Summary

1. Fluorenone oxime has been shown to undergo a normal Beckmann rearrangement, yielding phenanthridone.
2. Oximation of 2-nitrofluorenone has been shown to yield mainly, if not entirely, one of two possible stereo-isomers.
3. Beckmann rearrangement of this 2-nitrofluorenone oxime to 7-nitrophenanthridone has been effected in yields of 90% and the method shown to be of preparative significance.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 17]

THE REARRANGEMENT OF ISOPROPYLETHYLENE TO TRIMETHYLETHYLENE AND THE PYROGENIC DECOMPOSITION OF PENTENE-2 AND TRIMETHYLETHYLENE

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One of the major subjects under investigation in this Laboratory is the influence of structure on the reactivity of atoms and groups in organic compounds. The problem is being studied from two points of view; in one the rates at which the members of a series of analogous compounds react with a fixed substance is being studied;[2] in the other the conditions are being investigated under which certain molecular rearrangements take place and under which definite bonds are severed through the influence of heat and catalytic agents. This paper contains the preliminary results obtained in the study of three amylenes from the second point of view.

A detailed study of the properties of the amylenes is of particular interest on account of the fact that certain of these hydrocarbons are formed in the cracking of petroleum and are now of importance as sources from which amyl alcohols are prepared on a large scale.

The amylenes selected for study were pentene-2, trimethylethylene, and *iso*propylethylene. These compounds can be prepared readily from easily available substances and possess structures that make possible the study of the effect of the position of the double bond on rearrangements and the severing of the molecules under the influence of heat. In *iso*propylethylene the double bond is in position 1, in pentene-2 in position

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[1] From the thesis presented by Raymond Reuter in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1925. Grasselli Scholar in Chemistry 1924–1925.

[2] Norris and Ashdown, THIS JOURNAL, **47**, **837** (1925).

2 and in trimethylethylene there are two radicals in combination with one of the unsaturated carbon atoms.

The chemical reactivity of these isomers with inorganic acids varies greatly with their structure.[3] The work described below shows that similar differences are observed when the isomers are subjected to the action of heat.

It was found that *iso*propylethylene rearranged to trimethylethylene to the extent of 10% when the vapor was passed through a silica tube containing alumina heated to 450° and the contact time was $^1/_4$ minute. When aluminum sulfate was used as the catalyst 47% of the hydrocarbon underwent rearrangement. Phosphoric acid was found to facilitate the reaction but was not as efficient as aluminum sulfate.[4]

These results led to a detailed study of the influence of catalysts on the pyrogenic decomposition of *iso*-amyl alcohol, which furnishes the best method for the preparation of *iso*propylethylene. It was found that the presence of a catalyst and its nature affected markedly the product obtained. In the absence of a catalyst no rearrangement of the *iso*propylethylene produced was observed up to 450°; at higher temperatures partial rearrangement took place. When alumina was used the elimination of water took place at lower temperatures, but the catalyst did not materially alter the proportions in which the two isomers were formed. When, however, *iso*-amyl alcohol was dehydrated under the influence of aluminum sulfate or phosphoric acid, the proportion of trimethylethylene formed was largely increased. The results of three experiments are illustrations of these conclusions. At 375° with alumina (contact time $^1/_4$ minute) 48% of the alcohol passed through the tube was decomposed and there was no rearrangement of the *iso*propylethylene formed. At the same temperature with aluminum sulfate, about 90% of the alcohol was decomposed and 70% of the product was trimethylethylene. With phosphoric acid a higher temperature was necessary to get appreciable dehydration; at 405°, 50% of the alcohol was decomposed and about 50% of the product was trimethylethylene.

The fact that catalysts of an acidic nature caused the rearrangement of *iso*propylethylene to trimethylethylene led to a detailed study of the action of sulfuric acid on the former. It was found that contrary to the behavior of other olefins of this type it could not be converted into a secondary alcohol. When the acid used was sufficiently strong to react with the hydrocarbon the chief product was a polymer. A small amount of tertiary amyl alcohol was formed from the trimethylethylene produced as the result of rearrangement.

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[3] Norris and Joubert, THIS JOURNAL, **49**, 873 (1927).

[4] Ipatiew, *Ber.*, **36**, 2000 (1903), has studied the rearrangement of *iso*propylethylene at higher temperatures in the presence of alumina, but he reports no results with other catalysts.

Experiments were carried out to determine whether or not trimethylethylene would rearrange to *iso*propylethylene; under the conditions used by us no rearrangement was observed.

When pentene-2 was heated under a variety of conditions there was no evidence of the formation of branched-chain hydrocarbons.

The Pyrogenic Decomposition of Pentene-2 and Trimethylethylene

Pentene-2.—The hydrocarbon was passed through a silica tube at such a temperature and rate that it was not completely decomposed. These conditions were used to prevent excessive cracking of the primary products of decomposition. The reaction was studied in detail at 600° when the hydrocarbon was passed through the tube at such a rate that the contact time was 15 seconds. The interior of the silica tube was covered with a thin coating of carbon deposited from the gas before the decomposition was brought about. This was done to avoid the catalytic effect of the silica surface at the beginning of the experiment. Under these conditions about two-thirds of the hydrocarbon was decomposed.

The quantitative determination of the components of the complex mixture formed presented a difficult task. There are no satisfactory methods for the analysis of mixtures of paraffins, olefins or di-olefins. The methods used in this investigation gave results of sufficient accuracy, however, to warrant conclusions as to a probable mechanism of the decompositions studied.

The mixture of products obtained as the result of the decomposition of pentene-2 in a carefully carried out experiment at 600° consisted of ($^1/_3$) hydrocarbons having a molecular weight greater than pentene and ($^2/_3$) hydrocarbons of a lower molecular weight. The former, which appear to be unsaturated, have not yet been fully investigated.

