Chlorination of Ethylpentachlorobenzene at 180°.—Redistilled ethylpentachlorobenzene (1000 g.) was illuminated with a 500-watt bulb and chlorinated at 180° to a gain in weight of 132 g. and then reacted with benzene as above. Distillation gave the following fractions: (1) 229 g. of b. p. 100–160° at 0.15 mm.; (2) 546 g. of b. p. 168–180° at 0.2 mm.; (3) 60 g. of b. p. 186–205° at 0.3 mm.; (4) 123 g. of b. p. 210–232° at 0.8 mm.; (5) 36 g. of b. p. 232° at 2.5 mm. Fraction 1 was separated into material soluble in trichloroethylene in the cold and material insoluble in trichloroethylene in the cold. The insoluble material was crystallized from trichloroethylene yielding 11 g. of hexachlorobenzene. The soluble material was crystallized from ethanol yielding 110 g. of ethylpentachlorobenzene. Fraction 2 was crystallized as in the previous case from trichloroethylene-alcohol yielding 403 g. of V and 94 g. of IV. Fraction 3 was also crystallized from trichloroethylene-alcohol and gave only 32 g. of V. When Fraction 4 was crystallized from trichloroethylene–alcohol (1:2) both rods and a powder deposited. The two were separated by floating off the powder with mother liquor and were then crystallized separately to yield pure VII, m. p. 132–133° and pure VI, m. p. 143–143.5°. In all we isolated only 11 g. of VII and 7 g. of VI. Crystallization of Fraction 5 from trichloroethylene–alcohol (2:1) gave only 10 g. of hexachlorobenzene.

Summary

To determine the relative amounts of α- and β-chlorination of ethylpentachlorobenzene at 70–75° and 180° the crude chlorination products were treated in the Friedel–Crafts reaction with benzene and the products of this reaction were then separated by standard methods. To identify the products formed 1-pentachlorophenyl-1-phenylethane, 1-pentachlorophenyl-2-phenylethane and 1-pentachlorophenyl-1,2-diphenylethane were synthesized from starting materials of known structure.

At 70–75° the ratio of β- to α-chlorination is approximately 1.6:1 and at 180° almost 4.6:1, thus indicating a lower activation energy for the α-chlorination. This lends support to the mechanism previously postulated to account for the difference in the direction of chlorination and bromination of ethylpentachlorobenzene.

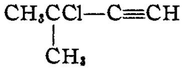
RECEIVED AUGUST 5, 1948

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Reaction of Dialkylethynylcarbinols with Acidic Reagents

BY CHARLES D. HURD AND WARREN D. MCPHEE[1]

Several branched isomers of the formula C_6H_7Cl are reported in the literature. One such is 3-chloro-3-methyl-1-butyne (I) formed by reaction of dimethylethynylcarbinol with hydrochloric acid (at 20°) in the presence of cupric (or cuprous) chloride and ammonium chloride.[2] Apparently it was stable during distillation, b. p. 74–76°. The compound reacted with ammoniacal silver nitrate and underwent hydrolysis in the presence of calcium carbonate to the original carbinol. On standing in the presence of cuprous and ammonium chlorides, (I) gradually rearranged into isomers which were indifferent toward ammoniacal silver nitrate and which were assigned structures II (b. p. 101–104°) and III (b. p. 97.5–98°, d^{20}_4 0.9543). II was indifferent, but III was reactive toward maleic anhydride, giving rise to four products of m. p. 210, 239, 298, 352°. Oxidation of II by potassium permanganate yielded acetone and α-hydroxyisobutyric acid.

