stance melting at 126–32° was obtained. Further chilling of the filtrate yielded a very small amount of a material melting at 158–159°. The low-melting fraction was recrystallized from methanol and then from ethanol–water, m. p. 141°. The mother liquors from the recrystallization yielded the high melting material, m. p. 161°. When potassium bisulfate was used as a condensing agent, small amounts of the material melting at 185° which was obtained from the hydrogen chloride condensation could be isolated. All these substances will be subjected to further study.

1,4,1',3',5',1'',3'',5''-Octamethyl-3,5,4',4''-tetracarbethoxytripyrrylmethane. (a) **Hydrogen Chloride Method.** —One gram of 1,4-dimethyl-2-formyl-3,5-carbethoxypyrrole and 1.56 g. of 1,2,4-trimethyl-3-carbethoxypyrrole were dissolved in 30 cc. of dry ether, 5 cc. of ether saturated with hydrogen chloride at 0° was added and the mixture allowed to stand for twenty hours. The precipitate was filtered off, washed with ether, dissolved in chloroform and chilled in dry ice. When crystallization had started several volumes of ether were added and the solution chilled in dry ice. The colorless crystals were recrystallized from alcohol–water; m. p. 178°, yield 1.3 g. Lead dioxide and hydrogen chloride or hydrogen chloride in air gave a lavender color but hydrogen chloride in an inert atmosphere produced no color change.

(b) **Fusion Method.**—Two grams of the N-methyl aldehyde and 2.7 g. of the N-methyl α-free pyrrole were ground together and fused at 210° for twelve minutes. After cooling 50 cc. of methanol was added. Solution took place followed by rapid deposition of colorless crys-

tals. These were filtered off, and washed with methanol; m. p. 175°, yield 1.6 g. An additional 0.9 g. was obtained by chilling the mother liquors in dry ice. Recrystallization from alcohol–water raised the m. p. to 178°; no m. p. depression with the material from acid condensation.

Anal. Calcd. for $C_{33}H_{45}O_8N_3$: C, 64.79; H, 7.41. Found: C, 64.86, 64.91; H, 7.58, 7.55.

Summary

1. A tripyrrylmethane has been isolated as a by-product in the aldehyde synthesis of a dipyrrylmethene.

2. The stability of one "negatively substituted" tripyrrylmethane has been shown to be illusory.

3. It has been demonstrated that varying courses of dipyrrylmethene and tripyrrylmethane syntheses can be accounted for on the basis of varying reaction velocities.

4. Conditions have been defined under which the aldehyde synthesis may proceed directly without an intervening tripyrrylmethane.

5. A hindering action of N-methyl groups has been discovered.

6. By-products have been observed in the Feist fusion for tripyrrylmethanes.

2,5,5-Trimethyl-1,3-hexadiene and its Hydrogen Bromide Addition Product
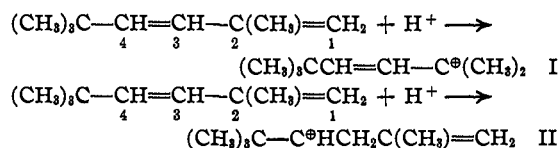
BY KENNETH N. CAMPBELL[1]

During work in this Laboratory on the rearrangements of compounds containing a neopentyl system[2] it was considered of interest to study the addition reactions of a conjugated hydrocarbon containing such a system. The hydrocarbon chosen for study was 2, 5, 5 - trimethyl- 1, 3-hexadiene, one of the simplest compounds fulfilling the requirements.

The addition of one molecule of hydrogen bromide to this hydrocarbon could take place in several ways. Applying the theory current in this Laboratory,[3] addition of a proton would be most likely to occur at carbon atom (1) or carbon atom (3) of the conjugated system, giving the two positive fragments, I and II.

$(CH_3)_3C$—$\underset{4}{CH}$=$\underset{3}{CH}$—$\underset{2}{C(CH_3)}$=$\underset{1}{CH_2}$ + H^+ ⟶

$(CH_3)_3CCH$=CH—$C^{\oplus}(CH_3)_2$ I

$(CH_3)_3C$—$\underset{4}{CH}$=$\underset{3}{CH}$—$\underset{2}{C(CH_3)}$=$\underset{1}{CH_2}$ + H^+ ⟶

