Zinc Alkali Reduction of 2,2'-Dimethoxybenzoin Methyl Ether to 2,2'-Dimethoxydesoxybenzoin.—One and three-tenths g. of 2,2'-dimethoxybenzoin methyl ether[7] was boiled for three hours with 15 cc. of 15% aqueous potassium hydroxide, 45 cc. of alcohol and 3 g. of zinc dust. The solution was filtered from zinc, acidified, diluted and extracted with ether. The ether solution was washed with water, dried and evaporated. The ether residue crystallized on seeding with 2,2'-dimethoxydesoxybenzoin. The yield was quantitative. A part was recrystallized from petroleum ether and melted at 57°, which is in agreement with the figure reported for dimethoxydesoxybenzoin.[5]

Anal. Calcd. for $C_{16}H_{16}O_3$: $2CH_3O$, 24.21. Found: CH_3O, 24.01, 23.91.

Summary

A new hydroxy derivative of deguelin has been prepared by peroxide oxidation in alcoholic alkali solution. The compound is isomeric with the two known tephrosins, but, unlike these, it is not dehydrated by mineral acids. By the same method a corresponding compound isorotenolone-C has been obtained from isorotenone together with another isomer, isorotenolone-D both of which are also stable to dehydrating agents.

Isorotenolones-I and -II corresponding to the normal rotenolones were obtained by the iodine method and by air oxidation of isorotenone. Isorotenolones-I and -II are dehydrated by mineral acids yielding dehydroisorotenone.

All four isorotenolones are converted into their methyl ethers by silver oxide and methyl iodide.

Methyl isorotenolone-II is transformed into methyl isorotenolone-I by acids but methyl isorotenolone-C and -D are stable.

The four isorotenolones-I, -II, -C and -D all undergo the derritol-rotenol reaction and yield isoderritol and isorotenol.

From the facts presented, it appears that isorotenolone-II is an unstable form having the methoxyl group on the same carbon atom as methyl isorotenolone-I. It is not possible to decide whether the hydroxyl group in the isorotenolones is located on the alpha or beta carbon atom of the dihydro-γ-benzopyrone system. The isomerism of the four isorotenolones may be due to a combination of optical and geometric isomerism due to the presence in the several compounds of different planes of asymmetry of the ring systems joined to the two asymmetric carbon atoms in the dihydro-γ-pyrone systems.

WASHINGTON, D. C. RECEIVED MAY 3, 1934

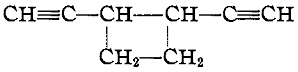
[CONTRIBUTION NO. 130 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & COMPANY]

Acetylene Polymers and their Derivatives. XXI. Polymerization of Vinylacetylene

BY HARRY B. DYKSTRA

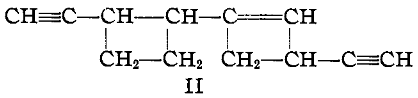
The facts that vinylacetylene is the simplest possible enyne and is conjugated confer some importance on a knowledge of its polymerization. In the first paper of this series,[1] it was reported that the polymerization of vinylacetylene in the presence of cuprous chloride gave a dimer, "acetylene tetramer," which was considered to be octatriene-1,5,7-yne-3. Thermal polymerization, on the other hand, was stated to convert vinylacetylene into viscous drying oils and finally into hard resinous solids. It was suggested that this reaction involved only the ethylenic linkages and resulted in a chain bearing primary acetylenic groups at alternate carbons.

While a decisive demonstration of the structure of the thermal polymers of vinylacetylene is extraordinarily difficult, some evidence has now been obtained that the above view is incorrect; the products more likely consist of cyclobutane and cyclobutene derivatives, such as I, II and III.