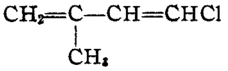


$CH_3\underset{CH_3}{C}Cl-C\equiv CH$

I

$(CH_3)_2C=C=CHCl$

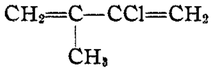
II



$CH_2=\underset{CH_3}{C}-CH=CHCl$

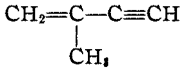
III

Another isomer is 2-chloro-3-methyl-1,3-butadiene (IV). It was prepared by Carothers and Coffman[3] by addition of hydrochloric acid to methylbutenyne (V) in the presence of ammonium chloride and cuprous chloride. It possessed constants (b. p. 93° with some polymerization, 37° (105 mm.), d^{20}_4 0.9593, n^{20}_{D} 1.4689) which are remarkably close to those given for III. The substance was volatile in steam and polymerizable to a jelly on standing for five days in a tube containing a trace of air. It underwent the Diels–Alder reaction with α-naphthoquinone, the yield of adduct not being given. Oxidation of the adduct gave the known 2-chloro-3-methylanthraquinone, which is confirmatory evidence for structure IV.



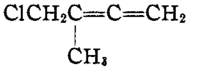
$CH_2=\underset{CH_3}{C}-CCl=CH_2$

IV



$CH_2=\underset{CH_3}{C}-C\equiv CH$

V



$ClCH_2\underset{CH_3}{C}=C=CH_2$

VI

The present work also deals with a product of formula C_6H_7Cl which was obtained by interaction of hydrochloric acid with dimethylethynylcarbinol. A chloride of structure IV would be expected (via V + HCl) on the basis of the behavior of other related ethynylcarbinols[4] toward acidic reagents. Certain facts agreed with this expecta-

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[1] Holder of Commercial Solvents Corporation Fellowship, 1938–1940. Present address: G. D. Searle and Company, Chicago, Illinois.

[2] Favorskiĭ and Favorskaya, *Compt. rend.*, **200**, 839 (1935); Favorskaya, *J. Gen. Chem.* (*U. S. S. R.*), **9**, 386, 1237 (1939); Favorskaya and Zakharova, *ibid.*, **10**, 446 (1940).

[3] Carothers and Coffman, THIS JOURNAL, **54**, 4071 (1932); Carothers and co-workers, *ibid.*, **53**, 4203 (1931); **54**, 4066 (1932).

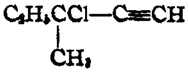
[4] Hurd and Jones, *ibid.*, **56**, 1924 (1934); Hurd and Christ, *ibid.*, **59**, 118 (1937).

tion. It was volatile in steam. It polymerized to a brown-black gum if kept for a few hours at room temperature. It underwent the Diels–Alder reaction (42% yield). The adduct with maleic anhydride melted at 124–126°. On the other hand, it was not distillable without polymerization unless quite low pressures were used. Also, the refractive index of the distilled material was low (n^{20}_{D} 1.445). Any allene isomer VI that might have been present (also via V + HCl) should have caused a higher index of refraction, not a lower one. This follows from the observation that for the pair of lower homologs, 4-chloro-1,2-butadiene and chloroprene, the compound with the allene structure possesses[3] the higher refractive index (1.4775 and 1.4583, respectively).

In view of the above facts, ozonolysis was undertaken to help elucidate the structure. A compound of structure I should yield acids but no aldehydes, whereas IV should yield formaldehyde and acetic (or pyruvic) acid in a 2:1 ratio. Our chloride did yield formaldehyde in this operation. It was identified by its reaction with 2-naphthol, a procedure used by Carothers[3] in the identification of formaldehyde following ozonolysis of 4-chloro-1,2-butadiene. Reaction of the formaldehyde (present work) with methone revealed a yield of 36%. The quantity of IV actually present must, therefore, have been far in excess of 36%, since this value corresponds to the isolated yields[5] of aldehydes obtained by ozonolysis of olefins. A quantitative determination of acetic acid showed that two moles of formaldehyde were obtained on ozonolysis for each mole of acetic acid obtained after further oxidation. Direct oxidation of the substance also afforded acetic acid, characterized by means of Duclaux constants and its *p*-bromophenacyl ester. Since none of the other isomers could behave in this manner, this provides strong support for structure IV.