The hydrocarbons having molecular weights lower than that of pentene were studied in some detail. The only saturated hydrocarbon found to be present was methane. There appeared to be no free hydrogen produced. The number of moles of methane was approximately equal to the sum of the number of moles of the other hydrocarbons present. This fact indicates that the decomposition consisted in the removal of a methyl group from the end of the chain of pentene-2[5] and a similar removal in the case of the decomposition of the products formed as the cracking progressed. The carbon atom numbered 1 in pentene-2 or the one numbered 5 may be removed in this way. It is possible that the hydrocarbon decomposes in the two ways, but it is probable, for the following reasons, that in the decomposition the larger proportion of pentene loses carbon 5. In order to bring about the same percentage decomposition of trimethyl-

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[5] Gault and Altchidjian, *Ann. chim.*, [10] **2**, 209 (1924), obtained a similar result with other hydrocarbons.

ethylene and pentene-2 a higher temperature is required in the case of the former. This fact indicates that it is more difficult to break the bond between a methyl radical and an unsaturated carbon atom than between the radical and a saturated atom.

If it is first assumed that the carbon atom numbered 5 is removed, the decomposition can be formulated as follows. The breaking of the bond results in the formation of two radicals

$$CH_3CH_2CH{=}CHCH_3 = CH_3{-} + {-}CH_2CH{=}CHCH_3$$

The addition of hydrogen to these radicals leads to the formation of methane and butene-2

$$CH_3{-} + {-}CH_2CH{=}CHCH_3 + 2H = CH_4 + CH_3CH{=}CHCH_3$$

The hydrogen necessary is produced as a result of the partial or complete decomposition of some hydrocarbon, since carbon is deposited in the tube. It is also formed during the conversion of the butylene radical into butadiene

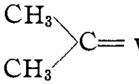
$${-}CH_2CH{=}CHCH_3 = CH_2{=}CH{-}CH{=}CH_2 + H$$

The amounts of butene and butadiene-1,3 formed were approximately the same. The sum of the number of moles of butene and of butadiene was two-thirds of the number of moles of methane—a fact that indicates that a part of the butene radical, the primary product of decomposition, underwent subsequent cracking with the formation of methane. The presence of propylene and ethylene in the gas was demonstrated. It is possible that some propadiene was formed from the butylene, but if present its amount was too small for identification.

If a decomposition of pentene-2 takes place in which the carbon numbered 1 is split off, the reactions would be similar to those just described, with the difference that butene-1 instead of butene-2 would be formed. The method of analysis used in the work did not differentiate between these hydrocarbons. The butene present was converted into a butyl chloride by adding hydrochloric acid. Both butenes give 2-chlorobutane.

In the mixture of hydrocarbons showing molecular weights lower than the molecular weight of pentene the components were found to be present approximately in the molecular ratios: CH_4, 100; C_4H_6, 30; C_4H_8, 27; C_3H_6, 21; C_2H_4, 15. The percentages by weight of the products obtained were approximately as follows: pentene-2 recovered, 33; hydrocarbons of higher molecular weight than that of pentene-2,15; methane, 7.8; butadiene, 8; butene, 8; propylene, 4; ethylene, 2.

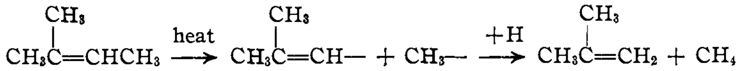
As has been noted, these conclusions are drawn from the results of the use of analytical methods which are in part but roughly quantitative. The determinations of methane were accurate as the usual combustion method was used. The determination of total unsaturated gases and of ethylene was also reasonably accurate. The butadiene was determined as the tetrabromide, which was isolated from the product formed as the result of the addition of bromine to the unsaturated compounds. The tetrabromide was obtained in part by crystallization from the solvent used in the bromination and in part by distilling the bromides formed. The amounts of butylene and propylene were calculated from (1) the amounts of the several products formed in the fractionation of the dibromides and (2) the result of the fractionation of the chlorides produced by adding hydrochloric acid to the unsaturated hydrocarbons. The quantitative results in the case of butylene and propylene are, therefore, approximations only.

Trimethylethylene.—At 625° the extent of decomposition of trimethylethylene was about one-half that of pentene-2 at 600°, and at 650° the decomposition was slightly more. At the latter temperature about 70% of the hydrocarbon was decomposed when the contact time, as in the case of pentene-2, was 14-15 seconds. The product of decomposition as in the case of the isomer consisted of approximately $^1/_3$ hydrocarbons of higher and $^2/_3$ lower molecular weights. As before, no free hydrogen was formed and about $^1/_2$ of the gases was methane. In the examination of the products formed as a result of the decomposition of trimethylethylene, analyses were made for the proportion in which compounds containing the grouping  $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C\!=$ were present. Such compounds react rapidly with 60% sulfuric acid and with concentrated hydrochloric acid. About 30% of the gas produced in the reaction was rapidly absorbed by concentrated hydrochloric acid. About 20% of the gas consisted, therefore, of straight-chain unsaturated compounds. This latter conclusion is open to question, because the behavior of gaseous di-olefins with concentrated hydrochloric acid is not known. The 30% absorbed by the acid is, accordingly, a minimum figure for the olefins containing two methyl groups attached to an unsaturated carbon atom.

The liquid condensate from the decomposition was examined with 60% sulfuric acid for hydrocarbons of the type just mentioned. About 70% dissolved in acid of this strength. This fact leads to the conclusion that the higher hydrocarbons formed contained an appreciable amount of compounds having straight chains. No butadiene was found to be present in the gases.

