

largely the result of experimental inaccuracies, the agreement is quite good. In general, the refractive indices can be calculated, with or without measurements of the densities, to within a few units in the fourth decimal place. (It should be noted that none of the compounds for which reliable data are available contain bonds between two quaternary carbon atoms. Hence, there is as yet no check on the constant ( $-0.35$ ) in the corresponding term of Equation 23 or Equation 24.)

#### Discussion

In many instances, the difference between experimental and calculated values, both for densities and for refractive indices, is less than the probable experimental inaccuracy. It seems hardly worth while to refine the treatment further than has been done, until more or better data are available. The calculations are, however, being extended to non-paraffin hydrocarbons and to other organic compounds.

A theoretical interpretation of the meaning of the regularities observed and of the magnitudes of the constants will be postponed until later. In the meantime, it is hoped that the equations obtained will prove useful.

**Acknowledgment.**—The writer is glad to acknowledge the able assistance of Miss Dorothy Owen with the calculations reported in this paper. He also wishes to express his indebtedness to Mr. S. S. Kurtz, Jr., of the Sun Oil Company, for a helpful discussion of some of the points involved in the present treatment.

#### Summary

1. Molal volumes of normal paraffins are given quite accurately by an equation of the form  $V_n = a + bn + (c/n)$ .

2. Molal volumes of several series of non-normal paraffins are given quite accurately by relations of the form  $V = V_n + d$ .

3. Molal refractions of paraffins in general are, quite accurately, the sums of characteristic bond refractions. The magnitude of a C-C or C-H bond refraction depends on the number of C and H atoms attached to each of the carbon atoms concerned. Simple equations for computing molal refractions (and refractive indices) of paraffins from their formulas have been deduced and tested.

KODAK RESEARCH LABORATORIES  
ROCHESTER, NEW YORK

RECEIVED AUGUST 7, 1940

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

## A New Optically Active Reagent for Carbonyl Compounds; the Resolution of *dl*-Camphor

BY ROBERT B. WOODWARD,<sup>1</sup> T. P. KOHMAN,<sup>2</sup> AND G. CHRIS HARRIS

Only a few instances of the resolution of racemic carbonyl compounds have been described in the literature. Using *l*-menthylhydrazine,<sup>3</sup> Neuberger<sup>4</sup> resolved *r*-arabinose, and shortly thereafter the same worker with Federer<sup>5</sup> accomplished the resolution of *r*-galactose, using *as*-phenyl-*d*-amylhydrazine.<sup>6</sup> Wilson, *et. al.*, have succeeded in resolving *r*-benzoin through its derivatives with  $\delta$ -[*d*-( $\alpha$ -phenylethyl)]-semicarbazide and its enantiomer,<sup>7a</sup>  $\delta$ -[*l*-menthyl]-semicarbazide,<sup>7b</sup> and  $\delta$ -[*d*-( $\alpha$ -phenylpropyl)]-semicarbazide,<sup>7c</sup> but were

not able to resolve *dl*-camphor, or *dl*-3-methylcyclohexanone with these reagents.

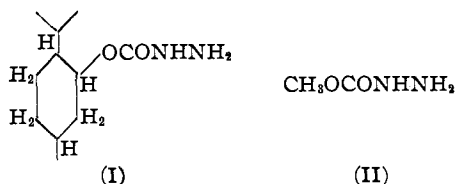
Several optically active hydrazine derivatives whose value as resolving agents has not been demonstrated, but which might potentially be of use in this connection, have been described, *viz.*, *d*-bornylhydrazine,<sup>8</sup> *as*-methyl-*d*-bornylhydrazine,<sup>9</sup> *as*-ethyl-*l*-menthylhydrazine,<sup>3</sup>  $\psi$ -camphorylsemicarbazide,<sup>10</sup> *l*-menthylglycine hydrazide,<sup>11</sup> and *d*-*neo*-menthylglycine hydrazide.<sup>11</sup> Of these compounds (including those used successfully by Neuberger and Wilson) several have not been obtained in a state of purity, the majority are oils or low-melting solids, and, with the exception of the last three, the substances are unstable either in

(1) Member of the Society of Fellows.  
(2) Mr. Kohman participated in this research in pursuance of a Chemistry 5 special problem.  
(3) Kishner, *J. Russ. Phys.-Chem. Soc.*, **27**, 524 (1895).  
(4) Neuberger, *Ber.*, **36**, 1192 (1903).  
(5) Neuberger and Federer, *ibid.*, **38**, 868 (1905).  
(6) Neuberger and Federer, *ibid.*, **38**, 866 (1905).  
(7) (a) Hopper and Wilson, *J. Chem. Soc.*, 2483 (1928); (b) Crawford and Wilson, *ibid.*, 1122 (1934); (c) Little, McLean and Wilson, *ibid.*, 336 (1940).

