cule, with the complex probably having properties similar to those of the reaction products.[9]

It has been shown by LaMer[10] that the activation energy terms, for a reaction involving electrostatic effects, may be divided into three terms. Thus, for the entropy

$$\Delta S^* = \Delta S_0^* + \Delta S_D^* + \Delta S_{\text{In}}^* \qquad (8)$$

where ΔS_0^* is the entropy freed from electrostatic effects, ΔS_D^* is the portion due to the change in dielectric constant from this ideal state, and ΔS_{In}^* the portion due to ionic strength effects. In the present case ΔS_{In}^* may be considered negligible. It has been pointed out by Warner[11] that $\Delta S_D^* = 0$ when temperatures coefficients are measured in iso-dielectric media.

The entropy values of Table III are therefore free of electrostatic effects in the usual sense. The value of ΔS_0^* should, however, be a constant independent of the medium, whether its magnitude meets the requirements of the collision theory or not. Evidently another variable term should be added to equation (8)

$$\Delta S^* = \Delta S_0^* + \Delta S_D^* + \Delta S_{\text{In}}^* + \Delta S_x^* \qquad (9)$$

where ΔS_x^* varies with the medium but is not a normal electrostatic term. In view of the dilute solutions used it cannot correspond to a normal non-electrostatic term such as that in the complete Laidler–Eyring equation (ref. 6, p. 330).

A possible explanation of the variable term ΔS_x^* may be found in the different degrees of hydration of the hydroxyl ion in the different media. Formation of the critical complex must require a simultaneous displacement of the hydration equilibrium. While in a mixed solvent hydrophilic ions tend to remain hydrated, the normal equilibrium must be considerably disturbed. Tables II and III show that the activation energy approaches the expected value in high dioxane concentrations (*i. e.*, $\Delta S^* \rightarrow 0$) and this would correspond to a minimum of hydration displacement in formation of the critical complex. A reaction involving hydrogen ion would be less subject to such an effect because of the greater stability of the hydrated ion in mixed solvents; this is seen in the reaction of hydrogen ion and azodicarbonate ion.[12]

The authors wish to thank Mr. Seymour Zenchelsky and Mr. Myron Lover, who carried out a number of the experiments reported here.

Summary

The rate of decomposition of nitrosotriacetoneamine catalyzed by hydroxyl ion, has been measured at five temperatures from 15 to 35°, in solutions of water and dioxane up to 40% dioxane.

It has been shown that the effect of changing the dielectric constant and temperature does not agree with the simplified forms of present theory. Factors which may cause the deviations have been discussed.

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(9) Ref. (5), pp. 22, 24 and 418.

(10) LaMer, *J. Frank. Inst.*, **225**, 709 (1938).

(11) Warner, *Ann. N. Y. Acad. Sci.*, **39**, 345 (1940).

(12) King and Josephs, THIS JOURNAL, **66**, 767 (1944).

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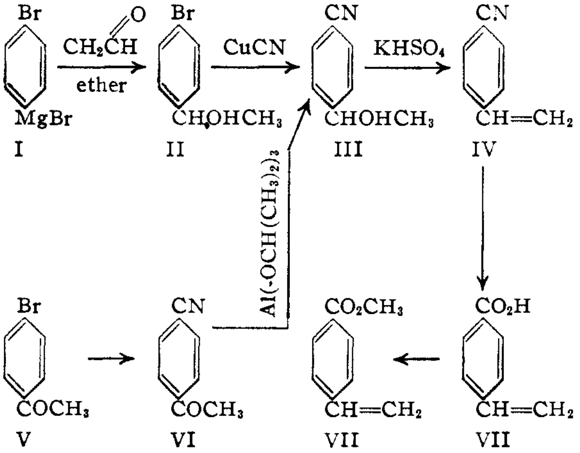
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Preparation and Polymerization of *p*-Cyanostyrene, *p*-Vinylbenzoic Acid and its Methyl Ester[1,2]

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

This paper describes the synthesis of *p*-cyanostyrene and its conversion to *p*-vinylbenzoic acid and its methyl ester as outlined in the chart. *p*-Cyanophenylmethylcarbinol (III) was prepared by two routes, one through the Grignard reagent from *p*-dibromobenzene (I) and the other from *p*-bromoacetophenone (V). By either route the final yield was low. The ease with which *p*-cyanostyrene polymerized during its preparation or storage caused considerable difficulty in the synthesis. These new styrene derivatives have been polymerized by standard procedures in order



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(1) A part of the work described in this manuscript was done under Contract RuRSR 95 between Rubber Reserve Company and the University of Illinois.