$(CH_3)_3C$—$C^{\oplus}HCH_2C(CH_3)$=CH_2 II

Fragment I could become stabilized by the addition of a bromide ion, giving the 1,2-hydrobromide, III, $(CH_3)_3CCH$=CH—$C(CH_3)_2Br$, or a shift of an electron pair could occur, resulting in fragment IV, $(CH_3)_3C$—$C^{\oplus}H$—CH=$CH(CH_3)_2$. This then could add a bromide ion to give the 1,4-hydrobromide, V, $(CH_3)_3C$—$CHBr$—CH=$CH(CH_3)_2$, or it could appropriate an electron pair, together with the attached methyl group from the adjacent carbon atom, and addition of a bromide ion to the resulting fragment would yield the rearranged bromide, VI, $(CH_3)_2CBr$—$CH(CH_3)$—CH=$C(CH_3)_2$. Such a rearrangement would be analogous to that of *t*-butylethylene to

(1) Present address: Department of Chemistry, University of Notre Dame.

(2) Whitmore and Laughlin, THIS JOURNAL, **55**, 3732 (1933); Whitmore and Meunier, *ibid.*, **55**, 1106, 3721 (1933).

(3) Whitmore, *ibid.*, **54**, 3274 (1932).

tetramethylethylene.[4] Addition of a bromide ion to fragment II would give the 3,4-hydrobromide, VII, $(CH_3)_3C—CHBr—CH_2C(CH_3)=CH_2$, or fragment II could undergo a rearrangement, and addition of a bromide ion to the new fragment would result in compound VIII, $(CH_3)_2$-$CBr—CH(CH_3)—CH_2C(CH_3)=CH_2$.

Kharasch and his students[5] have shown recently that the mode of addition of hydrogen bromide to butadiene is profoundly affected by the presence of peroxides. In the absence of peroxides 1,2-addition occurs, to give methylvinylcarbinyl bromide; in the presence of peroxides crotyl bromide is the main product. Winstein and Young[6] have found that methylvinylcarbinyl bromide and crotyl bromide form an equilibrium mixture in which crotyl bromide predominates. In the light of these investigations, it might be expected that a large amount of the 1,4-addition product (V) or the rearranged bromide (VI) would be formed if peroxides were not excluded.

One mole of dry hydrogen bromide gas was added to one mole of the conjugated hydrocarbon in chloroform solution. No effort was made to exclude air or peroxides. An oily bromide was obtained, which was not very stable. It could be distilled under reduced pressure without decomposition if suitable precautions were taken. When pure it could be kept in a refrigerator over potassium carbonate for a few days without much decomposition, but on standing at room temperature it quickly turned brown and evolved hydrogen bromide.

The bromide was dissolved in petroleum ether and treated with ozone. The clear ozonide solution was decomposed with water and zinc dust by the method of Whitmore and Church.[7] All the fractions so obtained gave negative tests for formaldehyde and acetone. Trimethylacetaldehyde and α-hydroxyisobutyraldehyde, in the form of their 2,4-dinitrophenylhydrazones, were isolated, and a viscous oil was also obtained, whose boiling point (136° under 28 mm.) corresponded to that of polymeric α-hydroxyisobutyraldehyde.[8] Another portion of the bromide was

oxidized with potassium permanganate and sodium dichromate according to the procedure of Farmer and Marshall.[9] From the oxidation products the p-nitrobenzyl ester of α-hydroxyisobutyric acid was isolated.

The formation of trimethylacetaldehyde and α-hydroxyisobutyraldehyde shows that addition of hydrogen bromide to the conjugated hydrocarbon occurred in the 1,2-positions. Since no trace of acetone or formaldehyde could be found in the decomposition products of the ozonide, the possibility that the hydrobromide could contain any appreciable amounts of the 1,4- or 3,4-addition products (compounds V and VII) or of the rearranged bromides, VI and VIII, is excluded. These results indicate that the 1,4- and 1,2-addition products are not in the mobile equilibrium shown to exist in the case of the hydrogen bromide addition compounds of butadiene.

Trimethylacetaldehyde was prepared from methyl formate and t-butylmagnesium chloride by a modification of the method of Bouveault.[10] The aldehyde was condensed with acetone in the presence of sodium ethylate to give a ketol, which was dehydrated readily with iodine to form 5,5-dimethyl-3-hexene-2-one. Addition of hydrogen halide to this ketone should give a new type of substituted neopentyl halide, $(CH_3)_3$-$CHCl—CH_2COCH_3$. The rearrangements of this type of halide would be of interest in view of those of other neopentyl compounds.[2] Hydrogen chloride was added to the unsaturated ketone, but the resulting chloride was so unstable that further work on this line was dropped.