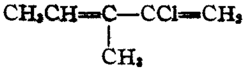
The question arises why this material differs from the chloroisoprene obtained by Carothers and Coffman. No certain answer is at hand, but since it was prepared from dimethylethynylcarbinol, possibly it contains some I as well as IV. This would explain the lower refractive index but would not account for the instability during vacuum distillation. Furthermore, if Carothers' sample of IV contained a little VI, the latter would bring about a higher refractive index. These questions cannot be answered definitely with the present evidence.

The study was extended to methylethylethynylcarbinol. Campbell[6] used concentrated hydrochloric acid, whereas Favorskaya and Zakharova[2] used this acid in the presence of cuprous and ammonium salts. Structure VII was assigned to the product. The chlorine in this compound (b. p. 48–50° (100 mm.), 51–52° (135 mm.), n^{20}_{D} 1.4331) should be reactive, and we found that a comparable sample of it (n^{20}_{D} 1.4332) did readily convert silver nitrate solution into silver chloride That some isomeric VIII was present also was confirmed by ozonolysis and characterization of formaldehyde. VIII has been synthesized previously (b. p. 57–60° (96 mm.), n^{20}_{D} 1.4671) from 3-methyl-3-penten-1-yne.[3]



$C_2H_5CCl{-}C{\equiv}CH$ with CH_3 on the CCl carbon

VII



$CH_3CH{=}C(CH_3){-}CCl{=}CH_2$

VIII

Reaction of dimethylethynylcarbinol with formic acid has been stated by Rupe[7] to yield isopropylideneacetaldehyde, $(CH_3)_2C{=}CHCHO$, but no direct proof of this structure was offered. Traces of it may have been formed,[8] but probably the bulk of any C_5H_8O– material was the isomeric[4] 1-methylvinyl methyl ketone, $CH_2{=}C(CH_3){-}COCH_3$. In the present investigation it was found that dimethylethynylcarbinol yields only traces of a carbonyl derivative when treated with formic acid. The main product was methylbutenyne (V), indicating that the initial reaction was one of dehydration. 1-Methylvinyl methyl ketone was obtained by first hydrating the ethynylcarbinol in the presence of mercuric acetate to 3-methyl-3-hydroxy-2-butanone and then dehydration of the latter by means of *p*-toluenesulfonic acid. This unsaturated ketone had been prepared previously by Morgan[9] in poor yield by the condensation of formaldehyde with methyl ethyl ketone followed by dehydration. Synthesis by this method demonstrated the identity from the two sources. The compound was shown to possess the structure indicated rather than ethyl vinyl ketone by ozonization to formaldehyde and diacetyl. Oxidation with chromic acid[10] gave 1.2 moles of acetic acid per mole of ketone. Hydrogenation of the unsaturated ketone afforded methyl isopropyl ketone, identified by its carbonyl derivatives.

Experimental

Reactions of Dimethylethynylcarbinol

Hydrochloric Acid.—When shaken at room temperature for ten to twenty minutes with an excess of concentrated hydrochloric acid, dimethylethynylcarbinol is easily converted to an organic chloride. In a typical experiment, 10 ml. (0.1 mole) of dimethylethynylcarbinol was shaken in a separatory funnel for fifteen minutes with 30 ml. (0.3 mole) of concentrated hydrochloric acid. The solution turned from light to dark green, and a light green-yellow oil separated. This was removed and dried in the refrigerator with anhydrous potassium carbonate. The weight of dried liquid after filtration was 7.5 g. or 73%.

Sometimes the oil was removed from the reaction mixture by distillation, then separated and dried. In general, the purity of the material isolated this way was no higher than if it was simply separated from the reaction mixture, because polymerization set in during distillation. The yields (60–70%) were usually less for the same reason.

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(5) Church, Whitmore and McGrew, THIS JOURNAL, **56**, 176 (1934).

(6) Campbell, Campbell and Eby, *ibid.*, **60**, 2882 (1938).

(7) Rupe and Kambli, *Helv. Chim. Acta*, **9**, 672 (1926); Rupe, U. S. Patent 1,670,825 (1928).

(8) Chanley, THIS JOURNAL, **70**, 244 (1948).