As in the case of pentene-2 the ethylene formed was approximately 10 molar per cent. of the methane formed; also, the amount of propylene was greater than that of ethylene.

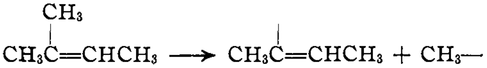
The facts established by the work up to the present indicate that the decomposition in the case of trimethylethylene can be formulated in a way similar to that given in the case of pentene-2



$$CH_3\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CHCH_3 \xrightarrow{\text{heat}} CH_3\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH{-} + CH_3{-} \xrightarrow{+H} CH_3\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH_2 + CH_4$$

The radical from *iso*butene cannot form a butadiene without the severing of a carbon-carbon bond followed by the recombination of the carbon atoms in a straight chain. As this kind of rearrangement is improbable, the fact that no butadiene-1,3 was found appears reasonable.

It is possible that the hydrocarbon may break as indicated below



$$CH_3\overset{CH_3}{\overset{|}{C}}{=}CHCH_3 \longrightarrow CH_3\overset{|}{C}{=}CHCH_3 + CH_3—$$

The unsaturated radical could by loss of hydrogen form butadiene-1,2, which might rearrange to butadiene-1,3, although the only rearrangement yet observed is one which produces an acetylene derivative. The addition of hydrogen would produce butene-2, which by subsequent decompositions and recombinations would produce compounds with a straight chain. The butene formed would on subsequent decomposition be converted into propylene and ethylene.

The work on the two pentenes suggests that for a full understanding of the changes involved the pyrogenic decomposition of propylene, the butylenes and the dienes of low molecular weight should be studied. The investigation will be continued in this direction.

The work involved the development of analytical methods. As relatively large quantities of the hydrocarbons were made, an opportunity was offered to prepare samples in a high state of purity for the redetermination of certain physical properties. These results are given in detail in the experimental part of the paper.

Experimental Part

The Preparation of the Compounds Studied

Isopropylethylene.—A number of methods for the preparation of this hydrocarbon have been described.[6] The directions for the method outlined briefly here are more specific than those previously given and are based on a detailed study of the effects of the various factors involved.

*Iso*propylethylene was prepared by passing *iso*-amyl alcohol over an alumina catalyst heated at 375–450°. When an electrically heated silica tube 4 feet long and 1 inch in internal diameter was used and the alcohol was passed through at the rate of 1.6 moles per hour (contact time $^1/_4$ minute) about 50% of the alcohol was converted into amylene and most of the rest was recovered.

Since the *iso*-amyl alcohol used contained about 10% of active amyl alcohol it was necessary to remove from the crude amylene the unsymmetrical methylethylethylene formed and any trimethylethylene produced by rearrangement of *iso*propylethylene. This was accomplished by shaking the crude amylene for an hour at 30–35° with an equal volume of 60% sulfuric acid. The two substances were contained in a stout bottle closed by a tightly fitting rubber stopper which was wired in place and through which a thermometer passed. The bottle was attached to a shaking machine in the form of a

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[6] See Norris and Joubert, (ref. 3) for references—also Adams, Kamm and Marvel, *Univ. Ill. Bull.*, **16**, No. 43, 10 (1919), and This Journal, **40**, 1950 (1918).

swing agitated by a motor. By placing an electric light bulb over the bottle and covering the machine with a towel the temperature could be maintained at 30–35°.

After the treatment a few cubic centimeters of the hydrocarbon should be tested by shaking at 30–35° with 4 volumes of the acid. If there is no change in volume in 15 minutes the separation of trimethylethylene and unsymmetrical methylethylethylene from the *iso*propylethylene is complete. If the decrease in volume is marked the treatment of the entire amount is repeated. The number of treatments is determined by the proportions in which the isomers are present.

The hydrocarbon purified in this way was washed with a dilute solution of sodium hydroxide, dried over calcium chloride, refluxed with sodium and distilled. The *iso*propylethylene obtained boiled at 20–21°.

After standing for four days, a hydrocarbon separated from the sulfuric acid solution used in the purification of *iso*propylethylene. It boiled at 153–155°, a small fraction boiled up to 160°. The main fraction was apparently the dimer of unsymmetrical methylethylethylene. Its index of refraction was n_D^{20}, 1.4382.

Trimethylethylene.—A number of methods have been given for the preparation of this hydrocarbon. The material used in this research was made by heating tertiary amyl alcohol with 46% sulfuric acid. The alcohol dissolves in acid of this strength and when the mixture is gently heated trimethylethylene separates and distils off.

One experiment gave the following results: 610 cc. (491 g.) of tertiary amyl alcohol was added to a cold mixture of 400 cc. of concentrated sulfuric acid and 800 cc. of water. On distillation 360 g. of hydrocarbon (92% of the theoretical amount) was obtained. A careful study of the product, which boiled at 36.7–38.7°, showed that it contained a small amount of unsymmetrical methylethylethylene.

Pentene-2.—This hydrocarbon was prepared by dehydrating the secondary amyl alcohol manufactured from petroleum. The alcohol is slowly dehydrated when one volume of it is heated with 1.5 volumes of 46% sulfuric acid. It is prepared most readily by using 60% acid. The yield is 90% of the hydrocarbon boiling between 36.5 and 40°.

Pentene-2 Dibromide.—This compound is described by Wagner and Saytzeff,[7] who found that it boiled at 178° (uncorrected). It was prepared in order to ascertain its index of refraction, which was used in the examination of the material obtained as a result of the addition of bromine to the products of the cracking of pentene-2. It was made by adding to pentene-2 (b. p. 36.3–36.4°) bromine dissolved in 4 volumes of carbon tetrachloride at about —20°. The product was fractionated through a column. It was found to boil with slight decomposition at 180.2 to 180.8° (thermometer in vapor) at 754 mm. The fraction boiling at 180.2 to 180.5° had an index of refraction n_D^{10} 1.5149 and n_D^{20} 1.5098.

