[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

# THE HYDRATION AND CYCLIZATION OF SOME DIVINYLACETYLENES[1, 2]

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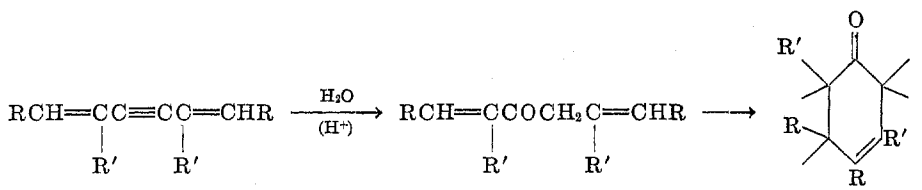
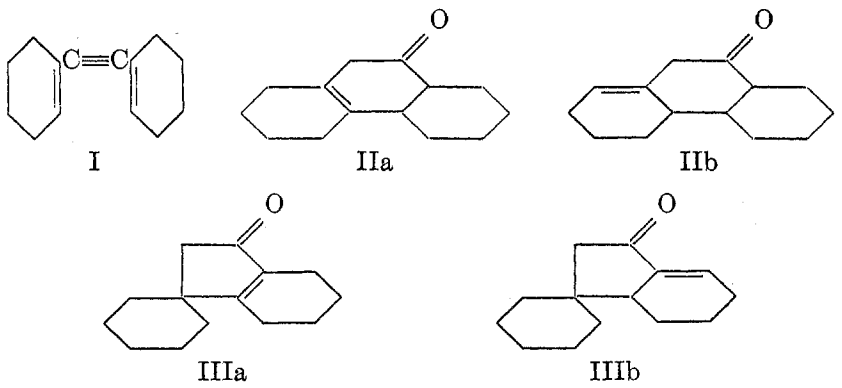
One of the most controversial problems in the whole field of acetylene chemistry concerns the manner in which divinylacetylenes are converted to cyclic ethylenic ketones by treatment with strong acids. The initial observations were due to Marvel and associates, who claimed in a series of thirteen papers (1) that the reaction path is substantially the following.




This formulation (2) was criticized, in the case of dicyclohexenylacetylene (I), by a number of investigators (3–6) who presented good evidence that the product is a mixture of two spiroindanones[3] (III) instead of the dodecahydrophenanthrones (II).



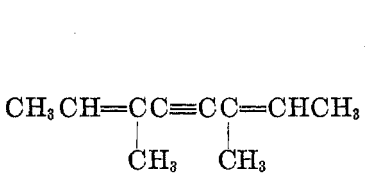

I IIa IIb IIIa IIIb

[1] Paper LVII on substituted acetylenes; previous paper, *J. Am. Chem. Soc.*, **73**, in press (1951).

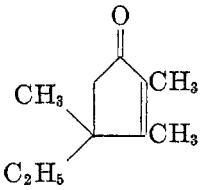
[2] This paper is based on a dissertation by Rev. Ralph B. Davis, C.S.C., in partial fulfillment of the requirements for the Ph.D. degree in the University of Notre Dame, August, 1951.

[3] The indanone structure appears well established by Schwartzman (ref. 6) who chose structure IIIb although ultraviolet absorption data (ref. 5) suggests that IIIa may be the major product.

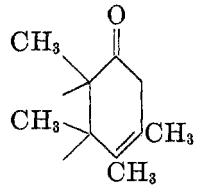
Marvel's claim has also been contradicted for 3,6-dimethyl-2,6,-octadiene-4-yne (IV), which was stated by Nazarov (7) to cyclize to V rather than VI (8).



IV



V

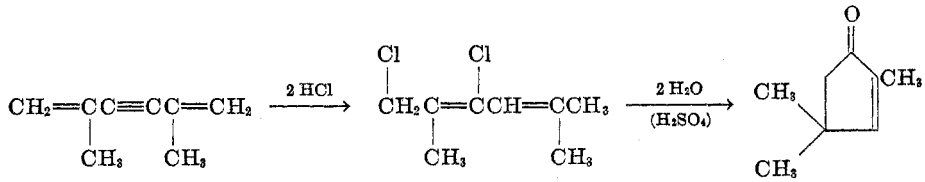


VI

By way of generalization, there are clearly two aspects to the controversy: whether the cyclization step produces a five or a six-membered ring; and whether or not the ethylenic portion is in conjugation with the carbonyl group.

