TABLE I

SUBSTITUTED PHENYLETHYNYLCARBINOLS[a]

Substituents	Yield, %	M. p., °C.	Empirical formula	OCH₃, % Calcd.	OCH₃, % Found	Mol. wt. Calcd.	Mol. wt. Found	Acetate M. p., °C.	Acetate Empirical formula	Acetate OCH₃, % Calcd.	Acetate OCH₃, % Found	Acetate Acetyl, % Calcd.	Acetate Acetyl, % Found
4-OH-3-CH_3O[f]	77	83–84	$C_{10}H_{10}O_3$	17.4	17.3	178	169	93.5–94	$C_{14}H_{14}O_5$	11.8	11.7	32.8	32.3
3,4-Dimethoxy[g]	78	99	$C_{11}H_{12}O_3$	32.3	32.3	192	206	42–42.5	$C_{13}H_{14}O_4$	26.5	26.6	18.4	17.9
4-C_2H_5O-3-CH_3O[h]	91	81–82.5	$C_{12}H_{14}O_3$	30.1[e]	30.3[e]	206	201	64.5–65[c]	$C_{14}H_{16}O_4$	25.0[e]	25.3[e]	17.3	16.6
3,4-CH_2O_2[b,i]	93	34.5–35	$C_{10}H_8O_3$	...	...	...	...	55.5–56.5[d]	$C_{12}H_{10}O_4$	...	...	19.7	19.8

[a] Phenylethynylcarbinol, obtained in 79% yield, melted at 29–30°, n^{20}D 1.5511. The reported values are: m. p., 22°,[4] n^{20}D 1.5508,[2] 1.5505,[3] n^{21}D 1.5482.[4] The benzoyl derivative m. p. was 82–84° and the mercury derivative m. p. was 162–163° (reported m. p., 167–168°[4]). [b] $n^{20.5}$D 1.5696. [c] n^{20}D 1.5292. [d] $n^{20.5}$D 1.5375. [e] Total alkoxyl calculated as methoxyl. [f] Yielded a mercury derivative as an unstable salt unsuitable for characterization. [g] Mercury deriv. obtained in 91% yield, m. p. 147.5–150°. *Anal.* Calcd. for $C_{22}H_{22}O_6Hg$: methoxyl, 21.3. Found: methoxyl, 21.5. [h] Mercury deriv. obtained in 96% yield, m. p. 140–142°. *Anal.* Calcd. for $C_{24}H_{26}O_6Hg$: alkoxyl (as methoxyl), 20.3. Found: alkoxyl, 20.1. [i] Mercury deriv. obtained in 76% yield, m. p. 170–171°. *Anal.* Calcd. for $C_{20}H_{14}O_6Hg$: Hg, 36.4. Found: Hg, 35.6.

color was dispelled a solution of 0.5 mole[6] of the aldehyde in anhydrous ether was added dropwise and the mixture stirred six hours. The flow of acetylene was continued throughout the reaction period. Ammonium chloride (0.5 mole) was then added and the ammonia evaporated overnight under nitrogen. The carbinol was separated from the salt with ether and recovered from the washed and dried ether solution in a suitable manner. In the reaction with benzaldehyde the carbinol was recovered by fractional distillation. The crude carbinols from veratraldehyde and 4-ethoxy-3-methoxybenzaldehyde, which were crystalline and only slightly soluble in ether, were separated by filtration and purified by recrystallizing from ethanol. The dried ether solutions from the reactions with piperonal and vanillin were added to petroleum ether to precipitate the carbinols as oils which crystallized. The carbinol from piperonal was purified by distillation and that from vanillin by several recrystallizations from toluene.

The acetyl derivatives were prepared using excess acetic anhydride in pyridine at room temperature and the mercury derivatives were obtained by the procedure of Johnson and McEwen.[7]

(6) In the case of vanillin one-fourth mole was used because one equivalent of sodium acetylide was lost through reaction with the phenolic hydroxyl.

(7) Johnson and McEwen, THIS JOURNAL, **48**, 469 (1926).

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Steric Inhibition of Resonance in Pentachlorostyrene

BY TURNER ALFREY, JR., AND W. H. EBELKE

Ross[1] has recently reported that the ultraviolet absorption spectrum of 2,6-dichlorobenzoic acid shows characteristics which may be attributed to steric inhibition of resonance.

