Synthesis.—A solution of 5 g. of benzalpinacoline in 50 cc. of absolute ether was saturated with hydrogen chloride. By evaporation of the ether in a vacuum at room temperature, a white residue of 1-chloro-1-phenyl-4,4-dimethyl-pentanone-3 resulted. This somewhat unstable substance, without further purification, was dissolved in 50 cc. of absolute ether and treated with 0.8 g. of sodium wire chips. After the reaction moderated the flask contents were refluxed and intermittently shaken for an hour, and then allowed to stand for 12 hours. A white precipitate of sodium chloride appeared. The excess of sodium was carefully removed and 50 cc. of water added. No evolution of gas was observed, the salt dissolved and white crystals collected at the liquid interface. These were separated and another small amount was later deposited from the ether layer; yield, 0.4 g., or 7.9%. Some benzalpinacoline was recovered. The product thus prepared melted alone at 208.5°, the dimolecular reduction product of benzalpinacoline behaved similarly, and a mixture of the two compounds likewise melted at 208.5°. They are, therefore, identical.

Summary

1. Benzalpinacoline, reduced by catalytic means and by metal combinations, yielded 3 new substances.

2. The structure of 2 of these, ω-benzylpinacoline and 2,2,9,9-tetramethyl-5,6-diphenyl-decandione-3,8, have been established by independent syntheses.

3. The third compound, presumably β-phenylethyl-*tert*-butyl carbinol, is still under investigation.

MIDDLETOWN, CONNECTICUT

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

POLYMERIZATION OF ALLYL CINNAMALACETATE[1]

BY F. F. BLICKE

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Acrylic acid, because of its unsaturated nature, is very readily polymerized; the same behavior characterizes the substituted acrylic acids of the type R—CH=CH—COOH.

β-Phenylacrylic acid (cinnamic acid) occurs naturally in several polymeric forms, and in the form of its allyl ester polymerizes under the influence of heat;[2] the ethyl and propyl esters do not polymerize under the same conditions.

Some years ago it was shown that another analog of acrylic acid, β-furfuracrylic acid, when converted into its allyl ester, is also prone to polymerization.[3]

At the suggestion of C. Liebermann, made shortly before his death, a

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[1] This investigation was begun at the Technische Hochschule, Berlin, in 1914, and completed at the University of Michigan.

[2] (a) Liebermann and Zsuffa, *Ber.*, **44**, 841 (1911). (b) Liebermann and Kardos, *ibid.*, **46**, 1055 (1913). Seeligmann, *Dissertation*, Karlsruhe, **1906**.

[3] Blicke, *Ber.*, **47**, 1352 (1913).

study was undertaken of the behavior of the allyl ester of cinnamalacetic acid (cinnamenylacrylic acid) toward heat.

When subjected to heat the liquid, monomolecular allyl cinnamalacetate gradually became more and more viscous and, if heated long enough, was finally converted into an amber-like solid. Analysis of this material showed that it had the same percentage composition as the monomolecular ester.

The polymerized ester was readily hydrolyzed to an amorphous acid; an analysis showed that this acid had the same percentage composition as cinnamalacetic acid.

Monomolecular cinnamalacetic acid, when heated with barium hydroxide, loses carbon dioxide and yields not phenylbutadiene, as would be expected, but a mixture of several liquid, polymeric modifications of the latter substance.[4]

The amorphous acid, when heated with barium hydroxide, yielded a small amount of an oil of aromatic odor resulting, undoubtedly, from the elimination of carbon dioxide from the acid. It was thought that the identification of this oil would throw light on the constitution of the amorphous acid. The oil boiled over a range of 100°, under 10 mm. pressure, thus indicating that it consisted of a mixture of at least 2 compounds; no constant-boiling portion could be isolated from the small amount of oil obtained and the expense of the material made the preparation of larger amounts impossible. The oil decolorized bromine in dissolved carbon disulfide, and also aqueous potassium permanganate, proving the presence of at least 1 unsaturated constituent. Analytical results obtained with 1 fraction of the crude oil did not quite correspond to those calculated for phenylbutadiene.

It is very probable that the commercial grades of allyl alcohol and allyl chloride also undergo spontaneous polymerization. A commercial allyl alcohol, which had remained in a preparation closet for a number of years, in a cork-stoppered bottle, was found to be in a sirupy condition. Although monomolecular allyl alcohol is very soluble in water, a considerable amount of the sirup was found to be insoluble in this solvent. The viscous, water-insoluble substance dissolved readily in chloroform and, on the addition of ether to the solution, a yellow gum was precipitated. Prolonged treatment with ether during the course of several weeks converted the gum into a hard, brittle resin. Analysis of this material gave results which, although comparable with those calculated for allyl alcohol, showed greater variation than could be attributed to analytical errors. Nevertheless, considering the amorphous nature of the product and the great difficulty in purifying such material, it is quite possible that

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[4] Liebermann and Riiber, *Ber.*, **33**, 2400 (1900); **35**, 2696 (1902). Doebner and Staudinger, *ibid.*, **36**, 4318 (1903).

the amorphous substance really represented polymerized allyl alcohol. When the material was subjected to heat a considerable amount of allyl alcohol was driven off, probably formed by depolymerization of the resinous material. The allyl alcohol was identified by its characteristic odor and by its melting point.

