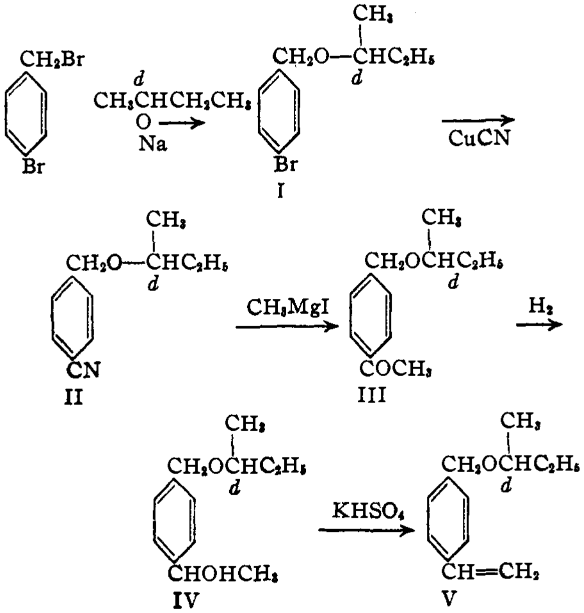
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

An Optically Active Styrene Derivative and its Polymer[1]

BY C. S. MARVEL AND C. G. OVERBERGER

The polymerization of optically active vinyl monomers[2] has been found useful in studying the kinetics of polymerization. The present work was undertaken to increase the number of optically active vinyl monomers available for this type of research.

The method used to obtain the optically active styrene derivative is outlined



Many of these reactions were first carried through with the methyl benzyl ether series so that there would be the least possible waste of the optically active *s*-butyl alcohol in the final synthesis. Since some of these derivatives are new, they are recorded in the experimental part of this paper.

The optically active styrene derivative (V) obtained in this synthesis had a specific rotation of +12.07° when prepared from *d*-*s*-butyl alcohol with a rotation of +11.5°. The change in specific rotation during polymerization was not great; the polymer had a specific rotation of +10.15° based on the monomer unit. In kinetic work this means an observed rotation change of 0.92° to 0.77° over a period of twenty-seven hours. The readings made at two to three hours intervals varied only by 0.03 to 0.04°. Since the polarimeter cannot be read with greater accuracy than ±0.01°, due to convection currents, the progress of this polymerization cannot be very accurately followed by polarimetric methods. However, taken as a whole the experiment plotted in the curve indicates that the polymerization follows first order kinetics.

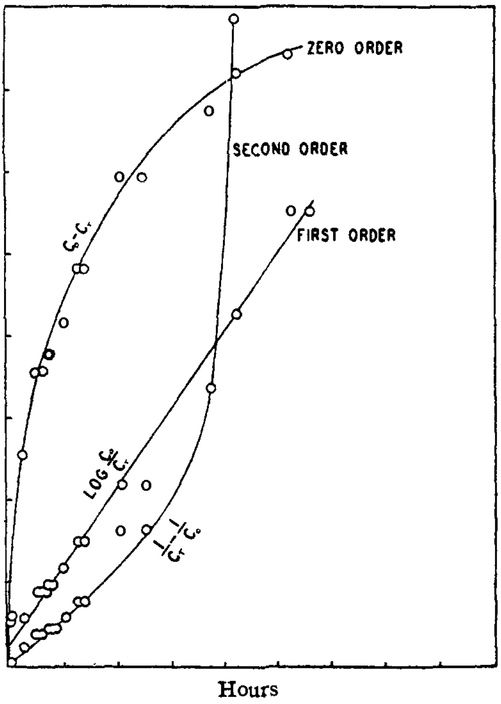


Fig. 1.

Experimental Part

***p*-Bromobenzyl *d*-*s*-Butyl Ether (I).**—The method of Sah and Lei[3] for making benzyl ethers was modified for this reaction.

