Summary

l-Menthol may be converted by a facile synthesis into *l*-menthydrazide (*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 specific 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.[1] 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,[2] HERBERT I. BERNSTEIN[3] 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[4] 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[5] 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,[6] b. p. 21° at 740 mm., $n^{20}\text{D}$ 1.3659, and $d^{20}{}_4$ 0.6604, are so close to those of 3-methyl-1-butene, b. p. 18.8° at 740 mm., $n^{20}\text{D}$ 1.3640, and $d^{15}{}_4$ 0.6332, it was obvious that the constants reported[5] for the reaction product, namely, b. p. 19.8° at 740 mm., $n^{20}\text{D}$ 1.3656, and $d^{14.4}{}_4$ 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.[7] The mixed m. p. of the synthetic dimethylcyclopropane and the Wurtz reaction product was $-113.5°$ to $-110.6°$.

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(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.

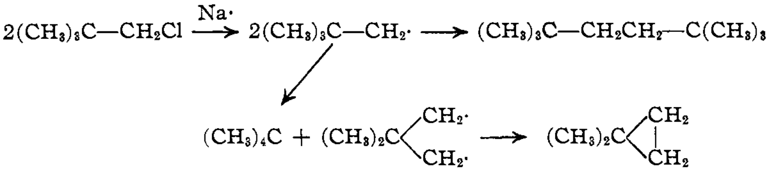
The reaction was repeated, but five moles of neopentyl chloride was added to one mole of sodium. The yields, based on sodium, were 41% of neopentane, 51% of 1,1-dimethylcyclopropane and 1.4% of impure 2,2,5,5-tetramethylhexane. Comparison of these products with those from the first experiment shows the absence of isobutylene and a decrease in the amount of coupling product.

The decreased yield of coupling product in the presence of large excess of the halide agrees with the suggestion that coupling occurs through the alkylsodium.[8] The disproportionation between a free radical and a methyl group in the solvent molecule has also been suggested by other workers.[9]

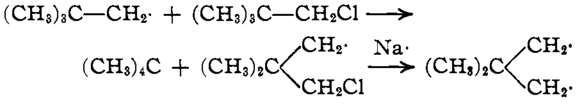
Discussion

The ordinary products of the Wurtz reaction in a case like that of an ethyl halide and sodium are *n*-butane, ethane and ethylene. These are often explained by the following assumptions.[10] The atomic sodium, which is a free radical in the sense that it has an odd electron, reacts with the alkyl halide to give a molecule of sodium halide and a free ethyl radical. If two of these ethyl radicals collide in such a way that their two odd electrons make contact, the product is *n*-butane. If, on the other hand, the odd electron end of a free radical strikes the methyl end of another radical, a hydrogen atom, including its odd electron, may attach itself to the first free radical forming a saturated molecule of ethane. The other partner of the collision will now have an odd electron on each of its two carbon atoms. This is stabilized as a molecule of ethylene. If the same mechanism is followed in the reaction of neopentyl chloride with sodium, there will be a certain chance of the union of two free radicals to form the coupled product 2,2,5,5-tetramethylhexane. On the other hand, there will be an increased probability of the odd electron end of one free radical contacting one of the three methyl groups of another free radical. In this case one of the products would be neopentane. The other would be a neopentyl system having an odd electron on each of two of the carbons. Such a structure cannot form an olefin by any ordinary means, but instead gives the equivalent which is 1,1-dimethylcyclopropane. A similar result would follow the collision of a free neopentyl radical with a molecule of neopentyl chloride. In this case a chlorine atom would be released and would react with sodium.

The processes involved may be indicated as follows



On this basis, the yields of neopentane and of dimethylcyclopropane should be equal and about three times that of the coupled product.



$$(CH_3)_3C—CH_2\cdot + (CH_3)_3C—CH_2Cl \longrightarrow (CH_3)_4C + (CH_3)_2C{<}\begin{matrix}CH_2\cdot\\ CH_2Cl\end{matrix} \xrightarrow{Na\cdot} (CH_3)_2C{<}\begin{matrix}CH_2\cdot\\ CH_2\cdot\end{matrix}$$

The large excess of neopentyl chloride would cut down the yield of coupled product.

