

THE THERMAL DECOMPOSITION OF ALLYLTRIMETHYL- AMMONIUM HYDROXIDE

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Current studies in this Laboratory involve the thermal decomposition of certain allylic trimethylammonium hydroxides. The observation that quite appreciable amounts of dimethylamine and saturated carbonylic compounds are formed in these reactions has led to the belief that these quaternary bases rearrange to some extent during the pyrolysis, giving vinylic trimethylammonium bases. Although it is conceivable that the carbonylic products might be formed by the rearrangement of allylic alcohols derived from the unrearranged quaternary bases, the only readily understood mechanism by which dimethylamine could be formed involves the hydrolysis of a vinyl dimethylamine, formed by an S_N2 attack by hydroxyl ion upon a methyl group of the vinyl trimethylammonium ion. The products of such a reaction would be methanol and a vinyl dimethylamine, which would be hydrolyzed (in the dilute acid commonly used to absorb the bases formed in Hofmann degradations) to dimethylamine and a saturated carbonylic compound.² A thorough examination of the products formed in the thermal decomposition of the simplest allylic trimethylammonium hydroxide (I) was considered worth while to substantiate these findings and postulates.

The pyrolysis of I has not been studied for over half a century,³ and then only cursorily. In an obscure publication which appeared in 1886 and has since been overlooked or discredited, Bono (3) heated allyltrimethylammonium iodide with potassium hydroxide and obtained an aldehyde, $C_6H_{10}O$, whose boiling point, 130–135° (as he pointed out) corresponded to that of α -methyl- β -ethylacrolein (IV), the only aldehyde of that formula known at that time; since our findings (see below) substantiate Bono's identification of this product,⁴ the question mark appearing in Beilstein's account (5) of his work should be deleted. A short time

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² A similar hydrolysis has been proposed by Buchman, Schlatter, and Reims (1) to explain the formation of cyclobutanone and dimethylamine in the thermal decomposition of trans-1,2-cyclobutane-bis-(trimethylammonium)hydroxide; this decomposition presumably proceeds stepwise, over an intermediate vinylic (or allylic) trimethylammonium base.

³ Quite recently, with reference to application of the decomposition of an allylic quaternary ammonium base to the synthesis of vitamin A, Milas (2) has written that "trimethylallylammonium hydroxide gives, on heating, chiefly trimethylamine and allyl alcohol" without any further substantiation of this statement.

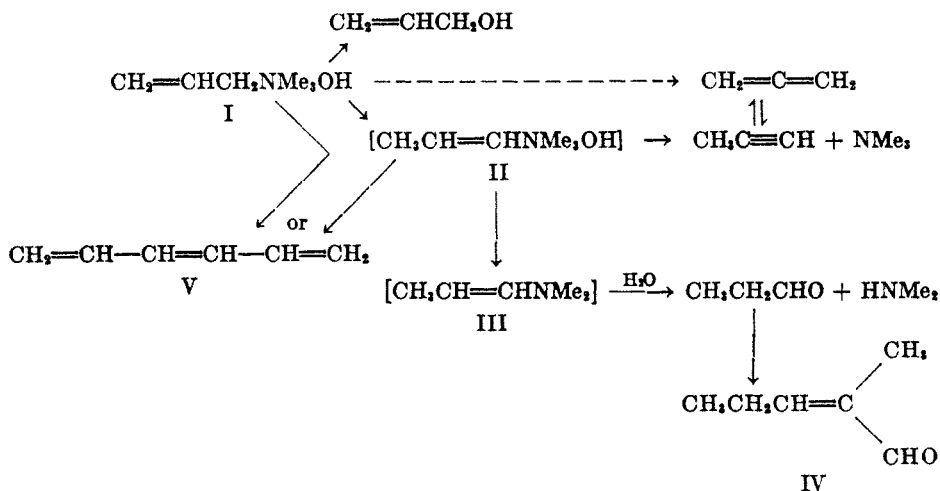
⁴ It seems highly probable that the "ketone", $C_6H_{10}O$, b.p. 130–140°, semicarbazone m.p. 192°, reported by von Braun (4) as one of the pyrolysis products of propane-1,3-bis-(trimethylammonium)hydroxide, is in reality IV, formed *via* I. The formation of rather large amounts of allyl dimethylamine in this reaction probably involves a different intermediate [(3-dimethylaminopropyl)trimethylammonium hydroxide] in view of our investigation of the bases formed in the pyrolysis of I.

