TABLE I

PHYSICAL CONSTANTS AND ANALYTICAL DATA

Compound	B. p. or m. p., °C.	Formula	Analyses, % Calcd.		Found
β-Pyridyl-methylamine[13]	112 (18 mm.)	$C_6H_8N_2$	N,	25.93	26.06
Picrate[13,14]	210–211 dec.	$C_{12}H_{11}N_5O_7$			
3-(α-Aminoethyl)-pyridine[14]	223 (740 mm.) 112–113 (22 mm.)	$C_7H_{16}N_2$	N,	22.95	23.12
Phenylthiourea	139–140	$C_{14}H_{15}N_3S$	N,	16.34	16.29
Chloroplatinate	280 dec.	$C_7H_{10}N_2 \cdot H_2PtCl_6$	Pt,	36.68	36.66
Picrate	204–205	$C_{13}H_{13}N_5O_7$	N,	19.31	19.46
Di-(β-pyridylmethyl)-amine	147–148 (mm.)	$C_{12}H_{13}N_3$	N,	21.11	20.81
Chloroplatinate	>300	$C_{12}H_{13}N_3 \cdot H_2PtCl_6$	Pt,	35.96	35.68
Picrate	218–220	$C_{18}H_{16}N_6O_7$	N,	18.96	18.80
[Di-α,α′-(3-pyridyl)]-diethylamine	152–153 (1 mm.)	$C_{14}H_{17}N_3$			
Chloroplatinate	292, 161–163	$C_{14}H_{17}N_3 \cdot H_2PtCl_6$	Pt,	34.76	34.64
Picrate	205 dec.	$C_{20}H_{20}N_6O_7$	N,	18.38	18.56
Oxime of 2,4-dimethyl-3-acetyl-5-carbethoxypyrrole	197–198	$C_{11}H_{16}N_2O_3$	N,	12.50	12.47
Oxime of 2,4-dimethyl-3-carbethoxy-5-acetylpyrrole	162–163	$C_{11}H_{16}N_2O_3$	N,	12.50	12.63
Monoxime of 2,4-dimethyl-3,5-diacetylpyrrole	240 dec.	$C_{10}H_{14}N_2O_2$	N,	14.43	14.08
2,4-Dimethyl-3-vinyl-5-carbethoxypyrrole	110.5–112	$C_{11}H_{15}NO_2$	N,	7.25	7.57
Benzoate of 2,4-dimethyl-3-(α-aminoethyl)-5-carbethoxypyrrole	179–180	$C_{18}H_{22}N_2O_3$	N,	8.92	9.01
Benzoate of 2-(α-aminoethyl)-pyrrole	149–150	$C_{13}H_{14}N_2O$	N,	13.08	12.91
2,4-Dimethyl-3-acetyl-5-ethylpyrrole	159–160	$C_{10}H_{15}NO$	N,	8.48	8.58
2,4-Dimethyl-3-carbethoxy-5-ethylpyrrole	106–107	$C_{11}H_{17}NO_2$	N,	7.18	7.38
Ethyl β-(3-pyridyl)-acrylate hydrochloride	186–187	$C_{10}H_{11}NO_2 \cdot HCl$	C,	56.20	56.35
			H,	5.62	5.78
			Cl,	16.65	16.62

a picrate, m. p. 210–211° dec., a dihydrochloride, m. p. 222°, and a *p*-nitrobenzoate, m. p. 188–189°. The picrate of the secondary amine had a m. p. of 218–220°.

Ethyl nicotinoacetate (30 g.) took up 1 mole of hydrogen per mole of ester at 85° within two and one-half hours. Fractional distillation of the product gave 11 g. of a compound, b. p. 136–138° (3 mm.), believed to be β-(3-pyridyl)-acrylic ester. The ester polymerized so rapidly that within twenty-four hours the refractive index had fallen from 1.5518 to 1.4612; however, a stable hydrochloride, m. p. 185–186°, was obtained.

Summary

The hydrogenations over Raney nickel of eight oximino, keto and cyano derivatives of pyrrole and pyridine have been described.

