# NOTES.

## *The Mechanism of Anionotropic Change and the Fate of the Mobile Anion.* By HAROLD BURTON.

IT has been shown (J., 1928, 1650) that the mobile group X (= $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{O}$) in the system $\text{Ph}\cdot\text{CHX}\cdot\text{CH}\!:\!\text{CH}_2$ (I) $\rightleftharpoons$ $\text{Ph}\cdot\text{CH}\!:\!\text{CH}\cdot\text{CH}_2\text{X}$ (II) undergoes ionic dissociation promoted by some molecular property of the solvent closely related to its dielectric constant. This conclusion was reached from a study of various points which are summarised as follows : (1) The change (I) $\longrightarrow$ (II) was not catalysed by strong or weak acids. (2) Isomerisation occurred smoothly in boiling acetic anhydride. (3) The possibility of a mechanism in which the mixed *p*-nitrobenzoic–acetic anhydride reacted with cinnamyl acetate (formed as an intermediate) was excluded. (4) The change (I) $\longrightarrow$ (II) occurred smoothly in benzonitrile at 140°, more slowly in chlorobenzene, and much less readily in *p*-xylene. (5) When α-phenylallyl *p*-nitrobenzoate was heated with an equivalent of tetramethylammonium acetate in acetic anhydride, a mixture of cinnamyl acetate (II; with $\text{X}_1 = \text{CH}_3\cdot\text{CO}\cdot\text{O}$ replacing X) and cinnamyl *p*-nitrobenzoate, in which the former preponderated, was obtained.

Further evidence regarding the above hypothesis can be obtained by investigating any change that may occur when cinnamyl *p*-nitrobenzoate is heated with tetramethylammonium acetate in acetic anhydride under the same conditions of time, temperature, and concentration as those originally used in (5). The non-formation of any appreciable quantity of cinnamyl acetate under such conditions would definitely exclude the possibility that, in (5), cinnamyl *p*-nitrobenzoate is first produced and then reacts with the tetramethylammonium acetate to give cinnamyl acetate. That such a reaction does not occur to any marked extent has been shown as follows :

A mixture of cinnamyl *p*-nitrobenzoate (10 g.), tetramethylammonium acetate (4·7 g.), and acetic anhydride (20 c.c.) was boiled for 6 hours, and the dark reaction mixture poured into warm water. The resulting precipitate (8 g.), m. p. 75° after being washed with water and cold alcohol, gave after one crystallisation from alcohol pure cinnamyl *p*-nitrobenzoate, m. p. and mixed m. p. 77—78°. The alcoholic washings contained a dark oil with the characteristic odour of cinnamyl acetate, but the quantity was too small for examination. A small amount of *p*-nitrobenzoic acid separated from the acidic aqueous mother-liquor on keeping.

This experiment, together with (5), shows that the substitution of X by $X_1$ occurs during, and not after, the change; and since $X_1$ was introduced in the negatively charged form, the experiments constitute a self-contained proof that the separation of X with a negative charge is a condition essential to migration.—THE UNIVERSITY, LEEDS. [*Received, May 24th,* 1934.]

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### *Electronic versus Ionic Mechanisms for Intramolecular Rearrangements.* By FRANK C. WHITMORE and GEO. H. FLEMING.

MOST molecular rearrangements have been discovered as isolated aberrations from the normal course of organic reactions. It is not strange, then, that diverse explanations of them have appeared, involving various types of ring structure, olefins, univalent nitrogen, bivalent carbon, and uni- and bi-valent ions. The British school of organic chemists has focused attention on the electronic nature of these changes (*Ann. Reports*, 1923—1930). Recently the conviction has grown that all rearrangements have much in common and should be explicable on a common basis. The electronic hypothesis used in this laboratory (*J. Amer. Chem. Soc.*, 1932, **54**, 3274; 1933, **55**, 4153) fits the facts remarkably well and is a valuable tool in experimental work. The presentation of this hypothesis and its applications has been faulty, however, in that many chemists have been left with the impression that it is an " ionic mechanism " such as the one used to explain rearrangements of alcohols and related compounds which can undergo at least a minimal ionisation (Meerwein *et al.*, *Annalen*, 1927, **455**, 227). This ionic mechanism failed, however, in the Hofmann, Lossen, Curtius, and Beckmann rearrangements, and in processes such as the action of nitrous acid with primary amines (*J. Amer. Chem. Soc.*, 1932, **54**, 3435, 3441). The confusion of the present electronic hypothesis with the earlier ionic mechanism extends to *Ann. Reports* (1933, **30**, 177), where it is implied that the hypothesis does not apply to the Hofmann rearrangement of *d*-3 : 5-dinitro-2-α-naphthylbenzamide into *d*-3 : 5-dinitro-2-α-naphthylaniline (Wallis and Moyer, *J. Amer. Chem. Soc.*, 1933, **55**, 2598). Actually, this rearrangement of the sterically hindered diphenyl derivative without racemisation offers the best existing proof of the soundness of the hypothesis used in our work (*ibid.*, 1934, **56**, 1729).

The misconception can best be corrected by a more detailed application of the electronic hypothesis to our study of the reaction between *neo*pentyl iodide, $CMe_3{\cdot}CH_2I$, and silver acetate. In conductivity glacial acetic acid at 60° in 36 hrs., this gives *tert.*-amyl acetate and mainly trimethylethylene, no *neo*pentyl acetate, the normal product, being detected. This result corresponds to that obtained with *neo*pentyl alcohol and halide acids (*ibid.*, 1932, **54**, 3431). The *tert.*-amyl acetate was treated with fuming hydrochloric acid, the resulting chloride was converted into the Grignard reagent, and treated with phenyl *iso*cyanate; dimethylethylacetanilide was formed, m. p. and mixed m. p. 90—91°, thus proving the tertiary structure.

We picture this reaction as follows : (1) The formation of silver iodide removes an iodine with a complete octet of electrons, thus leaving one carbon of the *neo*pentyl system with only six electrons, an open sextet. This fragment is unstable and reactive, resembling a " positive " chlorine atom with only six electrons; neither of the systems shows the properties of an ordinary positive ion having a complete octet. (2) The fragment must undergo a change which will eliminate the open sextet; this could be effected by one of the following mechanisms. (*a*) Union with an acetate ion; but failure to detect *neo*pentyl acetate indicates that this does not take place to any appreciable extent. (*b*) Attraction of an electron pair from the next atom in the same molecule; this process requires no special mechanism : the methyl group, held by the shifting electron pair, moves with it to form a *tert.*-amyl system, in which the tertiary carbon has an open sextet. It is unreasonable to assume either that the electron pair or the methyl group, with or without electrons, leaves the molecule during the process. The transfer from one atom to the next takes place entirely intramolecularly, as Wallis and Moyer have shown so clearly in their rearrangement (*loc. cit.*). (3)(*a*) The electronically deficient *tert.*-amyl fragment formed as in (2) (*b*) can and does satisfy its deficiency by union with an acetate ion; hence, the " life " of this fragment is apparently longer than that of the corresponding *neo*pentyl fragment, in agreement with the known facts about primary and tertiary compounds. (*b*) The deficiency can be satisfied *intramolecularly* by the shift of an electron pair from an adjacent atom to form a double bond and liberate a proton; this change would give trimethylethylene and 2-methyl-1-butene.—THE PENNSYLVANIA STATE COLLEGE, STATE COLLEGE, PENNA. [*Received, April 20th,* 1934.]