We have studied the copolymerization behavior of pentachlorostyrene, with styrene and with methyl methacrylate. Our results indicate a similar steric effect in pentachlorostyrene. Apparently the two ortho chlorine atoms and the vinyl group are sufficiently large so that the latter is forced out of the plane of the benzene ring, reducing the extent of conjugation and therefore the reactivity of this styrene derivative with free radicals. (Lewis and Mayo[2] have postulated a similar steric inhibition of resonance in esters of maleic acid, to explain the low copolymerization reactivities of maleates as compared with the corresponding fumarates.)

(1) Ross, THIS JOURNAL, **70**, 4039 (1948).

(2) Lewis and Mayo, *ibid.*, **70**, 1533 (1948).

The low reactivity of pentachlorostyrene is apparent from the reactivity ratios and particularly from the low Q value reported below. The Q–e values indicate that the substitution of chlorine atoms in the ring has made the vinyl double bond more positive, as expected, but has *reduced* the average reactivity to about 20% of that of styrene. Since in other ring chlorinated styrenes either a slight increase, or no change, in reactivity is observed, the suggestion of steric inhibition of resonance in pentachlorostyrene seems reasonable. We would expect a similar reduction in copolymerization reactivity in the case of 2,6-dichlorostyrene. Marvel and co-workers[3] have reported copolymerization of 2,6-dichlorostyrene with butadiene at a single monomer ratio; their results are in harmony with this expectation, although the point cannot be definitely established from this single measurement.

Experimental

Pentachlorostyrene, provided by Dr. S. Ross and the Sprague Electric Company, was purified by recrystallization (m. p. 110.5–112°) and was copolymerized to low conversion at 70° with styrene and methyl methacrylate, using benzoyl peroxide as catalyst. Copolymers were precipitated with methanol, and monomers were removed by extraction with ether and repeated precipitation from benzene. Copolymer composition was determined by chlorine analysis, using a Parr Bomb method. Reactivity ratios were evaluated graphically with the aid of the well-known copolymerization equation

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]}$$

Q and e values for pentachlorostyrene were also estimated graphically, using as reference standards the values initially assigned to styrene and methyl methacrylate by Alfrey and Price[4] in their semi-empirical scheme for resolving the copolymeriza-

(3) Marvel, Inskeep, Deanin, Juve, Schroeder and Goff, *Ind. Eng. Chem.*, **39**, 1486 (1947).

(4) Alfrey and Price, *J. Polymer Sci.*, **2**, 101 (1947).

tion behavior of a monomer into a "reactivity" term Q, correlated with the degree of conjugation, and a "polarity" factor e. Experimental data are summarized in Tables I, II and III.

TABLE I

STYRENE (M_1)–PENTACHLOROSTYRENE (M_2) SYSTEM

Monomer composition Mole fraction M_2	Polymer composition % Cl	Polymer composition Mole fraction M_2
0.070	8.4	0.054
.159	15.2	.105
.274	24.8	.192
.428	31.1	.261
.654	42.2	.420
.842	48.6	.541
1.000	64.0	.999

$r_1 = 1.31 \pm 0.2$ $r_2 = 0.10 \pm 0.02$

TABLE II

METHYL METHACRYLATE (M_1)–PENTACHLOROSTYRENE (M_2) SYSTEM

Monomer composition Mole fraction M_2	Polymer composition % Cl	Polymer composition Mole fraction M_2
0.2	8.6	0.051
.4	21.7	.156
.6	33.9	.289
.8	49.7	.553
.9	56.0	.715
1.0	63.9	.994

$r_1 = 4.0 \pm 0.4$ $r_2 = 0.35 \pm 0.05$

TABLE III

Monomer	Q	e
Styrene	1.0	−1.0
Methyl methacrylate	0.64	0.0
Pentachlorostyrene	0.2	+0.25

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Heterocyclic Basic Compounds. XII. 7-Bromo- and 7-Iodo-quinolines[1]

BY A. E. CONROY,[2] HARRY S. MOSHER[3] AND FRANK C. WHITMORE[4]

Various workers[5–8] have synthesized N-substituted 4-amino-7-halogen quinolines, certain of which possess considerable antimalarial activity. Outstanding among these is 4-(7-chloro-4-quinolylamino)-2-diethylaminomethylphenol,[9] SN 10,751.[10] The present note describes the synthesis of the 7-bromo- (SN 13,167) and the 7-iodo- (SN 13,168) analogs, which were obtained by coupling, according to Burckhalter, *et al.*,[9] 4-amino-2-diethylaminomethylphenol and the appropriate 4-chloro-7-haloquinoline. The 4-chloro-7-haloquinolines were prepared by the method of Price and Roberts[7] starting with the *m*-haloaniline and ethoxymethylenemalonic ester. The intermediate 4-hydroxy-7-haloquinolines and 4-chloro-7-haloquinolines have also been prepared by Surrey and Hammer[6] by another method. The melting points reported by these authors do not agree in certain cases with those found in this work.