(13) Craig and Hixon, THIS JOURNAL, **53**, 4369 (1931).

(14) Erlenmeyer and Epprecht, *Helv. Chim. Acta*, **20**, 690 (1937).

MADISON, WISCONSIN RECEIVED JUNE 16, 1941

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF SPRAGUE ELECTRIC CO.]

Preparation of Substituted Styrenes

BY LESTER A. BROOKS

Our interest in a study of the electrical characteristics of the polymers of various halogen substituted styrenes has necessitated the preparation of the corresponding monomers. Since the results of the electrical measurements are not complete and will be reported in a later paper, we are describing the preparation of several monomeric styrene derivatives at this time.

A knowledge of the electrical properties of materials is of value in the communications field and considerable work has been reported on various organic compounds.[1,2,3] However, it appears that little investigation has been made of specific styrene derivatives.

A modification of the styrene molecule accomplished by the introduction of a halogen atom in the ring will raise the dielectric constant. Any advantage due to increased dielectric constant will be nullified if a correspondingly large increase in dielectric loss occurs, or if the resulting polymer is not chemically stable in an electric field. It is well known that many iodine compounds are thermally unstable even at moderate temperatures. Bromine compounds also show this behavior but to a less extent, as, for example, in the case of the isomeric polybromostyrenes.[4]

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(1) White and Bishop, THIS JOURNAL, **62**, 8 (1940).

(2) White, Biggs and Morgan, *ibid.*, **62**, 16 (1940).

(3) Mead and Fuoss, *ibid.*, **65**, 2067 (1943).

(4) Marvel and Moon, *ibid.*, **62**, 45 (1940).

The discoloration produced on aging may be attributed to the liberation of bromine. This bromine liberation would be intensified by an electric field and the bromine would be in a form which would result in high dielectric loss.

In the case of non-polymeric materials, McLean and co-workers[5] have shown that common commercial dielectrics such as chlorinated diphenyl eventually liberate hydrogen chloride in an electric field. This effect would probably be much smaller than that which would occur in the corresponding brominated diphenyl. It seemed, therefore, that thermal and electrical stabilities, as determined by dielectric loss measurements, would be higher in polyfluorostyrenes than in polychlorostyrenes.

The following compounds are described for the first time with the exception of *m*-chlorostyrene and *p*-chlorostyrene. These two chlorostyrenes have recently been reported; they were prepared by methods different from those which have been used in this work. The monomers were prepared by the batch dehydration of the carbinols using not over 1% of fused potassium bisulfate in conjunction with suitable pressures. In this manner excellent yields of the corresponding styrenes were obtained. The carbinols were prepared by reduction of the corresponding ketone or by addition of a Grignard reagent to an aldehyde. When the styrenes were purified by repeated distillation, polymerization occurred more readily. The dichlorostyrenes were least stable in this respect and the fluorostyrenes most stable. The lessened stability of the chlorostyrenes might be attributed to the presence of traces of hydrogen chloride. An analogous situation would be unlikely in the case of the fluorostyrenes.

Experimental[6]

***o*-Chlorophenylmethylcarbinol.**—A suspension of methylmagnesium bromide was prepared by bubbling commercial methyl bromide into 1-liter of anhydrous ether which covered 26.7 g. of magnesium turnings. When the magnesium was almost dissolved 140 g. of redistilled commercial *o*-chlorobenzaldehyde, dissolved in 500 cc. of anhydrous ether, was added dropwise with stirring. The reaction mixture was then worked up in the usual manner. The yield was 119 g. (76%) of a colorless liquid, b. p. 108–109° (7 mm.); d^{20}_4 1.355; n^{20}_{D} 1.5457.

Anal. Calcd. for C_8H_9OCl: C, 61.34; H, 5.75. Found: C, 60.80; H, 5.68.