Trimethylethylene Dibromide.—The boiling point of this compound at atmospheric pressure and its index of refraction are not recorded. It was prepared in the way described above and was found to boil with slight decomposition at 170–173°. The fraction boiling at 170–172° had the index n_D^{20} 1.150 and the one boiling at 172–173°, n_D^{20} 1.511.

2-Chloropentane.—This compound has been prepared by Przewalski[8] who reports the boiling point 96–97° and index $n_D^{19.6}$ 1.4062. Clough and Johns[9] give 96° (760 mm.). It appeared advisable to examine carefully the product formed as a result of the addition of hydrogen chloride to pentene-2. The formation of two isomers is possible, 2-chloropentane and 3-chloropentane. The latter compound is reported to boil at 103–105°.

A very pure sample of pentene-2 was used, which boiled at 36.4° at 760 mm.

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[7] Wagner and Saytzeff, *Ann.*, **179**, 307 (1875).

[8] Przewalski, *Chem. Zentr.*, **II**, 793 (1909).

[9] Clough and Johns, *Ind. Eng. Chem.*, **15**, 1030 (1923).

When 20 cc. of the hydrocarbon was shaken with 9 volumes of concentrated hydrochloric acid for five and one-half hours at room temperature and then allowed to stand for fifteen hours, only about 40% of the hydrocarbon reacted. When a similar mixture was shaken for ten hours and left standing eight hours, almost two-thirds of the hydrocarbon was converted into chloride. The combined products were fractionated. The chloride obtained boiled at 96.87–96.96° at 759 mm.; index, n_D^{20} 1.4084. It is probable that the chloride formed in this way is in large part, or wholly, 2-chloropentane.

Determination of Physical Properties

Boiling Points.—Samples of the compounds studied, prepared in the ways just described, were subjected to fractional distillation. As the hydrocarbons boiled at low temperatures, precautions were taken to avoid superheating during distillation and efficient cooling of the vapors was secured.

Two fractionating columns were used. One, referred to as the 20-inch column, measured 18 inches from the bottom to the side neck and 1.25 inches in diameter. It was filled with pieces of 5 mm. glass tubing approximately 10 mm. long, set on end. The tower was furnished with a still head through which water could be circulated. A thermometer was so placed in the side neck that the mercury was completely immersed in vapor.

A similar column of similar construction 10 inches long and 0.5 inch in diameter was used when small amounts of liquid were fractionated.

The boiling points of the three hydrocarbons were determined with an Anschütz thermometer, graduated in fifths of a degree, which had been calibrated against a standard thermometer graduated in twentieths of a degree and calibrated at the Physikalisch-Technische Reichsanstalt. The boiling point of tertiary amyl alcohol was determined with a thermometer graduated in fifths of a degree and calibrated at the Reichsanstalt.

Melting Points.—The melting points of the hydrocarbons were determined by cooling 5cc. samples contained in 6-inch test-tubes with liquid air, and taking the temperature of the change in state with a pentane thermometer graduated in degrees.

The melting point of tertiary amyl alcohol was determined with a 125cc. sample which was frozen and then introduced into a carefully dried Dewar tube. The melting point was observed with a thermometer graduated in twentieths of a degree which had been calibrated at the Reichsanstalt.

Density.—The density determinations were made with samples contained in a 14cc. Sprengel tube or in a specific gravity bottle. Two determinations were made at 15 and at 25°. Single determinations were made at the other temperatures. A thermostat which remained constant to 0.005° was used for the measurements at 25°. A battery jar 6 by 8 inches was used as a thermostat at 15 and 20°. When the temperature of the room was within 2 degrees of that of the bath, the temperature of the latter remained within 0.1 degree for fifteen minutes or more. The observations at 30° were made in a similar way, but the temperature of the bath remained within 0.1 degree for about five minutes only. The weights are reduced to a vacuum basis.

Index of Refraction.—An Abbé refractometer was used which was supplied with a calibrated thermometer graduated in whole degrees. Duplicate observations checked to 3 in the fourth decimal place.

*Iso*propylethylene.—The slow distillation of 200 cc. of the hydrocarbon prepared as described above showed that the boiling point of the pure compound lies between 20.0 and 20.2° at 759 mm. An 85cc. sample, separated between these limits, was redistilled at 759 mm. through the 10-inch column. The result was as follows: boiling point at the beginning of the distillation 20.0°; when 3 cc. had condensed 20.05°; total distillate 7 cc., 20.10°; 65 cc., 20.15°; 75 cc., 20.20°. About 80% of the hydrocarbon boiling within 0.2° distilled between 20.10 and 20.15°. It is safe to say that the boiling point of *iso*propylethylene at 759 mm. is 20.10 ± 0.05°.

Pentene-2.—Two liters of the hydrocarbon boiling within 1 degree was fractionated with the 20-in. column at 771 mm. The portion measuring 500 cc. which boiled between 36.50 and 37.00° when redistilled yielded 375 cc. boiling between 36.70 and 36.90° and of this 265 cc. boiled between 36.70 and 36.75°. From these results the boiling point of pentene-2 appears to be 36.72 ± 0.05° at 771 mm.

The same sample was redistilled when the barometer registered 760 mm. The boiling point at this pressure was 36.39 ± 0.03°.

Trimethylethylene.—In preparing the hydrocarbon to be used in the determination of physical properties a sample of tertiary amyl alcohol was used which boiled within 0.1° and melted within 1°. It was thought that a pure hydrocarbon might be produced in this way. The result proved that dehydration of the alcohol takes place in more than one way. The chief product is trimethylethylene but some unsymmetrical methylethylethylene, which is said to boil at 31–33°, is also formed. There is no way of separating the isomers by chemical means.