(2) This is the nineteenth communication on vinyl polymers. For the eighteenth see THIS JOURNAL, **66**, 475 (1944).

that the properties of the polymers may be compared with those of their vinylogs[3] from acrylonitrile, acrylic acid and methyl acrylate, respectively. The solubilities of the new polymers agree with predictions based on this relationship. Poly-*p*-cyanostyrene is not soluble in benzene or chloroform but does dissolve in dimethylformamide and nitromethane. Poly-*p*-vinylbenzoic acid is slightly soluble in benzene and completely soluble in nitromethane, chloroform and 5 per cent. sodium hydroxide solution. Polymethyl-*p*-vinylbenzoate is very soluble in benzene.

Experimental

***p*-Bromophenylmethylcarbinol (II).**—This alcohol was prepared by the procedure of Ziegler and Tiemann[4] from *p*-bromophenylmagnesium bromide and acetaldehyde. The yield starting with 250 g. (1.06 moles) of *p*-dibromobenzene was 120 g. (0.60 mole) (56%) of a product boiling at 114–117° at 10 mm.

***p*-Cyanophenylmethylcarbinol (III) from the Corresponding Bromo Alcohol (II).**—The general procedure was that of "Organic Syntheses"[5] for replacing an aryl bromide by the —CN group. In a 250-cc. round-bottomed flask equipped with ground-glass joint and condenser were placed 60 g. (0.298 mole) of *p*-bromophenylmethylcarbinol, 55 cc. of dry pyridine, 30 g. (0.34 mole) of cuprous cyanide, two small crystals of cupric sulfate, two drops of *p*-tolunitrile and 1 g. of hydroquinone. This mixture was refluxed for fifteen hours at 200–215°. The reaction mixture was worked up as described in "Organic Syntheses."[5] The yield was 16 g. (0.109 mole) (36%) of a water-white liquid boiling at 136–140° (5 mm.) n^{20}D 1.5477.

Anal.[6] Calcd. for C_9H_9ON: C, 73.44; H, 6.16. Found: C, 73.69; H, 6.18.

***p*-Cyanoacetophenone (VI).**—The procedure was a modification of that of Helberger and v. Rebay, who prepared *o*-cyanoacetophenone.[7] Into a 2-liter round-bottomed flask equipped with a ground-glass joint and condenser, were placed 163 g. (1.82 moles) of cuprous cyanide, 850 cc. of dry pyridine, 325 g. (1.63 moles) of *p*-bromoacetophenone, two small crystals of cupric sulfate and two drops of *p*-tolunitrile. The mixture was heated at 130° for six hours. The reaction mixture was treated as described by Helberger and v. Rebay.[7] This reaction mixture may also be treated as described in "Organic Syntheses."[5] The yield was 176 g. (1.21 moles) (74%) of a white solid; m. p. 54–56°; b. p. 122–125° (3 mm.) After recrystallization from aqueous ethanol, the melting point changed to 58–59°. Ohrens[8] prepared this product by diazotization and replacement of the amino group in *p*-aminoacetophenone and recorded the melting point as 60–61°.

***p*-Cyanophenylmethylcarbinol (III) by Reduction of *p*-Cyanoacetophenone (VI).**—In a 24-liter round-bottomed flask equipped with a small column were placed 1045 g. (7.23 moles) of *p*-cyanoacetophenone, 525 g. (2.58 moles) of aluminum isopropoxide, 5225 cc. of dry isopropyl alcohol and 8700 cc. of dry toluene. The mixture was slowly refluxed for one hour without removing any distillate and then partially refluxed over a period of twenty-four hours while the acetone and some of the isopropyl alcohol slowly distilled. The toluene was then removed under a slight vacuum until the volume of solution was 1500 cc. The reaction complex was decomposed with 800 cc. of concentrated hydrochloric acid in 800 cc. of water. The resulting solution was extracted with 2 liters of ether, dried over magnesium sulfate, the drying agent and solvent were removed and the residue was distilled through one-foot helix-packed column. The yield was 936 g. (6.37 moles) (88%) of a slightly yellow liquid; b. p. 155–158° (6 mm.), n^{20}D 1.5474.

***p*-Cyanostyrene (IV).**—In a 50-cc. Claisen flask equipped with a dropping funnel, capillary and thermometer were placed 6 g. of fused, finely ground potassium bisulfate and 2 g. of hydroquinone. Nitrogen, freed from oxygen and water, was introduced by means of the capillary beneath the surface of the potassium bisulfate. The flask was heated to 205–220° and evacuated to 50–60 mm. The *p*-cyanophenylmethylcarbinol (16 g., 0.109 mole) was slowly dropped onto the potassium bisulfate, and the dehydrated product then slowly distilled out of the reaction flask. The distillate was dissolved in 80 cc. of ether. The ether solution was washed with 30 cc. of five per cent. aqueous sodium hydroxide and with 30 cc. of a saturated calcium chloride solution. It was dried over calcium chloride, filtered, and the ether removed. The resulting liquid was distilled from a 15-cc. modified Claisen flask. The yield was 4 g. (0.031 mole) (29%) of a water-white, sweet-smelling liquid; b. p. 102–104° (9 mm.), n^{20}D 1.5781.