later Collie and Schryver (6) studied the thermal decomposition of I with the object of preparing allyldimethylamine, traces of which were apparently identified; they claimed that another product of the reaction was acrolein, "recognized by its smell and the power it possessed of reducing a silver solution". Although other products of the pyrolysis of I may well have been responsible for these qualitative observations of Collie and Schryver, it is interesting that Hey and Ingold (7) have claimed the identification of acrolein (as its *p*-nitrophenylhydrazone) among the products of the decomposition of diallyldibenzylammonium hydroxide; in accord with our views of the changes effected by heating bases of this type, Hey and Ingold also reported the formation of dibenzylamine in this reaction; but the other hydrolysis product (propionaldehyde) of the supposed intermediate (β -methylvinyl)dibenzylamine was not detected by them.

Rothstein (8) has shown that the isomerization (I \rightarrow II) of allyltrimethylammonium chloride in strongly basic media does not occur to any appreciable extent under conditions considerably milder than those employed in our experiments; he noticed that some dimethylamine was formed under less mild conditions, but failed to comment on this observation. We have attempted without success to identify the rearranged base (II) in a sample of partially pyrolyzed I; II evidently decomposes quite rapidly, once formed.⁵

To the best of our knowledge, the purely olefinic products of the thermal decomposition of I have not been investigated.

The substances we have identified among the products of this reaction (carried out at 310–325°) and the manner in which we believe they are formed are indicated in the following diagram:



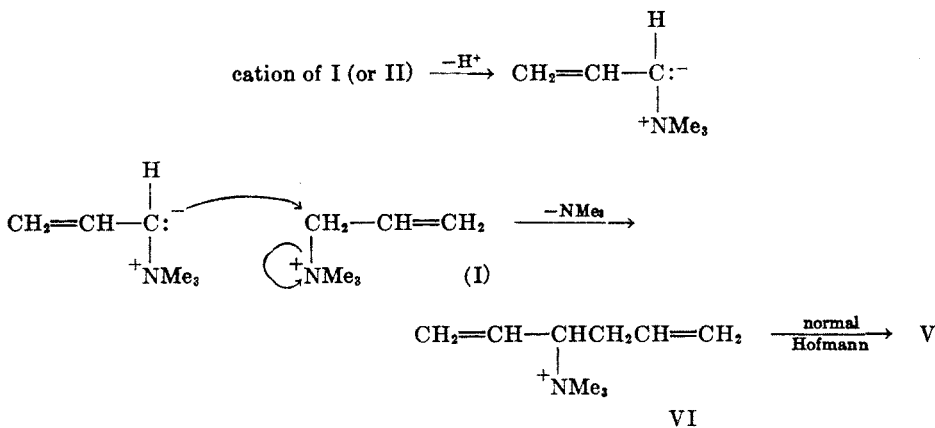
⁵ In connection with this discussion of rearrangements occurring in the decomposition of allylic quaternary ammonium bases, recent work of Tarbell and Vaughan (9) with allylphenyldimethylammonium 2,6-dimethylphenoxide is of interest; *N,N*-dimethylaniline and the allyl ether of 2,6-dimethylphenol are formed in good yield. The predominant direction of this reaction to give this allyl ether (in analogy with the formation of allyl alcohol from I) is probably attributable to the different basic strength of the dimethylphenoxide ion.