A sample of 1700 cc. of the mixed hydrocarbons was fractionated. The first distillation yielded 1450 cc. boiling between 36.7 and 38.7°. There was no break in the curve when volumes of the distillate were plotted against temperature. The hydrocarbon was redistilled six times, rejecting each time the lower-boiling fractions. It was only in the sixth distillation that a fraction was obtained which when redistilled boiled within the original temperature range. This fraction contained 300 cc. and boiled from 38.23 to 38.48°; 205 cc. boiled between 38.31 and 38.42°; and 145 cc. between 38.38 and 38.42°. These results indicate that trimethylethylene boils at 38.40 ± 0.04° at 759 mm. When redistilled at 770 mm. the hydrocarbon boiled at 38.78 ± 0.04°.

Tertiary Amyl Alcohol.—A sample of the alcohol prepared from petroleum was used.[10] The material was refluxed with barium oxide and fractionated with a 20-inch column. A fraction containing 785 cc. when refractionated at 755 mm. yielded 695 cc. boiling between 101.50 and 101.61°. Of this, 570 cc. boiled between 101.55 and 101.61°.

These results indicate that tertiary amyl alcohol boils at 101.58 ± 0.03° at 755 mm. The sample when redistilled at 766 mm. boiled at 101.97 ± 0.03°.

The results of the determination of physical properties are given in the following table.

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[10] We are indebted to A. D. Little, Inc., for the tertiary amyl alcohol used in this research.

TABLE I

PHYSICAL PROPERTIES OF PENTENE-2, *Iso*PROPYLETHYLENE, TRIMETHYLETHYLENE AND TERTIARY AMYL ALCOHOL

Pentene-2

B. p. 36.39 ± 0.04° at 760 mm. dt/dp, 0.030° per mm. (760–770) M. p. —138 ± 2°
$\text{Density}_{4°}$ 15°, 0.65551 20°, 0.65054 25°, 0.64537 ± 0.00003 30°, 0.64021
n_D 5.3°, 1.3899 10°, 1.3868 15°, 1.3839 20°, 1.3808 30°, 1.3744

*Iso*propylethylene

B. p. 20.10 ± 0.05° at 760 mm. M. p., a thick sirup at —180°
$\text{Density}_{4°}$ 15°, 0.63197 ± 0.00002
n_D 0°, 1.3762 10°, 1.3707 15°, 1.3675

Trimethylethylene

B. p. 38.42 ± 0.04° at 760 mm. dt/dp, 0.036° per mm. (760–770) M. p. —123 ± 2°
$\text{Density}_{4°}$ 15°, 0.66708 ± 0.00002 25°, 0.65694 ± 0.00002
n_D 10°, 1.3939 15°, 1.3908 20°, 1.3878 30°, 1.3814 35°, 1.3781

Tertiary Amyl Alcohol

B. p. 101.76 ± 0.04° at 760 mm. dt/dp, 0.035° per mm. (755–765) M. p. —11.9 ± 0.5°
$\text{Density}_{4°}$ 15°, 0.81382 ± 0.00002 25°, 0.80475 ± 0.00002
n_D 10°, 1.4104 15°, 1.4078 20°, 1.4052

The Action of Heat on *Iso*propylethylene, Trimethylethylene and Pentene-2

Apparatus.—The tube which was used for studying rearrangement and cracking was made of silica. It was four feet long, one inch in internal diameter, wound with No. 18 Chromel "A" resistance wire and covered with asbestos magnesia pipe covering. Three and one-half inches of the tube projected at the inlet end and 8.5 inches at the outlet end. This arrangement made possible the use of corks. The outlet end was connected with a four foot, quarter-inch spiral condenser made of copper. The receiver was a 250-cc. flask, set in ice water and connected with a gasometer.

Temperature measurements were made with two thermocouples. The junctions were so placed that they were 11 and 5 inches from the inlet and outlet ends, respectively, of the heated part of the tube. At the higher temperatures it was necessary to heat the inlet end of the tube with a flame in order to realize an even temperature throughout. In a tube of this length it is necessary to have two pyrometers in order to be sure of the temperature throughout the length of the tube.

Catalysts.—The substances used were (1) aluminum sulfate. A sample of commercial alum was heated in an iron dish until the water of crystallization was just driven off. The porous material was used in the form of small lumps. (2) Aluminum oxide. The material used was Merck's precipitated "aluminum hydroxide" powder. It was heated for about ten minutes at 900° in the silica tube and then allowed to cool to the desired temperature in a stream of air. (3) Phosphoric acid. The catalyst was prepared by heating lumps of pumice which had been soaked in sirupy phosphoric acid.

Methods of Analysis.—In studying the rearrangement of *iso*propylethylene into trimethylethylene it was necessary to devise a method for the quantitative determination of the two hydrocarbons in the presence of each other.

When no other substance is present, a determination of the index of refraction of the mixture serves as a reliable method of analysis. The index of a mixture of the two hydrocarbons in equal quantities was found to be within 0.5% of the mean of the indices of the two hydrocarbons. The same agreement was found in the case of mixtures of trimethylethylene and pentene-2.

A large number of experiments were carried out with the three hydrocarbons alone and with binary mixtures in an endeavor to develop a method of analysis based on the use of sulfuric acid. The effects of temperature, concentration of the acid, time of shaking and the relative amounts of the components in the mixtures were studied. The temperature finally selected was 33–35°. When small quantities of the materials were used they were contained in glass tubes $^1/_2$ inch in diameter and having a capacity of 20 cc. Changes in volume were measured by means of a millimeter scale. The tubes were shaken by hand in a bath, the temperature of which varied less than two degrees.