When the unsaturated ketone was treated with methylmagnesium chloride an unsaturated alcohol was obtained, which readily lost water to give a hydrocarbon. This hydrocarbon was shown to be 2,5,5-trimethyl-1,3-hexadiene in the following ways. The exaltation of the molecular refraction showed that it contained a conjugated system. The carbon skeleton was established by catalytic reduction by the Adams method to a saturated hydrocarbon whose physical properties agreed with those recorded by Noller[11] and Kishner[12] for 2,5,5-trimethylhexane. Since there can be but one conjugated hydrocarbon with such a skeleton, the diolefin must be 2,5,5-tri-

(4) Laughlin, Nash and Whitmore, This Journal, 56, 1395 (1934). Unpublished work carried out in this Laboratory indicates that the addition of hydrogen bromide to t-butylethylene may or may not result in a similar rearrangement, depending on the conditions.

(5) Kharasch, Margolis and Mayo, J. Org. Chem., 1, 393 (1936).

(6) Winstein and Young, This Journal, 58, 104 (1936).

(7) Whitmore and Church, ibid., 54, 3710 (1932).

(8) Franke, Monatsh., 21, 213 (1900); Dworzak, ibid., 52, 141 (1929); ibid., 53-54, 588 (1929).

(9) Farmer and Marshall, J. Chem. Soc., 129 (1931).

(10) Bouveault, Compt. rend., 138, 1108 (1904).

(11) Noller, This Journal, 51, 594 (1929).

(12) Kishner, J. Russ. Phys.-Chem. Soc., 45, 957, 973 (1913); Chem. Centr., 84, II, 2131 (1913).

methyl-1,3-hexadiene. Confirmatory evidence for this structure was found in the fact that it could be reduced by aluminum amalgam to an olefin which on ozonization gave acetone and *t*-butyl-acetaldehyde.

Experimental

Trimethylacetaldehyde.—This was prepared by a modification of the method of Bouveault[10] which is in general use in this Laboratory. *t*-Butylmagnesium chloride was prepared from 120 g. of magnesium turnings, 550 cc. of *t*-butyl chloride and 1750 cc. of dry ether. The Grignard reagent was filtered in an atmosphere of dry nitrogen, and found to contain 3.1 moles of Grignard reagent, as shown by titration. This material was added dropwise with stirring to 600 cc. of methyl formate. The temperature of the reaction mixture was kept below −40°. The Grignard complex so obtained was hydrolyzed in the usual way with ice and sulfuric acid, and the aldehyde taken up in ether. The ethereal solution of the aldehyde was dried over potassium carbonate, and 2 g. of hydroquinone were added to protect it from oxidation. The ether was removed by distillation through a 17 × 650 mm. helix-packed column, and the residue fractionated through a 13 × 390 mm. helix-packed column. The product from two such runs gave 15 fractions and a residue of 135 g. Fractions 4–13, b. p. 67–74° (730 mm.), n^{20}D 1.3795–1.3791, were sufficiently pure for subsequent work. Their combined weight was 255 g. Fractions 9–13, b. p. 71–74° (730 mm.), n^{20}D 1.3791, were pure trimethylacetaldehyde. They weighed 187 g., a 35% yield, based on the Grignard reagent used.

5,5-Dimethyl-3-hexene-2-one.—This was prepared by the condensation of trimethylacetaldehyde with acetone. When 12% aqueous sodium hydroxide was used as the condensing agent, an 18% yield of impure ketone was obtained. By the use of sodium ethylate, the yield of pure product was raised to 40–50%. A sodium ethylate solution, prepared from 6 g. of metallic sodium and 100 cc. of absolute ethanol, was added to 350 cc. of acetone, which had been dried over potassium carbonate and purified by distillation from a small amount of potassium permanganate. Over a period of twelve hours, 116 g. of trimethylacetaldehyde was added to the mixture with mechanical stirring. The reaction flask was cooled in an ice-bath during this process. The reddish brown mixture was allowed to stand overnight, and then was poured into 1 liter of cold water. It was made neutral with 50% sulfuric acid and then extracted with ether. The ether extract was dried over potassium carbonate, and most of the ether was removed by distillation. A few crystals of iodine were added to the residue, which was then fractionated through a 13 × 390 mm. helix-packed column under reduced pressure, to give twelve fractions and a residue of 56 g. of tar. Fractions 5–10, b. p. 78–80° (40 mm.), n^{20}D 1.4430, weighed 68 g., and represented a 40% yield of ketone, based on the trimethylacetaldehyde used.