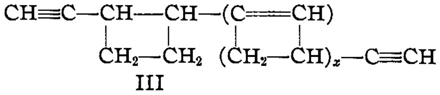
$$\begin{array}{l} CH\equiv C-CH-CH-C\equiv CH \\ \qquad\quad\ |\qquad | \\ \qquad\ CH_2-CH_2 \end{array}$$

I



$$\begin{array}{l} CH\equiv C-CH-CH-C=CH \\ \qquad\quad\ |\qquad |\qquad |\qquad | \\ \qquad\ CH_2-CH_2\ \ CH_2-CH-C\equiv CH \end{array}$$

II



$$\begin{array}{l} CH\equiv C-CH-CH-(C=CH) \\ \qquad\quad\ |\qquad |\qquad\ |\qquad | \\ \qquad\ CH_2-CH_2\ \ (CH_2-CH)_x-C\equiv CH \end{array}$$

III

A very unexpected observation made in the course of this study was that the thermal polymerization of vinylacetylene in the presence of certain acidic materials, *e. g.*, acids, acid anhydrides and phenols, leads to the formation of styrene. Resinous products are also formed, but under suitable conditions approximately one-half of the polymer consists of the dimer, styrene.

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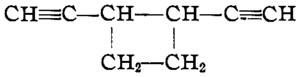
[1] Nieuwland, Calcott, Downing and Carter, THIS JOURNAL, **53**, 4197 (1931).

It is evident from the foregoing remarks that vinylacetylene can undergo at least three distinct types of polymerization. The varied character of the products is clearly shown in Table I, which gives data for the dimers.

TABLE I

DIMERS OF VINYLACETYLENE

Type	Catalyst used	Structure	B. p. (30 mm.), °C.	d_4^{20}	n_D^{20}
A	Cu_2Cl_2	$CH_2{=}CH{-}C{\equiv}C{-}CH{=}CH{-}CH{=}CH_2$	50	0.830	1.576
B	None	 $\begin{array}{l} CH{\equiv}C{-}CH{-}CH{-}C{\equiv}CH \\ \quad\quad\quad\ \vert \quad\ \ \vert \\ \quad\quad\ \ CH_2{-}CH_2 \end{array}$	50–53	.873	1.508
C	Acids	$C_6H_5{-}CH{=}CH_2$	54	.907	1.545

The higher polymers obtained in conjunction with the dimers or by direct polymerization of the latter also exhibit pronounced differences. Polymers of A do not contain acetylenic hydrogen, become insoluble on exposure to air and cannot be depolymerized by heat but decompose violently. Polymers of B contain acetylenic hydrogen, become insoluble on exposure to air and decompose with explosive violence when heated above approximately 110°. Higher polymers of C (polystyrene) as is known do not contain acetylenic hydrogen, do not become insoluble on exposure to air and can be cracked by heat to yield styrene.

Discussion

The mixed polymer obtained by heating vinylacetylene in the absence of a catalyst is a soft, light-colored resin having an average molecular weight equivalent to 6.4 vinylacetylene units. Zerewitinoff determinations indicate the presence of one acetylenic hydrogen for each 3.2 units of vinylacetylene, *i. e.*, two acetylenic hydrogen atoms per molecule of polymer. This is in accordance with the structures I, II and III.

The mixed polymer contains only a very small amount of dimer which can be removed by vacuum distillation. The physical properties of the dimer, particularly its density (Table I), indicate that it has a cyclic structure. The dimer contains two acetylenic hydrogens. On hydrogenation it gives C_8H_{16} (presumably diethylcyclobutane) whose physical properties also suggest a cyclic structure. On the basis of these data, it is concluded that the dimer is diethynylcyclobutane (1). The fact that an analogous structure for the thermal polymers of divinylacetylene has already been established[2] makes this conclusion seem more probable. Cyclobutane structures have also been proposed for allene polymers with some evidence by Lebedev.[3]

Owing to the tendency of vinylacetylene polymers to decompose when heated, only the dimer could be separated from the polymer by ordinary distillation methods. Higher polymers were separated in the hydrogenated form, however, by catalytically hydrogenating the mixed polymer and fractionally distilling the product. In this way there was obtained a trimer, two tetramers and an impure pentamer. The results indicated that the original polymer contained approximately 1% dimer, 3% trimer, 16% tetramer, 8% pentamer and 72% higher polymers. The physical and analytical data for these products (Tables II and III), with the data obtained on the acetylenic hydrogen content of the original mixed polymer, suggest that the products are chain structures of Type III, containing $x-1$ cyclobutane (or cyclobutene) rings for each x units of vinylacetylene.