It is thus shown experimentally that under conditions which can give free radicals the neopentyl system does not undergo the change to a *t*-amyl system which is characteristic of processes which can leave the neopentyl system with an open sextet of electrons.[4] Moreover, added confirmation is given to the conception of the Wurtz reaction as involving free radicals.

Experimental

The Reaction between One Mole of Neopentyl Chloride and One Mole of Sodium.—The apparatus consisted of a two-necked flask equipped with a dropping funnel and a reflux condenser. The reflux condenser was connected to a dry-ice–acetone trap, and uncondensed gases were then collected over a saturated sodium chloride solution.

To 23 g. (1 mole) of sodium cut into small strips was added 106 g. (1 mole) of neopentyl chloride,[11] b. p. 84° at 741 mm. and $n^{20}D$ 1.4042. The reaction was initiated by heat but, once it had begun, it was so exothermic that an ice-bath was necessary to cool it. When the ice-bath was removed, refluxing again began due to the heat of the reaction. The ice-bath was alternately raised and lowered for two hours, after which time the reaction mixture was a solid. Gas was emitted for one hour after this time. All the residual gas was then driven off by heating the reaction mixture in an oil-bath at 150°, and passing a stream of nitrogen through the system. No hydrogen was detected.

The gases condensed in the dry-ice–acetone trap were fractionated through a low temperature column in the Cryogenic Laboratory of The Pennsylvania State College. Obtained were fractions: 1, wt. 2.81 g., b. p. 0.0–7.8° at 720 mm.; 2–5, 25.8 g., 8.3° at 720 mm. to −4.0° at 360 mm.; 6–7, 16.9 g., 1.0–2.0° at 360 mm. Fraction 1 was

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(8) Morton and Massengale, THIS JOURNAL, **62**, 120 (1940).

(9) (a) Marvel, Rieger and Mueller, *ibid.*, **61**, 2769 (1939); (b) Bamford and Norrish, *J. Chem. Soc.*, 1531 (1938).

(10) *Cf.* Bachmann and Clark, THIS JOURNAL, **49**, 2089–2098 (1927).

(11) Whitmore and Fleming, *ibid.*, **55**, 4161 (1933).

vaporized and by gas analysis, absorption in 62.4% sulfuric acid, was shown to contain 17% isobutylene. This was checked by the gas density, mol. wt. 66.0. Fractions 2–5, f. p. −19 to −20°, represented a 36% yield of neopentane. Fraction 7, wt. 12.5 g., was redistilled through a packed micro-column at 742 mm. to give fractions: 8, wt. 0.8 g., b. p. 18.7–19.8°, $n^{20}{}_{\mathrm{D}}$ 1.3656; 9–12, 7.0 g., 19.8°, 1.3656, $d^{14.4}{}_{4}$ 0.6681. These constants check with those of 1,1-dimethylcyclopropane,[6] and fractions 6–7 represent a 25% yield.

The residual solid of the reaction mixture was treated with 200 cc. of methyl alcohol. There was no evolution of hydrogen. To this mixture was added 200 cc. of water, and the aqueous mixture extracted twice with 75-cc. portions of ether. The ethereal solution was washed three times with water, and dried over anhydrous potassium carbonate. Distillation through a packed column at 736 mm., after the ether had been removed, yielded fractions: 13, wt. 5.2 g., b. p. 81–82°, $n^{20}{}_{\mathrm{D}}$ 1.3972; 14, 0.5 g., 82–131°, 1.4022; 15, 2.2 g., 131–135°, 1.4042; 16–17, 7.1 g., 135°, 1.4049–1.4050; residue, 4.2 g. Fraction 13 was mostly recovered neopentyl chloride. The last three fractions represent a 13% yield of 2,2,5,5-tetramethylhexane. This compound had also been prepared by Fleming and Buechele by the electrolysis of sodium *t*-butylacetate.[12] Their constants were b. p. 136.1° at 735 mm., $n^{20}{}_{\mathrm{D}}$ 1.4057.