Occasionally the product had the same boiling point but an index of refraction of 1.4420. In the cases where the product of lower index was obtained there was a larger forerun of undehydrated ketol, which, when redistilled

over a few crystals of iodine, gave more unsaturated ketone, n^{20}D 1.4420. This may be a case of geometrical isomerism, as observed by Eccott and Linstead in the case of the closely related isobutylidene acetone.[13] This would explain the difference in the ease of dehydration of different preparations of the ketol.

The semicarbazone, prepared in the usual way from ketone of index n^{20}D 1.4430, was recrystallized from alcohol as large white needles, which melted at 178°.

Anal. Calcd. for $C_9H_{17}ON_3$: C, 58.95; H, 9.23; N, 22.94. Found: C, 58.8; H, 9.39; N, 22.86.

The 2,4-dinitrophenylhydrazone of the ketone of index 1.4430 was recrystallized from benzene to give red crystals, m. p. 159–161°.

Addition of Hydrogen Chloride to the Ketone.—Eleven grams of the ketone were treated, in an ice-bath, with dry hydrogen chloride gas for two hours. The dark red solution was fractionated under reduced pressure through a 10 × 300 mm. helix-packed column to give 6 fractions and 0.5 g. of tarry residue. Fractions 3–4, b. p. 63–70° (40 mm.), n^{20}D 1.438, weighed 4.9 g., and probably were impure chloride. This material darkened and decomposed very rapidly.

2,5,5-Trimethyl-1,3-hexadiene.—A solution of 186 g. of 5,5-dimethyl-3-hexene-2-one in 500 cc. of dry ether was added slowly with stirring to an ethereal solution of methylmagnesium chloride, prepared from 72 g. of magnesium turnings. The reaction flask was cooled in an ice–salt bath during the addition, which required eight hours. The Grignard complex was allowed to stand at room temperature overnight, and then was hydrolyzed with ice and sulfuric acid. The ether extract was dried over potassium carbonate and the ether removed. The residue was treated with 1 g. of iodine and distilled. The distillate was a mixture of water and hydrocarbon. The hydrocarbon layer, after drying over sodium sulfate, was redistilled through a 13 × 390 mm. helix-packed column to give 13 fractions and a tarry residue of 3 g. Fractions 7–12, b. p. 128° (732 mm.), n^{20}D 1.4489, d^{20}_4 0.7478, weighed 51 g., a 27% yield of 2,5,5-trimethyl-1,3-hexadiene, based on the weight of ketone used. The hydrocarbon had a sharp mint odor: MRD observed, 44.50, calcd. 42.83; ED observed, 35.85, ED calcd. 34.51. For a singly disturbed conjugated system the exaltation of ED should be at least 1.10.[14]

Catalytic Hydrogenation of 2,5,5-Trimethyl-1,3-hexadiene.—A solution of 18 g. of the diolefin in 150 cc. of methyl alcohol was reduced with the Adams catalyst, using 0.35 g. of platinum oxide and an initial hydrogen pressure of 45 lb. (3 atm.). An azeotropic mixture of the hydrocarbon and alcohol was formed. This was diluted with water, the hydrocarbon extracted with ether, the ether solution dried and most of the solvent removed. The residue was fractionated carefully through a 10 × 300 mm. helix-packed column to give 11.0 g. of material of b. p. 121–122° (731 mm.), n^{20}D 1.4000. This product was refractionated to give 6.5 g. of hydrocarbon of b. p. 122.9–123.0° (736 mm.), n^{20}D 1.3997, d^{20}_4 0.7081, MRD calcd. 43.76, MRD obsd. 43.82. The physical constants given by Noller[11] for 2,5,5-trimethylhexane are: b. p.

(13) Eccott and Linstead, *J. Chem. Soc.*, 917 (1930).
(14) Auwers and Eisenlohr, *Ber.*, 45, 806 (1910).

121–123°, n^{20}D 1.3997, d^{20}_4 0.7091. Kishner[12] reported the following constants for this hydrocarbon: b. p. 126° (764 mm.), nD 1.3987, d^{20}_0 0.7082.