Anal. Calcd. for C_9H_7N: C, 83.68; H, 5.46. Found: C, 83.69; H, 5.31.

***p*-Vinylbenzoic Acid (VII).**—Into a 200-cc. round-bottomed flask were placed 4 g. (0.031 mole) of *p*-cyanostyrene, 0.2 g. of hydroquinone, and 6.5 g. of potassium hydroxide dissolved in 50 cc. of alcohol. The mixture was gently refluxed on a steam-cone overnight. A precipitate of the potassium salt of the acid appeared during the night. This was removed by filtration and dissolved in 50 cc. of water and the free acid precipitated by dilute hydrochloric acid. The *p*-vinylbenzoic acid was removed by filtration and dried. The acid took up bromine in carbon tetrachloride immediately. After recrystallization (with small amounts of hydroquinone present) from a mixture of 80% water and 20% ethanol, the acid melted at 140–141°. Repeated recrystallizations raised this melting point to 143–144°. The yield was 3.0 g. (0.0203 mole) (67%) of white, fluffy, plate-like crystals.

Anal. Calcd. for $C_9H_8O_2$: C, 72.97; H, 5.44. Found: C, 72.87; H, 5.49.

Methyl *p*-Vinylbenzoate (VIII).—One and one-half grams (0.0102 mole) of *p*-vinylbenzoic acid was dissolved in 40 cc. of 5% methanolic hydrogen chloride which was cooled in an ice-bath. The solution was allowed to stand at 0° for twenty-four hours. The methanol was allowed to evaporate in the air and a dirty white solid separated from the solution. Upon cooling, more solid appeared. This material was filtered and recrystallized from aqueous ethanol containing a very small amount of hydroquinone. A white solid melting at 35–36° was obtained. It took up bromine immediately and gave a negative test for halogen. The yield was 0.79 g. (0.0049 mole) (47%).

Anal. Calcd. for $C_{10}H_{10}O_2$: C, 74.05; H, 6.21. Found: C, 74.04; H, 6.42.

Polymerization of *p*-Cyanostyrene, Methyl *p*-Vinylbenzoate and *p*-Vinylbenzoic Acid.—In a Pyrex test-tube was placed 1 g. of methyl *p*-vinylbenzoate. The test-tube was suspended under an ultraviolet lamp and left there until a hard polymer had been formed (twenty-four hours). The polymer was dissolved in 50 cc. of benzene and precipitated by slowly dropping the solution into 300 cc. of methanol with vigorous mechanical stirring. This process of purification was repeated and the powder obtained was dried for one week in a vacuum desiccator. An approximate molecular weight was determined by viscosity measurements with the use of an equation developed by Kemp and Peters[9] for the determination of the molecular weight of polystyrene using the *k* value for styrene.

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[3] Fuson, *Chem. Rev.*, **16**, 1 (1935).

[4] Ziegler and Tiemann, *Ber.*, **55**, 3414 (1922).

[5] Newman, "Organic Syntheses," Vol. 21, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 89.

[6] Microanalyses reported in this paper were done by Miss Theta Spoor and Mr. Howard S. Clark.

[7] Helberger and v. Rebay, *Ann.*, **531**, 284 (1937).

[8] Ohrens, *Ber.*, **20**, 2956 (1887).

[9] Kemp and Peters, *Ind. Eng. Chem.*, **34**, 1097 (1942).

TABLE I

Polymer from	Approx. mol. wt.	Softening point, °C.	Solubility: Nitromethane	Solubility: Chloroform	Solubility: Benzene	Empirical formula	Analyses, %: Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
p-Cyanostyrene[a]	5310	200–225	+	−	−	C_9H_7N	83.72	5.42	10.85	81.86	5.49	10.46
p-Vinylbenzoic acid[b]	4710	165–200	+	+	−	$C_9H_8O_2$	72.97	5.40		68.85	5.17	
Methyl *p*-vinylbenzoate	45000	205–212	+	+	+	$C_{10}H_{10}O_2$	74.07	6.17		71.96	5.72	

[a] Also soluble in dimethylformamide. [b] Also soluble in 5 per cent. sodium hydroxide solution.

