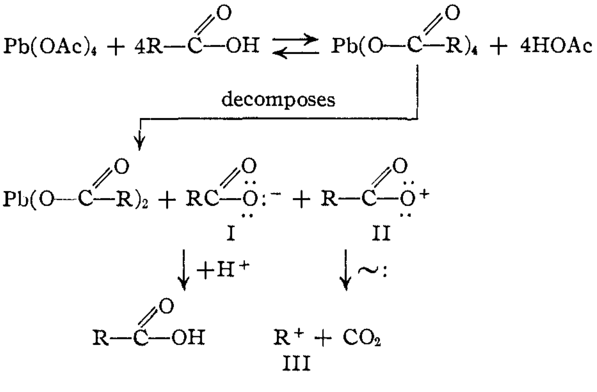
Previous workers have shown that lead tetraacetate decomposes in acetic acid to give carbon dioxide, methane, acetoxyacetic acid and methylene diacetate. We have extended this reaction to include a variety of organic acids (formic acid, triphenylacetic acid, trimethylacetic acid, isobutyric acid and isovaleric acid) in a study of the mechanism involved. The products obtained may be readily explained by the following ionic scheme: interchange first occurs between lead tetraacetate and the organic acid present; decomposition of the Pb^{++++} salt yields the corresponding Pb^{++} compound, the negative ion of the acid and positive ion such as $R\text{–CO–O}^+$. This electronically deficient oxygen-containing ion may then decompose to carbon dioxide and a carbonium ion which may stabilize itself by losing a proton to form an olefin, by reacting with solvent anion to form esters, or by abstracting a hydride ion from a molecule of solvent to give rise to a more stable carbonium ion and hydrocarbon gas. No evidence of free radical decomposition was observed.

The decomposition of lead tetraacetate in acetic acid has been reported by Kharasch[1] and coworkers, and a mechanism involving trivalent lead radicals proposed. Previous work[2] in this Laboratory, however, has suggested that benzpinacolyl alcohol was oxidized by lead tetraacetate in good yield to benzaldehyde and triphenylcarbinol *via* an ionic cleavage reaction involving an electronically deficient oxygen intermediate. In an attempt to determine the generality of ionic reactions of lead tetraacetate, a systematic study has been made of the decomposition of tetravalent lead salts of organic acids of varying structure. Table I presents a concise summary of the conditions and products of the reactions investigated.

A careful study of the products obtained in the above reactions indicated a pronounced mechanistic trend which led us to interpret the reaction from the ionic viewpoint rather than the free radical concept advanced by Kharasch.[1]

The oxidation of formic acid[3] appeared to be a convenient starting point in the present mechanistic study because this molecule offers to the oxidizing agent only two possible points of attack—the aldehyde function and the hydroxylic function. Because it is a well established fact that aldehydes under the conditions employed are stable to lead tetraacetate, it was suspected that the hydroxyl group must be the center of attack by the oxidizing agent. The following generalized mechanism is proposed



$$Pb(OAc)_4 + 4R\text{—}\overset{\overset{O}{/\!/}}{C}\text{—}OH \rightleftharpoons Pb(O\text{—}\overset{\overset{O}{/\!/}}{C}\text{—}R)_4 + 4HOAc$$

$$\xrightarrow{\text{decomposes}} Pb(O\text{—}\overset{\overset{O}{/\!/}}{C}\text{—}R)_2 + \underset{\text{I}}{RC(=O)\text{—}\ddot{O}\!:^-} + \underset{\text{II}}{R\text{—}C(=O)\text{—}\ddot{O}^+}$$

$$\text{I} \xrightarrow{+H^+} R\text{—}\overset{\overset{O}{/\!/}}{C}\text{—}OH \qquad \text{II} \xrightarrow{\sim:} \underset{\text{III}}{R^+} + CO_2$$

There is other evidence[4] for the rejection of the classical aldehyde theory of oxidation of formic acid.

In support of this mechanism, the tetravalent lead salt of trimethylacetic acid has been prepared and decomposed in trimethylacetic acid solvent. The products obtained from this reaction were nearly identical to those found when lead tetraacetate itself was decomposed under similar con-

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[1] M. S. Kharasch, H. N. Friedlander and W. H. Urry, *J. Org. Chem.*, **16**, 533 (1951).

[2] W. A. Mosher and H. A. Neidig, THIS JOURNAL, **72**, 4452 (1950).

[3] J. M. Grosheintz, *ibid.*, **61**, 3379 (1939).

[4] *Cf.* Paul Haas, *Nature*, **167**, 325 (1951).