Aluminum Amalgam Reduction of 2,5,5-Trimethyl-1,3-hexadiene.—Aluminum amalgam was prepared by the method of Wislicenus.[15] Small amounts of water were added occasionally to a well-stirred mixture of 19 g. of 2,5,5-trimethyl-1,3-hexadiene, 30 g. of aluminum amalgam and 400 cc. of ether, over a period of twelve hours. The mixture was then filtered from unused amalgam, made neutral with dilute hydrochloric acid and extracted with ether. Distillation of the ethereal extract gave a small amount of material of b. p. 72° (735 mm.), n^{20}D 1.4019. Two and one-half grams of this product was dissolved in 175 cc. of petroleum ether (b. p. 5–30°) and ozonized for thirty-five minutes. The ozonide was decomposed with water and zinc dust.[7] The first portion of the aqueous distillate from the decomposition gave a good iodoform test for acetone, and negative tests for formaldehyde. A small amount of a 2,4-dinitrophenylhydrazone was isolated. After repeated crystallizations this melted at 137°. A mixture with an authentic sample of the derivative of t-butylacetaldehyde, m. p. 146°, melted at 145–146°. There was not enough material for further purification.

Anal. Calcd. for $C_{12}H_{16}O_4N_4$: C, 51.43; H, 5.71. Found: C, 51.14; H, 5.29.

2,5,5-Trimethyl-1,3-hexadiene Hydrobromide.—Hydrogen bromide gas was passed, with stirring, into a solution of 66 g. of the diolefin in 100 cc. of chloroform until the gain in weight was 35 g. The reaction mixture was cooled in an ice–salt bath during this process. Excess hydrogen bromide was removed from the purple solution with solid potassium carbonate, and most of the chloroform was removed by distillation under reduced pressure. The residue was fractionated through a 13 × 390 mm. helix-packed column at 50 mm. pressure to give 50 g. of material of b. p. 75–77° (50 mm.), n^{20}D 1.4770–1.4773, d^{20}_4 1.1045. The hydrobromide could be kept for a few days if stored in the refrigerator in perfectly clean bottles over potassium carbonate. Otherwise, the substance quickly turned brown and evolved hydrogen bromide.

A solution of 25 g. of the hydrobromide in 275 cc. of petroleum ether (b. p. 5–35°) was ozonized for two and a quarter hours. The clear ozonide solution was decomposed with water and zinc dust by the method of Whitmore

(15) Wislicenus, *J. prakt. Chem.*, **54**, 54 (1897).

and Church.[7] The aqueous distillate and residue gave negative tests for acetone and formaldehyde. The material in the 2,4-dinitrophenylhydrazine trap was composed of two substances, which were very difficult to separate. One fraction, composed chiefly of impure trimethylacetaldehyde derivative, melted at 192°. The other fraction was composed of orange-red needles of m. p. 142°. This material gave analytical values which indicated that it was probably the derivative of α-hydroxyisobutyraldehyde.

Anal. Calcd. for $C_{10}H_{12}O_5N_4$: C, 44.78; H, 4.48. Found: C, 44.97; H, 3.80.

Distillation of the contents of the ether traps gave a fraction of b. p. 78° (732 mm.), n^{20}D 1.371, which smelled strongly of trimethylacetaldehyde. The constants of pure trimethylacetaldehyde are: b. p. 74° (730 mm.), n^{20}D 1.379. The 2,4-dinitrophenylhydrazone obtained from this material melted at 195°. A mixture with the derivative of trimethylacetaldehyde (m. p. 209°) melted at 204–205°.

Distillation of the oily fraction from the ozonide decomposition gave 2 g. of an extremely viscous oil, b. p. 136° (28 mm.). This corresponds to the recorded boiling point of polymeric α-hydroxyisobutyraldehyde.[8]

A portion of the hydrobromide was oxidized with potassium permanganate and cold dichromate by the method of Farmer and Marshall.[9] The reaction product was made alkaline and steam distilled to remove any unoxidized glycol. The residue was acidified with sulfuric acid and extracted with ether. The ether extract was concentrated by evaporation and converted to the p-nitrobenzyl ester by the procedure of Reid and Lyons.[16] A white crystalline substance was isolated which melted at 80° after recrystallization from alcohol. The p-nitrobenzyl ester of α-hydroxyisobutyric acid melts at 80.5°.[16]

Summary

1. 5,5-Dimethyl-3-hexene-2-one and 2,5,5-trimethyl-1,3-hexadiene have been synthesized.

2. The addition of hydrogen bromide to 2,5,5-trimethyl-1,3-hexadiene has been studied, and found to occur in the 1,2-positions, with no rearrangement.

(16) Reid and Lyons, THIS JOURNAL, **39**, 1727 (1917).