(9) Morgan and Holmes, *J. Chem. Soc.*, 2667 (1932); British Patent 404,317; Morgan and Griffith, *ibid.*, 841 (1937).

(10) Hurd and Pollack, *ibid.*, **3**, 550 (1939).

Distillation at reduced pressure from a water-bath at 30–40° did not prevent polymerization nor give a purer product. The presence of such substances as hydroquinone or picric acid were ineffectual as inhibitors and a considerable tar was formed even when they were taken. Refractive index ($n^{20}\mathrm{D}$) of product isolated in this manner ranged from 1.431 to 1.441.

Dry Hydrogen Chloride.—Dry hydrogen chloride was passed into 10 ml. (0.1 mole) of dimethylethynylcarbinol at 0° for thirty hours. The mixture became deep red, but never tarry or immobile as was often the case at higher temperatures. The product was treated with anhydrous sodium carbonate. The top layer was separated and dried with fresh carbonate. The yield of product, $n^{20}\mathrm{D}$ 1.4440, was 6 g. or 52%.

Anal. Calcd. for C_5H_7Cl: Cl, 34.7. Found: Cl, 35.0.

In another experiment, 30 ml. (0.3 mole) of dimethylethynylcarbinol was saturated with dry hydrogen chloride at 0°. In thirteen hours the reaction mixture gained 13 g. in weight, after which it gained no more. The mixture was always mobile and free from tar. The product was worked up as in the preceding experiment; $n^{20}\mathrm{D}$ 1.4447, yield 20 g. or 67%.

Distillation.—A 20-g. sample of the crude reaction product was distilled through a Davis column.[11] The flask was maintained at 0° in an ice-bath and the head of the column was cooled to −35° with Dry Ice and acetone. Pressure was lowered and adjusted until reflux was established. Ten grams of colorless distillate was collected at −8 to −7° and 5–6 mm.; $n^{20}\mathrm{D}$ 1.4453.

Ozonization.—Five grams of product, $n^{20}\mathrm{D}$ 1.4435, dissolved in 40 ml. of anhydrous carbon tetrachloride, was treated at 0° with the theoretical amount of ozone. After decomposition[5] of the ozonide, the total volume of aqueous solution was 38 ml. Five ml. of this solution was decolorized with Norit and then refluxed with one drop of concentrated hydrochloric acid and 0.1 g. of 2-naphthol. The crystals of methylenedi-2-naphthol were separated from the boiling solution and were recrystallized from dilute alcohol. The m.p.[12] and mixed m.p. was 203–204°.

The 2-naphthol method is not quantitative for formaldehyde. Dimethyldihydroresorcinol (methone), however, precipitates[13] formaldehyde from very dilute solutions (0.0018 g. per 100 ml.). To 2 ml. of the solution from the ozonization, after decolorization and neutralization, was added 250 ml. of an aqueous solution containing 1.5 g. of dimethyldihydroresorcinol. After twelve hours, 0.55 g. (0.0019 mole) or 36% yield of methylenebis-dimethyldihydroresorcinol was collected. It melted[14] at 187–188° after recrystallization from alcohol.

Another 5 ml. of the ozonized solution was treated with 50 ml. of 3% hydrogen peroxide.[15] The solution was refluxed until gases were no longer evolved (ninety minutes), then distilled. Since the Duclaux constants (7.7, 8.7, 10.8) corresponded to no acid, the solutions were recombined and oxidized for fifteen minutes with refluxing chromic acid solution[16] (6 g. of potassium dichromate, 15 ml. of concd. sulfuric acid, 100 ml. of water). The volatile acid was removed completely by exhaustive distillation[10] and shown to contain 0.0028 mole of acid. That it was acetic acid was shown by Duclaux constants: 6.5, 6.9, 7.4. The neutralized solutions were evaporated and the sodium salt was placed in reaction with 0.5 g. of *p*-bromophenacyl bromide to form *p*-bromophenacyl acetate, m.p. and mixed m.p. 84°.

