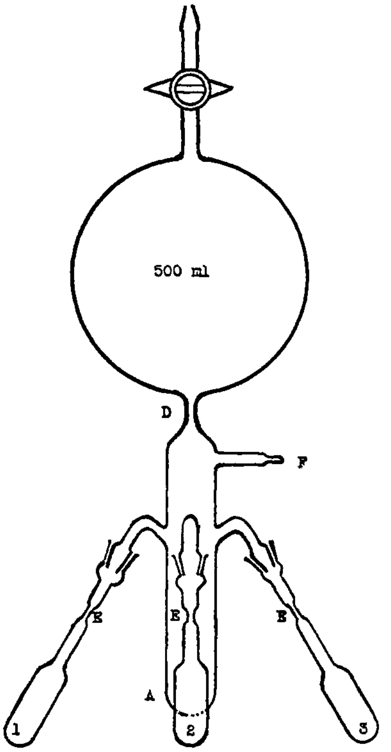

Fig. 1.—Apparatus used for the preparation of carbonyl-cyanyl compounds.

monoxide. Nickel carbonyl (perhaps due to disproportionation of a cyanyl-carbonyl) was condensed in a trap and decomposed on a hot glass surface, with collection and measurement of carbon monoxide. Finally all solids were dissolved in concentrated hydrochloric acid and analyzed for nickel by dimethylglyoxime and potassium by the cobaltinitrite method,[6] using aliquots of the solution.

One result was 43.4% KCN, 25.9% Ni, and 31.3% CO, corresponding perfectly to the formula $(KCN)_3Ni_2(CO)_5$. This could mean equal molar proportions of $K_2Ni(CN)_2(CO)_2$ and $KNiCN(CO)_3$. The average of all the results was: 39.8% KCN, 26.3% Ni, and 35.6% CO, corresponding to $(KCN)_4Ni_3(CO)_8$, or two moles of $KNiCN(CO)_3$ to one of $K_2Ni(CN)_2(CO)_2$. These simple formulas probably are fortuitous since the mixtures seem to vary continuously as indicated by measurements of carbon monoxide evolved in numerous experiments in which the composition of the solute was not determined.

It is also to be noted that in some experiments an insoluble yellow solid was obtained. This was not collected for analysis.

Reaction of $K_4Ni(CN)_4$ with CO.—The displacement of cyanide ion from $K_4Ni(CN)_4$ by the action of carbon monoxide was qualitatively demonstrated as follows. A sample of the salt $K_4Ni(CN)_4$ was prepared by the reaction of $K_2Ni(CN)_4$ with potassium in liquid ammonia.[2] After evaporation of all the ammonia *in vacuo*, methyl cyanide was distilled into the reaction tube, partially dissolving the copper-colored solid. Carbon monoxide now was introduced to a total pressure of 726 mm. During a week, at constant temperature (25°), the pressure fell to 654 mm. and a white precipitate (presumably KCN) appeared. A yellow solid apparently distinct from $K_4Ni(CN)_4$ also was noticed. More carbon monoxide was added and the pressure fell to the same point, 656 mm. Although the question of an established equilibrium was quite uncertain in this and preceding experiments, the fact that carbon monoxide could be either absorbed or evolved depending upon the conditions left no doubt of the reversibility of a series of displacements.

Discussion.—In view of the higher base strength of cyanide ion, it would seem surprising that carbon monoxide is capable of displacing it. The apparent similarity in the strength of bonding to nickel can be understood in terms of the double bonded situation in nickel carbonyl and the argument that the cyanide is chiefly single bonded.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF SOUTHERN CALIFORNIA
LOS ANGELES 7, CALIFORNIA
RECEIVED MARCH 26, 1949

---

[6] L. V. Wilcox, *Ind. Eng. Chem., Anal. Ed.*, **9**, 137 (1937).

Preparation of Arylethynylcarbinols[1]

BY E. T. CLAPPERTON AND W. S. MACGREGOR

Vanillin, veratraldehyde, 4-ethoxy-3-methoxybenzaldehyde and piperonal were converted to the corresponding arylethynylcarbinols by reaction with sodium acetylide in liquid ammonia.[2,3,4] The yields, Table I, ranged from 77 to 93% only when anhydrous conditions were carefully maintained. Hurd and McPhee[5] found that 0.0032 mole of water in a one-fifth mole reaction of acetone with sodium acetylide reduced the yield of dimethylethynylcarbinol from 86 to 49%. In the reaction of benzaldehyde 0.02 mole of water reduced the yield of phenylethynylcarbinol in a one-half mole reaction to 17.5%. The water in this case caused incomplete reaction and induced side reactions yielding nitrogen-free polymers, benzoic acid and benzyl alcohol.

When sodium acetylide and a nine-fold excess of benzaldehyde reacted in the presence of excess acetylene, 139% of phenylethynylcarbinol (based on sodium) was isolated. The high yield would be expected if the anion of phenylethynylcarbinol and acetylene were in equilibrium with the free carbinol and the acetylide anion as suggested by Campbell, Campbell and Eby.[2]

Acknowledgments.—The authors wish to express their appreciation of a grant from Research Corporation in support of this work.

Experimental

General Procedure.—The procedure used was adapted from those previously described.[2-5] The reactions were run in a 2-liter 3-neck flask fitted with a Hershberg stirrer having a hollow shaft for introducing gases. All outlets were protected from atmospheric moisture by Drierite tubes. Commercial acetylene, passed through water, a calcium chloride tube and a Dry Ice trap, was bubbled through a stirred mixture of one-half mole of sodium and 500 ml. of refrigeration-grade ammonia. After the blue

---

[1] From the thesis of E. T. Clapperton presented in May, 1948, in partial fulfillment of the requirements for the Master of Science Degree at the University of Portland. Presented before the Cellulose Division of the American Chemical Society at the 114th meeting.

[2] Campbell, Campbell and Eby, THIS JOURNAL, **60**, 2882 (1938).

[3] Hennion and Murray, *ibid.*, **64**, 1220 (1942).

[4] Jones and McCrombie, *J. Chem. Soc.*, 733 (1942).

[5] Hurd and McPhee, THIS JOURNAL, **69**, 239 (1947).

TABLE I

SUBSTITUTED PHENYLETHYNYLCARBINOLS[a]

Substituents	Yield, %	M. p., °C.	Empirical formula	OCH$_3$, % Calcd.	OCH$_3$, % Found	Mol. wt. Calcd.	Mol. wt. Found	Acetate M. p., °C.	Acetate Empirical formula	Acetate OCH$_3$, % Calcd.	Acetate OCH$_3$, % Found	Acetate Acetyl, % Calcd.	Acetate Acetyl, % Found
4-OH-3-CH$_3$O[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$_2$H$_5$O-3-CH$_3$O[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$_2$O$_2$[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).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF PORTLAND
PORTLAND 3, OREGON

RECEIVED MARCH 30, 1949

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.)

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-

---

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

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

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

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