For open-chain divinylacetylenes (*e.g.*, IV) Marvel employed a mixture of acetic and sulfuric acids at 0° and reported poor yields. Nazarov (7) tried various acids and conditions and found that heating IV at 70° with concentrated hydrochloric acid produced V in excellent yield (82%). It is certain that cyclization of a divinylacetylene cannot occur prior to an addition reaction across the triple bond. The hydration of divinylacetylenes, even in the presence of mercury catalysts, is surprisingly difficult. It would seem, therefore, that the remarkable success of the hydrochloric acid method is due to an initial addition of HCl, which occurs far more readily than hydration. We have observed that this is indeed the case, since under suitable conditions divinylacetylene hydrochlorides can be isolated. When these are heated with various acids, cyclization and hydrolysis occur. With 3,6-dimethyl-2,6-octadiene-4-yne (IV) the three reactions (addition of HCl, cyclization, and hydrolysis) proceed together. The same is true of 3,6-diethyl-2,6-octadiene-4-yne (VII), but not for 2,5-dimethyl-1,5-hexadiene-3-yne (IX). The latter (IX) forms a dihydrochloride which is best cyclized by subsequent treatment with 85% sulfuric acid. It is significant that Mitchell and Marvel (8) were unable to affect the cyclization of IX with their acetic-sulfuric acid mixture. The tendency to cyclic ketone formation, no matter how done, is much enhanced by the presence of terminal alkyl groups as in I, IV, and VII.

The cyclization of IX was accomplished in two steps and thus produced 2,4,4-trimethyl-2-cyclopenten-1-one (XI), whose structure was proved by ozonization and ultraviolet absorption. The intermediate dihydrochloride (X) had



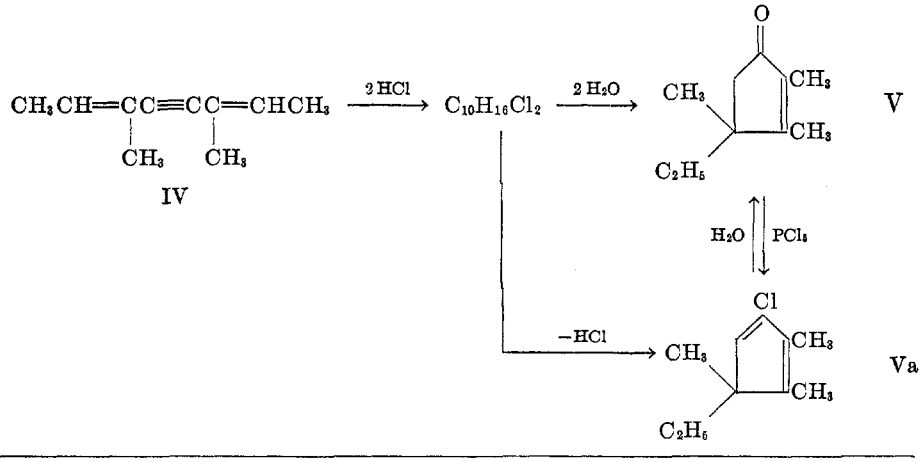
IX X XI

the correct analysis; no attempt was made to establish the structure. The assigned formula (X) appears justified, since it agrees with the structure of ordinary

divinylacetylene dihydrochloride (9) and is compatible with the end-product (XI). It should be mentioned that Nazarov (10) produced XI from IX in another way, namely hydration of the triple bond (to the corresponding dienyl ketone) and cyclization with a mixture of formic and phosphoric acids.