Styrene was formed when the thermal polymerization of vinylacetylene was carried out in the presence of such acidic materials as acetic acid, chloroacetic acid, benzoic acid, malonic acid, abietic acid, hydrogen chloride, acetic anhydride, phthalic anhydride, pyrogallol and methanol. The conversion of vinylacetylene to styrene during six hours heating at 105° in the presence of 1–10% of the acidic compound generally ranged from 10–15% and the yield based on recovered vinylacetylene ranged from 20–50%. The by-product consisted of resinous material of the type obtained in the absence of a catalyst; no polystyrene could be isolated.

The direct trimerization of acetylenes to aromatics is well known, but this case involving the intermediate dimer, vinylacetylene, apparently represents a new type since 1,4 addition must be involved. The reaction is probably analogous to the dimerization of butadiene (Diels–Alder diene reaction), and may be represented as follows:

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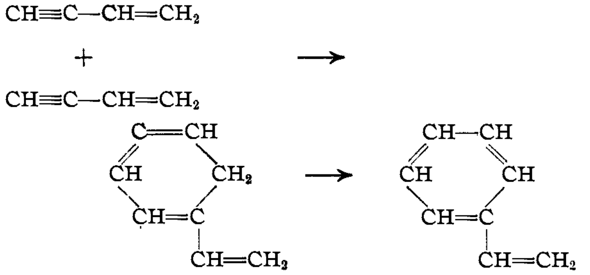
(2) Carothers and Cupery, THIS JOURNAL, **56**, 1167 (1934).

(3) Lebedev, *J. Russ. Phys.-Chem. Soc.*, **43**, 820 (1911); Lebedev and Merezhkorskii, *ibid.*, **45**, 1249 (1913).



IV

The structure of IV, which is shown as a six-membered ring containing a pair of contiguous double bonds, appears to be practically impossible stereochemically. It is conceivable that IV is not actually formed as an intermediate but that a triad shift occurs concurrently with the combination so that styrene is formed directly.

Experimental

Polymerization of Vinylacetylene.—Four steel bombs (200-cc. capacity) each containing 104 g. of vinylacetylene were heated at 105° for six hours. The contents of the bombs were combined and freed from vinylacetylene by distillation under reduced pressure. The residue (140 g.) was a soft, light-colored resin which was readily soluble in acetone, ethyl acetate and benzene, partly soluble in alcohol and insoluble in ligroin. It became relatively insoluble in all solvents when exposed to air. Other properties observed for the mixed polymer are: d_4^{20} 1.0503; n_D^{20} 1.5942; mol. wt. 332, 324, 350; acetylenic hydrogen per unit of vinylacetylene, 0.314, 0.322, 0.303.

Anal. Calcd. for $(C_4H_4)_x$: C, 92.25; H, 7.75. Found: C, 92.10, 92.64; H, 7.87, 7.89.

Hydrogenation of Mixed Polymer.—Hydrogenation of the mixed polymer in ethyl acetate solution using platinum oxide gave varying results, the absorption ranging from 0.62 to 0.84 mole of hydrogen per vinylacetylene unit. For the separation of the lower polymers it was found advantageous to hydrogenate only the alcohol-soluble fraction of the mixed polymer and subject the latter to distillation. In a typical experiment 104 g. of alcohol-soluble vinylacetylene polymer (obtained from 212 g. of the mixed polymer) dissolved in 300 g. of ethyl acetate was found to absorb 1.88 moles of hydrogen. On heating the hydrogenated product to 225° under 1 mm. pressure, 58 g. of clear liquid distillate was obtained. Physical and analytical data for the principal fractions obtained on redistillation are given in Tables II and III.