In a 500-cc., three-necked, round-bottomed flask equipped with condenser, stirrer and dropping funnel were placed 35 g. of *d*-*s*-butyl alcohol ($[\alpha]^{23}D$ +11.5°), 200 cc. of dry benzene and 10.9 g. of sodium (small shavings). The reaction mixture was allowed to reflux on the steam-bath with stirring for fifteen hours until all the sodium had dissolved. To this was added with stirring 118 g. of *p*-bromobenzyl bromide dissolved in 200 cc. of dry benzene. The addition took about fifteen minutes. The reaction mixture was then stirred for five hours while refluxing on a steam cone. The sodium bromide which precipitated was filtered and washed with two 75-cc. portions of benzene. The benzene layer was extracted with two 100-cc. portions of water to remove sodium bromide, the layers were separated and the benzene solution was dried over sodium sulfate. The solvent was removed and the resulting solution distilled through a column. The ether boiled at 109–110° at 8 mm. The yield was 70 g. (49.1%) $n^{20}D$ 1.5331; d^{24}_{24} 1.255; $[\alpha]^{23}D$ +10.2° (α, 0.39°, 0.1921 g. made up to 10 cc. with 95% ethanol in a 2-dm. tube).

Anal. Calcd. for $C_{11}H_{15}OBr$: C, 54.33; H, 6.22. Found: C, 53.80; H, 5.90.

***p*-Cyanobenzyl Methyl Ether.**—This ether has been prepared by von Braun and Zobel[4] by a different and more involved set of reactions.

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[1] This is the eighteenth communication on vinyl polymers. For the seventeenth see THIS JOURNAL, **65**, 2054 (1943).

[2] Marvel, Dec and Cooke, *ibid.*, **62**, 3499 (1940); Marvel and Frank, *ibid.*, **64**, 1675 (1942).

[3] Sah and Lei, *Science Reports, National Tsing Hua Univ.*, Ser. **AI**, 193–195 (1932); see *C. A.*, **26**, 5927 (1932).

[4] Von Braun and Zobel, *Ber.*, **56**, 691 (1923).

In a dry, 200-cc., round-bottomed flask fitted with a ground-glass condenser and protected from moisture with a calcium chloride tube was placed 50 g. of *p*-bromobenzyl methyl ether, 22.3 g. of dry powdered cuprous cyanide and 35 cc. of pyridine dried over potassium hydroxide. This mixture was heated in a Wood's metal bath at 215–225° for fifteen hours. The reaction mixture was poured while still hot (100°) into 150 cc. of aqueous ammonia (sp. gr. 0.90) and 150 cc. of water. One hundred and forty cubic centimeters of benzene was added and the flask was stoppered and shaken until all the lumps had disintegrated. After the mixture was cooled to room temperature, 100 cc. of ether was added and the mixture filtered. The filtrate was transferred to a 1-liter separatory funnel and 100 cc. more of ether was added to facilitate separation and the aqueous layer separated. The ether-benzene layer was washed four times with dilute aqueous ammonia, until the wash water was colorless, and then twice with two 100 cc. portions of 6 *N* hydrochloric acid. A precipitate settled out at this point and was filtered. The benzene solution was then washed with two 100-cc. portions of water and two 100-cc. portions of a saturated sodium chloride solution. The ether and benzene were boiled off and the remaining solution distilled through a four plate column. The yield was 25 g. (68%) of a water-white liquid boiling at 108–110° at 9 mm.; n^{20}_{D} 1.5265.

***p*-Cyanobenzyl *d*-*s*-Butyl Ether (II).**—By the same procedure, except the addition of ten small crystals of cupric sulfate and two drops of *p*-tolunitrile, 40 g. of *p*-bromobenzyl *d*-*s*-butyl ether, 16 g. of powdered cuprous cyanide, and 40 cc. dry pyridine were heated at 215–225° for fifteen hours. The yield was 28 g. (90%) of a product boiling at 134–137° at 9 mm.; n^{20}_{D} 1.5080; $[\alpha]^{23}_{\mathrm{D}}$ +10.9°; (α, 0.39°, 0.1780 g. made up to 10 cc. with 95% ethanol in a 2-dm. tube).

This compound contained bromine and it was found impossible to separate completely the *p*-bromobenzyl *d*-*s*-butyl ether from the *p*-cyanobenzyl *d*-*s*-butyl ether by fractional distillation. Three analyses, one of which was made on the optically inactive cyano compound, proved to be almost identical.