When larger quantities were used the materials were placed in oil sample bottles and shaken in a machine provided with an electric light bulb so placed that the temperature of the bottles covered with a towel measured nearly constant at 33–35°. Although the temperature is above the boiling point of *iso*propylethylene, a tightly fitting rubber stopper wired in place withstood the pressure, which at 35° was about 1.5 atmospheres. The best conditions for analysis of mixtures containing trimethylethylene are as follows. One volume of the mixture is shaken at 33–35° with 4 volumes of 60% sulfuric acid until the volume of the upper layer remains constant. When 3 to 4 cc. of the mixture of hydrocarbons is used solution of the trimethylethylene is complete in about fifteen minutes The volume of the residual hydrocarbon layer is a measure of the amount of *iso*propylethylene or pentene-2 in the mixture.

When these conditions are used with mixtures, neither *iso*propylethylene nor pentene-2 is attacked nor do they contain any polymer produced from trimethylethylene. The method was tested with mixtures containing as much as 85% of trimethylethylene and was found to be accurate within 3% at the higher concentrations and more accurate than this with lower percentages of the soluble hydrocarbon.

The great difference between the rates at which hydrochloric acid, contained in a concentrated aqueous solution, adds to olefins that yield tertiary chlorides and to those that yield secondary chlorides led to the study of the reactions with the expectation of developing a method of analyzing mixtures of these types of unsaturated hydrocarbons.

While the results did not lead to an exact analytical method, they showed that a close approximation could be obtained of the minimum amounts of trimethylethylene and *iso*butene present in mixtures of hydrocarbons which did not contain two radicals linked to an unsaturated carbon atom.

A mixture of air and the vapor of the hydrocarbons was analyzed in an apparatus for gas analysis. The mixture was treated first with concentrated hydrochloric acid and then with a solution of sodium hydroxide. The process was repeated as long as the volume of the mixture decreased appreciably. There are two sources of error in the method. The hydrocarbons that form secondary chlorides react very slowly with the acid; consequently the absorption does not come to a definite end when the hydrocarbons forming tertiary chlorides are removed. A second source of error is due to the fact that the tertiary chlorides produced have an appreciable vapor pressure at room temperature. One error tends to counteract the other; the results obtained are not exact but approximate the truth sufficiently to be useful.

The Results.—The hydrocarbons were heated at various temperatures up to that at which decomposition began. Incipient cracking was recognized by the evolution of gas. The results are given in Table II.

Table II

The Action of Heat on *Iso*propylethylene, Trimethylethylene and Pentene-2

No.	Hydrocarbon	Catalyst	Temp., °C.	Contact time, seconds	Rate, moles per hour	Hydrocarbon passed, moles	Hydrocarbon recovered, %	Conversion, %	Gas, liters at 22°
1	*Iso*propylethylene	Alumina	450	16	1.71	0.90	79	10 (trimethylethylene	0
2	*Iso*propylethylene	Aluminum sulfate	425	16	1.81	.38	74	47 (trimethylethylene)	0
3	*Iso*propylethylene	Phosphoric acid	500	14	1.60	.36	90	29 (trimethylethylene)	0
4	Hydrocarbon recovered from No. 3	Phosphoric acid	500	21	1.24	.31	91	15 (trimethylethylene)	0
5	Trimethylethylene	Alumina	450	21	1.30	.38	90	No *iso*propylethylene	Trace
6	Trimethylethylene	Phosphoric acid	500	20	1.27	.38	90	No *iso*propylethylene	Trace
7	Pentene-2	Aluminum sulfate	350	15	2.1	.71	77	No *iso*propylethylene	0
8	Pentene-2	Aluminum sulfate	450	16	1.7	.38	70	No isomers formed	0.1
9	Pentene-2	Phosphoric acid	525	12	2.0	.47	88	No isomers formed	0

*Iso*propylethylene rearranged to trimethylethylene, the extent of the change varying with the catalyst used. With one passage through the tube, alumina at 450° caused 10% conversion; phosphoric acid at 500°, 29%; and aluminum sulfate at 425°, 47%. The experiments in each case were carried out at the highest temperature at which cracking did not occur.

In experiment numbered 4 a mixture of *iso*propylethylene and trimethylethylene containing 29% of the latter was passed through the tube. Fifteen per cent. conversion took place, as the hydrocarbon recovered contained 44% of trimethylethylene.

Pentene-2 was not converted into any of its isomers under the conditions used.

The Rearrangement of *Iso*propylethylene to Trimethylethylene under the Influence of Sulfuric Acid.—Up to the present no one has succeeded in preparing the corresponding secondary alcohol from *iso*propylethylene, either by the addition of hydriodic acid[11] and subsequent hydrolysis or by treatment with sulfuric acid.[3]

The action of sulfuric acid on *iso*propylethylene was studied under conditions other than those already reported. Norris and Joubert did not observe any conditions under which *iso*propylethylene dissolved in sulfuric acid. We have found that when 1 cc. of the hydrocarbon is shaken with 1 cc. of 84% sulfuric acid at 35° for about ten minutes, a clear solution is obtained which almost immediately deposits an oil. Dilution of the clear solution as soon as formed yielded only a polymer which boiled at about 150°. When 69% sulfuric acid was used, the small amount of alcohol obtained proved to be tertiary amyl alcohol formed from the trimethylethylene produced as the result of the rearrangement of the *iso*propylethylene.