Chromic acid solution as prepared above will oxidize formic acid quantitatively without affecting acetic acid. Hence the total acetic acid in the total ozonization mixture was 0.0213 mole. The total formaldehyde was 0.0365 mole. The ratio of formaldehyde to acetic acid was, therefore, 1.7 to 1.

Reaction with Maleic Anhydride.—Five ml. of the product (C_5H_7Cl) was treated with 2.3 g. of maleic anhydride. The mixture was boiled gently and the anhydride dissolved to form an amber solution. The solid obtained on cooling was recrystallized twice from dry pyridine. The white needles of 1,2,3,6-tetrahydro-4-chloro-5-methylphthalic anhydride melted at 124–126°; yield, 2 g. (42%). It dissolved readily in water.

Anal. Calcd. for $C_9H_9ClO_5$: equiv. wt., 100.3. Found: equiv. wt., 102.3, 98.06.

Reaction of Methylethylethynylcarbinol with Hydrochloric Acid.—Forty grams (0.4 mole) of methylethylethynylcarbinol was shaken for fifteen minutes with 200 ml. (2 mole) of concentrated hydrochloric acid. The mixture became warm and dark on shaking. The light yellow top layer was separated, dried at 0° with potassium carbonate, filtered, and distilled through a 60-cm. column packed with nichrome helices. The material was not of uniform composition, since of the 23 g. (48% yield) collected in several fractions, between 100–103°, $n^{20}\mathrm{D}$ values change from 1.4222 to 1.4385. Of this, 10 g. had b.p. 102.5–102.7°, $n^{20}\mathrm{D}$ 1.4332, which corresponds to the chloride described by Campbell.[4] This material is exceptionally more stable than the lower homolog obtained from dimethylethynylcarbinol.

Oxidation.—A mixture of 5.5 g. of this chloride (b.p. 102.5–102.7°) and 100 ml. of water was added to a chromic acid solution (48 g. potassium dichromate, 120 ml. concd. sulfuric acid, 400 ml. distilled water). The mixture was refluxed for three hours and the volatile acid was completely removed by exhaustive distillation. Titration revealed 0.0943 mole of acid, or 2.0 moles of acid per mole of substance oxidized. The distillate gave no test for sulfate or chloride. Duclaux constants were satisfactory for acetic acid (7.1, 7.5, 7.9). One gram of the dry salt, obtained by neutralizing the acid, was converted to *p*-bromophenacyl acetate, m.p. and mixed m.p. 84–85°.

Ozonization.—The product (9.1 ml.), b.p. 102.5–102.7°, was dissolved in 50 ml. of dry carbon tetrachloride and treated with ozone as above outlined to yield 35 ml. of an aqueous solution of formaldehyde, from which methylenedi-2-naphthol, m.p. 203–204°, was obtained by reaction as before with hydrochloric acid and 2-naphthol.

Reaction of Dimethylethynylcarbinol with Formic Acid.—When this reaction was carried out in the manner outlined by Rupe,[7] a pure product was never isolated. A typical run consisted in refluxing 24 ml. (0.6 mole) of 85% formic acid with 9.8 ml. (0.1 mole) of dimethylethynylcarbinol for two and one-half hours. The solution soon became dark. It was cooled, extracted thrice with ether, and the extracts were washed with sodium carbonate solution, dried and distilled. Three grams of the carbinol was collected between 100–107° ($n^{20}\mathrm{D}$ 1.421) and 1.1 g. of distillate was collected in three fractions between 107–130° ($n^{20}\mathrm{D}$ 1.425, 1.429, 1.447). All fractions, even the carbinol collected, gave semicarbazones of m.p. 214°. Rupe gives the m.p. of "isopropylideneacetaldehyde" semicarbazone as 244°, but recrystallization never raised the m.p. of our semicarbazone above 214°.

