

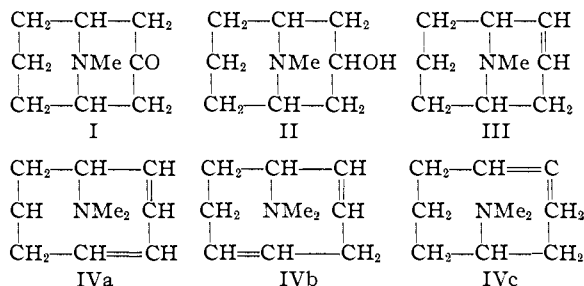
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Validity of the Structure Assigned to Cyclooctatetrene: Pyrolysis of *bis*-Quaternary Ammonium Hydroxides Related to 1,2- and 2,3-Butenes

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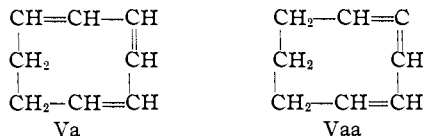
The evidence for the structure of 1,3,5,7-cyclooctatetrene, discovered by Willstätter and Waser¹ and used so widely in theoretical discussions concerning the structure of the aromatic nucleus, rests chiefly on its mode of synthesis from pseudo-pelletierine and on its hydrogenation to cyclooctane. The hydrogenation evidence does not establish the position of the double bonds at 1,3,5,7 for any cyclooctatetrene should hydrogenate to cyclooctane. In the evidence of synthesis there was the tacit assumption that exhaustive methylation would give rise to conjugate unsaturation; but this was the very feature they were trying to establish. Of course, if other types of unsaturation were present, the structural similarity to benzene would disappear. As is well known, cyclooctatetrene is reactive and displays no such inertness as is found in benzene or diphenylhexatriene,² $C_6H_5-(CH=CH)_3-C_6H_5$.

These steps were involved in Willstätter and Waser's synthesis. Pseudo-pelletierine (I) was reduced to II, which was dehydrated to *N*-methylgranatenine (III). Next, III was converted to a quaternary ammonium salt with methyl iodide, then subjected to a Hofmann degradation. The reaction product was assigned structure IVa,

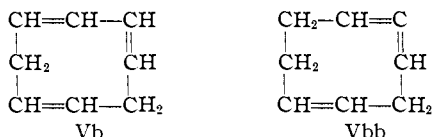


without submitting evidence, however, to show that this cyclooctadiene skeleton must possess 1,3-unsaturation as in (a) to the exclusion of 1,4- or 1,2-unsaturation as in (b) or (c).

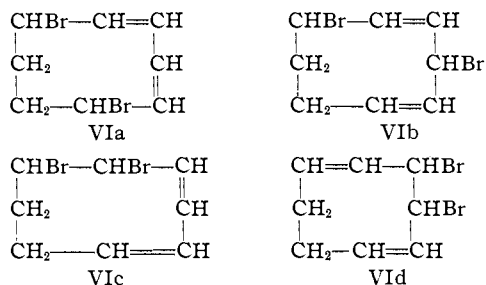
From IVa, a cyclooctatriene was prepared by another process of exhaustive methylation. Its structure was listed as Va, but Vaa may have been produced concurrently. Furthermore, if IVb



and IVc were involved in the exhaustive methylation, two other isomers would appear, namely, Vb and Vbb.



The next step was one of bromine addition to convert C_8H_{10} into $C_8H_{10}Br_2$. If all four cyclooctatrienes participated in this reaction, fourteen such dibromides would be anticipated by normal addition at 1,2- or 1,4- or 1,6-positions (four isomers each from Va and Vaa, and three each from Vb and Vbb). Even if Va were the only isomer, as Willstätter and Waser assumed, these four isomers would be reasonable reaction products



but only from VIa would it be possible to synthesize the conjugated cyclooctatetrene, unless molecular rearrangements were assumed. No evidence eliminated VIb, VIc or VIId as reaction products and no evidence was submitted to uphold VIa.

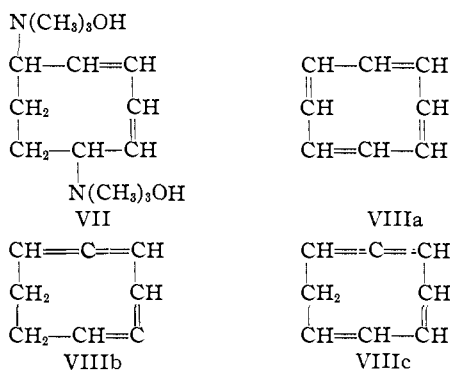
Next, the dibromide (or the dibromide mixture) was heated in benzene with dimethylamine to obtain the *bis-t*-amine, $C_8H_{10}(NMe_2)_2$. Willstätter mentions that this material was not homogeneous but consisted chiefly of an amine which was stable toward acids together with a lesser quantity of an amine which could be hydrolyzed readily. Structures such as $C-C-C-NMe_2$ or $C=C-C-NMe_2$ are stable toward hy-

(1) Willstätter and Waser, *Ber.*, **44**, 3433 (1911); Willstätter and Heidelberger, *ibid.*, **46**, 517 (1913)

(2) Kuhn and Winterstein, *Helv. Chim. Acta*, **11**, 87 (1928).

drolytic scission, but $C=C-NMe_2$ is a structure which hydrolyzes with acids. It is an ammonio analog of the enol ethers and as such it should hydrolyze readily with acids. Structures Vaa and Vbb would yield dibromides which, in turn, would generate the *bis-t*-amines containing the hydrolyzable group $C=C-NMe_2$. It is evident that if Vaa and Vbb are present, this makes a strong case for the presence of all the other isomers.