(8) Taipale, *Ber.*, **63**, 246 (1930).  
(9) Forster, *J. Chem. Soc.*, **75**, 942 (1899).  
(10) Forster and Fierz, *ibid.*, **87**, 722 (1905).  
(11) Galloway and Read *ibid.*, 1222 (1936).

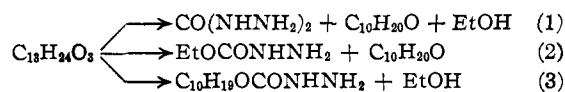
the pure state or in solution. Moreover, none of the compounds yields readily crystalline derivatives on reaction with a variety of carbonyl compounds. Further we should expect that the asymmetric disubstituted hydrazines would fail to react or at best react with difficulty with ketones, even though suitable derivatives have been obtained from aldehydes in a very few instances. Finally, all of the substances were prepared either by a difficult synthesis or from rather difficultly accessible and sensitive intermediates.

In this communication we report the synthesis of *l*-menthyl N-aminocarbamate (I), a stable, beautifully crystalline, optically active reagent which forms well-defined crystalline derivatives with a large number of carbonyl compounds of



widely differing function and, further, demonstrate its applicability as a resolving agent by a remarkably facile resolution of *dl*-camphor.

Following an observation of Diels,<sup>12</sup> who prepared methyl N-aminocarbamate (II) in excellent yield from dimethyl carbonate and hydrazine, we investigated the action of the latter reagent on di-*l*-menthyl carbonate, prepared from dimethyl carbonate and excess *l*-menthol in the presence of sodium. The di-*l*-menthyl carbonate, however, showed great resistance to attack by hydrazine under all conditions, *e. g.*, the ester was recovered unchanged after boiling for long periods with "100 per cent." hydrazine hydrate. This result, although eliminating one possibility for the preparation of *l*-menthyl N-aminocarbamate, indicated that the cleavage of the ester link in the latter would not be a complicating factor in the reactions of the reagent, and further pointed the way to the final solution of the problem. By the action of ethyl chloroformate in the presence of a small quantity of pyridine, we converted *l*-menthol into ethyl *l*-menthyl carbonate in excellent yield. On treatment of this ester with hydrazine, we found that of the three possible reactions



(12) Diels, *Ber.*, **47**, 2187 (1914).

reaction (3) predominated under all conditions. Best results were obtained when the hydrazinolysis was carried out in boiling cellosolve with a slight excess of hydrazine. Under these conditions *ca.* 70% of the ester was used in reaction (3), the remainder of the 90% which could be accounted for appearing as *l*-menthol, formed in reactions (1) and (2).

*l*-Menthylhydrazide<sup>13</sup> crystallized from aqueous alcohol or ligroin in splendid needles, melting sharply at 101.5–102°, and had  $[M]^{25}_D -171^\circ$ . It formed solutions which were stable indefinitely in the usual organic solvents, and was insoluble in cold, but soluble in hot dilute mineral acids. Under a wide variety of conditions it formed with representative carbonyl compounds nicely crystalline, sharp-melting derivatives. Table I in the experimental part summarizes the properties of a number of derivatives and the conditions under which they were obtained. For the general characterization of aldehydes and ketones these derivatives are advantageous in that they possess definite specific rotations in addition to sharp melting points.

