TABLE I

REDUCTION PRODUCTS OF *m*-NITROSTYRENE

Compound	Yield, %	Color	M. p., °C., cor.	Empirical formula	Analyses, % Carbon Calcd.	Found	Hydrogen Calcd.	Found	Nitrogen Calcd.	Found
3,3′-Divinylazoxybenzene	78	Yellow	39.5–41	$C_{16}H_{14}N_2O$	76.78	76.81	5.64	5.65	11.20	11.30
3,3′-Divinylazobenzene	81.5	Orange	84	$C_{16}H_{14}N_2$	82.02	82.21	6.02	6.16	11.96	11.87
3,3′-Divinylhydrazobenzene	74.5	Faint yellow	96.5-97	$C_{16}H_{16}N_2$	81.32	81.14	6.81	6.92	11.86	11.87
2,2′-Divinylbenzidine	30	White	123	$C_{16}H_{16}N_2$	81.32	81.06	6.81	6.92	11.86	12.10
3-Aminostyrene hydrochloride polymer	84	Brown	Dec.	$C_8H_{10}NCl$	...	...	..	..	9.00	9.17

the experimental part. The azoxy compound was formed with zinc and ammonium chloride instead of the hydroxylamine usually obtained with this reagent. Polymeric products were obtained in the reduction of nitro to amino with zinc and hydrochloric acid; of nitro to azo with stannous chloride; of azoxy to azo with iron filings; and of azo to hydrazo with zinc and alcoholic sodium hydroxide. The azoxy compound polymerized on heating with benzoyl peroxide and the benzidine and azo compounds on heating without catalyst. The hydrazo compound decomposed on heating with benzoyl peroxide apparently without polymerization.

Experimental

Yields, physical properties, and analyses for the following products are listed in Table I.

***m*-Nitrostyrene** was prepared by the decarboxylation of *m*-nitrocinnamic acid by a procedure similar to that previously attempted.[2] A mixture of 20 g. of *m*-nitrocinnamic acid (E. K. Co.), 75 ml. of quinoline, and 3 g. of copper powder were heated at 185–190° so as to produce a steady evolution of carbon dioxide. After one and one-half hours of heating the mixture was acidified with 50% excess 3 *N* hydrochloric acid and steam distilled. The distillate was extracted with chloroform and the combined extracts were dried over anhydrous sodium sulfate. After distilling off the chloroform, the residue was fractionated from a modified Claisen flask to give 9.3 g., 60% of the theoretical amount, of *m*-nitrostyrene, b. p. 90–96° (3.5 mm.), $n^{20}D$ 1.5836. Refractionation through a partial take-off column, 0.75 × 8 in. packed with Fenske rings gave a center cut, b. p. 96° (3.5 mm.), $n^{20}D$ 1.5830. With larger quantities longer reaction times were required and lower yields were obtained than in the above experiment.

3,3′-Divinylazoxybenzene was prepared by the reduction of *m*-nitrostyrene with sodium methoxide in methanol[3] or by reduction with zinc and ammonium chloride in aqueous ethanol.[4] Heating the fused solid at 80° with 0.5% benzoyl peroxide gave an insoluble, infusible polymer.

3,3′-Divinylazobenzene.—To 0.68 g. of 3,3′-divinylhydrazobenzene in 75 ml. of ethanol was added 10 g. of ferric chloride hexahydrate in 25 ml. of hot water. After fifteen minutes water was slowly added to precipitate the azo compound which was twice recrystallized from alcohol-water. Oxidation with sodium hypobromite or air in alcoholic sodium hydroxide also converted the hydrazo to the azo compound. Attempts to convert the azoxy to the azo compound by heating with iron filings gave polymeric products. The sample analyzed melted at 84° (cor.); Komppa[1] reported a m. p. of 38°. Heating at 110° for twenty-four hours gave an insoluble polymer which decomposed before melting when heated.