Careful fractional recrystallization of the picrates prepared from the basic products of the decomposition showed that they consisted almost entirely of di- and tri-methylamines in a ratio of 1:2; we were unable to detect allyldimethylamine.

Among the neutral products boiling above room temperature, the following compounds were identified (by conversion to solid derivatives and comparison of these with authentic samples): propionaldehyde (trace), allyl alcohol (2.4%), and α -methyl- β -ethylacrolein (IV) (9.2%); higher-boiling materials, probably consisting of propionaldol and other aldehyde and polyene condensation products, were isolated but not identified. From the most volatile portion of this neutral fraction, a water-insoluble oil was isolated and shown (by its ultraviolet absorption spectrum, Figure 1, upper curve) to contain about 2% (yield at least 0.06% from I) of 1,3,5-hexatriene (V);⁶ the presence in this oil of a conjugated diene was also indicated by the absorption spectrum [compare products reportedly formed by the dimerization of allene (12)].

Distillation of the more volatile neutral products gave a 34% yield of a mixture of methylacetylene and, presumably, allene; the identification of the former as the major constituent was indicated by the boiling point (principally at -23°) and confirmed by the preparation of mercuric methylacetylide from it in good yield. Analysis of a small sample of gas withdrawn from this mixture provided data from which it was possible to estimate its composition as 87.2% methylacetylene and 12.8% allene. According to Slobodin (13), an equilibrium mixture of 61.5% methylacetylene and 38.5% allene is rapidly formed on passing

⁶ The detection of this product recalls an example of the so-called "1,1-elimination" described by Ingold and Jessup (10); analogy with this work would represent the formation of V by the dimerization of $\text{CH}_2=\text{CH}\ddot{\text{C}}\text{H}$ (which could be formed from I or II by abstraction of a proton and loss of trimethylamine), but it is difficult to see how such a reactive intermediate would have sufficient opportunity to dimerize to give detectable amounts of V. The following mechanism seems more reasonable:



Note that Kharasch and co-workers (11) have shown that intermediates analogous to VI are involved in the formation of 1,3,5-hexatrienes from allyl chlorides by the action of sodamide.

either of the pure gases over "floridin" at 325°. It is thus clear that the methylacetylene formed in the pyrolysis of I at 310–325° is not an isomerization product of allene; in fact, although some of the allene may arise directly from I (see broken arrow in diagram), all of it may well be formed from methylacetylene.

In agreement with the postulated step II \rightarrow III, the pyrolysis of neurine (vinyltrimethylammonium hydroxide) is reported (14) to yield some vinyltrimethylamine; acetaldehyde and trimethylamine were also formed, but whether or not any acetylene was produced is not indicated.

The author wishes to acknowledge his indebtedness to Dr. E. R. Buchman for helpful discussions during the course of the investigation; and to The Research Corporation for the support of this research.

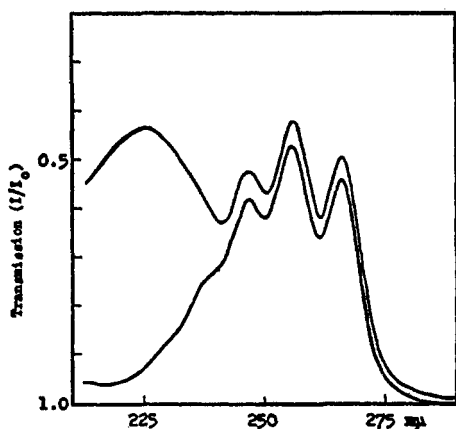


FIGURE 1. Upper curve: 1.8 mg. hydrocarbon (b.p. 52–72°) in 25 ml. *n*-hexane. Lower curve: 2.9 mg. authentic 1, 3, 5-hexatriene in 2.5 l. *n*-hexane.

EXPERIMENTAL PART

All melting points are corrected. Microanalyses were done at this Institute by Dr. G. Oppenheimer and her staff. Absorption spectra were obtained using a Beckman Model DU Spectrophotometer.