Special attention was given to the tetramethyldivinylacetylene (IV) on account of the Marvel (8)-Nazarov (7) disagreement. Repetition of Marvel's procedure (8) for the cyclization and hydration of IV gave only 6% yield of product, whereas refluxing of IV with 85% formic acid produced a 17% yield of 4-ethyl-2,3,4-trimethyl-2-cyclopenten-1-one (V). Strong hydrochloric acid at 70° proved far superior, *provided vigorous agitation was employed*, affording a 59% yield. Since it was now suspected that the latter method involved *in situ* cyclization of a mono- or a di-hydrochloride, the HCl method was repeated with the addition of cuprous and ammonium chlorides (9) and a little cetyldimethylamine as emulsifying agent. The Nazarov procedure was thereby greatly improved, IV giving an 83% yield of V. Each of the four methods was repeated several times to permit careful study of the products. *All methods gave the same material, proved by ozonization and ultraviolet absorption to be 2,3,4-trimethyl-4-ethyl-2-cyclopenten-1-one* (*V*). Unfortunately, the HCl methods, although affording high yields, gave a product persistently contaminated with a chlorine-containing impurity.

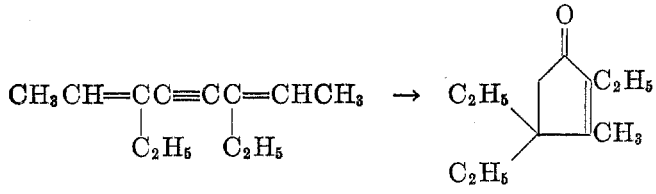
That IV is converted to V by way of intermediate hydrochlorides, though not proved conclusively, is indicated by the following. Reaction of IV with HCl gas in ether produced a mixture of mono- and di-hydrochlorides. When this mixture was treated with aqueous hydrochloric acid, conversion to the ketone (V) proceeded rapidly in good yield. When V was treated with phosphorus pentachloride two products, a monochloro and a dichloro derivative, were obtained. The former, for which structure Va appears reasonable, was readily hydrolyzed back to V; indeed treatment of Va with 2,4-dinitrophenylhydrazine precipitated the 2,4-dinitrophenylhydrazone of V directly.[4] The following mechanism thus fits these facts.




[4] The facile hydrolysis of Va in acidic media seems reasonable on the basis of I-strain theory. *cf.* Brown, *et al.*, *J. Am. Chem. Soc.*, **72**, 2926 (1950); **73**, 212 (1951).

The intermediate dihydrochloride, $C_{10}H_{16}Cl_2$, probably has the structure 2,4-dichloro-3,6-dimethyl-3,5-octadiene. Since this permits of an exceedingly large number of structural, geometrical, and optical isomers, no attempt was made to deduce the exact nature of it.

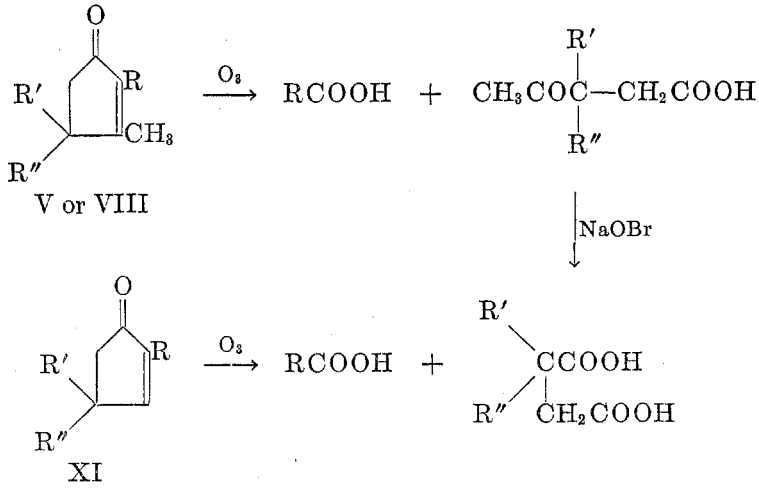
The cyclization of the dimethyldiethyldivinylacetylene (VII) was carried out in various ways, corresponding to the treatments of IV. Marvel's procedure gave a 16% yield. Using the hydrochloric acid-copper catalyst mixture described above, the process was greatly improved, the yield being 65%. All samples proved to be 2,4,4-triethyl-3-methyl-2-cyclopenten-1-one (VIII).