The polymer of *p*-cyanostyrene was prepared in a similar manner. It was purified by dissolving in 30 cc. of nitromethane and reprecipitated by slowly dropping this solution into 250 cc. of methanol. This process of purification was repeated and the powder obtained was dried for several days. This polymer was insoluble in benzene and chloroform but did dissolve in dimethylformamide as well as nitromethane.

The polymer of *p*-vinylbenzoic acid was obtained in the purification of the monomer. Upon successive recrystallization of *p*-vinylbenzoic acid from an aqueous ethanol solution, without an inhibitor present, the polymer precipitated from solution upon gentle refluxing for several hours. This polymer was removed by filtration and dried in a vacuum desiccator for several weeks. It was only slightly soluble in benzene but completely soluble in chloroform and nitromethane.

The analyses and physical properties of these three polymers are described in the table.

The analytical figures indicate that these substituted styrene polymers like the polymer of styrene itself take up a considerable amount of oxygen as a part of the molecule during polymerization.[10]

Summary

p-Cyanostyrene, *p*-vinylbenzoic acid and methyl *p*-vinylbenzoate have been synthesized and the corresponding vinyl polymers briefly characterized.

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[10] Price and Tate, THIS JOURNAL, 65, 517 (1943).

URBANA, ILLINOIS RECEIVED AUGUST 22, 1945

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF PARKE, DAVIS AND COMPANY]

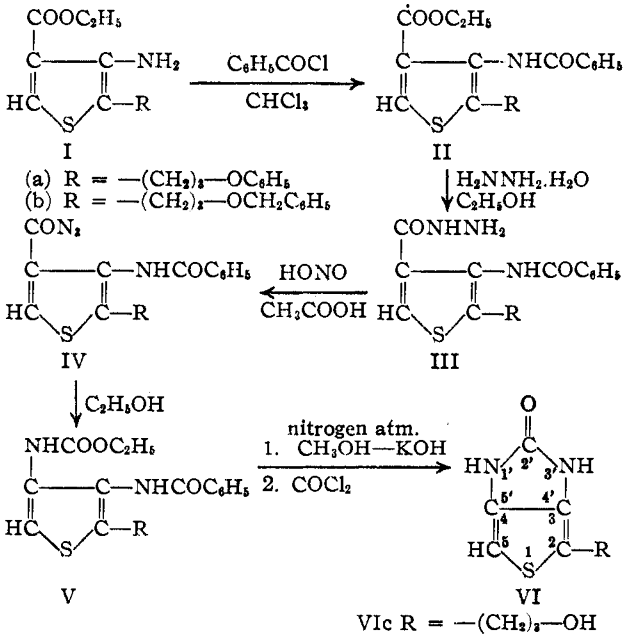
Derivatives of 2′-Keto-3,4-imidazolidothiophene

BY LEE C. CHENEY AND J. ROBERT PIENING

The aromatization of ethyl 3-keto-2-γ-phenoxypropyl-4-tetrahydrothiophenecarboxylate oxime[1] afforded in a favorable yield the hitherto unknown ethyl 3-amino-2-γ-phenoxypropyl-4-thiophenecarboxylate (Ia). Because the readily accessible parent keto ester had been prepared by an unambiguous ring closure,[2] the structure of Ia could be assigned without reservation, thus rendering the compound particularly well suited as a model in experiments aimed toward the ultimate synthesis of 2,3,4,5-tetradehydrobiotin.[3]

By means of the sequence of reactions featuring the Curtius degradation as pictured on the flow sheet, an unequivocal synthesis of 2′-keto-3,4-imidazolido-2-γ-phenoxypropylthiophene (VIa) was achieved. The corresponding benzyl ether (VIb) was then prepared from Ib by an extension of the same general method.

The amino esters (I) were first benzoylated by a modification of the method of Jacobs and Heidelberger.[4] However, the more convenient procedure of refluxing a chloroform solution of the weakly basic amines with an excess of benzoyl chloride was found to give satisfactory results. The hydrazides (III) were obtained in yields of 88–95% by boiling an alcoholic solution of the acylated amino esters (II) with an excess of 85% hydrazine hydrate. Inasmuch as the hydrochlorides and sulfates of the hydrazides (III) were practically insoluble in water, the conventional procedure for carrying out the Curtius degradation[5] was considered inappro-



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[1] Cheney and Piening, THIS JOURNAL, 67, 729 (1945).

[2] Cheney and Piening, *ibid.*, 67, 2213 (1945).

[3] Cheney and Piening, *ibid.*, 66, 1040 (1944); 67, 731 (1945).

[4] Jacobs and Heidelberger, *ibid.*, 39, 1439 (1917).

[5] Pertinent examples are the following: Windaus and Dalmer, *Ber.*, 53, 2304 (1920); Robinson and Todd, *J. Chem. Soc.*, 1743 (1939).