The pyrolyses were carried out in an apparatus similar to that used previously in this Laboratory (15). The decomposition chamber was prepared by blowing a test-tube bottom on the female half of a 24/40 standard taper joint to give a tube 11 cm. in depth; the male half was similarly closed off 2 cm. above the grinding and a 50-ml. Squibb funnel sealed into it in such a way that the tip of the funnel extended almost to the ground part of the joint; a 16-cm. straight condenser set for downward distillation was also sealed to this (male) half of the joint, near the point-of-entrance of the funnel stem. Both halves were fitted with hooks so that they might be held together snugly (with small springs) during the decomposition. The condenser (cooled by circulating ice-water) led to a wash-bottle (in the larger experiment described below an empty vessel preceded this) containing an appropriate amount of 6 *N* hydrochloric acid and cooled in ice; any products passing this bottle were conducted through a small amount of calcium chloride and into a series of two traps cooled in Dry-Ice-dibutyl ether (no appreciable amount of material collected in the second of these, whose exit was protected from moisture by a calcium-chloride tube). Before running a pyrolysis, the apparatus was swept out with nitrogen and the decomposition chamber charged with about 4 g. of 20–40 mesh powdered Pyrex glass and heated (in a

metal-bath extending about 5 cm. up the chamber) to 310–325°. A concentrated aqueous solution of I was then introduced dropwise from the funnel under a water-head of about 45 cm.

First experiment. A concentrated aqueous solution of 11.4 g. (0.0633 mole) of dry allyltrimethylammonium bromide (16) was shaken for 15 minutes with silver oxide prepared from 17.0 g. (0.1 mole) of C.P. silver nitrate and carbonate-free aqueous sodium hydroxide (17). Solids were filtered from the solution and the filtrate freed of most of its water *in vacuo* (water-aspirator) at 40–50°. The residual syrup was pyrolyzed (as indicated above) over a period of about two hours; the acid-wash bottle (initially charged with 15 ml. of acid) now contained a floating layer of yellow oil, and about 1 ml. of colorless mobile liquid had collected in the Dry-Ice trap.

The aqueous phase of the distillate was saturated with sodium sulfate, washed with three 10-ml. portions of ethyl ether, and divided into three equal parts. The bases in one of these portions were converted to picrates by treating with 5.0 g. (theory 1.2 g.) of sodium hydroxide pellets in an evacuated manifold in communication with a flask containing 500 ml. (slight excess) of a 1% solution of picric acid in ethyl ether; after the manifold had stood overnight at room temperature, the crude picrates, filtered off, washed with ether, and air-dried, weighed 4.7 g. Recrystallization of this material from methanol, followed by mechanical separation of the bright yellow needles (trimethylamine picrate, m.p. 224–225°) from the rugged dark, red-brown prisms (dimethylamine picrate, m.p. 158–161°) gave 3.12 g. (51.3%) of the former and 1.49 g. (25.7%) of the latter—total recovery 4.61 g.⁷

Another third of this solution of the bases formed in the pyrolysis was cooled and treated with 1.2 ml. (0.01 mole) of benzoyl chloride and 10 ml. (0.05 mole) of 5 N sodium hydroxide; after warming to room temperature, the strongly basic mixture (which no longer smelled of benzoyl chloride) was extracted with benzene. Drying and evaporating this benzene extract gave 0.81 g. (25.8%) of N,N-dimethylbenzamide, crude m.p. 43–44°, not raised by recrystallization from ethyl acetate. The benzene distilled from this derivative of dimethylamine was extracted with 10 ml. of 6 N hydrochloric acid and this extract placed in the receiver of a distilling apparatus in the boiler of which the basic aqueous solution (from which the dimethylbenzamide was extracted with benzene, above) was heated until its vapors were no longer basic. Evaporation of the distillate to dryness left 1.11 g. of white hygroscopic crystalline material; a negligible part of the bases (in which any dimethylallylamine should presumably be concentrated) liberated from this salt boiled above room temperature.