VII VIII

Structures of the end-products, namely the ketones V, VIII, and XI, are based on the following facts. Each one shows exaltation of the molar refraction and produces a scarlet-red 2,4-dinitrophenylhydrazone, suggesting conjugation. The UV-absorption spectra of V, VIII, and XI demonstrated conjugation, but the maxima, at 237, 238, and 229 mμ, respectively, are about 10 mμ lower than predicted by Woodward's rules (5, 12). This is especially significant since Gillam and West (11) have pointed out that 2-cyclopentenones do not obey Woodward's rules, the UV-absorption maxima occuring at wave lengths lower than expected. Conjugate cyclohexenones, on the other hand, follow the rules reasonably well (13).

Conclusive evidence for structures V, VIII, and XI was obtained by ozonization and oxidation of the γ-ketoacids thus produced. In this way V ultimately



V or VIII

XI

gave acetic acid and α-methyl-α-ethylsuccinic acid; XI also produced acetic acid, the other product being α,α-dimethylsuccinic acid. Similarly VIII gave propionic acid and α,α-diethylsuccinic acid. We were especially concerned about the α-methyl-α-ethylsuccinic acid obtained from V since Marvel (8) claimed one of the ozonization products to be α,β-dimethyl-γ-ketovaleric acid. This could not be confirmed and the authenticity of our α-methyl-α-ethylsuccinic acid was established by comparison with an independent sample (14) kindly furnished by Dr. P. A. Smith of the University of Michigan.

## EXPERIMENTAL

*Preparation of substituted divinylacetylenes.* Acetylenic-γ-glycols were prepared from acetone, methyl ethyl ketone, and diethyl ketone, each by reaction with sodium acetylide as described by Macullum (15). The dehydrations to divinylacetylenes were carried out by heating with 50% sulfuric acid (7, 8).

*2,5-Dimethyl-1,5-hexadiene-3-yne dihydrochloride* (X). The dimethyldivinylacetylene (IX) (78 g., 0.735 mole) was stirred vigorously (60°, four hours) in a mixture of 550 ml. of concentrated hydrochloric acid, 2 g. of cuprous oxide, 4 g. of ammonium chloride, 1 g. of copper-bronze powder, and 1 g. of cetyldimethylamine. Carbon dioxide was passed over the surface continuously to avoid contact with air. The mixture was cooled, diluted with 250 ml. of water, and extracted three times with 100-ml. portions of ether. The combined ether extract was washed with 10% sodium carbonate, with water, dried over calcium chloride, and fractionated through a glass helix-packed column. The portion boiling at 79–84° at 18 mm. (79 g., 60% yield), $n_D^{25}$ 1.4868–1.4935, was retained. The middle fraction boiled at 81.5° at 18 mm.; $n_D^{25}$ 1.4923; $d^{25}$ 1.0648.

*Anal.*[5] Calc'd for $C_8H_{12}Cl_2$: C, 53.65; H, 6.75; Cl, 39.59.
Found: C, 53.55; H, 6.88; Cl, 39.47.

*Cyclization of 1,3-dichloro-2,5-dimethyl-2,4-hexadiene* (X). This compound (X, 51 g., 0.286 mole) was stirred rapidly at 60–70°, under carbon dioxide, with 340 g. of conc'd sulfuric acid and 60 g. of water for 24 hours. Water (100 ml.) was then added and stirring continued for two hours at 60–70°. The mixture was then cooled, diluted with 200 ml. of water, and extracted three times with 100-ml. portions of ether. The ethereal solution was washed with 10% sodium carbonate, with water, and dried over calcium chloride. Distillation through a helix-packed column gave 14 g. (39% yield) of 2,4,4-trimethyl-2-cyclopenten-1-one (XI), b.p. 66° at 20 mm.; $n_D^{25}$ 1.4573; $d^{25}$ 0.9044.

*Anal.* Calc'd for $C_8H_{12}O$: C, 77.37; H, 9.74; MR, 36.50.
Found: C, 77.23; H, 9.86; MR, 37.41.

The *semicarbazone* melted at 169–170° [lit. (10) 171–172°] and the 2,4-dinitrophenylhydrazone at 215–216° (uncorr.).