Anal. Calcd. for $C_{12}H_{15}ON$: C, 76.15; H, 7.98; N, 7.40. Found: Sample 1, C, 74.63; H, 7.94; Sample 2, C, 74.32; H, 7.49; Sample 3, C, 74.33; H, 7.93; N, 6.85.

Sample (3) was made with *dl*-*s*-butyl alcohol. By calculation, the amount of *p*-bromobenzyl *d*-*s*-butyl ether in the mixture is 8.3%. No further attempt to separate the compound was made as this intermediate is relatively unimportant and the next compounds in the series proved to have the correct analyses.

Hydrolysis of *p*-Cyanobenzyl *dl*-*s*-Butyl Ether.—In order to have evidence of the quality of the cyano compound, it was converted to the acid by hydrolysis. In a 200-cc. round-bottomed flask equipped with condenser was placed 15 g. of potassium hydroxide dissolved in 50 cc. of 95% ethyl alcohol. To this was added 5 g. of *p*-cyanobenzyl *d*-*s*-butyl ether. This was then refluxed by means of an oil-bath for thirty hours. The solution was filtered and the sodium salt dissolved in 20 cc. of water. The solution was then acidified with dilute hydrochloric acid and the precipitate filtered. Upon purification by treatment with Norite and recrystallization from a water-95% alcohol mixture a small amount of a white solid was obtained melting at 77–78°.

Anal. Calcd. for $C_{12}H_{16}O_3$: C, 69.20; H, 7.74. Found: C, 69.09; H, 7.69.

***p*-Acetobenzyl Methyl Ether.**—In a 200-cc., three-necked, round-bottomed flask equipped with a stirrer, condenser, and dropping funnel was placed 8.56 g. of magnesium covered with 30 cc. of dry ether. To this with stirring was added over a period of one-half hour, 50 g. of methyl iodide dissolved in 120 cc. of ether (to give 3 moles excess of methylmagnesium iodide). The mixture was allowed to stir for fifteen minutes after all the iodide had been added. To this Grignard reagent was added with stirring 26 g. of *p*-cyanobenzyl methyl ether in 100 cc. of ether. This addition took ten minutes. The mixture was then heated under a reflux condenser for two hours. The complex was decomposed in iced, dilute hydrochloric acid. Benzene was added (about 200 cc.) and the organic layer separated. Fifty cubic centimeters of a 2% hydrochloric acid solution was added to the benzene layer and the solution refluxed for one hour. The water layer was then separated, the benzene layer dried, benzene removed and the resulting solution distilled through a four-plate column. The yield was 15 g. (52%) of a water-white liquid boiling at 104–105° at 9 mm., n^{20}_{D} 1.5280.

The ketone was converted to the 2,4-dinitrophenylhydrazone by the standard method[5] and this derivative was recrystallized from ethyl acetate, m. p. 170–171°.

Anal. Calcd. for $C_{16}H_{16}O_5N_4$: C, 55.80; H, 4.68. Found: C, 55.56; H, 4.67.

***p*-Acetobenzyl *d*-*s*-Butyl Ether (III).**—Using the same procedure 9.26 g. of magnesium, 52 g. of methyl iodide and 17 g. of *p*-cyanobenzyl *d*-*s*-butyl ether gave 12 g. (65%) of product boiling at 129–130° at 10 mm., n^{20} 1.5110; d^{24}_{24} 1.019; $[\alpha]^{20}_{\mathrm{D}}$ +10.8° (α +0.91°, 0.4952 g. made up to 10 cc. with 95% ethanol in a 2 dm. tube).

Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 75.36; H, 8.56.

This ketone gave a 2,4-dinitrophenylhydrazone which melted at 158–159° after recrystallization from ethyl acetate.

Anal. Calcd. for $C_{19}H_{22}O_5N_4$: N, 14.50. Found: N, 14.45.