Identification of 1,1-Dimethylcyclopropane

A. **Solubility in 66% Sulfuric Acid.**—1,1-Dimethylcyclopropane dissolves in 66% sulfuric acid in ten minutes at 0°, while 3-methyl-1-butene is insoluble under similar conditions.[6] To 0.1 cc. of the unknown material was added 2.5 cc. of cold 66% sulfuric acid. Shaking for ten minutes at 0° resulted in solution. 3-Methyl-1-butene (see below), treated similarly, did not dissolve in two hours.

B. **Reaction with Dilute Alkaline Potassium Permanganate.**—1,1-Dimethylcyclopropane is fairly stable toward dilute alkaline potassium permanganate while 3-methyl-1-butene immediately decolorizes the latter solution.[5] Four drops of the unknown solution did not decolorize 0.1 cc. of a 0.5% alkaline potassium permanganate solution in thirty minutes, whereas 4 drops of 3-methyl-1-butene produced instant decoloration in a similar solution.

C. **Reaction with Ozone.**—An adapter was placed at the outlet of an ozonolysis apparatus to enable ozone to pass through two tubes simultaneously. Each tube led to a vial containing a dilute starch-potassium iodide solution. In the first tube was placed 0.3 g. of the unknown in 20 cc. of low-boiling saturated hydrocarbon, and in the second a similar solution of 3-methyl-1-butene. The tubes were immersed in a dry ice–acetone bath, and ozone passed through both solutions at the rate of one bubble per second. Within three minutes the starch–iodide solution connected to the tube containing the unknown turned blue, while the sample of 3-methyl-1-butene absorbed ozone so readily that no blue coloration was observed for over two hours. This was conclusive proof of the non-olefinic nature of the unknown.

D. **Reaction with Bromine in Carbon Tetrachloride.**—In three tubes were placed 20 drops of the unknown, 20 drops of synthetic 1,1-dimethylcyclopropane (see below), and 20 drops of synthetic 3-methyl-1-butene (see below), all diluted with 10 cc. of carbon tetrachloride. On the addition of 10 drops of a dilute solution of bromine in carbon tetrachloride to each solution at 0°, only the last tube showed decoloration. The first two tubes were brown after thirty minutes of standing.

It is therefore certain that the substance in question was 1,1-dimethylcyclopropane.

Addition of Five Moles of Neopentyl Chloride to One Mole of Sodium.—Into a 3-liter flask under a packed column set for total reflux was placed 23 g. (1 mole) of sodium and 532.5 g. (5 moles) of pure neopentyl chloride. The column was connected to a dry-ice–acetone trap and a gas collector. Heat was needed to start the reaction, and then an ice-bath was used to control it. In one hour the reaction subsided. It was heated at 72° for one hour, and at 95° for six hours. At this point the temperature of the material refluxing at the top of the column was 35°. Distillation was then begun at 732 mm. to yield fractions: 1, wt. 2.1 g., b. p. 35–69°, $n^{20}{}_{\mathrm{D}}$ 1.3932; 2, 3.2 g., 69–83°, 1.3950; 3–9, 389.1 g., 83.5°, 1.4030–1.4040. The last seven fractions were neopentyl chloride. The residue, white solid sodium chloride, was extracted with 250 cc. of anhydrous ether in three portions. The ether extract was then fractionated to give 1.0 g. of substance, b. p. 128–135° at 734 mm., $n^{20}{}_{\mathrm{D}}$ 1.4012–1.4078. This represented a 1.4% yield of impure 2,2,5,5-tetramethylhexane.