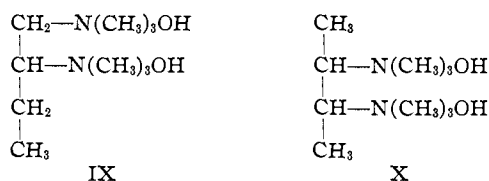
The final step of the synthesis was conversion of the *bis-t*-amine to the *bis*-quaternary ammonium hydroxide, $C_8H_{10}(NMe_3OH)_2$, and pyrolysis of the latter in a Hofmann degradation. The above argument points to the presence of between one and fourteen isomeric quaternary hydroxides. Let us, however, assume the presence of only one of these isomers, namely, the isomer (VII) required by Willstätter and Waser.



Its breakdown should not necessarily follow an exclusive course leading to 1,3,5,7-cyclooctatetrene (VIIIa). There should be concurrent production of the 1,2,4,5- and 1,2,4,6-isomers (VIIIb and VIIIc, respectively). Of course, other isomers would appear if any of the other fourteen hydroxides entered the reaction.

The question involved may be restated as follows. Must a *bis*-quaternary ammonium hydroxide give rise to conjugate double bonds wherever possible and avoid the production of cumulative double bonds? To obtain evidence on this point it was decided to study the decomposition of some simple *bis*-quaternary bases so that the results would be determined unambiguously. The bases selected for study were the 1,2- and the 2,3-disubstituted butanes, IX and X. The products anticipated from IX by pyrolysis would be methylallene and ethylacetylene, but not 1,3-butadiene. From X one would expect 1,3-

butadiene, methylallene and dimethylacetylene.



It is possible to analyze either type of gas mixture volumetrically by absorbing ethylacetylene in alkaline potassium iodomercurate solution, 1,3-butadiene in molten maleic anhydride,³ and methylallene or dimethylacetylene in 82% sulfuric acid. By so doing it was established that IX yielded a mixture containing 44% of ethylacetylene and 56% of methylallene. There was no 1,3-butadiene. The hydrocarbons from X did contain 1,3-butadiene as expected, but it was only to the extent of 42–47% instead of being quantitative. The other 58–53% was a mixture of methylallene and dimethylacetylene. The fact that none of the conjugated hydrocarbon came from IX, and that 1,3-butadiene was not the exclusive product from X casts serious doubt on the structure of Willstätter's cyclooctatetrene.

Experimental Part

Reagents.—Trimethylamine was prepared by the method given in "Organic Syntheses."⁴ It was distilled from a Davis column, b. p. 3–4.5°. The synthesis of pure 1-butene and pure 2-butene was described by Hurd and Goldsby.⁵ Both of these hydrocarbons were available from this source and were used in the present work. The purity of both was reestablished, however, by analytical distillation through the Frey-Hepp column. Pure 1-butene also was prepared in the present investigation by pyrolysis of *n*-butyltrimethylammonium hydroxide.

The pure 1-butene was converted into 1,2-dibromobutane by gradual addition of it into a solution of bromine in carbon tetrachloride at –10°. Purification was by distillation through an efficient vacuum-jacketed column. The fraction collected distilled at 165–166°. Similarly, pure 2,3-dibromobutane, b. p. 158–159°, was prepared from pure 2-butene.

***n*-Butyltrimethylammonium Bromide.**—This salt was prepared by mixing 30 g. of *n*-butyl bromide (b. p. 100°) with 12 g. of trimethylamine in a stoppered flask at 0°. After twelve hours, crystals were noticeable. The mixture was then left at room temperature for a week. The nearly solid mass was crystallized several times from butanol, washed a few times with ether, and centrifuged. The salt was deliquescent. In a sealed tube it melted at 197–198°. The yield was 39.7 g. or 92.5%.

Anal. Calcd. for $C_7H_{13}NBr$: Br, 40.8. Found: Br, 40.8, 40.6.

(3) Tropsh and Mattox, *Ind. Eng. Chem.*, **6**, 104 (1934).

(4) "Organic Syntheses," Coll. Vol. I, 1932, pp. 514–519.

(5) Hurd and Goldsby, *THIS JOURNAL*, **56**, 1813 (1934).

1-Butene.—To 6.65 g. of the bromide dissolved in 30 cc. of water, 3.94 g. of silver oxide was added. The mixture was shaken intermittently for one hour and the silver bromide filtered off. The filtrate was placed in a modified 50-cc. Claisen flask attached in series to a 50-cc. receiver, a small bubbler containing concd. hydrochloric acid, and a 2.5-liter bottle filled with salt solution. The bottle was disconnected at the outset.