The resolution of *dl*-camphor through the diastereomeric *d*- and *l*-camphor *l*-menthylhydrazones offered little difficulty, the latter derivative being very much less soluble in alcohol or aqueous alcohol than the former. Nearly pure *l*-camphor-*l*-menthylhydrazone crystallized directly on cooling a solution of equimolecular quantities of *dl*-camphor and *l*-menthylhydrazide in alcohol, containing a little acetic acid and sodium acetate, which had been boiled for nine days, provided a sufficiently large amount of solvent had been used. On the other hand, if only sufficient hot alcohol was used to effect the initial solution of the reactants, both diastereomers crystallized out almost completely and in excellent yield on cooling, and the filtered material was easily separated by a short systematic fractional crystallization. Pure *l*-camphor-*l*-menthylhydrazone crystallized from absolute alcohol in well-formed shining needles,  $[M]^{25}_D -101^\circ$ , m. p. 193–194°, while *d*-camphor-*l*-menthylhydrazone, also crystallizing in shining needles, had  $[M]^{25}_D -236^\circ$ , m. p. 177–178°. Hydrolysis of these derivatives with dilute aqueous alcoholic sulfuric acid gave

(13) Each of the formally correct designations of the reagent is cumbersome, particularly in the naming of aldehyde and ketone derivatives. We suggest tentatively that the semi-trivial name *l*-menthylhydrazide on the one hand reveals the character of the reagent as a hydrazide of an acid containing the *l*-menthyl group, and on the other lends itself readily to the formation of derivative names, *e. g.*, benzaldehyde *l*-menthylhydrazone.

*l*-camphor,  $[M]^{25D} - 64^\circ$ , m. p. 177–178°, and *d*-camphor  $[M]^{25D} + 62^\circ$ , m. p. 177–178°.

As a result of our experiments, *l*-camphor, hitherto obtainable only as a rather rare and inaccessible natural product, may easily be prepared from readily available commercial *dl*-camphor. Since *l*-menthylhydrazide is easily prepared from a substance readily obtainable in a state of optical purity, since in our hands it has invariably given crystalline derivatives with carbonyl compounds,<sup>14</sup> and since its value in the resolution of a racemic ketone has been demonstrated, we anticipate its use in such problems as those involving resolution of synthetic racemic ketones or aldehydes into active forms for comparison with natural products, e. g., oestrone, muscone, etc.<sup>15</sup>

### Experimental

**Di-*l*-menthyl Carbonate.**—100 grams of *l*-menthol, 50 g. of dimethyl carbonate and 14 g. of sodium, cut into pieces about the size of a pea, were placed in a flask equipped for distillation and heated for six hours in a metal bath at 200°. Methyl alcohol distilled off slowly as the reaction proceeded. The yellow reaction mixture was then cooled, an equal volume of 75% ethanol was added, and the crystalline product filtered. After crystallization from alcohol-benzene, 60 g. of pure di-*l*-menthyl carbonate was obtained as beautiful shining leaflets, m. p. 105–106°. Twenty-five cc. of absolute alcohol containing 0.5445 g. had  $\alpha - 3.96^\circ$  ( $t = 25^\circ$ ,  $l = 2$  dm.),  $[M]^{25D} - 308^\circ$ . Erdmann,<sup>16</sup> who obtained the ester from menthol and phosgene in the presence of pyridine, reported m. p. 106°,  $[M]^{25D} - 313^\circ$  (benzene).

**Ethyl *l*-Menthylcarbonate.**—*l*-Menthol was dissolved in 1–2 times its weight of ethyl chloroformate, a small amount of pyridine was added as catalyst, and the reaction mixture refluxed until the evolution of hydrogen chloride had ceased (eight to twelve hours). After two distillations *in vacuo*, ethyl *l*-menthyl carbonate was obtained in 90% yield. The substance was a colorless oil, of pronounced orange odor, b. p. (9 mm.) 121°, b. p. (43 mm.) 163°, m. p. 20.5°.

*Anal.* Calcd. for  $C_{18}H_{24}O_3$ : C, 68.38; H, 10.59. Found: C, 68.42; H, 10.68.