TABLE II

PHYSICAL CONSTANTS OF DISTILLABLE HYDROGENATED POLYMERS

Fraction	Original polymer, %	B. p., °C.	Mm.	d_4^{20}	n_D^{20}	M_R[a] Calcd.	M_R[a] Found
1	1	*ca.* 120	760	0.772	1.4270	36.94	37.29
2	3	36	0.5	.8591	1.4704	53.22	53.69
3	11	83–6	.5	.8843	1.4808	69.49	70.85
4	5	97–8	.5	.9290	1.5010	69.49	69.83
5	8	140–160	.5	.9739	1.5321	85.58	86.00

[a] Calculations based on formulas given in Table III.

The hydrogenated dimer, trimer and tetramer are colorless mobile liquids, while the pentamer which is probably a mixture of isomers is a straw-colored, viscous liquid. The density of the products is considerably higher than that of acylic hydrocarbons of the same general composition, and definitely indicates that the products are cyclic. The hydrogenated derivatives, particularly the higher members, are probably not completely saturated; they readily discolor solutions of bromine and of potassium permanganate and react exothermically (with partial solution) with concentrated sulfuric acid. The analyses also point to incomplete hydrogenation and indicate the presence of a small amount of oxygen. The hydrogenated pentamer was observed to absorb oxygen from the air.

Vinylacetylene Dimer.—A flask containing 140 g. of crude vinylacetylene polymer was heated at 110° under 1 mm. pressure until distillation ceased. The product collected (1 g.) boiled almost exclusively at 50–53° (30 mm.). It yielded a mercury derivative which rapidly became insoluble on exposure to air. Other properties observed for the dimer are: d_4^{20} 0.873; n_D^{20} 1.5081.

Determination of Acetylenic Hydrogen in Dimer.—A solution of 0.1800 g. of vinylacetylene dimer in 5 cc. of *n*-butyl ether was treated with an excess of methylmagnesium iodide in *n*-butyl ether. Methane was evolved slowly and collected in a gas buret. The mixture was heated to 95° to complete the reaction. A total of 67.8 cc. of gas measured at 29° and 755 mm. was collected. This is equivalent to 1.57 active hydrogens per molecule of dimer, as compared with a theoretical value of 2.00 for diethynylcyclobutane. The low value is believed to result from polymerization of a portion of the dimer during the reaction with the Grignard reagent, for the dimer was found to polymerize readily even in the absence of air.

Hydrogenation of Dimer.—A mixture of 0.762 g. of dimer, 10 g. of ethyl alcohol and 0.1 g. of platinum catalyst was hydrogenated in a Burgess–Parr reduction machine.

TABLE III

ANALYTICAL DATA FOR DISTILLABLE HYDROGENATED POLYMERS

Fraction	Product	Formula[a]	Calcd., % C	Calcd., % H	Calcd., % Mol. wt.	Found, % C		Found, % H		Found, % Mol. wt.[b]	
1	Dimer	C_8H_{16}	85.61	14.39	112	83.35		13.55		..	
2	Trimer	$C_{12}H_{22}$	86.65	13.35	166	87.01	87.32	12.94	13.12	181	175
3	Tetramer	$C_{16}H_{28}$	87.18	12.82	220	87.67	87.37	12.32	12.35	229	220
4	Tetramer	$C_{16}H_{28}$	87.18	12.82	220	87.18	86.65	10.91	11.56	237	226
5	Pentamer	$C_{20}H_{34}$	87.50	12.50	274	87.84	87.18	11.21	10.92	281	269

[a] Assuming cyclobutane structure and complete hydrogenation.

[b] Freezing point method in benzene.

Absorption of hydrogen was very rapid. The mixture was diluted with water and the insoluble portion separated, dried and distilled. Physical and analytical data for the hydrogenated product, probably somewhat impure, are given in Tables II and III.

Polymerization of Vinylacetylene to Styrene.—A solution of 5 g. of acetic acid in 104 g. of vinylacetylene was heated in a steel bomb for six hours at 105°. On distilling the mixture under reduced pressure 70 g. of vinylacetylene, 5 g. of acetic acid and 13 g. of styrene were obtained. The residue (13 g.) consisted of a soft, straw-colored resin apparently identical with the polymer obtained in the absence of acid. The styrene was purified by washing with dilute alkali, drying over calcium chloride and distilling over hydroquinone. The properties observed are: b. p. 144° (54° (30 mm.)); d_4^{20} 0.9065; n_D^{20} 1.5450. The styrene was further characterized by its dibromide, m. p. 73.5°, as compared with a recorded value of 73°,[4] by its oxidation to benzoic acid and by its substantially quantitative conversion to meta-styrene when treated with stannic chloride.