***o*-Chlorostyrene.**—In a 500-cc. modified Claisen flask were placed 200 g. of *o*-chlorophenylmethylcarbinol, 2 g. (1%) of powdered, fused potassium bisulfate, and 2 g. of hydroquinone. The flask was immersed in an oil-bath heated to 200–210°, and the pressure was adjusted to 110–130 mm. The styrene, water and carbinol distilled at 125–140° in about one and one-half to two hours. The distillate was dissolved in ether. The ether solution was washed with 5% sodium hydroxide, then with a saturated calcium chloride solution, and finally dried over calcium chloride. After removal of the ether 81 g. (70%) of *o*-chlorostyrene, b. p. 62–64° (4 mm.) was distilled. The temperature of the oil-bath was raised and 69 g. of unreacted carbinol was collected. Redistillation of the styrene gave a product which boiled at 60–61° (4 mm.); d^{20}_4 1.100; n^{20}_{D} 1.5648.

Anal. Calcd. for C_8H_7Cl: C, 69.31; H, 5.05. Found: C, 69.25; H, 5.04.

***m*-Chlorophenylmethylcarbinol.**—This material was prepared by essentially the same method as that described for the *ortho* compound. From 142 g. of *m*-chlorobenzaldehyde there was obtained 118 g. (76%) of *m*-chlorophenylmethylcarbinol, b. p. 102–104° (3 mm.); d^{20}_4 1.174; n^{20}_{D} 1.5438.

Anal. Calcd. for C_8H_9OCl: C, 61.34; H, 5.75. Found: C, 61.10; H, 5.76.

***m*-Chlorostyrene.**—Marvel and Schertz[7] recently prepared *m*-chlorostyrene and *p*-chlorostyrene from the corresponding carbinols. They employed an alternate method for the synthesis of the carbinols. The details of the carbinol dehydration are offered here because an improvement in the yields has been obtained, and the physical constants found in this work are somewhat different from those now in the literature.

The amounts of material used were the same as described for the preparation of the *ortho* derivative. The oil-bath temperature was held at 200–210° and the pressure at 120–130 mm. The mixture distilled at 130–145°. A residue (17 g.) remained in the flask after the distillation. After working up the mixture as previously described there was obtained 47 g. of unreacted carbinol and 114 g. (83%) of styrene, b. p. 59–62° (6 mm.). Upon redistillation the styrene boiled at 62–63° (6 mm.); d^{20}_4 1.090; n^{20}_{D} 1.5619.

Anal. Calcd. for C_8H_7Cl: C, 69.31; H, 5.05. Found: C, 69.19; H, 5.07.

***p*-Chlorophenylmethylcarbinol.**—From 141 g. of *p*-chlorobenzaldehyde there was obtained 134 g. (86%) of *p*-chlorophenylmethylcarbinol; b. p. 87–89° (2 mm.); d^{20}_4 1.171; n^{20}_{D} 1.5633.

Anal. Calcd. for C_8H_7OCl: C, 61.34; H, 5.75. Found: C, 61.40; H, 5.88.

***p*-Chlorostyrene.**—*p*-Chlorophenylmethylcarbinol (200 g.), potassium bisulfate (2 g.), and hydroquinone (2 g.) were heated to 200–210° under a pressure of 100–120 mm. *p*-Chlorostyrene (127 g., 86%) distilled at 53–56° (3 mm.). The recovered carbinol amounted to 33 g. Upon redistillation the pure *p*-chlorostyrene boiled at 53–54° (3 mm.); d^{20}_4 1.090; n^{20}_{D} 1.5658.

Anal. Calcd. for C_8H_7Cl: C, 69.38; H, 5.05. Found: C, 69.13; H, 5.07.

***o*-, *m*- and *p*-Fluorobenzaldehyde.**—The *o*-, *m*- and *p*-fluorobenzaldehydes were made by the method described in "Organic Syntheses"[8] for the preparation of *p*-chlorobenzaldehyde. In each case 220 g. (2 moles) of the fluorotoluene was used. The yields and boiling points of the isomeric fluorobenzaldehydes were as follows

	Boiling point °C. at 45 mm.	Yield, G.	%
o-Fluorobenzaldehyde	90–91	118	48
m-Fluorobenzaldehyde	92–93	109	44
p-Fluorobenzaldehyde	93–94	120	49

***o*-Fluorophenylmethylcarbinol.**—This compound was prepared in the manner described for the preparation of *o*-chlorophenylmethylcarbinol. From 99 g. of *o*-fluorobenzaldehyde there was obtained 87 g. (78%) of *o*-fluorophenylmethylcarbinol which boiled at 117–118° (45 mm.); d^{20}_4 1.123; n^{20}_{D} 1.5031.