***l*-Menthylhydrazide.**—Ethyl *l*-menthyl carbonate (400 g.) and pure hydrazine hydrate (140 g.) were dissolved in just enough cellosolve (*ca.* 500 cc.) to effect complete solution. The reaction mixture was boiled for seventy-two hours on the metal bath, and then subjected to distillation in the vacuum of the water pump. Approximately 700 cc. of

very low boiling material (cellosolve, alcohol, water, hydrazine, etc.) was distilled off, then about 200 cc. of an oily liquid boiling in the range 100–150° at 28 mm. The residue (201 g.) immediately solidified to a hard mass. The oily liquid was then distilled more carefully, and after some low-boiling material (b. p. 65–100 at 19 mm.) had been collected, about 60 g. of *l*-menthol passed over at 100–105° (19 mm.). The residue from this distillation (55 g.) also solidified immediately on cooling, and was combined with the residue from the first distillation to give 257 g. of crude *l*-menthylhydrazide (68%). This material was crystallized from *ca.* 2700 cc. of hot middle-boiling ligroin, which freed it from a small amount of ligroin-insoluble amorphous impurity, and gave pure *l*-menthylhydrazide (*ca.* 225 g.) as splendid long needles, m. p. 101.5–102°. Twenty-five cc. of an absolute alcohol solution containing 0.4903 g. had  $\alpha - 3.13^\circ$  ( $t = 25^\circ$ ,  $l = 2$  dm.);  $[M]^{25D} - 171^\circ$ .

*Anal.* Calcd. for  $C_{11}H_{22}O_2N_2$ : C, 61.65; H, 10.35. Found: C, 61.70; H, 10.32.

**Formation of *l*-Menthylhydrazones.**—Table I summarizes the properties of the derivatives and the manner in which each was prepared.

As revealed by an inspection of Table I, all of these *l*-menthylhydrazones could be obtained by direct combination in solution of equimolecular portions of reagent and carbonyl compounds in the absence of catalysts. However, as would be expected, we found that all of the condensations were accelerated by such catalysts as acetic acid, sodium acetate, or acetic acid-sodium acetate buffer solutions. As a result of our experience in this direction we suggest for the preparation of *l*-menthylhydrazones of new or unknown compounds the following procedure, which has been uniformly successful in our hands.

The carbonyl compound (1 mole) and *l*-menthylhydrazide (1 mole) are dissolved in the smallest possible amount of a solution prepared by dissolving 2 g. sodium acetate and 1 cc. acetic acid in 100 cc. alcohol, and the reaction mixture is boiled under reflux for one to two hours. If the derivative does not separate on cooling (and occasionally after standing overnight), either it is too soluble in alcohol, and water must be added to throw it out, or the carbonyl group may be hindered, in which case considerably longer boiling is necessary. In the case of camphor, for example, only a small amount of *l*-menthylhydrazone was formed in four hours, while after nine days (not necessarily a minimum time) the derivative separated almost quantitatively.

**Hydrolysis of *l*-Menthylhydrazones.**—All of the above derivatives were completely hydrolyzed on short boiling with 5–10% sulfuric acid. Practically quantitative recovery of the simple carbonyl compounds as well as of the *l*-menthylhydrazide was easily effected. In the case of ketones or aldehydes of relatively low molecular weight, recovery was most efficaciously effected by direct steam distillation of the hydrolysis mixture (acetone, methyl ethyl ketone, benzaldehyde). The polyfunctional compounds, on the other hand, underwent further change under the influence of the acid, and could not be recovered by this method (ethyl acetoacetate, ethyl levulinate, benzalacetophenone).

**Resolution of *dl*-Camphor.**—(1) In a preliminary experiment, 20 g. of *dl*-camphor and 28 g. of *l*-menthylhydrazide

(14) Derivatives from cyclopentanone, cyclohexanone, cycloheptanone, cyclooctanone, and cyclononanone, as well as *o*-methylcyclohexanone, benzoin, and ethyl  $\alpha$ -phenyl- $\beta$ -benzoylpropionate, already in our hands, will be described subsequently.

(15) Mention should be made of the use of the reagent in following polarimetrically the complicated course of the reaction of carbonyl compounds with hydrazines. A start in this direction has been made in this Laboratory, but as yet the results are too involved to admit of ready interpretation with the material at hand.

(16) Erdmann, *J. prakt. Chem.*, [2] **56**, 43 (1897).

