Summary

The acidic ionization constant of the ampholyte glycine has been determined by measurement of the electromotive forces of the cell $H_2/Z^{\pm}$ (m_1), HZCl (m_2), X%D, Y%H_2O/AgCl–Ag and subsequent calculations.

The measurements were carried out in media containing 20, 45 and 70% dioxane by weight, and over a temperature range from 0 to 50° inclusive.

The thermodynamic ionization constants may be expressed by equation (7) the constants of which were determined by the method of least squares. By use of equations (8) through (11) and the constants in Table III the numerical evaluation of the thermodynamic functions is possible. These values at 25° have been given for the ionization in solutions containing 0, 20, 45 and 70% dioxane.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

A Synthesis of Cinnamic Acids from Methyl Acrylate or Acrylonitrile and Diazonium Salts

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From a study of a number of examples, Meerwein and his co-workers[1] concluded that the coupling of diazonium salts with α,β-unsaturated compounds led to the attachment of an aryl group to an α-carbon atom. But the only products whose structures were rigorously proved were those derived from α,β-unsaturated compounds already arylated in the β-position.

Because such coupling reactions of diazonium salts probably involve free aryl radicals[2] and because nitrobenzene reacts readily and leads to *o*- and *p*-nitrobiphenyls,[3] it appeared possible that steric factors might be more important than the direction of polarization of the α,β-unsaturation in determining the carbon atom to which the aryl group became attached. For this reason the behaviors of acrylonitrile and of methyl acrylate toward diazonium salts have been studied.

It has been found that these substances couple readily, and that in every case the product is formed through the union of an aryl group with the β-carbon.

$$ArN_2Cl + CH_2{=}CHCN \longrightarrow ArCH_2CHClCN$$

Since the products are formed in fairly good yields, and since they can be transformed into derivatives of cinnamic acid, the reaction has some promise as a preparative method.

Further studies are being carried out to determine the effect of various substituents in the unsaturated component on the proportion of α- to β-arylation which it undergoes.

Experimental

In a large number of orienting runs it was established that certain conditions, already noted by Meerwein and his collaborators, were almost essential for a successful coupling. These were the presence of acetone, the presence of cupric salt, and the maintenance of the proper *p*H. It was found, however, that this latter condition could be fulfilled as well by using a sodium acetate buffer as by using the chloroacetate of Meerwein.

The following procedure gave generally satisfactory results. A mixture of 0.5 mole of amine with 50 ml. of water was treated with 100 ml. of concd. hydrochloric acid, warmed if necessary to effect solution, then cooled by adding ice, and finally diazotized by adding a concentrated solution of 35 g. of sodium nitrite. This diazonium salt was added dropwise to a stirred mixture kept at 25° prepared by neutralizing 30 g. of acetic acid in 100 ml. of water with 40% sodium hydroxide, adding 15 g. of cupric chloride, 250 ml. of acetone, and 25 g. of acrylonitrile (or 43 g. of methyl acrylate). After the diazonium solution had been added, the mixture was warmed slowly to 35–40°, and stirring was continued for two hours or until no more nitrogen was evolved. The *p*H was then about 6; it was changed to *p*H 2 by adding hydrochloric acid, the oil was separated and the aqueous part was washed once with ether.

In the cases where a nitrodiazonium salt was used, the combined oil and extract was diluted with 250 ml. of ether, causing the separation of a dark red tar. This was extracted five times with 50-ml. portions of ether, and the combined ether solutions were then concentrated. The residue crystallized and was fairly pure α-chloronitrohydrocinnamonitrile; for complete purification this substance was distilled in small quantities under reduced

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(1) Meerwein, Buchner and van Emster, *J. prakt. Chem.*, **152**, 237 (1939); *cf.* British Patent 480,617; Bergmann and Weinberg, *J. Org. Chem.*, **6**, 134 (1941).

(2) Haworth, Heilbron and Hey, *J. Chem. Soc.*, 372 (1940).

(3) France, Heilbron and Hey, *ibid.*, 369 (1940); Elks, Haworth and Hey, *ibid.*, 1284 (1940).