The material (*ca.* 1 ml., see above) collected in the Dry-Ice trap was allowed to warm to room temperature and thus (except for about 0.1 ml. of higher-boiling material) distilled through a short tube of Drierite into an ampule cooled in Dry-Ice, yield 0.67 g. (34%)⁷ of a mixture of methylacetylene and allene (see below); the action of Nessler's reagent on this material, following the directions of Johnson and McEwen (18), gave 1.03 g. (44%) of crude mercuric methylacetylde; continuous extraction with acetone gave white flaky crystals, m.p. 209° dec. [lit. (18), m.p. 203–204° (uncorr.)].

Second Experiment. A concentrated aqueous solution of allyltrimethylammonium bromide was prepared as follows: in a flask kept cold by immersion in an ice-bath, 65 g. (0.50 mole) of allyl bromide (Eastman White Label) was carefully layered with 120 g. (theory 115.6 g.) of a 25.5% solution of trimethylamine in water; as the two layers slowly merged, the mixture was cautiously swirled from time to time; solution of the last of the allyl bromide was accomplished by shaking the mixture at room temperature for a short time. Excess trimethylamine was then expelled by bringing the solution to its boiling point. After cooling, it was shaken for 15 minutes with silver oxide from 100 g. (theory 85 g.) of silver

⁷ From the fact that only 77% of the theoretical quantity of bases is obtained, it must be concluded that about 23% of the starting quaternary ammonium base is lost during the concentration *in vacuo* at 40–50°; this conclusion is taken into consideration in calculating the yields of products.

nitrate. The resulting aqueous solution of I was concentrated (seven hours) and pyrolyzed (two hours) as before.

Redistillation of the liquid collected in the Dry-Ice trap gave 5.59 g. (34%)⁷ of material boiling principally at -22.7° (pentane thermometer immersed in boiling liquid) at 746 mm., in agreement with a recent value given (19) for the boiling point of methylacetylene. A 43.5-ml. sample of gas removed from this liquid was analyzed in a modified Bunte apparatus (20), absorbing the methylacetylene in Nessler's reagent and the allene in 82.5% sulfuric acid (21); from the values thus obtained (16.6% allene in methylacetylene) and the vapor-pressure-temperature equations given by Livingstone and Heisig (22) for these two substances, it can be calculated that the liquid from which this small sample of gas was removed contained 12.8% allene.

Somewhat less than 1 ml. of the original methylacetylene-allene fraction was not volatile at room temperature; this brownish oil was added to the two-phase distillate collected just before the acid-wash bottle (see above); with cooling, the contents of the latter were also added. The oily epiphase, which decreased somewhat in volume during this acidification, was taken up in ether (after saturating the aqueous phase with sodium sulfate), dried over sodium sulfate and magnesium sulfate, and the ether carefully fractionated off at atmospheric pressure. The residual oil (somewhat less than 10 ml.) was transferred to a smaller flask and divided into the following fractions by distillation through a 10-cm. Vigreux column: A, 1.28 g., b.p. $25-27^{\circ}$ at 100 mm. B, 1.38 g., b.p. up to 60° at 100 mm. C, 1.87 g., b.p. $53-50^{\circ}$ at 50 mm. D, 1.15 g., b.p. up to 70° at 0.6 mm. The residue weighed 1.95 g. (Total yield of neutral materials, about 70%).⁷

