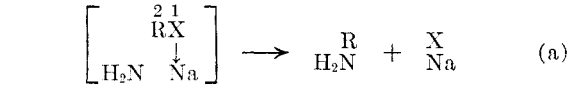
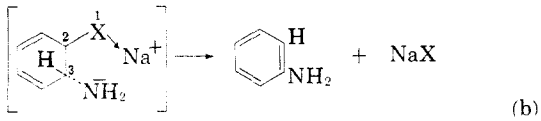
tween alkali metal salts and halogen compounds begin with proton removal and follow with halogen ejection. Essentially the intermediate is a stripped-down molecule, an acetylenic system in a 6-membered ring. Lately the idea has been adopted for a Wurtz-Fittig reaction.[3] It is interesting to apply the ion-pair concept to this amination. Here the intermediate would be essentially an additive product, a built-up molecule approaching the type of dihydrobenzene. In succeeding paragraphs, this idea will be developed. The ordinary reaction, usually called displacement, will be pictured as 1,2-addition, halogen being numbered 1. *Meta* amination would begin as 1,3-addition followed by common steps that permit accounting for all of the effects so far observed.

For all cases the carbon-halogen bond is presumed to have a degree of unsaturation. The polar end of the carbo-halyl system has unshared electrons and at the instant of reaction is adjacent to the positively charged cation. This contact is denoted in (a) with an arrow, probably as a coordination. As sodium halide emerges from the complex the amino group adds to carbon. The over-all process is 1,2-addition as unsaturation develops at the carbon end



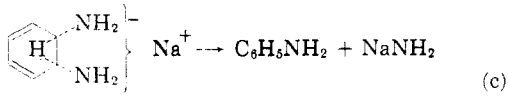
(a)

A 1,3-addition is shown in (b). The amino group might add (dotted line) at the 3-position as sodium halide emerges and hydrogen shifts. A random mix-



(b)

ture of 1,2- and 1,3-additions might occur. However the halogen has become very labile and of the type of an activated aliphatic halogen atom. Its displacement by an amide ion would give the complex in (c) from which a loss of sodamide in one of two equivalent ways would give aniline. All facts



(c)

connected with C^{14} halobenzenes would thereby be accounted for and with an intermediate far less strained than a "benzyne" structure.

This general picture for halogen removal is made more complete by an example of 1,4-addition. The novel formation of allenes[4,5] from some chloromethylacetylenes and lithium hydride (from lithium aluminum hydride) fits nicely into this category. As lithium chloride emerges from the complex illustrated in (c), addition occurs at the 4-position. Accompanying shifts produce a double bond between

(d)

the 2- and 3-positions, just as in many other 1,4-processes.

These additions involve both ions of the reagent. Electrons and charges move into appointed places, but such features and numerous details are avoided as far as possible in order to keep in focus the main issue of an intermediate that is achieved by stripping off atoms to give an acetylenic type structure *versus* one which is reached by adding atoms or ions to give a complex in which an unstrained dihydroaromatic system is approached. This discussion is not to be construed as a statement that the "benzyne" intermediate is wrong, but all facts so far presented[2] in its behalf can be interpreted equally well by some variant of the ion-pair concept.

CHEMISTRY DEPARTMENT
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE 39, MASSACHUSETTS

(3) Jenny and Roberts, *Helv. Chim. Acta.* **38,** 1248 (1955).
(4) Wotiz, *J. Am. Chem. Soc.*, **73,** 693 (1951).
(5) Bailey and Pfeifer, *J. Org. Chem.*, **20,** 95 (1955).

A New Technique for the Chromatographic Separation of Organic Compounds

ROGER SARGENT AND WM. RIEMAN III

Received February 29, 1956

Ion-exchange resins have been used as the stationary phase in chromatographic separations of the following types: (1) separation of two or more ions by elution with a solution of an electrolyte, (2) separation of an electrolyte from a nonelectrolyte by elution with water (ion exclusion),[1,2,3] and (3) separation of two or more nonelectrolytes by elution with water.[2] The purpose of this communication is to report that the separation of nonelectrolytes is greatly improved simply by using a salt solution instead of water as the eluant.

For example, the elution with water of a mixture of diethylene glycol and dipropylene glycol on a 70-cm. column of Dowex 1X8, sulfate form, 200–300 mesh, yields no separation, whereas elution on a 10-cm. column with 3.0 *M* ammonium sulfate yields a quantitative separation, diethylene glycol emerging from the column first. As illustrated in Fig. 1, the separation of methanol, ethanol, and propanol-1 is much better with 3.0 *M* ammonium sulfate as

(1) Wheaton and Bauman, *Ind. Eng. Chem.*, **45,** 228 (1953).
(2) Simpson and Wheaton, *Chem. Eng. Progr.*, **50,** 45 (1954).
(3) Simpson and Bauman, *Ind. Eng. Chem.*, **46,** 1958 (1954).