TABLE I

<i>l</i> -Menthylidrazone	Formula	Crystal form	Solvent	M. p., <sup>a</sup> °C.	$c^b$	$\alpha$	$[M]^{25D}$	Nitrogen, %	
								Calcd.	Found
Acetone <sup>c</sup>	C <sub>14</sub> H <sub>20</sub> O <sub>2</sub> N <sub>2</sub>	Large hex, prisms	Acetone	191-192	0.0218	-0.71°	-163°	11.02	10.96
Ethyl methyl ketone <sup>d</sup>	C <sub>16</sub> H <sub>28</sub> O <sub>2</sub> N <sub>2</sub>	Long needles	Aq. alc.	146-147	.0394	-1.23°	-156°	10.45	10.37
Acetophenone <sup>e</sup>	C <sub>19</sub> H <sub>20</sub> O <sub>2</sub> N <sub>2</sub>	Needles	Alcohol	164-165	.0240	-0.90°	-187°	8.86	9.03
Benzalacetophenone <sup>f</sup>	C <sub>26</sub> H <sub>32</sub> O <sub>2</sub> N <sub>2</sub>	Needles	Isopr. alc.	169-170	.00892	-.22°	-123°	6.93	7.00
Ethyl acetoacetate <sup>g</sup>	C <sub>17</sub> H <sub>30</sub> O <sub>4</sub> N <sub>2</sub>	Very small needles	Aq. alc.	92-93	.0636	-2.04°	-160°	8.59	8.56
Ethyl levulinate <sup>h</sup>	C <sub>15</sub> H <sub>28</sub> O <sub>4</sub> N <sub>2</sub>	Silky needles	Aq. MeOH	117-117.5	.0221	-0.82°	-186°	8.23	8.18
Benzaldehyde <sup>i</sup>	C <sub>15</sub> H <sub>20</sub> O <sub>2</sub> N <sub>2</sub>	Large rect. prisms	Alcohol	164-164.5	.0515	-1.87°	-182°	9.27	9.34
Cinnamic aldehyde <sup>j</sup>	C <sub>20</sub> H <sub>28</sub> O <sub>2</sub> N <sub>2</sub>	Small white needles	Aq. alc.	176-177	.0625	-2.01°	-161°	8.54	8.50
<i>d</i> -Glucose <sup>k</sup>	C <sub>17</sub> H <sub>32</sub> O <sub>7</sub> N <sub>2</sub>	Long stout needles	Aq. alc.	187-189	.0115	-0.52°	-226°	7.44	7.52
<i>d</i> -Camphor <sup>l</sup>	C <sub>21</sub> H <sub>36</sub> O <sub>2</sub> N <sub>2</sub>	Needles	Aq. alc.	177-178	.0574	-2.71°	-236°	8.04	7.90
<i>l</i> -Camphor <sup>l</sup>	C <sub>21</sub> H <sub>36</sub> O <sub>2</sub> N <sub>2</sub>	Silky needles	Alcohol	193-194	.0287	-0.58°	-101°	8.04	8.12

<sup>a</sup> All melting points uncorrected. <sup>b</sup> Concentrations are in moles per liter. The solvent was in each case absolute alcohol, the temperature 25°, and the rotations were taken in a 2 dm. tube. <sup>c</sup> Precipitation of the derivative from a nearly saturated solution of the reagent in acetone was complete in about an hour. <sup>d</sup> A solution of the reactants in alcohol was allowed to stand for fifteen hours after adding as much water as was possible without precipitation. <sup>e</sup> The derivative crystallized quantitatively when an absolute alcohol solution of the reactants was allowed to stand overnight. <sup>f</sup> The reactants were dissolved in absolute alcohol, water was added just until precipitation began, the reaction mixture was boiled for half an hour, cooled and allowed to stand. The precipitated material (which was occasionally contaminated with a small amount of oil) was recrystallized directly from isopropyl alcohol. <sup>g</sup> The derivative sometimes precipitated as an oil on adding water to an absolute alcohol solution of the reactants which had stood one week. On chilling, the oil solidified and could be crystallized further with ease. <sup>h</sup> Crystallized quantitatively on adding water to an absolute alcohol solution of the reactants which had stood one week. <sup>i</sup> Precipitated directly as large crystals from an absolute alcohol solution which had stood one week. <sup>j</sup> Precipitated from an absolute alcohol solution of the reactants in four hours. The substance turned yellow without alteration of the melting point on standing for a short time. <sup>k</sup> Addition of water to an absolute alcohol solution of the reactants which had stood for two weeks precipitated an oil, from which glucose *l*-menthylidrazone was obtained by repeated fractional crystallization from aqueous alcohol. <sup>l</sup> See below.