Preliminary qualitative tests on A showed that it contained some carbynylic constituent and was only partly water-soluble; it was shaken with 2.0 g. of saturated aqueous sodium bisulfite and the insoluble oil carefully pipetted off, dried over magnesium sulfate, and distilled at atmospheric pressure, giving 0.51 g. of colorless, brilliant oil, b.p. $52-72^{\circ}$, having a characteristic olefinic odor. The ultraviolet absorption spectrum of a solution of 1.8 mg. of this material in 25 ml. of pure *n*-hexane showed four peaks, λ_{\max} 225, 247, 256, and 266 $m\mu$; the shape and location of the three peaks at longer wavelengths were indistinguishable from those observed (see Fig. 1) on a solution of authentic 1,3,5-hexatriene (see below). The intensity of absorption at 256 $m\mu$ ($I/I_0 = 0.422$) compared with that of the same peak of pure authentic hexatriene indicated the presence of 1.86% of this triene in the above water-insoluble fraction, representing a yield of 0.064%⁷ from I; this must be regarded as a minimum yield because of the sensitive nature of this triene and the fact that it was an unexpected product and no special precautions were exercised during its concentration. The 225- $m\mu$ peak is quite alien to the spectrum of 1,3,5-hexatriene and may indicate the presence of some conjugated diene in this fraction; such a diene may also be the source of a crystalline product (rugged colorless granules left on spontaneous evaporation of a ligroin-benzene solution, m.p. $141-144^{\circ}$) obtained (in amount too small for analysis) by refluxing 0.20 g. of this fraction with a benzene solution of 0.24 g. of maleic anhydride [the maleic-anhydride-addition product of 1,3,5-hexatriene melts at about 50° (23)].

Treatment of the above bisulfite extract of fraction A with 7.0 g. of saturated aqueous sodium carbonate gave an ether extract having a distinct odor of propionaldehyde; the extract was treated dropwise with a 2,4-dinitrophenylhydrazine sulfate solution (24a) until a precipitate no longer formed in the drops descending through the ether solution. On shaking, this precipitate dissolved in the ether-phase, which was evaporated to dryness; the residue was twice recrystallized from acetonitrile, clusters of orange needles, m.p. $154.7-155.7^{\circ}$, undepressed by admixture with an authentic sample of propionaldehyde (25) 2,4-dinitrophenylhydrazine.

Fraction B, which gave a strong alcohol-test with ceric-nitrate reagent (24b), was redistilled at atmospheric pressure, giving 0.58 g. (2.4%)⁷ of fairly pure allyl alcohol, b.p. $91-97.5^{\circ}$. Treatment of 0.12 g. of this material with pyridine and 3,5-dinitrobenzoyl chloride (0.5 equivalent) according to Suter (26) gave 0.20 g. of crude allyl 3,5-dinitrobenzoate, m.p. $45-48.5^{\circ}$ (a like sample of authentic allyl alcohol, similarly treated, also

gave 0.20 g. of crude ester, m.p. 48–49°); this derivative was converted to the α -naphthylamine complex (26), dark red needles from ligroin-benzene, m.p. 121–122°, unaffected by admixture with an authentic sample.

Fraction C was identified as α -methyl- β -ethylacrolein (IV) (9.2%)⁷ by conversion of a sample to the 2,4-dinitrophenylhydrazone, bright orange-red clustered plates from acetic acid-acetonitrile, m.p. 161–162°; this material did not depress the melting point of the dinitrophenylhydrazone prepared from authentic IV [b.p. 54–56° at 47.5 mm.; prepared in 41% yield according to Grignard and Abelmann (27)]. The semicarbazone of this aldehyde has been reported to melt anywhere from 187–188° (28) to 207° (29) [see reference in footnote 4 to a compound, m.p. 192°, described by von Braun (4), which may be IV-semicarbazone]. As prepared by us, this derivative is apparently homogeneous (cis-trans isomerism of IV and syn-anti isomerism of its semicarbazone lead to the prediction of four possible forms), sparsely-clustered rough colorless bars from ethanol-water (Anal. Calc'd for $C_7H_{13}N_3O$: C, 54.17; H, 8.44; N, 27.08. Found: C, 54.49; H, 8.24; N, 27.48.), but the melting point varies considerably with the manner in which this constant is secured; heated very slowly from 180°, it melts at 192.2–192.5°; from 190°, at 202.9–203.4°; when inserted into baths maintained at constant temperatures, a clear melt was obtained in 24 seconds at 209° and in 16 seconds at 210°. The semicarbazone is thus not of very great value for the characterization of methylethylacrolein; literature values (30) for the melting point of the dinitrophenylhydrazone are all in substantial agreement.