Anal. Calcd. for C_8H_9OF: C, 68.57; H, 6.43. Found: C, 68.60; H, 6.47.

***o*-Fluorostyrene.**—The procedure followed in the preparation of *o*-chlorostyrene was used here. However,

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[5] McLean, Egerton, Kohman and Brotherton, *Ind. Eng. Chem.*, **34**, 101 (1942).

[6] Yields of styrenes are based on the unrecovered carbinols. Microanalyses by Mr. Royal A. Cutler, R.P.I., Troy, N. Y. All boiling points are uncorrected.

[7] Marvel and Schertz, THIS JOURNAL, **65**, 2056 (1943).

[8] "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1943, Coll. Vol. II, p. 133.

the carbinol dehydrated easier, and the bath was maintained at a lower temperature (185°). From 212 g. of *o*-fluorophenylmethylcarbinol and 2 g. each of potassium bisulfate and hydroquinone, there was obtained 109 g. (76%) of *o*-fluorostyrene which boiled at 32–34° (3 mm.); d^{20}_{4} 1.030; n^{20}_{D} 1.5197. Forty-eight grams of the carbinol was recovered.

Anal. Calcd. for C_8H_7F: C, 78.68; H, 5.74. Found: C, 78.68; H, 6.02.

***m*-Fluorophenylmethylcarbinol.**—From 99 g. of the *m*-fluorobenzaldehyde there was obtained 83 g. (74%) of *m*-fluorophenylmethylcarbinol boiling at 120–121° (45 mm.); d^{20}_{4} 1.1201; n^{20}_{D} 1.5012.

Anal. Calcd. for C_8H_7OF: C, 68.57; H, 6.43. Found: C, 68.96; H, 6.66.

***m*-Fluorostyrene.**—The preparation of this compound was identical with the procedure followed for the *ortho*-derivative. From 220 g. of the carbinol there was obtained 144 g. (80%) of *m*-fluorostyrene which boiled at 30–31° (4 mm.); d^{20}_{4} 1.025; n^{20}_{D} 1.5173. Twelve grams of the carbinol was recovered.

Anal. Calcd. for C_8H_7F: C, 78.68; H, 5.74 Found: C, 78.73; H, 6.03.

***p*-Fluorophenylmethylcarbinol.**—From 99 g. of *p*-fluorobenzaldehyde there was obtained 94 g. (84%) of *p*-fluorophenylmethylcarbinol which boiled at 122–123° (45 mm.); d^{20}_{4} 1.122; n^{20}_{D} 1.5001.

Anal. Calcd. for C_8H_9OF: C, 68.57; H, 6.43. Found: C, 68.20; H, 6.52.

***p*-Fluorostyrene.**—In a manner similar to that used in preparing the other fluoro isomers, there was obtained from 260 g. of the carbinol 172 g. (81%) of *p*-fluorostyrene, b. p. 29–30° (4 mm.); d^{20}_{4} 1.024; n^{20}_{D} 1.5158. Seventeen grams of the carbinol was recovered.

Anal. Calcd. for C_8H_7F: C, 78.68; H, 5.74. Found: C, 78.21; H, 5.89.

3,4-Dichlorophenylmethylcarbinol.—3,4-Dichloroacetophenone, prepared according to Roberts and Turner,[9] was reduced by the method of Marvel and Schertz.[7] From 110 g. of 3,4-dichloroacetophenone there was obtained 98 g. (91%) of 3,4-dichlorophenylmethylcarbinol, b. p. 127–128° (2 mm.); d^{20}_{4} 1.318; n^{20}_{D} 1.5628.

Anal. Calcd. for $C_8H_8OCl_2$: C, 50.26; H, 4.19. Found: C, 50.19; H, 4.24.