A very old specimen of allyl chloride was found to consist mainly of a black, tarry mass. The latter was soluble in ether, acetone and benzene but insoluble in alcohol. From an acetone solution of the material an oil was precipitated by the addition of alcohol. No solid product could be obtained.

Experimental Part

Allyl Cinnamalacetate, $C_6H_5CH : CHCH : CHCO_2CH_2CH : CH_2$.—One part of concd. sulfuric acid was added, drop by drop with constant agitation, to 3.5 parts of a well cooled technical grade of allyl alcohol.[5] After the addition of 2 parts of cinnamalacetic acid the mixture was heated in a bath for 15 hours, the bath temperature being kept at 90–95°. The reaction mixture was then poured into water, the oily ester dissolved in ether and the ether solution shaken with dil. sodium carbonate solution to remove unchanged cinnamalacetic acid. In order to purify the ester the crude material was subjected to a vacuum distillation. The distillate, b. $p._{20\ mm.}$ 195–215°, was redistilled; b. $p._{20\ mm.}$ 210°; it is light yellow and possesses a high index of refraction. The material is very soluble in alcohol, ether and acetone; yield, 45–50%.

The ester is readily hydrolyzed by dil. alcoholic potassium hydroxide; cinnamalacetic acid, m. p., 166°. A carbon disulfide solution of the ester decolorizes bromine and aqueous potassium permanganate instantly.

The molecular weight of the ester, using the boiling-point method with benzene as a solvent, was found to be 222; calc. 214.

Analysis. Calc. for $C_{14}H_{14}O_2$: C, 78.50; H, 6.54. Found: C, 78.12; H, 6.80.

As is well known, unsaturated compounds, under the influence of concd. acids or alkali, often undergo rearrangements due to a shifting of a double bond. It was not entirely certain, therefore, that the ester prepared by the above method would be the allyl ester, since an isomeric compound, the propenyl ester, might have been produced. However, positive results obtained with two simple tests showed that the ester was the desired allyl compound: (1) the deep red color produced by the addition of phloroglucinol-hydrochloric acid[6] to the material, and (2) the absence of a precipitate of mercurous acetate when the substance was mixed with mercuric acetate[7] have been shown to be reliable tests for distinguishing between the allyl and propenyl groups. Recently Claisen[8] has proved that the latter test must be applied with caution in the case of certain complicated allyl compounds.

Bromination of the Ester.—The ester, dissolved in ligroin, instantly decolorized an equal molecular equivalent of bromine, dissolved in carbon disulfide. Upon removal

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[5] The ester was also made from allyl alcohol (60–70%) obtained from a firm in this country. In this case the proportions of reacting materials used were: concd. sulfuric acid 2 parts, allyl alcohol 5 parts, and cinnamalacetic acid 2 parts. The mixture was heated to 70–80° in a bath for 30 hours. When the temperature was allowed to exceed 80° a sudden and violent reaction took place; yield, 45%.

[6] Kobert, *Z. anal. Chem.*, **46**, 711 (1907).

[7] Balbiano, *Ber.*, **36**, 3578 (1902).

[8] Claisen, *J. prakt. Chem.*, **105**, 69 (1922).

of the solvent a brown oil was obtained which could not be converted into a crystalline product; the oil decolorized aqueous potassium permanganate.

A carbon disulfide solution of bromine (2½ molecular equivalents) was slowly added to the ester (1 equivalent) dissolved in ligroin. The reaction was carried out in sunlight. After the addition of the first equivalent of bromine the decolorization of the latter took place slowly, toward the end of the reaction with the evolution of a small amount of hydrogen bromide. After removal of the solvent in a desiccator containing paraffin, a brown oil, mixed with crystals, was obtained. After severalre crystallizations from alcohol a colorless product, which melted at 111–112°, resulted, which was soluble in ether and benzene. The material thus obtained contained alcohol of crystallization. This was removed only very slowly by heating the substance in a vacuum. The alcohol-free product melted at 126°. It was found that the alcohol could be removed most effectively by dissolving the alcohol-containing material in acetone and adding small amounts of potassium permanganate, dissolved in the same solvent, until a slight, permanent permanganate color was obtained. After 2 recrystallizations from acetone and 1 from ether, beautiful crystals possessing a silky luster resulted; m. p., 126°. This material proved to be allyl cinnamalacetate hexabromide.

Analysis. Calc. for $C_{14}H_{14}O_2Br_6$: C, 24.22; H, 2.01; Br, 69.14. Found: C, 24.35; H, 2.28; Br, 69.50.