The experiment which showed that rearrangement takes place under the influence of sulfuric acid was carried out as follows: 100 cc. of carefully purified *iso*propylethylene (b. p. 20.1–20.2°) was shaken at 38° with 100 cc. of 60% sulfuric acid for one hour. The layer of hydrocarbon decreased 3.3% and that of acid increased 3.6%. The acid layer was neutralized with sodium hydroxide and distilled. Three cc. of an alcohol was obtained which boiled at 94–108°, three-fourths of it at 100–104°. Tertiary amyl alcohol boils at 102°. The alcohol dissolved in concentrated hydrochloric acid and was converted into a chloride which separated from the solution in about one minute. The *iso*propylethylene recovered was fractionated and yielded 3 cc. of a polymer which boiled below 160°.

The Rearrangement of *Iso*propylethylene to Trimethyethylene during the Dehydration of *Iso*-amyl Alcohol.—The fact that *iso*propylethylene rearranged to trimethylethylene under the influence of certain

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[11] Wischnegradsky, *Ber.*, **10**, 81 (1877) and *Ann.*, **190**, 328 (1878).

catalysts led to a study of the effect of these catalysts when *iso*-amyl alcohol is used to prepare "amylene." The commercial variety of pentene sold under this name varies greatly in composition. The study of the reaction was extended with the view of developing methods for the direct preparation of either *iso*propylethylene or trimethylethylene from *iso*-amyl alcohol.

A number of the experiments carried out are listed in Table III. The results of the experiments numbered 1 to 3 show that when no catalyst is used the silica tube affects favorably the dehydration of the alcohol. When freshly glowed, 33% of the alcohol was changed to hydrocarbon. In the third experiment when the tube contained a slight deposit of carbon from two previous runs the conversion dropped to 9%. Increase in the temperature from 515 to 555° caused appreciable cracking to gaseous hydrocarbons. Experiments 4 and 5 show the influence of the rate of passage of the alcohol; doubling the rate decreased the conversion of alcohol to hydrocarbon from 41 to 36% and decreased slightly the percentage of the rearrangement of *iso*propylethylene to trimethylethylene.

TABLE III

DECOMPOSITION OF *ISO*-AMYL ALCOHOL BY HEAT

No.	Catalyst	Temp., °C.	Contact time, seconds	Rate, moles per hour	Moles alcohol passed	Alcohol obtained as hydrocarbon, %	Alcohol recovered, %	*Iso*propylethylene in hydrocarbon, %	Gas, liters at 22°
1	None. Tube heated to redness before use	515	13	1.67	1.14	33	51	67	0.3
2	None. Tube from Exp. 1	555	12	1.87	1.12	17	66	79	4.0
3	None. Tube from Exp. 2	515	13	1.88	1.16	9	91	80	0.7
4	None. Tube heated to redness before use	515	12	1.80	1.26	36	57	62	.5
5	None. Tube heated to redness before use	515	19	0.97	1.21	41	53	67	.7
6	Al_2O_3 (Merck's "Aluminum Hydroxide") heated to redness before use	375	17	1.56	1.25	48	38	90	.5
7	Al_2O_3. Tube from Exp. 6	375	19	1.63	1.28	25	68	90	.6
8	Al_2O_3. Heated to redness before use	450	13	1.66	1.27	52	26	90	3.9
9	Al_2O_3. Tube from Exp. 8	450	13	1.70	1.28	57	31	90	3.5
10	Al_2O_3. Tube from Exp. 9	450	13	1.65	1.29	58	30	90	3.4
11	Al_2O_3. Tube from Exp. 10	500	12	1.68	1.29	67	17	79	8.1
12	Al_2O_3. Tube from Exp. 11 after standing for 11 days	450	17	1.78	3.72	63	31	90	6.7
13	$Al_2(SO_4)_3$. SO_2 formed during exp.	345	15	1.48	0.81	57	15	21	0
14	$Al_2(SO_4)_3$. Catalyst blackened during exp. Much H_2S formed	515	10	1.7	.5	25	..	22	6
15	Pumice with H_3PO_4	405	14	1.43	.88	50	25	40	0
16	Tube from Exp. 15	500	11	1.58	.90	64	9	42	0
17	Tube from Exp. 16	505	12	1.67	.78	83	6	40	0

The effect of alumina as a catalyst is shown in experiments 6 to 12. Up to 450° it caused no rearrangement of the *iso*propylethylene produced as the result of the dehydration of the alcohol. The hydrocarbon obtained contained 90% of *iso*propylethylene. The fusel oil amyl alcohol (b. p. 130–132°) used was shown by an optical test to contain 10% of active amyl alcohol. The latter yields when dehydrated unsymmetrical methylethylethylene. At 375° the catalyst appears to decrease in activity with repeated use without reactivation by heating to redness. At 450° decrease in activity was not observed. At 500° cracking to gaseous hydrocarbons and some rearrangement to trimethylethylene take place.

Aluminum sulfate is the most active of the catalysts studied. At 345° dehydration of the alcohol took place to a greater extent than when alumina was used at 375°. It also was efficient in bringing about the rearrangement of *iso*propylethylene; the product contained but 21% of the latter hydrocarbon.

Phosphoric acid closely resembled alumina in its catalytic influence on the dehydration of the alcohol. It caused, however, more rearrangement of the *iso*propylethylene produced, but at the higher temperatures did not produce the cracking to gases observed when alumina was used.

The results show clearly that if it is desired to prepare *iso*propylethylene from *iso*-amyl alcohol by catalytic dehydration by heat, alumina should be used as the catalyst and the temperature should be near 450°. If it is desired to get the largest yield of trimethylethylene by the reaction, aluminum sulfate at 345° is the best catalyst.

Comparison of the results of the study of the rearrangement of *iso*propylethylene when the pure hydrocarbon is heated and when the rearrangement takes place during the dehydration of *iso*-amyl alcohol shows that the relative effectiveness of the catalysts is the same in both cases. The extent of rearrangement was greater in all cases when the alcohol was dehydrated.

