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).

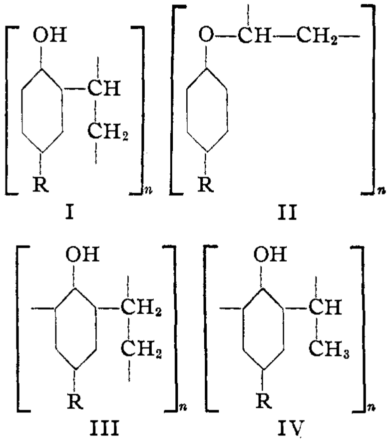
Urbana, Ill. Received January 9, 1948

[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 II III 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).

Since this result did not conform to structure I, some other reactions of Koresin were studied. In carbon tetrachloride solution, Koresin reacted with 0.94 mole of bromine per structural unit of the resin with evolution of hydrogen bromide. The product was a brittle, mahogany-colored resin which lost 60% of its bromine on refluxing for one and one-half hours with 1 *N* alcoholic potassium hydroxide. The brominated resin also lost hydrogen bromide on heating above 180° and, on further heating, gave an alkali-soluble distillate from which 4-*t*-butylphenol was isolated.

The presence of free hydroxyl groups in Koresin was confirmed by acetylation. The saponification equivalent of the ester indicated an acetyl content of 87% of that calculated.[4] This ester was fairly stable to pyrolysis but broke down at 340-400° to give a distillate which was partly soluble in alkali. While the alkali-soluble portion could not be crystallized, 4-*t*-butylphenol was isolated from the distillate by saponification of the alkali-insoluble portion.

The data obtained for acetylation and the degree of bromination are not in accord with structure II nor does the lability of the bromine introduced agree with either I or III The ease of bromination is thought to accord better with structure IV which contains a tertiary carbon atom than with III which was proposed by Kline.[2] Structure II would probably produce the alkylphenol on pyrolysis if its decomposition was similar to simple alkyl aryl ethers[7] but pyrolysis of the brominated product should yield a bromophenol. From an analogy with bibenzyl, structure III would be expected to yield a *t*-butylphenol having methyl groups *ortho* to the hydroxyl group.[8] While structure IV which has also been proposed by Zoss, *et al.*,[3] appears most probable for Koresin, the resin may not be homogeneous and it is not excluded that the other structures may occur to some extent. Structure IV also resembles the formulation of aldehyde-alkyl phenol resins[9] which are likewise said to be effective tackefiers for synthetic rubber. This structure is also in accord with that proposed by Nieuwland and Vogt[10] for the product obtained by the condensation of benzene and acetylene.

Experimental

Pyrolysis of Koresin.—Koresin[11] (20.0 g.) was heated rapidly over a free flame in a distilling flask. Significant formation of volatile material began at a pot temperature of 300°. In the course of one hour the temperature was raised from 300 to 400°. During this time there was steady distillation of an amber oil. Little uncondensable gas was formed. The residue was viscous and froze on cooling to a brittle, black solid, 4.9 g. The distillate was extracted with 5% sodium hydroxide solution, leaving an insoluble amber oil, 4.0 g. On acidification of the alkaline wash a pale yellow oil separated and soon crystallized, 11.0 g. The latter product was recrystallized from *n*-heptane and identified as 4-*t*-butylphenol (yield, 64%) by melting point, 97-98°, as well as by conversion to the benzoate, m. p. 81°, mixed with an authentic sample, 81°.

Bromination of Koresin.—To 1.76 g. of Koresin dissolved in 15 g. of carbon tetrachloride was added a solution of 2.40 g. of bromine (0.0150 mole) in 50 g. of carbon tetrachloride. The mixture soon gave off colorless fumes. After two hours at room temperature, the solution was washed with excess potassium iodide solution. Titration of the latter with standard thiosulfate showed 0.0056 mole of unreacted bromine to have been present, corresponding to a consumption of 0.0094 mole. The carbon tetrachloride solution was evaporated on a water-bath to a mahogany-colored brittle resin which was taken up in dioxane and evaporated again to remove carbon tetrachloride. The residue dried at 100° weighed 2.5 g. (98%). A weighed sample was hydrolyzed by refluxing for 1.5 hours with 1 *N* potassium hydroxide in ethanol and the solution was titrated with standard acid. Alkali consumption was 0.0023 mole per gram of brominated Koresin, calcd. 0.00376 if all the bromine were removed by alkali.