*Cyclization of 3,6-dimethyl-2,6-octadiene-4-yne* (IV). (a) *With hydrochloric acid and catalysts.* The divinylacetylene (IV), 128 g. (0.95 mole), was stirred rapidly under carbon dioxide (70°, three hours) with 400 ml. of conc'd hydrochloric acid containing 1 g. of cuprous chloride, 5 g. of ammonium chloride, 2 g. of copper-bronze powder, and 1.5 g. of cetyldimethylamine. The mixture was cooled, diluted with 400 ml. of water and extracted three times with 100 ml. of ether. The combined extract was washed with 10% sodium carbonate, with water, and dried with potassium carbonate. Fractional distillation (helix-packed column) gave 120 g. (83% yield) of 2,3,4-trimethyl-4-ethyl-2-cyclopenten-1-one (V), b.p. 81–82° at 8 mm.; $n_D^{25}$ 1.4793; $d^{25}$ 0.9268.

*Anal.* Calc'd for $C_{10}H_{16}O$: C, 78.89; H, 10.59; MR, 45.72.
Found: C, 78.18; H, 10.52; Cl, 2.41; MR, 46.61.

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[5] Analyses by Micro-Tech Laboratories, Skokie, Illinois.

The *semicarbazone* melted at 192–194° [lit. (7) 191–192°] and the *2,4-dinitrophenylhydrazone* at 163–164° [lit (8) 158–159°].

(b) *With hydrochloric acid.* Vigorous stirring of 88 g. (0.66 mole) of IV in 400 ml. of conc'd hydrochloric acid for five hours at 70°, the product isolated as described above, gave 59 g. (59% yield) of V; b.p. 86–87° at 10 mm.; $n_D^{25}$ 1.4799; $d^{25}$ 0.9283. Analysis showed 2.35% chlorine (Calc'd, none). Melting points and mixture melting points of derivatives were identical with those cited above.

(c) *With formic acid.* Gentle reflux, ten hours with stirring, of 77 g. (0.57 mole) of IV with 300 g. of 85% formic acid in a carbon dioxide atmosphere gave 14.5 g. of V (16.6% yield), b.p. 91–92° at 12 mm.; $n_D^{25}$ 1.4785; $d^{25}$ 0.9252. Derivatives melted as described above.

(d) *With acetic and sulfuric acids.* Compound IV (100 g., 0.75 mole) was stirred into 400 g. of glacial acetic acid and 270 g. of conc'd sulfuric acid maintained at 0°. The mixture was stirred for two hours and stored in the refrigerator overnight. The product was recovered as directed by Marvel (8). The yield was 7.1 g. (6.3%), b.p. 100° at 15 mm.; $n_D^{25}$ 1.4790. The semicarbazone and the 2,4-dinitrophenylhydrazone melted at 191–193° and 162–163°, respectively, not depressed by mixture with samples described above.

*Cyclization of 3,6-diethyl-2,6-octadiene-4-yne* (VII). (a) *With hydrochloric acid and catalysts.* Heating 123 g. (0.76 mole) of VII at 70° with vigorous stirring in 500 ml. of conc'd hydrochloric acid, 2 g. of cuprous oxide, 4 g. of ammonium chloride, 1 g. of copper-bronze powder, and 1 g. of cetyldimethylamine, as detailed above, gave 88 g. (65% yield) of 2,4,4-triethyl-3-methyl-2-cyclopenten-1-one (VIII), b.p. 117° at 13 mm.; $n_D^{25}$ 1.4780; $d^{25}$ 0.9136.

*Anal.* Calc'd for $C_{12}H_{20}O$: C, 79.94; H, 11.18; MR, 54.96.
Found: C, 79.00; H, 11.09; Cl, 0.98; MR, 55.85.

The *semicarbazone* melted at 198–199° and the *2,4-dinitrophenylhydrazone* at 139–140° [lit. (8) 138–139°].

(b) *With acetic and sulfuric acids.* Following Marvel's directions (8) 100 g. (0.62 mole) of VII in 400 g. of glacial acetic acid and 280 g. of conc'd sulfuric acid gave 17.5 g. (16% yield) of VIII, b.p. 107–109° at 8 mm.; $n_D^{25}$ 1.4780; $d^{25}$ 0.9114. The semicarbazone and the 2,4-dinitrophenylhydrazone melted as above.

