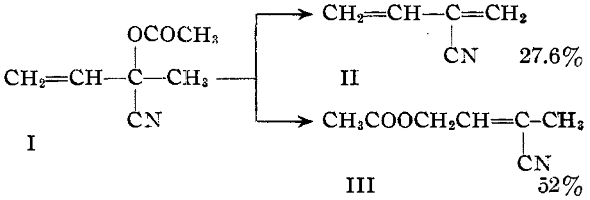
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

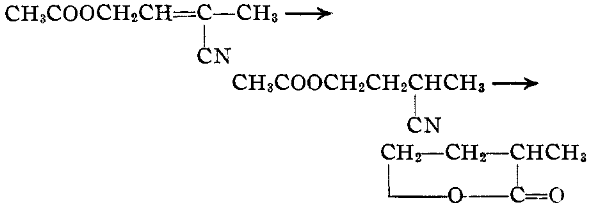
An Allylic Rearrangement in the Pyrolysis of 3-Acetoxy-3-cyano-1-butene[1]

BY C. S. MARVEL AND NEAL O. BRACE

2-Cyano-1,3-butadiene (II) has been prepared by Carter and Johnson[2] by the pyrolysis of 3-acetoxy-3-cyano-1-butene (I) but details on the yields or side reactions involved have not been reported. In repeating this preparation we have found that the main reaction is the allylic rearrangement of the acetoxy group to give 1-acetoxy-3-cyano-2-butene (III); only a small part of the original material is converted to 2-cyano-1,3-butadiene. When the rearrangement product (III) was recycled through the pyrolysis chamber it was recovered unchanged. This rearrangement is related to that reported by Heilbron, James, McCombie and Weedon[3] for 3-acetoxy-1,4-hexadiene.



The structure of the 1-acetoxy-3-cyano-2-butene was established by reduction of the olefin group and subsequent hydrolysis of the nitrile to yield α-methylbutyrolactone, which was identified by its physical properties and those of its hydrazide.[4]



The benzoate of the cyanohydrin of methyl vinyl ketone was also prepared and pyrolyzed. In this case only 10% yield of 2-cyano-1,3-butadiene was obtained and the major product was a rearranged ester isomeric with the starting material. This undoubtedly is also the result of an allylic shift of the benzoxyl group.

Experimental

Methyl Vinyl Ketone Cyanohydrin.—This was prepared by the procedure of Leupold and Vollmann[5] with potassium cyanide as the alkaline catalyst. It was necessary to control the temperature of the reaction mixture very carefully since little addition occurred below 5° and above 10° the product of addition was levulinonitrile.[6] It was also important to remove the phosphoric acid layer promptly at the end of the reaction. When these precautions were followed the yields of cyanohydrin were consistently between 60 and 70% when 200–400 g. of ketone was used. The product boiled at 60° under 5 mm. pressure, $n^{20}_{\rm D}$ 1.4264 (lit.[5] $n^{17.5}_{\rm D}$ 1.4264).

Acetate of Methyl Vinyl Ketone Cyanohydrin.—In a 1-liter, round-bottom flask were placed 428 g. (4.2 moles) of acetic anhydride and 5 g. of acetyl chloride. The flask was equipped with a Y-adapter fitted with a reflux condenser and dropping funnel. To the boiling mixture 388 g. (4.0 moles) of methyl vinyl ketone cyanohydrin was added slowly, and sufficient heat was applied to maintain gentle reflux. About two hours were required for the addition. Heating was continued for one-half hour. Distillation through a 10-in., helix-packed, electrically-heated column yielded 536 g. (96%) of 3-acetoxy-3-cyano-1-butene, b. p. 89–90° at 19 mm., $n^{20}_{\rm D}$ 1.4270, d^{20}_4 1.0070. The literature reports[3] b. p. 89–90° at 17 mm.

Anal.[7] Calcd. for $C_7H_9O_2N$: C, 60.27; H, 6.50; N, 10.04; *MR*, 35.47. Found: C, 60.53; H, 6.31; N, 10.24; *MR*, 35.48.

Benzoate of Methyl Vinyl Ketone Cyanohydrin.—To a mixture of 31.7 g. (0.3 mole) of methyl vinyl ketone cyanohydrin and 42 g. (0.3 mole) of benzoyl chloride in a 600-ml. beaker cooled in an ice–salt-bath was added slowly with stirring 40 g. (0.5 mole) of pyridine, so that the temperature was maintained between 8–15°. Care was taken to keep the mass that forms broken up, in order to aid in control of the temperature. After the pyridine had been added, the lumps were broken up and 500 ml. of water added with stirring. The suspended solid was collected on a Buchner funnel and washed with three 500-ml. portions of water. Recrystallization from a water–ethanol mixture yielded 47.5 g. (79%) of the benzoate of methyl vinyl ketone cyanohydrin, m. p. 49–50°. A small sample was recrystallized from a dioxane–water mixture, m. p. 53.5° and submitted for analysis.