Pyrolysis of Brominated Koresin.—To a solution of 17.6 g. of Koresin in 150 g. of carbon tetrachloride was added dropwise 16.0 g. of bromine. The solution was let stand overnight and then washed successively with water, sodium sulfite solution and water. The solvent was distilled and the residue destructively distilled. When the still temperature reached 180-190°, evolution of hydrogen bromide began and continued as the temperature was raised. Between 270 and 400° an amber liquid distilled, 6.5 g. The residue was a spongy black tar, 9.9 g. The gas absorbed in a water trap was shown by titration with silver nitrate to contain 0.048 mole hydrogen bromide. The liquid distillate was nearly all soluble in 5% sodium hydroxide and the oil separated by acidification of the alkaline solution partly crystallized on standing. The crystals were identified as 4-*t*-butylphenol after recrystallization from *n*-heptane by melting point, 97-98°, and mixed melting point, 97-99°.

Acetylation of Koresin.—Koresin (17.6 g.) was dissolved in 50 g. of acetic anhydride containing 0.5 g. of anhydrous sodium acetate. The mixture was refluxed for two hours and then poured into cold water. The precipitated resin was taken up in 100 ml. of ethyl ether and washed well with sodium hydroxide solution and then with water. The ether layer was dried over anhydrous calcium sulfate and evaporated to yield a brittle, yellow resin, 21 g. (96%); saponification equivalent (by refluxing with 1 *N* potassium hydroxide in ethanol for one hour), 251, calcd., 218.

Pyrolysis of Acetylated Koresin.—Acetylated Koresin (15 g.) was heated in a distilling flask. Decomposition began at a still temperature of 340° and continued slowly as the temperature was raised to 400°. The residue was a black tar, 6 g. The oily distillate, 6.5 g., smelled of acetic acid. The distillate was washed with sodium hydroxide solution and the insoluble portion, 4.5 g., was refluxed for one-half hour with 25 ml. of 10% potassium hydroxide in ethanol. Water was added, the ethanol distilled off and the residual solution acidified. The separated oil slowly crystallized and, after recrystallization from *n*-heptane, was identified as 4-*t*-butylphenol by melting point, 96-97°, and mixed melting point, 97°.

Summary

1. The principal product of pyrolysis of Koresin is 4-*t*-butylphenol.

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(7) Meyer and Hofmann, *Monatsh.*, **38**, 343 (1917).

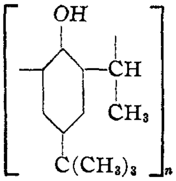
(8) Hurd, "The Pyrolysis of Carbon Compounds," The Chemical Catalog Co., Inc. (Reinhold Publ. Corp.), New York, N. Y., 1929, p. 30.

(9) G. E. P. Smith, Jr., J. C. Ambelang and G. W. Gottschalk, *Ind. Eng. Chem.*, **38**, 1166 (1946).

(10) J. A. Nieuwland and R. R. Vogt "The Chemistry of Acetylene," Reinhold Publishing Corp., New York, N. Y., Chap. 5, p. 154.

(11) Obtained from General Aniline and Film Corporation.

2. Koresin reacts with approximately one mole of bromine per structural unit of the resin. The bromine introduced is labile toward heat and toward alkali.
3. Acetylation of Koresin indicates approximately one free hydroxyl group per structural unit.
4. The probable structure of Koresin is



CHATTANOOGA, TENN. RECEIVED DECEMBER 1, 1947

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

The Mechanism of the Methane Fermentation

BY A. M. BUSWELL AND F. W. SOLLO, JR.[1]

Three possible mechanisms for the methane fermentation of acetic acid are suggested by the findings and reasoning of previous workers in this field. From the work of Omelianskii[2,3] and Söhngen[4,5] we would expect a preliminary decomposition of the acetic acid to hydrogen and carbon dioxide, with subsequent reduction of carbon dioxide to methane by the hydrogen. Barker's work[6] indicates that carbon dioxide would be directly reduced to methane and the acetic acid thereby oxidized to carbon dioxide. The reasoning of Buswell and Neave[7] leads to simple decarboxylation as the mechanism.