TABLE I

COUPLING PRODUCTS

No.	Compound	B. p. °C.	B. p. Mm.	M. p., °C.	Yield, % Crude	Yield, % Pure[a]	Formula	Calcd. C	Calcd. H	Found C	Found H
I	α-Chlorohydrocinnamonitrile	137–140	15	18– 21	..	34	C_9H_8ClN	65.3	4.8	65.8	4.9
II	α-Chloro-*m*-nitrohydrocinnamonitrile	215–225	13	83– 84	53	38	$C_9H_7ClN_2O_2$	51.3	3.3	52.8	3.4
III	α-Chloro-*p*-nitrohydrocinnamonitrile	...	..	111–112	61	48	$C_9H_7ClN_2O_2$	51.3	3.3	51.3	3.3
IV	α-Chloro-*p*-methylhydrocinnamonitrile	140–145	11	...	45	40	$C_{10}H_{10}ClN$	66.8	5.6	66.7	5.8
V	Methyl α-chloro-*p*-methylhydrocinnamate	135–145	11	...	23	..	$C_{11}H_{13}ClO_2$	62.1	6.1	64.6	6.5

[a] Because of the ease with which they lose hydrogen chloride, some of the coupling products could not be obtained completely pure (see analyses) in spite of many efforts. There can be no doubt as to the constitutions of these substances however, because they were all converted into cinnamic acid derivatives (Table II) and compared with the same derivatives prepared by standard methods.

TABLE II

CINNAMIC ACID DERIVATIVES

No.	Compound	Source	Yield, %	B. p., °C.	B. p., Mm.	M. p., °C.
VI	Cinnamonitrile	I	96	115–120	12	20[a]
VII	Cinnamic acid	VI	55	...	..	132–134
VIII	*m*-Nitrocinnamonitrile	II	72	205–208	11	157–160[a,b]
IX	*p*-Nitrocinnamonitrile	III	61	...	..	200–201[a,c]
X	*p*-Methylcinnamonitrile	IV	84	120–130	12	60– 70[d]
XI	Methyl *p*-methylcinnamate	V	81	110–130	8[e]	...
XII	*p*-Methylcinnamic acid	X	62	...	..	195–197[f]
XII	*p*-Methylcinnamic acid	XI	51	...	..	195–197[f]

[a] Alone or mixed with an authentic sample prepared by dehydrating the amide with thionyl chloride. [b] Brady and Thomas [*J. Chem. Soc.*, **121,** 2108 (1922)] report m. p. 160°. [c] $C_9H_6N_2O_2$ requires C, 62.1; H, 3.4. Found: C, 62.2; H, 3.2. Brady and Thomas (*loc. cit.*) report m. p. 202°. [d] Fiquet [*Ann. chim.*, [6] **29,** 483 (1893)] reports b. p. 180° (vac.), m. p. 79–80°. [e] Stoermer, Grimm and Laage [*Ber.*, **50,** 980 (1917)] report b. p. 164–165° (32 mm.). [f] Hanzlik and Bianchi [*ibid.*, **32,** 1289 (1899)] report m. p. 198–199°.

pressure and crystallized from alcohol. The distillation of the nitronitriles before the tar had been removed by the ether treatment, or the distillation of the partly purified substances in large quantities always resulted in explosions. The chloronitriles containing no nitro group could be distilled safely in small quantities in their crude states; some elimination of hydrogen chloride took place, but only by distillation could all the tarry by-products be removed. In addition to the chloronitriles, small amounts of the phenols and the aryl chlorides corresponding to the diazonium salts were isolated from the reaction mixtures.

In order to convert the chlorohydrocinnamonitriles to cinnamonitriles, the compounds were boiled for five minutes with five times their weight of diethylaniline. The base was then removed with dilute sulfuric acid, and the product was distilled under reduced pressure or crystallized. The cinnamic acids were obtained from the cinnamonitriles or directly from the chlorohydrocinnamonitriles by boiling them for one-half to one hour with 10% aqueous sodium hydroxide.

The author thanks the Dow Chemical Company of Midland, Michigan, for furnishing the acrylonitrile used in this investigation.

Summary

Diazonium salts react with acrylonitrile or with methyl acrylate to give α-chlorohydrocinnamic acid derivatives. This β-arylation is in contrast with the α-arylation reported to result when diazonium salts react with other α,β-unsaturated compounds.

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