Reduction of the Ketone (III) to the Carbinol (IV).—In a 250-cc., round-bottomed flask, attached by a ground-glass connection to a column was placed 13.2 g. of aluminum isopropoxide, 200 cc. of dry isopropyl alcohol and 10 g. of ketone (III). This mixture was slowly heated for one hour. After that time, acetone began to distill slowly. The reaction mixture was then heated for five hours and the isopropyl alcohol and acetone slowly distilled. An additional 100 cc. of freshly distilled dry isopropyl alcohol was added and this also was distilled slowly. When all but about 30 cc. of isopropyl alcohol had been distilled, the reaction mixture was poured slowly into dilute, iced hydrochloric acid. The resulting mixture was extracted with benzene, dried, the benzene removed and the solution distilled from a modified 25-cc. Claisen flask. The yield was 6 g. (60%) of a product boiling at 144–149° at 9 mm. n^{20}_{D} 1.5056, $[\alpha]^{23}_{\mathrm{D}}$ +11.2° (α, +0.91°, 0.4054 g. made up to 10 cc. with 95% ethanol in a 2-dm. tube).

Anal. Calcd. for $C_{13}H_{20}O_2$: C, 74.95; H, 9.67. Found: C, 75.76; H, 9.62.

***p*-Vinylbenzyl *d*-*s*-Butyl Ether (V).**—A mixture of 1.2 g. of fused, finely powdered potassium hydrogen sulfate and 0.2 g. of hydroquinone was fused in a 50-cc. modified Claisen flask fitted with a receiver and heated with a metal bath (200–220°). A stream of nitrogen, purified to remove oxygen and water, was introduced beneath the surface by means of a capillary tube through the same rubber stopper that contained a dropping funnel. The flask was evacuated to a pressure of 60–100 mm. Seven grams of the alcohol was dropped slowly (fifteen minutes) onto the molten potassium hydrogen sulfate at the temperature and pressure specified. About 4 g. of impure product was carried over into the receiver. The distillate was dissolved in 40 cc. of ordinary ether, washed with 20 cc. of a 5% sodium hydroxide solution, then with 20 cc. of a saturated calcium chloride solution and dried over calcium chloride. The solvent was removed and residue distilled in a 10-cc. modified Claisen flask. The yield was 3 g. (47%) of a product boiling at 111–113° at 8 mm., n^{20}_{D} 1.5179; $[\alpha]^{26}_{\mathrm{D}}$ 12.8; (α, +0.57, 0.4459 g. made up to 10 cc. with dry dioxane).

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.05; H, 9.53. Found: C, 82.10; H, 9.25.

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(5) Shriner and Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1940, p. 143.

Polymerization of *p*-Vinylbenzyl *d*-*s*-Butyl Ether.—A mixture of 0.7600 g. of the styrene derivative and 0.1748 g. of benzoyl peroxide was made up to 10 cc. in dry dioxane and placed in a 1-dm. water-jacketed polarimeter tube and held at 55°. The rotation of this solution when first measured was +0.917°. After heating at 55° for twenty-four hours the rotation had dropped to +0.722°. Readings were made at various intervals during this time and the results of the experiment are plotted in Curve I. It will be noted that the best curve is obtained when first order kinetics are assumed. The errors in reading any one rotation are probably about 10%. The polymer which precipitated from the solution at the end of the run by adding methyl alcohol was a soft mass which could not be obtained in a satisfactory state for further study. Evaporation of the solvent gave a brittle mass. In order to obtain a sample for analysis, a dioxane solution of this polymer was slowly dropped into 100 cc. of methyl alcohol with vigorous stirring. One cubic centimeter of concentrated hydrochloric acid was added, 10 cc. of water and the solution allowed to stand for over twelve hours. A gummy powder or a gum settled which hardened on standing. This was finely ground and dried for two weeks in a vacuum desiccator.

Anal. Calcd. for $(C_{12}H_{18}O)_n$: C, 82.05; H, 9.53. Calcd. for $C_6H_5CO_2[(C_{13}H_{18}O)_8(O)_{11}]_n$: C, 73.27; H, 8.25. Found: C, 73.47; H, 8.44.

Summary

p-Vinylbenzyl *d*-*s*-butyl ether, an optically active styrene derivative, has been prepared and polymerized. The rotation change during polymerization is not great and accurate kinetic studies are difficult to make. The indication is that the polymerization follows first order kinetics.