The first mechanism was based on the similarity of the hydrogen and methane fermentations, but the low concentration of hydrogen found in the gas from the methane fermentation of acetic acid is evidence against this mechanism. If we examine the data of Symons and Buswell[8] we find that only 3.5 liters of methane was formed over a period of one hundred days with regular circulation of hydrogen and carbon dioxide through a culture of 2.0 liters total volume. In the same time, such a culture fermenting acetic acid could be expected to form 75[8,9] liters of methane.

The second mechanism avoids this weakness by implying a direct reduction of the carbon dioxide, without the intermediate stage of free hydrogen. This mechanism seems rather indirect and involved, but parallels that found by Barker in the oxidation of alcohols.

The last mechanism appears to be the simplest and most direct. A similar reaction *in vitro* is the chemical decarboxylation of sodium acetate with sodium hydroxide. The internal oxidation reduction could be effected by the transfer of the hydrogen atom from the carboxyl to the methyl group. Evidence against this mechanism is found in Thayer's work.[10] He reasoned that this reaction was a decarboxylation, and that the fermentation of propionic and butyric acids should yield ethane and propane. However, his results were entirely negative, for no hydrocarbon other than methane was found. This has been confirmed in all work where the gas was analyzed. Therefore, if we are to accept this mechanism of simple decarboxylation for acetic acid, it must be as a special case, not applicable to the higher fatty acids.

Barker, Ruben and Kamen[11] found evidence for the reduction of carbon dioxide in the fermentation of acetic acid through the use of $C^{11}O_2$, but they stated that the radioactive methane found might have been due to the presence of methanol carried over with the inoculum. It should also be mentioned that these workers were using a pure culture of *Methanosarcina methanica*, and that even if methane should be formed by reduction of carbon dioxide in that case, that might not be the predominant mechanism in the general methane fermentation where a mixed culture is used.

This question of the mechanism of fermentation of acetic acid is of more than academic interest. Culture failure is almost invariably accompanied by, or preceded by, the accumulation of high concentrations of volatile organic acids, largely acetic. Thus any information concerning this mechanism might lead to methods of treatment or operation which would alleviate or prevent this accumulation of acids and possibly the failure of many cultures.

It may be seen at once that if the carbon of the carbon dioxide were marked isotopically, this question of mechanism could be settled. If either of the mechanisms involving reduction of carbon dioxide were involved, the methane produced should be similarly marked. If the reaction were a simple decarboxylation, the methane should not be so marked.

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(1) Present address: National Aluminate Corporation, 6216 W. 66th Place, Chicago, Illinois.

(2) W. Omelianskii, *Zentr. Bakt.*, II Abt., **8**, 193, 225, 257, 289, 321, 353, 385 (1902).

(3) W. Omelianskii, *ibid.*, II Abt., **11**, 369 (1904).

(4) N. L. Söhngen, *Rec. trav. chim.*, **29**, 238 (1910).

(5) N. L. Söhngen, *Proc. Roy. Acad. Amsterdam*, **8**, 327 (1905).

(6) H. A. Barker, *Arch. Mikrobiol.*, **7**, 404 (1936).

(7) A. M. Buswell and S. L. Neave, Ill. State Water Survey, Bull. No. 30, 1930.

(8) Ill. State Water Survey, Bull. No. 32, 1936, p. 47.

(9) D. Tarvin and A. M. Buswell, THIS JOURNAL, **56**, 1751 (1934), p. 1752, Table I.

(10) L. A. Thayer, *Bull. Am. Assoc. Petroleum Geol.*, **15**, 441 (1931).

(11) H. A. Barker, S. Ruben and M. D. Kamen, *Proc. Natl. Acad. Sci.*, **26**, 426 (1940).