Polymerization of the Ester.—The monomolecular ester was poured into small glass bulbs, each containing about 7 g. of the ester; the bulbs were then evacuated and sealed. The bulb of a vapor-jacket, such as is used in the Victor Meyer method for the determination of molecular weights, was partly filled with nitrobenzene. A number of the small bulbs were then suspended just above the surface of the nitrobenzene and the latter brought to the boiling point. The material was heated in the hot vapor (210°) continuously for 7 days.

The ester gradually became more and more viscous and after it had been heated for the required time it was converted into a light yellow, transparent mass which was almost solid. The glass bulbs were then crushed and the product was dissolved in warm acetone. After filtration, the solution, previously cooled to 0°, was poured into a large volume of cold alcohol. A finely divided, light yellow, amorphous precipitate was obtained. For further purification the material was extracted with absolute alcohol, for 8 hours, in an apparatus designed especially for this purpose.[9] The polymerized ester was finally obtained in the form of an amorphous, amber-like solid. The yield of solid product was about 25% of the amount of monomolecular ester used.

Analysis. Calc. for $(C_{14}H_{14}O_2)_x$, C, 78.50; H, 6.54. Found: C, 78.41; H, 6.79.

Monomolecular ester which had been exposed to the sunlight for some days in a loosely stoppered flask gradually became quite viscous, and upon addition of alcohol a white, gummy precipitate was obtained. The yield of the latter was so small, however, that the material could not be further investigated. It was, no doubt, a product of the monomolecular ester which had been polymerized by the action of light and air, similar to the polymerization products obtained by Liebermann and co-workers[10] with ethyl and allyl cinnamate.

It was found that the allyl ester of furfuracrylic acid under the above conditions also becomes very viscous after being exposed to bright light for 3 months. Upon the addition of ether, in which the monomolecular ester is very soluble, an amorphous product was obtained. Ester which had been exposed to the light in sealed tubes, or ester exposed to the air while protected from light, remained unchanged.

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[9] Blicke, *Chem.-Ztg.*, **67, 68,** 424 (1915).

[10] Ref. 2a, p. 842. Ref. 2b, p. 1056.

The Acid from the Polymerized Ester.—The polymerized ester was hydrolyzed by dissolving it in 15 parts of acetone and adding to the boiling solution 5 equivalents, based on the monomolecular ester, of alcoholic potassium hydroxide. The latter was added, drop by drop, at such a rate that the material remained in solution continually during the hydrolysis. After the mixture had been heated for 6 hours about $^2/_3$ of the solvent was removed by distillation, the solution diluted somewhat and the remainder of the solvent driven off with steam. The residue was poured into a considerable volume of water and ice and acidified with dil. sulfuric acid. After 8 hours the liquid was decanted from the precipitated material. The yield of the slightly yellow, amorphous acid thus obtained was quantitative.

Analysis. Calc. for $(C_{11}H_{10}O_2)_x$: C, 75.86; H, 5.74. Found: C, 75.51; H, 6.00.

The finely powdered acid was intimately mixed with 3 times its weight of anhydrous barium hydroxide and an equal weight of coarse sand. A layer of the mixture was placed in a combustion tube which was closed at one end. The tube was heated until the material had become somewhat viscous and a suction flask was then attached to the open end of the tube. The apparatus was evacuated through the suction flask and heat again applied to the tube. The amorphous material swelled, gradually decomposed and a dark colored oil was slowly driven into the receiver. The latter was dissolved in absolute ether and dried with fused sodium sulfate. A portion of the oil, b. p.$_{10\ mm.}$ 120–140°, was analyzed.

Analysis. Calc. for $C_{10}H_{10}$ (phenylbutadiene): C, 92.23; H, 7.77. Found: C, 90.65; H, 7.65.

Summary

1. The preparation of allyl ester of cinnamalacetic acid and its hexabromide is described.

2. When heated the ester polymerized to a considerable extent to an amorphous, amber-like material which had the same percentage composition as the monomolecular ester.

3. The polymerized ester was readily hydrolyzed to an amorphous acid which had the same percentage composition as cinnamalacetic acid. When the acid was heated with barium hydroxide a mixture of liquid compounds, undoubtedly hydrocarbons, resulted; the latter were formed by the elimination of carbon dioxide from the amorphous acid.

Ann Arbor, Michigan

[Contribution from the Chemical Laboratory of the University of Michigan]

THE NITRATION OF 1,1'-BINAPHTHYL

By C. S. Schoepfle

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In the course of an investigation it became necessary to prepare 4-nitro-1,1'-binaphthyl for use as an intermediate. A mononitro- and dinitro-1,1'-binaphthyl are described in the literature by Julius[1] who obtained the former by nitrating 1,1'-binaphthyl in acetic acid at room temperature with twice its weight of 47.5% nitric acid. In attempting to repeat this experiment we found that there was no appreciable nitration of the bi-

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[1] Julius, *Ber.*, **19**, 2550 (1886).