The Cracking of Pentene-2 and Trimethylethylene.—The results obtained in the study of these hydrocarbons are given in Table IV.

The gases formed were analyzed as follows: (1) Total unsaturation by means of bromine water; (2) unsaturated hydrocarbons other than ethylene by means of 87% sulfuric acid; (3) methane by explosion with air after removal of unsaturated compounds; (4) total unsaturated compounds by fractionating the dibromides obtained when the gas was treated at —20 to —10° with bromine dissolved in carbon tetrachloride; (5) fractionation of the compounds formed as the result of the addition of concentrated hydrochloric acid.

(6) The liquid condensate was treated with 60% sulfuric acid for compounds containing two radicals linked to an unsaturated carbon atom and was (7) fractionated and the part boiling below 34° was (8) treated with bromine at —17 to —10° and the product fractionated and (9) with concentrated hydrochloric acid and the products fractionated.

TABLE IV

CRACKING OF PENTENE-2 AND TRIMETHYLETHYLENE

	Pentene-2			Trimethylethylene	
	1	2	3	1	2
Temperature, °C.	575°	600	600	625	650
Time of contact, seconds	12	14	14	14	13
Input rate, cc./min.	3.5	2.5	2.5	2.5	2.5
moles/hr.	2	1.4	1.4	1.4	1.4
Charge, cc.	205	200	140	140	140
g.	132	129	90^+	92	92
moles	1.90	1.86	1.30	1.30	1.30
Recovered pentene, moles	1.2	0.9–0.6			0.3
fraction of charge	$^2/_3$	$^1/_3$			$^1/_4$
Decomposition products					
Temperature of condenser water, °C.	9	9	11	10	10
Liquid condensate	155	100	59	(About) 90	64
Charge by volume, %	77	50	42	(About) 64	46
Fractionation of liquid condensate					
% off at 30°	25	21			14
40°	96	71			59
70°		85			70
100°	99.5	89			78
150°	99.5^+	95			
200°		98			93
Gas, liters at 22°	9	33	28	15	27
liters per 100 cc. charge	4.4	16	20	11	19
moles per mole charge	0.19	0.72	0.88	0.48	0.85
Individual hydrocarbons produced					
Methane, moles/mole charge	0.01	0.34	0.31	0.26	0.46
Ethylene, moles/mole charge	.005	.05		.024	.047
Propylene, moles/mole charge	$.02^-$	$.07^+$		Greater than ethylene	
Butylene, moles/mole charge	.1	0.06–0.13		(?) 0.11	
Hexylene, 50–75° cut		0.03^-			
Butadiene, 50–75° cut	.003	0.13–0.09		Little or none	Little or none
Hydrocarbons available for tertiary alcohol formation					
% in gas (by HCl)	Absent	Absent	5–10	30	30
% in liquid condensate (by 60% H_2SO_4 solution), 33°, 15 min.	Absent	Trace (?)	..	..	69

Summary

1. The rearrangement of *iso*propylethylene to trimethylethylene produced by heat is markedly affected by catalysts. The efficiency increases in the order alumina, phosphoric acid, aluminum sulfate.

2. The rearrangement of *iso*propylethylene to trimethylethylene which takes place when *iso*-amyl alcohol is dehydrated by heat is slightly greater than when the hydrocarbon is heated. The efficiency of the catalysts in causing rearrangement is in the same order as in (1) above.

(3) Under the conditions used trimethylethylene did not rearrange to *iso*propylethylene.

(4) When pentene-2 was heated the results showed that no branched-chain hydrocarbons were formed.

(5) The pyrogenic decomposition of pentene-2 and trimethylethylene yielded gaseous and liquid hydrocarbons which were analyzed quanti-

tatively for the following hydrocarbons: methane, butene, butadiene, propylene, ethylene, higher hydrocarbons. The results lead to an interpretation of the mechanism of the decompositions.

(6) *Iso*propylethylene is stable toward diluted sulfuric acid but can be made to rearrange to trimethylethylene to a slight extent by the action of acid of such a concentration that polymerization does not take place appreciably.

(7) The boiling point, melting point, densities at various temperatures and index of refraction of trimethylethylene, pentene-2, *iso*propylethylene and tertiary amyl alcohol were redetermined with carefully purified material.

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THE REACTIVITY OF ATOMS AND GROUPS IN ORGANIC COMPOUNDS. II. SECOND CONTRIBUTION ON THE RELATIVE REACTIVITIES OF THE HYDROXYL-HYDROGEN ATOMS IN CERTAIN ALCOHOLS

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In a former paper[2] from this Laboratory the results were given of the study of the rates at which certain alcohols react with *p*-nitrobenzoyl chloride, and it was shown that the rates, which varied greatly, could be taken as a measure of the relative reactivities of the hydroxyl-hydrogen atoms in these alcohols. As certain striking relationships were indicated from the results obtained with the eleven alcohols investigated, the work was continued and eighteen additional compounds were studied. The alcohols were so selected that the results would show the influence of structure on the reactivity of the hydroxyl-hydrogen atom, especially as this reactivity is affected by lengthening of the carbon chain and by the position of a side chain with reference to the hydroxyl group.

Sufficient data have been obtained from the investigation of these twenty-nine alcohols to warrant definite conclusions. The results are in accord with the well-known qualitative differences in chemical behavior between the several types of alcohols; but they have, in addition, a quantitative significance, and throw some light on the change in the atomic bonding between oxygen and hydrogen produced by changes in the structure of the radical with which the hydroxyl group is combined.

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[1] From the thesis of Frank Cortese, Grasselli Fellow in Chemistry, 1925–1926, presented in partial fulfilment of the requirement for the degree of Doctor of Philosophy, 1926.

[2] Norris and Ashdown, THIS JOURNAL, **47**, 837 (1925).