Experimental[11]

3-Carbethoxy-4-hydroxy-7-bromoquinoline.—The intermediate ethyl α-carbethoxy-β-*m*-bromoanilinoacrylate was obtained in 40% yield (45 g.) by allowing a mixture of 50 g. of *m*-bromoaniline[12] and 63 g. of ethoxymethylenemalonic ester[13] to stand overnight. The resulting solid mass was twice recrystallized from a 1:1 solution of ether and ligroin; white needles, m. p. 70–71°. This material, 40 g., was cyclized by refluxing in diphenyl ether according to Price and Roberts.[7] After recrystallization from diphenyl ether, followed by thorough washing with diethyl ether, there was obtained a 44% yield (15 g.) of 3-carbethoxy-4-hydroxy-7-bromoquinoline as a white powder, m. p. 307–309°.

Anal. Calcd. for $C_{12}H_{10}O_3NBr$: C, 48.65; H, 3.38. Found: C, 48.74; H, 3.54.

3-Carbethoxy-4-hydroxy-7-iodoquinoline.—The intermediate ethyl α-carbethoxy-β-*m*-iodoanilinoacrylate was obtained in 43% yield (78 g.) by allowing a mixture of 90 g. of *m*-iodoaniline[12] and 89 g. of ethoxymethylenemalonic ester to stand overnight. The resulting solid mass was recrystallized once from acetone and once from a 1:1 solution of ether and ligroin; white needles, m. p. 92–93°. The product, 70 g., was cyclized and purified as in the above case. There was obtained a 45% yield (28 g.) of 3-carbethoxy-4-hydroxy-7-iodoquinoline as a white powder, m. p. 302–304°.

Anal. Calcd. for $C_{12}H_{10}O_3NI$: C, 42.00; H, 2.92. Found: C, 42.44; H, 3.17.

4-Hydroxy-7-bromoquinoline.—The intermediate 4-hydroxy-7-bromoquinoline-3-carboxylic acid was obtained in 70% yield (8 g.) by the hydrolysis of 13 g. of the 3-carbethoxy-4-hydroxy-7-bromoquinoline with 5% sodium hydroxide solution according to the method of Price and Roberts[7]; light yellow powder, m. p. 266° dec. The decarboxylation of 7 g. of this material was carried out by heating at 300° until the evolution of carbon dioxide ceased. The resulting crystalline cake was recrystallized from 95% ethanol giving 4 g. (68%) of 4-hydroxy-7-bromoquinoline as light tan crystals, m. p. 289–291° (lit.[6] 279–281°).

Anal. Calcd. for C_9H_6ONBr: C, 48.20; H, 2.68. Found: C, 48.01; H, 2.76.

4-Hydroxy-7-iodoquinoline.—The intermediate 4-hydroxy-7-iodoquinoline-3-carboxylic acid was obtained in 66% yield (15 g.) by the hydrolysis of 25 g. of the 3-carbethoxy-4-hydroxy-7-iodoquinoline with 5% sodium hydroxide solution; light grey powder, m. p. 263° dec. The

(1) Taken in part from a thesis submitted by Edward A. Conroy to The Pennsylvania State College in partial fulfillment of the requirements for the Ph.D. degree.

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(4) Deceased.

(5) Andersag, Breitner and Jung, U. S. Patent 2,333,970, *C. A.*, **35**, 3771 (1941); German Patent 683,692, *Chem. Zentr.*, **110**, II, 2446 (1939).

(6) Surrey and Hammer, THIS JOURNAL, **68**, 115 (1946).

(7) Price and Roberts, *ibid.*, **68**, 1206 (1946).

(8) Burckhalter, *et al.*, U. S. Patent 2,419,199, *C. A.*, **41**, 4815 (1947).

(9) Burckhalter, *et al.*, presented before the Medicinal Section of the American Chemical Society, April 9, 1946.

(10) The Survey Number, designated SN, serves to identify a drug in the Monograph "A Survey of Antimalarial Drugs, 1941–1945," F. Y. Wiselogle, editor, Edwards Brothers, Ann Arbor, Mich., 1946.

(11) All melting points are uncorrected. Analyses by Arlington Laboratories, Fairfax, Virginia.

(12) Winans, THIS JOURNAL, **61**, 3564 (1939).

(13) Fuson, Parham and Reed, *J. Org. Chem.*, **11**, 194 (1946)