There was no gas uncondensed by the dry-ice–acetone trap. The gases condensed in that trap were also fractionated through the low temperature column. Molecular weights were determined by gas density. Obtained were fractions: 10, 28.4 g., b. p. 9.8° at 760 mm., mol. wt. 71.6; 11, 1.2 g., −4.0 to +4.0° at 400 mm.; 12, 28.7 g., 6–8° at 400 mm., mol. wt., 70.2; 13, 7.5 g., residue, mol. wt. 70.7. Neopentane, fractions 10–11, was thus obtained in 41% yield, and 1,1-dimethylcyclopropane, fractions 12–13, in 51% yield. The m. p. of these fractions was −115.8 to −115.7°. Mixed m. p. with a synthetic sample (see below) of m. p. −108.4 to −107.3° was −113.5 to −110.6°.

Preparation of 3-Methyl-1-butene.—Isoamyl chloride, b. p. 97.5° at 741 mm., $n^{20}{}_{\mathrm{D}}$ 1.4081, was prepared from isoamyl alcohol, thionyl chloride, and pyridine. The chloride was treated with potassium hydroxide and absolute ethyl alcohol as described for the preparation of 2-ethyl-1-butene.[13] 3-Methyl-1-butene, b. p. 18.8° at 731 mm., $n^{20}{}_{\mathrm{D}}$ 1.3640, and $d^{15}{}_{4}$ 0.6332, was obtained in 11% yield. The rest of the material was the ethyl ether, which formed a constant boiling mixture with ethyl alcohol.

Preparation of 1,1-Dimethylcyclopropane. Preparation of 2,2-Dimethyl-1,3-propanediol.—Into a 3-liter flask fitted with a reflux condenser and a 1-liter dropping funnel was placed a solution of 175 g. of potassium hydroxide in 750 cc. of 95% ethyl alcohol. The funnel contained 500 cc. of 40% formaldehyde (Eastman Kodak Co.), 180 g. (2.5 moles) of isobutyraldehyde (Shell Tech.), and enough ethyl alcohol to give a homogeneous solution. This solution was dropped into the flask with frequent shaking in two hours. The mixture was refluxed for eighteen hours. The alcohol was then distilled off and the residue extracted with four 100-cc. portions of ether. The ether was distilled off and the residue distilled through a Claisen flask to give

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[12] Unpublished results from this Laboratory.

[13] Whitmore and co-workers, THIS JOURNAL, **62**, 796 (1940).

165 g. of a solid, b. p. 162–200° at atmospheric pressure. Recrystallization from a benzene–petroleum ether solution gave 130 g., or a 50% yield, of 2,2-dimethyl-1,3-propanediol, m. p. 126–128°.

Preparation of 2,2-Dimethyl-1,3-dibromopropane.—Into a 1-liter flask was placed 208 g. (2 moles) of 2,2-dimethyl-1,3-propanediol, and to this was slowly added 542 g. (2 moles) of redistilled phosphorus tribromide, the flask being cooled in an ice-bath. A reflux condenser and thermometer were then attached, and the reaction mixture allowed to come to room temperature. It was heated to gentle refluxing for eighteen hours, and the temperature then raised to cause vigorous boiling. In six hours a red precipitate had formed. The temperature of the reaction mixture was increased to 140° and held there for eighteen hours. After cooling, it was poured onto ice and the resultant mixture steam distilled. The gummy orange residue in the flask was also steam distilled. The combined organic layers were dried over potassium carbonate, and the resulting 200 g. of material was distilled through a small packed column. From 8 moles of 2,2-dimethyl-1,3-propanediol was obtained 635 g., or a 34.6% yield of 2,2-dimethyl-1,3-dibromopropane, b. p. 84° at 28 mm., $n^{20}\mathrm{D}$ 1.5050.