The air in the system was displaced by nitrogen, and the contents of the flask heated to incipient boiling. Then the bottle was connected. When all the water was distilled off, the oil-bath temperature was raised slowly to 250°. Vigorous bubbling took place and about 750 cc. of gas was collected in the bottle.

The gas was dried through a soda-lime tube and was liquefied at -80° in the bulb of the Frey-Hepp column.⁵ On distillation, 630 cc. of pure 1-butene was collected between -6.0° and -5.6° . There was no 2-butene.

1,2-Butane-*bis*-(trimethylammonium) Bromide.—A mixture of 22 g. of 1,2-dibromobutane and 10 g. of trimethylamine was left for two weeks at room temperature in a tightly-stoppered flask. The amount of crystals did not increase much after the first week. The excess of trimethylamine was boiled off and absorbed in hydrochloric acid. Then the excess of dibromobutane was decanted and the solid recrystallized from 20 cc. of butyl alcohol, rinsed repeatedly with dry ether, centrifuged, and stored in a vacuum desiccator over sulfuric acid; yield, 4.86 g. or 21%.

Anal. Calcd. for $C_{10}H_{26}N_2Br_2$: Br, 47.87. Found: Br, 47.77, 48.08.

Pyrolysis

Run 1.—A mixture of 4.26 g. (0.0128 mole) of this bromide, 30 cc. of water, and 3 g. (0.0128 mole) of silver oxide was shaken for one hour and the solution was filtered. The filtrate was heated first at 100°, then at 200–250° as described above for the decomposition of butyltrimethylammonium bromide. At the end of the reaction, the apparatus was filled with water to drive over the last portion of gas. In all, 300–310 cc. of gas was obtained.

Run 2.—The same quantities and apparatus were used as before, but this time the solution was allowed to drip into the hot flask (oil-bath at 250°) instead of warming the solution gradually. As before, the apparatus was filled with water at the end of the run. Three hundred thirty cc. of gas was secured.

Analysis.—No 1,3-butadiene was found. It was sought for by passing a sample of the gas through molten maleic anhydride³ at 100°. Ethylacetylene was determined by absorption⁶ in alkaline potassium iodomercurate solution. Methylallene, or a mixture of methylallene and dimethylacetylene, was determined by absorption in 83% sulfuric

(6) Hurd and Spence, *THIS JOURNAL*, **51**, 3356 (1929); Hurd and Meinert, *ibid.*, **53**, 294 (1931).

acid. Air made up 23.0–23.5% of the gas in both runs.

On an air-free basis, run 1 contained 44.5% ethylacetylene and 55.5% methylallene. Run 2 contained 45.5% ethylacetylene and 54.5% methylallene.

2,3-Butane-*bis*-(trimethylammonium) Bromide.—The same general procedure was used as that for the 1,2-analog. The quantities taken were 32 g. of trimethylamine and 52 g. of 2,3-dibromobutane. As before, a small quantity of oil separated in the first twelve hours only to be replaced by small cubical crystals in another twelve hours. The reaction was left for two weeks. After thorough purification, 4.9 g. (or 6.1%) of the salt was obtained.

Anal. Calcd. for $C_{10}H_{26}N_2Br_2$: Br, 47.87. Found: Br, 46.73, 48.90.

Pyrolysis.—Two runs were performed. Run 1 followed the conditions of run 1 of the 1,2-analog, with 3.72 g. of the salt in 30 cc. of water being treated with 2.6 g. of silver oxide. The volume of gaseous decomposition products was 250 cc. Run 2, with 4.00 g. of the salt, 30 cc. of water and 2.8 g. of silver oxide, corresponded in manipulative detail to run 2 of the 1,2-analog. About 240 cc. of gas was collected.

Gas Analysis.—On an air-free basis runs 1 and 2, respectively, analyzed as follows: 1,3-butadiene 42.5, 47.5; methylallene (or methylallene + dimethylacetylene) 57.5, 52.5. In both runs, there was 45–46% of air present.

Summary

Both 1,2- and 2,3-butane-*bis*-(trimethylammonium) bromides have been prepared from pure specimens of 1,2-dibromobutane and 2,3-dibromobutane. Pyrolysis of the *bis*-quaternary hydroxide from the 1,2-salt gave rise to ethylacetylene and methylallene, but no 1,3-butadiene. Pyrolysis of the *bis*-quaternary hydroxide from the 2,3-salt yielded 1,3-butadiene and methylallene (or methylallene + dimethylacetylene), the latter being slightly in excess of the 1,3-butadiene.

The assumption that conjugated unsaturation results exclusively during pyrolysis of the $-\text{CH}_2-\text{CH}-\text{CH}-\text{CH}_2-$ functional group is un-



justified. This assumption was made by Willstätter and Waser in their alleged synthesis of 1,3,5,7-cyclooctatetrene. The fact that 1,3-butadiene was not the exclusive product from 2,3-butane-*bis*-(trimethylammonium) hydroxide casts serious doubt on the structure of Willstätter's cyclooctatetrene.