*Reaction of 3,6-dimethyl-2,6-octadiene-4-yne* (IV) *with hydrogen chloride in ether.* A steady stream of dry hydrogen chloride gas was introduced beneath the surface of a mixture of 233 g. (1.74 mole) of IV, 150 ml. of anhydrous ether, 2 g. of cuprous chloride, 4 g. of ammonium chloride, and 1 g. of copper-bronze powder. Admission of hydrogen chloride was maintained for six hours with stirring at room temperature. The reaction mixture was then poured over 500 g. of ice. The ether layer was separated, washed several times with water, with dilute sodium carbonate, again with water, and dried over calcium chloride. Fractional distillation, accompanied by copious evolution of hydrogen chloride, gave 246 g. of product, b.p. 68–106° at 16 mm.; $n_D^{25}$ 1.4879–1.5195. Refractionation, again with evolution of hydrogen chloride, gave 186 g. of material boiling at 95–101° at 16 mm.; $n_D^{25}$ 1.5162–1.5190. Analysis of the middle fraction, b.p. 100° at 16 mm.; $n_D^{25}$ 1.5180; $d^{25}$ 0.9859, showed the product was a mixture of hydrochlorides of IV.

*Anal.* Calc'd for $C_{10}H_{15}Cl$: C, 70.37; H, 8.86; Cl, 20.77.
Calc'd for $C_{10}H_{16}Cl_2$: C, 57.98; H, 7.79; Cl, 34.24.
Found: C, 66.00; H, 8.56; Cl, 24.00.

*Reaction of the mixed hydrochlorides of 3,6-dimethyl-2,6-octadiene-4-yne with hydrochloric acid and catalysts.* The mixed hydrochlorides described above (b.p. 95–101° at 16 mm.) (72 g.) were heated at 70° for three hours under a carbon dioxide atmosphere with vigorous stirring in a mixture of 150 ml. of conc'd hydrochloric acid, 1 g. of cuprous oxide, 2 g. of ammonium chloride, 0.5 g. of copper-bronze powder, and 0.5 g. of cetyldimethylamine. After isolating the product in the usual manner, fractionation through a helix-packed column gave 47 g. of 2,3,4-trimethyl-4-ethyl-2-cyclopenten-1-one (V), b.p. 99° at 15 mm.; $n_D^{25}$ 1.4793; $d^{25}$ 0.9263; *semicarbazone*, m.p. 192–194°.

*Reaction of 2,3,4-trimethyl-4-ethyl-2-cyclopenten-1-one* (V) *with phosphorus pentachloride.*

To 229 g. (1.1 mole) of phosphorus pentachloride, cooled in an ice-bath, was added dropwise 152 g. (1.0 mole) of V over a period of two hours and the mixture then was heated at 60° for an additional two hours. Hydrogen chloride was evolved continuously. The product was poured on 1000 g. of ice, stirred cautiously for 30 minutes, and then extracted with three 100-ml. portions of ether. The ethereal solution was washed and dried in the usual way and fractionated, yielding 25 g. (15% yield) of a monochloride, presumably 1,2,5-trimethyl-5-ethyl-3-chloro-1,3-cyclopentadiene (Va), b.p. 69–71° at 13 mm.; $n_D^{25}$ 1.4892; $d^{25}$ 0.9649.

*Anal.* Calc'd for $C_{10}H_{15}Cl$: Cl, 20.77. Found: Cl, 20.50.

The reaction also produced an unidentified dichloride (108 g.) b.p. 89–90° at 13 mm.; $n_D^{25}$ 1.4930; $d^{25}$ 1.0590.

*Hydrolysis of 1,2,5-trimethyl-5-ethyl-3-chloro-1,3-cyclopentadiene* (Va.) Twenty grams of Va was treated with 100 ml. of conc'd hydrochloric acid containing 1 g. of cuprous oxide, 2 g. of ammonium chloride, 0.5 g. of cetyldimethylamine, and 0.5 g. of copper-bronze powder as directed above. The yield of ketone (V) was 11.2 g. (63%), b.p. 99° at 15 mm.; $n_D^{25}$ 1.4793; *semicarbazone*, m.p. 193–195°, not depressed by mixture with an authentic sample. Agitation of the chloride (Va) with 2,4-dinitrophenylhydrazine reagent gave an immediate copious precipitate of the *dinitrophenylhydrazone of V*, m.p. 159–161°.