Anal. Calcd. for $C_{12}H_{11}O_2N$: C, 71.62; H, 5.51; N, 6.96. Found: C, 71.44; H, 5.24; N, 6.75.

Pyrolysis of the Acetate of Methyl Vinyl Ketone Cyanohydrin.—Pyrolysis of the acetate of methyl vinyl ketone cyanohydrin was accomplished by passing the ester dropwise through a Pyrex tube (outside diameter 19 mm.) packed for a distance of 12 inches with 4-mm. glass beads and heated to 475° by means of an electrically-heated combustion furnace. The acetate was added at a rate of one drop every three seconds and a diluting stream of purified nitrogen gas was passed through the hot tube during pyrolysis. The pyrolysate was collected in a 500-ml. suction flask cooled by a Dry Ice-bath and connected with a vapor trap cooled with Dry Ice. The liquid pyrolysate was washed with four 100-ml. portions of an aqueous sodium chloride solution, and the organic material separated and dried over anhydrous sodium sulfate. About 0.1 g. of picric acid was added to prevent polymerization and the material was distilled through a 4-in., helix-packed column. From 219 g. (1.56 moles) of the acetate there was obtained 34 g. (27.6%) of 2-cyano-1,3-butadiene, b. p. 30–40° (4 mm.), $n^{20}_{\rm D}$ 1.4450 and 114.0 g. of an ester, b. p. 95° (10 mm.), $n^{20}_{\rm D}$ 1.4500, d^{20}_4 1.0280 that was not the acetate of methyl vinyl ketone cyanohydrin. This represents 52% of the original ester.

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[1] The work described in this communication was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

[2] Carter and Johnson, U. S. Patent 2,205,239 (June 18, 1940).

[3] Heilbron, James, McCombie and Weedon, *J. Chem. Soc.*, 88 (1945).

[4] (a) Adams and Rogers, THIS JOURNAL, **63**, 228 (1941); (b) Cavallito and Haskell, *ibid.*, **68**, 2332 (1946).

[5] Leupold and Vollmann, U. S. Patent 2,166,600 (July 18, 1939).

[6] Dykstra, U. S. Patent 2,188,340 (January 30, 1940).

[7] The microanalyses reported in this work were done by Mr. Howard Clark of the Illinois State Geological Survey.

Anal. Calcd. for $C_7H_9O_2N$: C, 60.27; H, 6.50; N, 10.04; *MR*, 35.47. Found: C, 60.53; H, 6.66; N, 10.29; *MR*, 36.36 (exaltation of 0.9).

Identification of the Ester Produced in the Pyrolysis.—Hydrogenation of 13.9 g. of the recovered ester dissolved in 100 ml. of absolute ethanol was accomplished in an Adams hydrogenation apparatus at room temperature using as catalyst 1 g. of 10% palladium on charcoal. The compound absorbed 82% of the theoretical amount of hydrogen. The catalyst was removed by filtration and the ethanol removed by distillation. Distillation of the residue through a 10-in., helix-packed column yielded 8 g. of a saturated derivative, b. p. 110° (18 mm.), $n^{20}D$ 1.4280.

Anal. Calcd. for $C_7H_{11}O_2N$: C, 59.56; H, 7.86; N, 9.92. Found: C, 58.89; H, 7.21; N, 9.65.

Six grams of the compound was added to a solution of 5 g. of sodium hydroxide in 20 ml. of distilled water in a 100-ml. round-bottom flask fitted with a reflux condenser. The mixture was refluxed for two hours, after which it was cooled in an ice-bath and 9 ml. of 50% sulfuric acid slowly added. The acidified solution was again refluxed for two hours. The organic layer was separated, and the aqueous layer extracted with two 15-ml. portions of benzene. The combined extracts and the original layer were dried over anhydrous magnesium sulfate, the drying agent removed by filtration, and the residue distilled through a 6-in. Vigreux column, giving 2.5 g. of a clear liquid, b. p. 197°, $n^{20}D$ 1.4320, d^{20}_4 1.0570.

Anal. Calcd. for $C_5H_8O_2$: C, 59.98; H, 8.05. Found: C, 59.70; H, 7.73.

