A Simple Application Technique for Paper Chromatography

COMPARATIVELY little use has been made of paper chromatography for micro or semimicro preparative purposes. A difficulty encountered in such work is that of applying relatively large quantities of material to the paper. The methods hitherto used are either time-consuming, for example, multiple, manual application of contiguous spots along a line some 24 in. in length, or require special apparatus, such as the kymograph method of Yanofsky, Wasserman and Bonner¹. The need for a quick and simple technique of application has led to the development of the following procedure.

A line is drawn parallel to, and 2 in. from, the edge of a large sheet of filter paper. The paper is now carefully folded along the line. Dipping the edge of the fold into the solution to be chromatographed results in the application of a band of solution which is both wide and uneven. This difficulty can be avoided by bringing the edge of the paper into contact with a strip of paper wetted with the solution.

Two or three long narrow strips of filter paper, preferably hardened, are placed one on top of the other in a trough. The solution to be used is poured into the trough in quantity (c. 10 ml. for three strips 24 in. by $\frac{3}{4}$ in.) just sufficient to wet the strips. The chromatogram is held taut between the thumb and second finger of each hand, the index finger being used to keep the two parts of the fold apart. The edge is now brought into contact with the strips for a short period. Regulation of the contact time controls the width of the band of material taken up by the chromatogram. After drying, the process is repeated until the desired concentration has been obtained. Sheets of paper up to 18 in. in width are easily handled. 24-in. sheets are best cut in half and spotted separately.

Typical of the results obtained by this method is the chromatogram of a mixture of glycine, alanine and valine run in phenol, A being the starting line (see photograph).

Paper chromatogram of a mixture of glycine, alanine and valine applied by the trough technique

Thanks are due to the South African Council for Scientific and Industrial Research for permission to publish this note.

L. NOVELLIE

National Chemical Research Laboratory,
Pretoria.
Nov. 2.

¹ Yanofsky, C., Wasserman, E., and Bonner, D. M., *Science*, 111, 61 (1950).

Bimolecular Nucleophilic Substitution with Anionotropic Rearrangement

WE have been concerned to establish bimolecular substitution with rearrangement, S_N2' , in anionotropic systems, for example, $\text{EtO}^- \text{CH}_2\text{CH}=\text{CH}-\text{X}$

$\text{CH(X)}-\text{Cl} \rightarrow \text{EtO}-\text{CH}_2-\text{CH}=\text{CH}-\text{X} + \text{Cl}^-$ (S_N2'). This has proved somewhat difficult, though, as it now appears, not for the reason that the mechanism is particularly uncommon, but because, in most simple cases, it is obscured by an accompanying substitution without rearrangement, S_N2 . The one fully established and unambiguous case is that recently reported¹, in which an isotopic substituting agent was employed to destroy the power of a faster S_N2 substitution to mask a slower S_N2' reaction. This work confirmed a suggestion, which had been made on theoretical grounds earlier², that what was needed to make S_N2' substitution observable without any necessity for such special measures was a suitable α -substituent in the allyl system, in order to retard selectively the S_N2 process.

On examining the literature, we noticed records to the effect that 1-chloro-3-ethoxypropene-1 had been isolated from the products of reaction of 3,3-dichloropropene-1 with sodium ethoxide³, and that the total process had been shown to have approximate second-order kinetics^{4,5}. Certainly, the fact that only part of the original chlorine is displaced in the reaction supports rearrangement, since substitution without rearrangement would produce an α -chloro-ether, which would readily lose its chlorine. This suggests that an α -chloro-substituent in an allyl halide system is, as might be supposed on other grounds, competent to favour the S_N2' reaction sufficiently to render it easily observable. (A halogen atom at the site of substitution inhibits mechanism S_N2 ; for example, for the reaction with Br^- at 25°, $k_{\text{CH}_3\text{Br}}/k_{\text{CH}_2\text{Br}_2} = 3,800$.)

We have therefore re-examined the products and kinetics of the reaction between 3,3-dichloropropene-1 and sodium ethoxide, and have established the following points:

(1) Substitution with rearrangement occurs concurrently with substitution without rearrangement, the rates of the two processes being of the same order of magnitude.

(2) *trans*-1-Chloro-3-ethoxypropene-1 is formed in considerable yields (for example, 25 per cent at 85°). The *cis*-isomer of this product is also obtained, but it participates more readily in further changes. From reactions which were discontinued before reaching their final stages, the dihalide was isolated unchanged.