were dissolved in just sufficient cold 95% ethanol (containing HOAc and NaOAc, *vide supra*) for complete solution. The reaction mixture was boiled for nine days, and then cooled, when 41 g. of nicely crystalline material separated. This was crystallized four times from 95% ethanol (about 250-275 cc.), the final crystallization giving pure *l*-camphor-*l*-menthylidrazone (5 g.) as fine needles, m. p. 193-194°. Twenty-five cc. of an absolute alcohol solution containing 0.250 g. had  $\alpha$  -0.58° ( $t = 25^\circ$ ,  $l = 2$  dm.),  $[M]^{25D} -101^\circ$ . Further crystallization failed to change the rotation.

*Anal.* Calcd. for C<sub>21</sub>H<sub>36</sub>O<sub>2</sub>N<sub>2</sub>: N, 8.04. Found: N, 8.12.

The mother liquor from the original crop of crystals was chilled, a small quantity of crystalline material which separated was filtered, and the filtrate was concentrated to one-third its volume. The material which separated on cooling as fine needles, m. p. 175-177°, was substantially *d*-camphor-*l*-menthylidrazone, though it was not as pure as our best sample (see below). Twenty-five cc. of an absolute alcohol solution containing 0.500 g. had  $\alpha$  -2.60° ( $t = 25^\circ$ ,  $l = 2$  dm.),  $[M]^{25D} -228^\circ$ .

(2) The original crop (40 g.) from an experiment similar to (1) was then subjected to a systematic five-stage fractional crystallization (95% ethanol), when 15 g. of *l*-camphor-*l*-menthylidrazone, and 8 g. of *d*-camphor-

*l*-menthylidrazone, fine needles, m. p. 177-178°, were obtained. Twenty-five cc. of an absolute alcohol solution containing 0.500 g. of the latter had  $\alpha$  -2.71° ( $t = 25^\circ$ ,  $l = 2$  dm.),  $[M]^{25D} -236^\circ$ .

*Anal.* Calcd. for C<sub>21</sub>H<sub>36</sub>O<sub>2</sub>N<sub>2</sub>: N, 8.04. Found: N, 7.90.

To regenerate the active ketone, 5 g. of *l*-camphor-*l*-menthylidrazone was boiled with 10 cc. of sulfuric acid in 45 cc. of water and 45 cc. of ethanol until complete solution had taken place, and then for one and one-half hours longer. The solution was then steam-distilled until about 75 cc. of liquid had passed over, an equal volume of water was added, and the camphor was extracted with three 20-cc. portions of petroleum ether (b. p. 20-40°). The petroleum ether solution was dried by filtering through anhydrous sodium sulfate, and boiled to dryness. The residual *l*-camphor was crystallized from 50% alcohol, filtered, and taken up again in petroleum ether. After drying, the solvent was again removed. In this way, 1.8 g. of *l*-camphor, m. p. 177-178°, was obtained. Twenty-five cc. of an absolute alcohol solution containing 0.300 g. had  $\alpha$  -1.01° ( $t = 25^\circ$ ,  $l = 2$  dm.),  $[M]^{25D} -64^\circ$ .

Similarly from *d*-camphor-*l*-menthylidrazone, *d*-camphor, m. p. 177-178°, was obtained. Twenty-five cc. of an absolute alcohol solution containing 0.300 g. had  $\alpha$  +0.98° ( $t = 25^\circ$ ,  $l = 2$  dm.),  $[M]^{25D} +62^\circ$ .

### Summary

*l*-Menthol may be converted by a facile synthesis into *l*-menthyldrazide (*l*-menthyl *N*-aminocarbamate). The latter substance is an excellent reagent for aldehydes and ketones, since it is a stable, beautifully crystalline substance, which with numerous carbonyl compounds gives stable, nicely crystalline, sharp melting derivatives, which have the further advantage for purposes of characterization that they possess definite spe-

cific rotations. Eleven such derivatives, *viz.*, those from acetone, methyl ethyl ketone, acetophenone, benzalacetophenone, ethyl acetoacetate, ethyl levulinate, benzaldehyde, cinnamic aldehyde, *d*-glucose, *d*- and *l*-camphor are described.