eluant than with water. Since the peak concentration of propanol-1 would appear at an effluent volume of 475 ml. with 3.0 *M* ammonium sulfate, the elution of this alcohol was hastened by changing the eluant to water after the elution of ethanol. Some precaution, such as taping the column, should be taken to guard against the hazard due to the

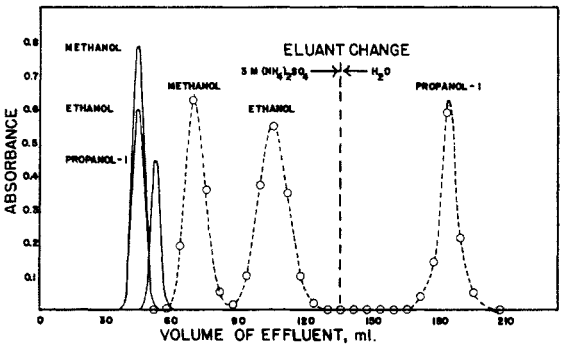


FIG. 1. COMPARISON OF THE SEPARABILITY OF ALCOHOLS WITH WATER AND 3.0 *M* AMMONIUM SULFATE. Eluants: water (————), 3 *M* ammonium sulfate (----------). Column: 25.7 cm. × 2.28 cm.², Dowex 1 × 4, 200–300 mesh, sulfate form. Flow rate: 0.5 cm./min.

swelling of the resin at this point. The quantity of the eluted alcohol in each fraction was determined by oxidation with dichromate in 50% sulfuric acid and the subsequent measurement of the absorbance of Cr(III).[4]

The beneficial effect of an electrolyte in the eluant is probably due to a selective salting-out of the organic compounds from the aqueous to the resinous phase. As the salt concentration in the water phase is increased, the solubility of the organic compound is decreased. Linear increases in the salt concentration produce roughly exponential increases in the abscissas of the peaks of the elution graphs.

RALPH G. WRIGHT CHEMICAL LABORATORY
RUTGERS UNIVERSITY
NEW BRUNSWICK, NEW JERSEY

(4) Sargent and Rieman, *Anal. Chim. Acta*, in press.

Methoxy- and Hydroxy-styryl Heterocycles

HENRY GILMAN, J. LEWIS TOWLE, AND ROBERT K. INGHAM

Received March 2, 1956

The marked antiseptic and trypanocidal activity of styrylpyridine and styrylquinoline derivatives has been reported;[1] styrylbenzothiazole compounds have been prepared and tested for similar chemotherapeutic properties.[2]

For use in connection with other studies, several

(1) (a) Ashley, Browning, Cohen, and Gulbranson, *Proc. Roy. Soc. (London)*, **B113**, 293 (1933); (b) Browning, Cohen, Ellingsworth, and Gulbranson, *J. Path. Bact.*, **27**, 121 (1924); (c) Browning, Cohen, Ellingsworth, and Gulbranson, *Brit. Med. J.*, **II**, 326 (1923).

(2) Stephens and Webberly, *J. Chem. Soc.*, 3336 (1950).

TABLE I

METHOXYSTYRYL COMPOUNDS

No.	Compound	M.p., °C.	Yield, %	Recrystallization solvent	Analyses S Calc'd	S Found	N Calc'd	N Found
I	2-(*p*-Methoxystyryl)benzothiazole	142–144	58[a]	Ethanol	11.95	12.00		
II	2-(2′,3′-Dimethoxystyryl)-benzothiazole	90–91	88	Dilute methanol	10.80	10.64		
III	2-(3′,4′-Dimethoxystyryl)-benzothiazole	150–151	67	95% Ethanol	10.75	11.00		
IV	2,6-Di-(2′,3′-dimethoxystyryl)-pyridine	140–141	50	Benzene-pet. ether (b.p. 60–70°)			3.48	3.62
V	2,6-Di-(3′-methoxy-4′-hydroxystyryl)pyridine	173–175	39.5	95% Ethanol			3.73	4.00
VI	2,3-Di-(*p*-methoxystyryl)quinoxaline	163–164	71[b]	Benzene				
VII	2,3-Di-(3′,4′-dimethoxystyryl)-quinoxaline	196–197[c]	64[c]	Benzene-pet. ether (b.p. 60–70°)			6.17	6.39
VIII	2-(*p*-Methoxystyryl)-6-methoxyquinoline	162–163	76	Benzene-pet. ether (b.p. 60–70°)			4.82	5.00
IX	2-(3′,4′-Dimethoxystyryl)-6-methoxyquinoline	137–138	75	95% Ethanol			4.36	4.31
X	2-(2′,3′-Dimethoxystyryl)-4-hydroxy-6-methoxyquinoline	278–280	60	Methyl Cellosolve[d]			4.15	4.27

[a] A 3% yield was obtained with piperidine as a catalyst. [b] Previously prepared in 10% yield (see ref. 7). [c] Reported m.p. 208°, in 10% yield (see ref. 7). [d] Trade mark for 2-methoxyethanol.