*Ozonizations.* (a) *Of V.* 2,3,4-Trimethyl-4-ethyl-2-cyclopenten-1-one (V) (25 g.) in 200 ml. of chloroform, cooled in an ice bath, was subjected to a stream of ozonized oxygen for 22 hours. The ozonide solution was added drop-wise to 100 ml. of distilled water with vigorous stirring. After three hours the temperature was raised to 50–60° and stirring continued for an additional ten hours. The mixture was cooled and neutralized with 10% sodium hydroxide. The aqueous layer was separated, acidified to Congo Red with 20% sulfuric acid, and extracted three times with 25-ml. portions of ether. The ether solution was washed twice with 10 ml. of water, dried with magnesium sulfate, and distilled, yielding 3.15 g. of 3-methyl-3-ethyl-4-ketovaleric acid, b.p. 137–138° at 4 mm.; $n_D^{25}$ 1.4532; N. E. calc'd 158.19; N. E. found, 158.17; *semicarbazone*, m.p. 158–159° [lit. (7) 149–150°].

The aqueous layers and washings from the above procedure were distilled and the distillate neutralized with 10% sodium hydroxide. Half of the neutralized solution was evaporated to 15 ml. and 25 ml. of alcohol and 3 g. of *p*-bromophenacyl bromide were added. After two hours at reflux temperature *p*-bromophenacyl acetate crystallized; m.p. 85–86°, not depressed by an authentic sample.

A sample (1.8 g.) of 3-methyl-3-ethyl-4-ketovaleric acid, described above, was added to a solution of 7 g. of bromine and 4.5 g. of sodium hydroxide in 45 ml. of water. A layer of bromoform separated and was recovered by extraction with ether. Distillation of the dried ether extract yielded 2.1 g. of bromoform, b.p. 150–151°. The aqueous layer was concentrated *in vacuo* to 10 ml. and strongly acidified with hydrochloric acid, yielding 1.2 g. of $\alpha$-methyl-$\alpha$-ethylsuccinic acid; N. E. calc'd, 80.08; N. E. found, 81.10; m.p. 103–105°, not depressed by an authentic sample (14).

(b) *Of VIII.* The above procedure was applied to 25 g. of 2,4,4-triethyl-3-methyl-2-cyclopenten-1-one, yielding 1.8 g. of propionic acid, b.p. 138–141°; m.p. −18°; *p*-bromophenacyl ester, m.p. 61–62°, and 1.6 g. of 3,3-diethyl-4-ketovaleric acid, b.p. 149° at 5.5 mm. Reaction of the latter (1.4 g.) with sodium hypobromite solution yielded 1.3 g. of bromoform, b.p. 150–151°, and 1.1 g. of $\alpha,\alpha$-diethylsuccinic acid, m.p. 110–111°; N. E. calc'd 87.1; N. E. found, 87.85.

(c) *Of XI.* Ozonization of 22 g. of 2,4,4-trimethyl-2-cyclopenten-1-one (XI) as described above gave acetic acid, identified as the *p*-bromophenacyl ester, m.p. 84–85° and 3.2 g. of $\alpha,\alpha$-dimethylsuccinic acid, m.p. 139–140°; N. E. calc'd 73.07; N. E. found, 73.05. As required by structure XI, treatment with sodium hypobromite was not needed to produce the succinic acid.

*Ultraviolet absorption spectra* were obtained in 95% alcohol solution, using a Beckman Model DU quartz spectrophotometer. Compound V, 4.09 mg. per liter, showed $\lambda_{max}$ at 237.5 m$\mu$, log $\epsilon$, 4.12. Compound VIII, 6.40 mg. per liter, $\lambda_{max}$ at 238.5 m$\mu$, log $\epsilon$, 4.16. Compound XI, 5.07 mg. per liter, $\lambda_{max}$ at 229 m$\mu$, log $\epsilon$, 4.08.

SUMMARY

1. The hydration and cyclization of three open-chain divinylacetylenes has been found to produce alkyl substituted cyclopentenones. That the latter possess five-membered rings and conjugate unsaturation has been proved by degradation and ultraviolet absorption studies.

2. An improved procedure for the cyclization of some divinylacetylenes is offered.

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