The value of the new reagent as a resolving agent for racemic carbonyl compounds is demonstrated by its use in the first successful resolution of *dl*-camphor.

CONVERSE MEMORIAL LABORATORY  
CAMBRIDGE, MASS.

RECEIVED OCTOBER 11, 1940

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

## The Common Basis of Intramolecular Rearrangements. VII.<sup>1</sup> Inapplicability of a Free Radical Mechanism. Formation of 1,1-Dimethylcyclopropane and Neopentane by the Action of Sodium on Neopentyl Chloride. Relation to the Mechanism of the Wurtz Reaction

BY FRANK C. WHITMORE, A. H. POPKIN,<sup>2</sup> HERBERT I. BERNSTEIN<sup>3</sup> AND JOHN P. WILKINS

Many reactions of neopentyl alcohol (*t*-butylcarbinol) and of neopentyl halides are accompanied by rearrangements of the carbon chain. In adapting a theory to explain these changes<sup>4</sup> the possibility of a free radical mechanism was carefully considered and discarded as inadequate. This was because the conditions used in such rearrangements do not correspond to those which are known to give free radicals. Moreover, the disproportionation products characteristic of reactions involving free radicals are not found as products of these rearrangements. This indirect negative evidence has now been confirmed by direct experiment.

The process most likely to give free radicals at ordinary temperatures and in solution is the Wurtz reaction. Consequently, it was decided to treat neopentyl chloride with metallic sodium. If the free neopentyl radicals behaved like the neopentyl fragments formed from neopentyl alcohol by the dehydration of that substance, then the chief products of the Wurtz reaction should be related to the *t*-amyl radical. As a matter of fact it was impossible to find any trace of any material containing the *t*-amyl grouping.

A previous communication<sup>5</sup> has described a reaction between one mole of sodium and one mole of neopentyl chloride to give a 13% yield of 2,2-

5,5-tetramethylhexane, a 36% yield of neopentane, and 16.9 g. of a substance whose physical constants checked closely with those of 1,1-dimethylcyclopropane. Also observed was a definite trace of isobutylene.

Since the physical constants of 1,1-dimethylcyclopropane,<sup>6</sup> b. p. 21° at 740 mm.,  $n_D^{20}$  1.3659, and  $d_4^{20}$  0.6604, are so close to those of 3-methyl-1-butene, b. p. 18.8° at 740 mm.,  $n_D^{20}$  1.3640, and  $d_4^{15}$  0.6332, it was obvious that the constants reported<sup>5</sup> for the reaction product, namely, b. p. 19.8° at 740 mm.,  $n_D^{20}$  1.3656, and  $d_4^{14.4}$  0.6681, would not alone serve for identification. This product has now been shown conclusively to be 1,1-dimethylcyclopropane and not 3-methyl-1-butene by reactions with 66% sulfuric acid, alkaline potassium permanganate, ozone, bromine in carbon tetrachloride, and finally by a mixed m. p. Synthetic 1,1-dimethylcyclopropane has a m. p. of -108.4 to -107.3°. The unknown material melted at -115.8 to -115.7°. Using the equation  $\Delta T = xRT^2/\Delta H$  in which  $x$  is the mole fraction of impurity and the heat of fusion is estimated at 1200 the unknown would contain 17% impurity. This is undoubtedly an upper limit since the heat of fusion of neopentane is 778 cal./mole.<sup>7</sup> The mixed m. p. of the synthetic dimethylcyclopropane and the Wurtz reaction product was -113.5° to -110.6°.

(1) Paper VI, THIS JOURNAL, 61, 1586 (1939).

(2) General Printing Ink Company, New York City.

(3) Frick Chemical Laboratory, Princeton University.

(4) Whitmore, THIS JOURNAL, 54, 3274 (1932).

(5) Whitmore, Popkin and Pfister, *ibid.*, 61, 1616 (1939).

(6) Gustavson and Popper, *J. prakt. Chem.*, [2] 58, 458 (1898).

(7) Private communication from J. G. Aston of this Laboratory.