To isolate methylbutenyne, 17.2 g. (20 ml.) of dimethylethynylcarbinol and 50 ml. of 85% formic acid were refluxed under a condenser maintained at 50–60°. Volatile material was conducted into a trap at 5° and another at −78°. After fourteen hours of refluxing, 10.2 g. of volatile product was condensed by the cold traps. The yield of methylbutenyne, b.p. 31–34°, $n^{20}\mathrm{D}$ 1.4105 was 9.7 g. or 72%. Similar boiling points were reported by Carothers[3] and Scheibler and Fischer.[17] The product gave definite voluminous precipitates with potassium mercuric iodide solution[18] and with ammoniacal silver nitrate.

Dehydration of 3-Methyl-3-hydroxy-2-butanone.—Thirty grams of 3-methyl-3-hydroxy-2-butanone, prepared by the method of Scheibler and Fischer,[17] was added

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[11] Davis, *Ind. Eng. Chem., Anal. Ed.*, **1**, 61 (1929).

[12] Hurd and Blunck, THIS JOURNAL, **60**, 2419 (1938), list 204°.

[13] Ionescu and Slusanschi, *Bull. soc. chim.*, [4] **53**, 908 (1933).

[14] Vorlander, *Ann.*, **294**, 253 (1896), lists 189°.

[15] Hurd and Williams, THIS JOURNAL, **58**, 962 (1936).

[16] Macnair, *Chem. News*, **55**, 229 (1887).

[17] Scheibler and Fischer, *Ber.*, **55**, 2903 (1922).

[18] Johnson and McEwen, THIS JOURNAL, **48**, 469 (1926).

dropwise to 5 g. of *p*-toluenesulfonic acid in a distilling flask in an oil-bath at 150°. Of the 30 g., 14.5 g. was recovered. The 1-methylvinyl methyl ketone steam distilled directly. It was dried with Drierite and distilled, b.p. 94–98°; yield, 10 g. The yield, based on the unrecovered starting product, was 74%.

The semicarbazone of this ketone was prepared from 1 g. of the ketone and recrystallized twice from water. It melted at 178°.

Anal. (method of Smith and Wheat[19]). Calcd. for $C_6H_{11}N_3O$: NNHCONH$_2$, 51.74. Found: NNHCONH$_2$, 51.63.

Preparation of 1-Methylvinyl Methyl Ketone.—A modification of Morgan's method[9] was used, taking 108 g. of methyl ethyl ketone, 225 g. of 40% formalin, and 25 ml. of 2 *N* sodium hydroxide solution. The initial reaction is vigorous and requires a long, efficient reflux condenser. There was obtained 36 g. of 3-methyl-4-hydroxy-2-butanone, b.p. 95–110° (18 mm.). This was dehydrated to 1-methylvinyl methyl ketone by distillation with a trace of iodine, instead of with potassium acid sulfate as used by Morgan. The yield was increased by this change. The product was dried (sodium sulfate) and distilled; b.p. 94–97°, n^{20}_D 1.4224. The yield of 14 g. is an over-all yield of 11%. Morgan reported 4%. The semicarbazone of this ketone (m.p. 178°) did not depress the m.p. of that prepared above.

Ozonization.—A solution of 5.2 g. of 1-methylvinyl methyl ketone in 50 ml. of carbon tetrachloride (dried with Drierite) was treated at 0° with ozone as outlined above to form an aqueous solution (35 ml.) neutral to litmus, containing aldehydes and ketones. A 5-ml. sample of the solution, treated with 0.5 g. of semicarbazide hydrochloride and 0.5 g. of anhydrous sodium acetate and kept at 0°, gave rise to 0.46 g. (31% yield) of biacetyl semicarbazone. After recrystallization from alcohol, it melted at 273–275° (d.). When mixed with an authentic specimen, the m.p. of 277–277.5° was not depressed.

Another 5-ml. portion was treated with 0.02 g. of 2,4-dinitrophenylhydrazine in 5 ml. of aqueous alcoholic sulfuric acid solution. Gradually at 0°, yellow crystals of formaldehyde 2,4-dinitrophenylhydrazone, m.p. 165–167° (d.), appeared.