3,4-Dichlorostyrene.—A mixture of 150 g. of 3,4-dichlorophenylmethylcarbinol, 1.5 g. of hydroquinone, and 1.5 g. of potassium bisulfate was placed in a 500-cc. modified Claisen flask and immersed in an oil-bath held at 210–215°. The pressure, initially at 110 mm., was gradually reduced to 15–20 mm. where the styrene–water mixture distilled at 130–150°. After working up the product in the usual manner there was obtained 90 g. (83%) of 3,4-dichlorostyrene boiling at 69–70° (4 mm.); d^{20}_{4} 1.256; n^{20}_{D} 1.5857. Thirty-one grams of carbinol was recovered.

Anal. Calcd. for $C_8H_6Cl_2$: C, 55.48; H, 3.47. Found: C, 55.72; H, 3.71.

2,5-Dichlorophenylmethylcarbinol.—2-Chloro-5-nitrobenzaldehyde was prepared according to the method of Erdmann.[10] The nitro group was reduced and replaced by chlorine exactly as described for the preparation of *m*-chlorobenzaldehyde in "Organic Syntheses."[11] From 110 g. of 2,5-dichlorobenzaldehyde there was obtained 110 g. (83%) of 2,5-dichlorophenylmethylcarbinol, b. p. 107–109° (2 mm.); m. p. 63–64°.

Anal. Calcd. for $C_8H_8OCl_2$: C, 50.26; H, 4.19. Found: C, 50.20; H, 4.09.

2,5-Dichlorostyrene.—This compound was prepared exactly according to the directions given for 3,4-dichlorostyrene. From 170 g. of 2,5-dichlorophenylmethylcarbinol and 1.7 g. each of hydroquinone and potassium bisulfate, there was obtained 44 g. (37%) of 2,5-dichlorostyrene. Thirty-nine grams of the carbinol was recovered. The product boiled at 72–73° (2 mm.); d^{20}_{4} 1.4045; n^{20}_{D} 1.5798.

Anal. Calcd. for $C_8H_6Cl_2$: C, 55.49; H, 3.47. Found: C, 55.55; H, 3.51.

Summary

The preparation of *o*-, *m*- and *p*-fluorostyrene, *o*-, *m*- and *p*-chlorostyrene, 3,4-dichlorostyrene and 2,5-dichlorostyrene has been described.

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(9) Roberts and Turner, *J. Chem. Soc.*, 1855 (1927).

(10) H. Erdmann, *Ann.*, **272**, 153 (1893).

(11) "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1943, Coll. Vol. II, p. 130.

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[Contribution from the Department of Biology and Biological Engineering, Massachusetts Institute of Technology]

X-Ray Diffraction Studies on Protein Fibers. I. The Large Fiber-Axis Period of Collagen

By Richard S. Bear

Most of the detailed deductions regarding protein fiber structure have been derived from wide-angle X-ray diffraction patterns, which yield information concerning the common inter-atomic distances of small magnitude. It has been known for some time that these fibers also exhibit small-angle patterns, resulting from very large structural periodicities. This paper reports in detail the evidence regarding the long spacings of collagenous tissues, briefly described in a previous Communication.[1]

Clark and Schaad,[2] on the basis of observation of diffractions corresponding to spacings of 202, 107, 72.6 and 57 Å., plus unspecified higher orders, concluded that the collagen large fiber-axis period was probably 216, 432 Å., or other multiple, favoring the second figure. Corey and Wyckoff[3] considered that their measurements of spacings at 103, 70.1, 54.6, 33.6, 26.9, 24.1 and 21.6 Å. indicated a period of 330 Å. The value 216 is one-third and 330 nearly half that now believed to be correct, but these early experiments lacked both the angular resolution and accuracy necessary to determine the true period.

Subsequent to the first report of the 640 Å. collagen period[1] it has been supported from two

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(1) R. S. Bear, This Journal, **64**, 727 (1942).

(2) G. L. Clark and J. A. Schaad, *Radiology*, **27**, 339 (1936).

(3) R. B. Corey and R. W. G. Wyckoff, *J. Biol. Chem.*, **114**, 407 (1936).