3,3′-Divinylhydrazobenzene was prepared by zinc and alcoholic sodium hydroxide reduction[5] of *m*-nitrostyrene. Attempts to reduce the azo to hydrazo compound with zinc and alcoholic sodium hydroxide gave only a polymer. On heating a mixture of solid the hydrazo compound and 0.5% benzoyl peroxide to 110° decomposition without apparent polymerization occurred.

2,2′-Divinylbenzidine was prepared in 30% yield by treating 3,3′-divinylhydrazobenzene with concd. hydrochloric acid in ether,[6] m. p. 123° (cor.); reported[1] m. p. 124°. Heating to 135° converted the benzidine to an infusible, insoluble polymer.

***m*-Aminostyrene Polymer.**—Reduction of *m*-nitrostyrene with zinc and hydrochloric acid gave a polymer which was precipitated as the hydrochloride on addition of excess hydrochloric acid to its aqueous acid solution.

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(2) Walling and Wolfstirn, THIS JOURNAL, **69**, 852 (1947).

(3) Sudborough and James, "Practical Organic Chemistry," D. Van Nostrand and Company, New York, N. Y., 1934, p. 252.

(4) Sudborough and James, *ibid.*, p. 253.

(5) Gattermann-Wieland, "Laboratory Methods of Organic Chemistry," The Macmillan Company, New York, N. Y., 1932, p. 174.

(6) Gattermann-Wieland, *ibid.*, p. 176.

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RECEIVED MARCH 13, 1948

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p-Alkoxybenzyl Grignard Reagents

BY M. G. VAN CAMPEN, DONALD F. MEISNER[1] AND STANLEY M. PARMERTER[2]

The alkoxybenzylmagnesium halides are valuable intermediates in the synthesis of stilbene derivatives particularly in the study of synthetic estrogenic agents. However, the general impression exists that these Grignard reagents cannot be prepared. This impression is probably due to the fact that in attempts to form the Grignard from such halides as *p*-methoxybenzyl chloride by the usual procedure, a nearly quantitative yield of the *p*,*p*′-dialkoxybibenzyl is obtained. By using a modification of the method reported by Gilman[3] for the preparation of allyl Grignard reagents, it is possible to prepare *p*-alkoxybenzylmagnesium chlorides in acceptable yields. This is accomplished primarily by the use of a large excess of magnesium powder and slow addition of a dilute ether solution of the benzyl halide to the magnesium. Using the following general procedure 90% yields of *p*-methoxybenzylmagnesium chloride and *p*-benzyloxybenzylmagnesium chloride are consistently obtained.

Procedure.—A mixture of 2 to 2.5 g. atoms of magnesium turnings and 2 to 2.5 g. atoms of magnesium

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(1) Present address: C. J. Patterson Co., Kansas City 2, Missouri.

(2) Present address: Eastman Kodak Research Laboratories. Rochester, New York.

(3) Gilman and McGlumphy, *Bull. soc. chim.*, [4] **43**, 1322 (1928).

powder is vigorously stirred under 1 liter of refluxing anhydrous ether. One mole of the alkoxybenzyl halide dissolved in 1 l. of ether is added over a two to five hour interval. The resulting Grignard reagent is then filtered through glass cotton to remove the finely divided magnesium powder, which if not removed usually reacts with objectionable vigor during the ultimate decomposition with water or dilute acid. The yield is estimated by the usual acidimetric titration.

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RECEIVED MARCH 8, 1948

COMMUNICATIONS TO THE EDITOR

CHEMICAL REACTIONS IN MOVING BOUNDARY SYSTEMS OF WEAK ELECTROLYTES

Sir:

In moving boundary systems containing partially neutralized weak acids or bases there exists the possibility of chemical reactions at the moving boundary which cause the mobility calculated from the boundary velocity and the conductivity of the leading solution to be lower than the ionic mobility.[1] This is illustrated by experiments 2 and 3 in which the indicator electrolyte is a salt of weak acid (cacodylic acid) having a higher *pK* than the leading weak electrolyte (acetic acid). The following reaction goes to completion to the right at the moving boundary so that none of the acetic acid remains behind that boundary.