Oxidation.—Two and one-half grams of 1-methylvinyl methyl ketone was heated with a solution of 21 g. of potassium dichromate, 52 ml. of concentrated sulfuric acid and 175 ml. of water. After the evolution of carbon dioxide ceased (thirty minutes), the mixture was refluxed for thirty minutes. It was then distilled.

Duclaux constants: 7.4, 7.5, 8.0; 7.5, 7.9, 8.6; 7.0, 7.5, 8.2, agree better for acetic acid, 6.8, 7.1, 7.4, than for propionic acid, 11.9, 11.7, 11.3. The neutral solution from the Duclaux measurements was evaporated to 2 ml. and converted into *p*-bromophenacyl acetate, m.p. 83–84°.

A sample (0.670 g. or 0.00796 mole) of 1-methylvinyl methyl ketone was oxidized as above, but with the oxidizing mixture diluted to half the previous concentration. The acetic acid was distilled slowly in an all-glass system until crystals formed. The distillate, which gave no test for sulfate, contained 0.00897 mole of acetic acid, or 1.2 moles of acid per mole of ketone oxidized.

Hydrogenation.—Twenty-six grams (0.31 mole) of 1-methylvinyl methyl ketone, dissolved in 25 ml. of pure pentane, was hydrogenated at 25° and 1000 pounds pressure in the presence of 3 g. of a reduced nickel catalyst.[20] The hydrogen absorbed was 0.31 mole. From the filtered solution was obtained 19.5 g. of methyl isopropyl ketone (75% yield), collected in several fractions. Of the total yield, 13.2 g. of the ketone had b.p. 93–98°, n^{20}_D 1.3875–1.3890.

All fractions also gave 2,4-dinitrophenylhydrazones, m.p. 119–122° after recrystallization from alcohol, and semicarbazones of m.p. 110–113° after recrystallization from water. The 2,4-dinitrophenylhydrazone of the known sample of methyl isopropyl ketone melted at 121° after recrystallization. Allen[21] lists the m.p. as 117°. The mixed m.p.'s were not depressed.

Reaction of Dimethylethynylcarbinol with Ketene.—The calculated quantity of ketene was passed into a cold (0°) solution of dimethylethynylcarbinol (10 ml.) in 10 ml. of dry carbon tetrachloride containing a drop of concentrated sulfuric acid. The solution was then neutralized with a little potassium carbonate and distilled to give 9.6 g. (74%) of a clear, pungent liquid, b.p. 126–128°. Nearly all the ester boiled sharply at 128°. Scheibler and Fischer[17] reported the b.p. as 128–136°. The dimethylpropargyl acetate gave a voluminous precipitate with ammoniacal silver nitrate solution. Its saponification equivalent was 125; calculated, 126.

Summary

The reaction of dimethylethynylcarbinol with hydrochloric acid is not one of simple metathesis but gives rise to an extensive production of 2-chloro-3-methyl-1,3-butadiene or chloroisoprene. This conclusion is based on methods involving oxidation, ozonolysis, and reactivity toward maleic anhydride.

Methylethylethynylcarbinol reacts with hydrochloric acid to yield the metathetic product, 3-methyl-3-chloro-1-pentyne, but evidence was found for 2-chloro-3-methyl-1,3-pentadiene in this material. The product was much more stable than that from dimethylethynylcarbinol.

Ketene reacts smoothly with dimethylethynylcarbinol to produce 1,1-dimethylpropargyl acetate. With formic acid, however, the carbinol undergoes dehydration into methylbutenyne which was capable of being hydrated to 3-methyl-3-hydroxy-2-butanone. Evidence for the structure of the latter was dehydration into 1-methylvinyl methyl ketone which underwent catalytic hydrogenation to methyl isopropyl ketone.

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[19] Smith and Wheat, *Ind. Eng. Chem., Anal. Ed.*, **11**, 200 (1939).

[20] Ipatieff and Corson, *Ind. Eng. Chem.*, **30**, 1039 (1938).

[21] Allen, THIS JOURNAL, **52**, 2955 (1930).