Adams and Rogers[4a] report the following constants for α-methylbutyrolactone: b. p. 200–201°, $n^{24}D$ 1.4282, d^{26}_4 1.047. A hydrazide of this material was prepared by treating 1.0 g. with 0.5 g. of 85% hydrazine hydrate in 10 ml. of absolute ethanol. The mixture was refluxed for eight hours and the hydrazide isolated by distillation,[8] b. p. 72–75° (12 mm.). Recrystallization of this material from ethyl acetate yielded white crystals, m. p. 90–91°. This corresponds to the melting point reported by Cavallito and Haskell,[4b] for the hydrazide of α-methylbutyrolactone.

Anal. Calcd. for $C_5H_{12}O_2N_2$: C, 45.43; H, 9.15; N, 21.20. Found: C, 45.70; H, 9.00; N, 20.78.

Pyrolysis of Benzoate of Methyl Vinyl Ketone Cyanohydrin.—Into the hot tube heated to 550° was dropped 169.5 g. of melted benzoate at a rate of one drop every two seconds using some nitrogen gas as a diluent. There was obtained by distillation of the pyrolysis mixture 7 g. (10%) of impure 2-cyanobutadiene, b. p. 24–31° (30 mm.). The remaining residue was washed several times with 5% sodium bicarbonate solution, and then twice with 100 cc. of 5% sodium hydroxide solution. The acid-free material was dried over anhydrous sodium sulfate and distilled from an oil-bath at high vacuum. A small amount of oil with an ester-like odor, b. p. 73–81° (5 mm.), came over first and then 12 g. of liquid, b. p. 150° (1 mm.), $n^{20}D$ 1.5315. This compound is nearly odorless and remained a liquid. It is isomeric with the original benzoate.

Anal. Calcd. for $C_{12}H_{11}O_2N$: C, 71.62; H, 5.51; N, 6.96. Found: C, 70.69; H, 5.28; N, 7.37.

Summary

Pyrolysis of the acetate of methyl vinyl ketone cyanohydrin gives a 27% yield of 2-cyano-1,3-butadiene but the major portion of the ester undergoes an allylic rearrangement to yield 1-acetoxy-3-cyano-2-butene. A similar rearrangement has been observed with the corresponding benzoate.

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(8) Darapsky, Beyer and Neuhaus, *J. prakt. Chem.*, **255**, 145 (1936).

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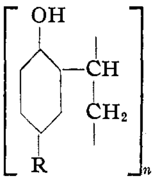
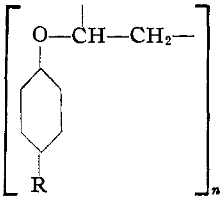
[Contribution from the Industrial Research Institute, University of Chattanooga]

The Pyrolysis of Koresin[1]

By J. W. LeMaistre and R. B. Seymour

Koresin, a synthetic resin used as a tackefier for synthetic rubber, is made[2,3] by condensation of acetylene with 4-*t*-butylphenol. Probable formulations for this resin include structures I–IV.[4]


I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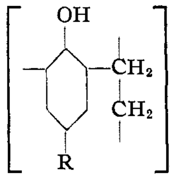
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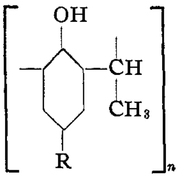
IV

R = *t*-butyl

The possibility of the polymeric material having structure I led us to study the pyrolysis of Koresin as a source of hydroxybutylstyrene. It has been shown[5,6] that vinyl polymers are thermally decomposed into the corresponding monomers or low polymers.

The pyrolysis of Koresin at 300–400° did not produce a substituted styrene but gave 55% (by weight) of 4-*t*-butylphenol, 20% of alkali-insoluble distillate and 25% of tarry non-volatile residue. The yield of 4-*t*-butylphenol was thus 65% of the theoretical.[4]

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(1) Presented at the Meeting-in-Miniature of the Chattanooga Section of the American Chemical Society, October 11, 1947.

(2) G. M. Kline, *Modern Plastics*, **23** [11], 151 (1946).

(3) A. O. Zoss, W. E. Hanford and C. E. Schildknecht, paper presented at the Sept. 1947 A. C. S. meeting, New York.

(4) Actually an excess of acetylene over the 1:1 molar ratio indicated by these structures is used in manufacture. The 1:1 ratio was, however, assumed for calculations of yields and analyses.

(5) R. B. Seymour, *Ind. Eng. Chem.* **40**, 524 (1948).

(6) G. B. Bachman, *et al.*, *J. Org. Chem.*, **12**, 108 (1947).