Some methyl ethers related to the intermediates were synthesized by new methods or for the first time and they were characterized.

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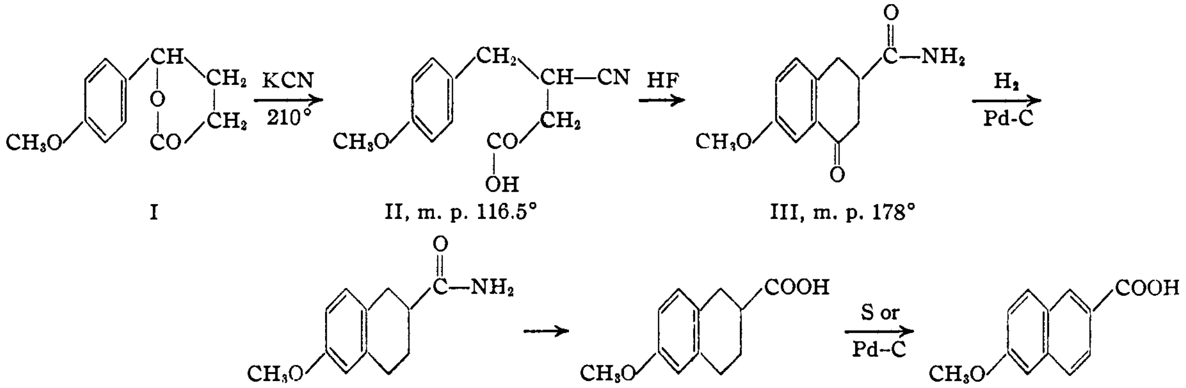
The Reaction of γ-Anisyl-γ-butyrolactone with Potassium Cyanide: 6-Methoxy-1,2,3,4-tetrahydro-2-naphthoic Acid

BY CHARLES C. PRICE AND WILLIAM KAPLAN

The reaction of γ-anisyl-γ-butyrolactone (I) with potassium cyanide[1] was studied in an attempt to prepare γ-anisyl-γ-cyanobutyric acid, which was desired for a projected synthesis of 6-methoxy-1,2,3,4-tetrahydro-1-naphthoic acid. However, the product finally obtained was shown to be 6-methoxy-1,2,3,4-tetrahydro-2-naphthoic acid (V), indicating that the reaction of potassium cyanide with γ-anisyl-γ-butyrolactone involves a rearrangement leading to the formation of γ-anisyl-β-cyanobutyric acid (II).



I

II, m. p. 116.5°

III, m. p. 178°

IV, m. p. 141°

V, m. p. 151°

VI, m. p. 196°

A similar rearrangement was observed by Blaise,[2] who found that the reaction of potassium cyanide with γ-methyl-γ-valerolactone yielded γ-methyl-β-cyanovaleric acid instead of the expected γ-cyano acid.

The structure of 6-methoxy-1,2,3,4-tetrahydro-2-naphthoic acid was established by dehydrogenation with sulfur or palladium on charcoal to yield 6-methoxy-2-naphthoic acid (VI). The identity of the dehydrogenation product was established by its melting point, the melting point of its amide and by a mixed melting point of each with authentic samples.[3]

Experimental

β-Anisoylpropionic Acid.—Following the directions of Fieser and Hershberg,[4] a 95% yield of β-anisoylpropionic acid, m. p. 144°, was obtained from the reaction between anisole (302 g.) and succinic anhydride (294 g.) in the presence of aluminum chloride (777 g.) when the precaution was taken of finely powdering the succinic anhydride crystals.

γ-Anisyl-γ-butyrolactone.—The keto-acid (140 g.) was added to 1 liter of absolute ethyl alcohol and the solution refluxed for several days, water being removed by calcium

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(1) Wislicenus, *Ann.*, **233**, 101 (1886).

(2) Blaise, *Compt. rend.*, **124**, 89 (1897).

(3) Fries and Schimmelschmidt, *Ber.*, **58**, 2840 (1925).

(4) Fieser and Hershberg, THIS JOURNAL, **58**, 2314 (1936).