Authentic 1,3,5-hexatriene (V) was prepared by the action of sodamide on a solution of allyl chloride in liquid ammonia, according to Kharasch and Sternfeld (23). The delicate nature of this triene is not sufficiently stressed by these authors in their directions for its preparation. In order to isolate appreciable quantities of the desired product, it is advisable to sweep vessels with nitrogen, use freshly-distilled ether, carry out distillations at reduced pressure, and add traces of hydroquinone to solutions of the triene which are to be allowed to stand for any length of time or are to be heated. A solution of the crude reaction product in ether was freed of ether and hexatriene by slowly reducing the pressure to 80 mm. and then heating the boiler slowly up to 100°; the distillate (b.p. up to 28°) was condensed in an efficient condenser cooled by circulating ice-water, and collected in a flask cooled in Dry-Ice. Toward the end of the distillation, the product crystallized on the tip of the condenser; this crystalline material (0.47 g.) was carefully removed and used as quickly as possible for the determination of the following physical constants: melting-range –35 to –28° (sample in a sealed capillary tube),⁸ Emich micro-b.p. 74.5° at 748 mm., d_4^{25} 0.7385, n_D^{25} 1.4770; the lack of agreement among previously reported physical constants for 1,3,5-hexatriene (32) undoubtedly reflects the delicate nature of this substance. Kharasch and Sternfeld (23) report the b.p. of V as 76–80°; their values for n_D^{20} (1.4330) and for d_4^{25} (0.7182) both seem low. The crystallization of 1,3,5-hexatriene apparently has not been observed until now.⁸ A solution of V in *n*-hexane gave an ultraviolet absorption spectrum (see Fig. 1) having the following characteristics: λ_{max} 247 m μ ($\epsilon \times 10^{-4}$, 1.63); 256 (2.24); 266 (1.85); data on this spectrum presented by its previous investigators (33) are insufficiently detailed for comparison. These three peaks, with the same relative intensities, but with hypso- or batho-chromic shifts of the group as a whole, are seen in the spectra of other compounds (34) having this system of three conjugated double bonds.⁹

⁸ While this manuscript was being prepared, we received an abstract (31) of a paper by Woods and Schwartzman in which the following constants are reported for a sample of 1,3,5-hexatriene prepared in a different way: m.p. –11°, b.p. 79–80°; the ultraviolet spectrum is also reported, but details of the curve are not included in the abstract.

⁹ Blout and Fields (35) do not present details of the spectrum of 2,4,6-octatriene, stating only that its peak of maximum intensity (at 263 m μ) has some fine structure. It is of interest that the ultraviolet absorption spectrum of 1,3,5-cyclooctatriene (36), in which the ring structure forces the three double bonds to maintain an "all-cis" configuration, is devoid of fine structure.

The remainder of the mixture of ether and V (*i.e.*, after removing the crystalline material as noted above) was treated with a few crystals of hydroquinone and distilled through a 20-cm. Vigreux column at 748 mm., giving, besides ether, a 0.7-ml. fraction, b.p. 68.3–74.7°, m.p. ca. –45° (thermometer in melt), and a 1.0 ml. fraction, b.p. 74.7–75.0°, m.p. ca. –35°.

SUMMARY

The thermal decomposition of allyltrimethylammonium hydroxide has been investigated.

Evidence is presented indicating that the pyrolysis of allylic quaternary ammonium hydroxides is accompanied by some isomerization to the corresponding vinylic quaternary ammonium bases.

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