TABLE I[a]

	Moving Boundary System[b] γ		β	α	$\frac{u \times 10^5}{(0° C.)}$
(1)	NaOAc(0.05)	$\longleftarrow$	NaCac	::NaCac	−17.47
(2)	NaOAc(0.05), HOAc(0.05)	$\longleftarrow$	NaCac, HCac	::NaCac	− 8.81
(3)	NaOAc(0.05), HOAc(0.01)	$\longleftarrow$	NaCac, HCac	::NaCac	− 5.85
(4)	NaOAc(0.05)	$\longleftarrow$	NaT	::NaT	—17.59
(5)	NaOAc(0.05), HOAc(0.05)	$\longleftarrow$	NaT, HOAc	::NaT	−16.54

[a] OAc, acetate; Cac, cacodylate; T, trichloroacetate. [b] The conventions recommended by Longsworth, THIS JOURNAL, **67**, 1109 (1945), are used.

$$\mathrm{Cac^-} + \mathrm{HOAc} \rightleftharpoons \mathrm{HCac} + \mathrm{OAc^-} \quad K_{25°} = 25 \quad (1)$$

The concentration of the sodium acetate is 0.05 *N* (at 0°) in all experiments, and it has been shown that the concentration and *p*H of the indicator electrolyte (α solution) is unimportant over a wide range.

The moving boundary equation[2] cannot be applied to acetate ion in the presence of acetic acid, but a term may be added for the acetic acid as follows so that the moving boundary equation for acetate constituent becomes

$$T^{\gamma}_{\mathrm{OAc^-}} = V^{\beta\gamma}(C^{\gamma}_{\mathrm{OAc^-}} + C^{\gamma}_{\mathrm{HOAc}}) = \frac{u^{\gamma}_{\mathrm{OAc^-}}C^{\gamma}_{\mathrm{OAc^-}}}{\kappa^{\gamma}\,1000/F} \quad (2)^3$$

From equation (2) we see that the mobility, u, calculated from the boundary velocity in this case is the "constituent" mobility. The acetate ion mobility, $u^{\gamma}_{\mathrm{OAc^-}}$

$$u = V^{\beta\gamma}\kappa^{\gamma}\frac{1000}{\mathrm{F}} = u^{\gamma}_{\mathrm{OAc^-}}\frac{(C^{\gamma}_{\mathrm{OAc^-}})}{(C^{\gamma}_{\mathrm{OAc^-}} + C^{\gamma}_{\mathrm{HOAc}})} \quad (3)$$

calculated from the constituent mobility obtained in experiments 2 and 3 by using equation (3) are -17.62×10^{-5} and -17.55×10^{-5} in agreement with the average value, -17.53×10^{-5}, obtained in experiments 1 and 4.

However, in systems containing weak electrolytes the constituent mobility is not always obtained as illustrated by experiment 5. Whether or not a chemical reaction takes place depends upon the *pK* and relative mobility of the indicator ion. In this experiment the mobility calculated is slightly lower than the ionic mobility because the acetate ion does not disappear in the $\beta\gamma$ boundary, owing to the slight dissociation of the acetic acid left behind the moving boundary.

Since proteins and buffers used in electrophoresis are weak electrolytes, reactions such as the above occur and must be considered in the quantitative interpretation of electrophoretic patterns.

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RECEIVED MAY 25, 1948

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[1] Dr. Harry Svensson, Institutes of Physical and Biological Chemistry, Upsala, Sweden, has independently recognized this fact in work initiated in September, 1946 (*Acta Chem. Scand.*, in press), personal communication.

[2] Weber, *Sitzungsber. Akad. Wissensch. Berlin*, 936 (1897); Svensson, *Ark. Kem. Min. Geol.*, **17A**, No. 14 (1943); Longsworth, THIS JOURNAL, **67**, 1109 (1945).

[3] The symbols have the meanings used by Longsworth ($C_{\mathrm{OAc^-}}$ is taken as negative).

SYNTHESIS OF DL-THREONINE

Sir:

The structure α-amino-β-hydroxy-*n*-butyric acid contains two dissimilar asymmetric carbon atoms and hence exists as four optical isomers and