Increase in temperature was observed to increase the rate of conversion of vinylacetylene to styrene but it failed to increase the yield on the basis of unrecovered vinylacetylene. Use of antioxidants in the reaction decreased the rate of resin formation (by-product) only slightly.

The author wishes to express his thanks to Dr. Wallace H. Carothers for his interest in this work and for his helpful suggestions.

Summary

The polymerization of vinylacetylene under various conditions is described. Evidence is presented which indicates that the dimer obtained by thermal polymerization in the absence of a catalyst is diethynylcyclobutane and that the higher polymers have polycyclobutene–cyclobutane structures. Hydrogenated derivatives of the lower polymers are characterized. Thermal polymerization of vinylacetylene in the presence of acidic materials is shown to give substantial quantities of the dimer, styrene.

WILMINGTON, DEL. RECEIVED MAY 3, 1934

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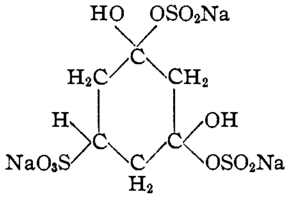
[4] Miller, *Ber.*, **11**, 1450 (1878).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

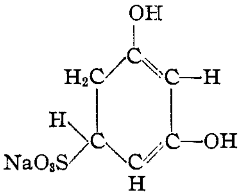
The Action of Sodium Bisulfite on Resorcinol

BY WALTER M. LAUER AND CARL M. LANGKAMMERER

Fuchs and Elsner[1] report the formation of an isolable product resulting from the addition of three molecules of sodium bisulfite to one of resorcinol. They postulate ketonization and accordingly assign structure I to this addition product. Upon treatment with aqueous sodium hydroxide, only two of the three added bisulfite molecules are removed; consequently these investigators assign structure II to the resulting product.

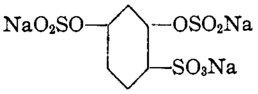


I

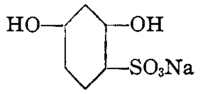


II

Bucherer and Hoffman[2] interpret the action of sodium bisulfite on resorcinol in a different manner and adopt structures III and IV for the addition product and the product obtained after hydrolysis.

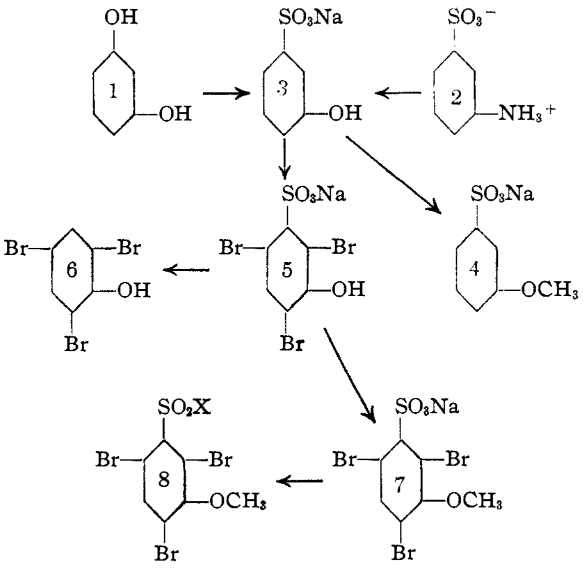


III



IV

On treating resorcinol with bisulfite, boiling the reaction mixture first with base and then with



X = Cl, NH_2, NHC_6H_5

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[1] Fuchs and Elsner, *Ber.*, **53**, 886–898 (1920).

[2] Bucherer and Hoffman, *J. prakt. Chem.*, [2] **121**, 113 (1929). See also Bucherer, *ibid.*, [2] **69**, 71 and 87 (1904); *Z. angew. Chem.*, **17**, 1073 (1904); German Patent 115,335.