Preparation of 1,1-Dimethylcyclopropane.—The method of cyclization was that of Hass and McBee.[14] Into a 1-liter three-necked flask fitted with a dropping funnel, reflux condenser and mercury-sealed stirrer were placed 130 g. (2 moles) of zinc dust, 14 g. of sodium iodide, 43 g. of sodium carbonate, and 250 g. of dry recrystallized acetamide. The reflux condenser was connected to a dry-ice–acetone trap. The flask was kept between 150–165°, and 380 g. (1.65 moles) of 2,2-dimethyl-1,3-dibromopropane in the funnel was added dropwise to the reaction mixture in five hours. The 1,1-dimethylcyclopropane collected in the dry-ice–acetone trap was dried by passage over potassium hydroxide followed by phosphorus pentoxide. This product decolorized neither a dilute solution of bromine in carbon tetrachloride nor an alkaline potassium permanganate solution. It was distilled through the low temperature column in the Cryogenic Laboratory at 605 mm. to give fractions: 1, 12 cc., b. p. 14.4°; 2, 52 cc., 14.7°; 3, 45 cc., 14.8°; 4, 25 cc., 14.9°; residue, 30 cc., $n^{20}\mathrm{D}$ 1.3873. Assuming dP/dT to be 30 mm./deg., the b. p. of fraction 2 at 760 mm. would be 19.9°. The m. p. was −108.4 to −107.3°.

Thanks are due to Dr. J. G. Aston for the use of the facilities of the Cryogenic Laboratory, and to Mrs. R. June Pfister, Mr. R. M. Kennedy, and Dr. Richard Greenberg for their invaluable assistance.

Summary

1. The products of the reaction of one mole of neopentyl chloride and one mole of sodium were 13% 2,2,5,5-tetramethylhexane, 36% neopentane, 25% 1,1-dimethylcyclopropane, and a trace of isobutylene.

2. The products of the reaction of five moles of neopentyl chloride and one mole of sodium were a trace of 2,2,5,5-tetramethylhexane, 41% neopentane, 51% 1,1-dimethylcyclopropane, and no isobutylene.

3. The bearing of these results on the mechanism of molecular rearrangements and of the Wurtz reaction has been discussed.

STATE COLLEGE, PENNA. RECEIVED JULY 15, 1940

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[14] McBee, Hass and Tarrant, Abstracts of the 97th Meeting, 1939, Am. Chem. Soc., Organic Section, p. 29, 1939.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

Scianthrene and the Synthesis of 1-Isopropyl-7-methylphenanthrene[1]

BY RUBY MURRAY ORCUTT AND MARSTON TAYLOR BOGERT

In a recent article,[2] Hidetaka Uota described an essential oil which he obtained by steam distillation of the finely divided twigs and leaves of the *Sciadopitys verticillata*, S. and Z., known as the "shade pine of South Japan." By distillation of this oil, in an atmosphere of carbon dioxide, at a pressure of 1 mm., he separated a fraction, b. p. 139–163° at 1 mm., from which there crystallized a new diterpene, sciadopitene, $C_{20}H_{32}$, m. p. 95–96°. Fusion of this solid with selenium, resulted in the production of a new hydrocarbon, $C_{18}H_{18}$, m. p. 86–87°, to which the author gave the name "scianthrene." A number of derivatives were prepared, and a series of reactions carried out which led him to the conclusion that this hydrocarbon was probably 1-isopropyl-7-methylphenanthrene, *i. e.*, an isomer of retene with the position of the two alkyl groups reversed.

Our laboratories being considerably interested in retene and related compounds, we have synthesized by two different methods what we believe to be the 1-isopropyl-7-methylphenanthrene, and the product so obtained does not agree in its properties with Uota's description of "scianthrene," as can be seen from the following comparison of melting points:

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[1] Presented in abstract before the Division of Organic Chemistry, at the Cincinnati Meeting of the Am. Chem. Soc., April 9, 1940.

[2] Uota, *J. Dept. Agr. Kyushu Imp. Univ.* **5**, 117–193 (1937); *C. A.*, **31**, 7416 (1937).