II.—*Influence of Poles and Polar Linkings on Tautomerism in the Simple Three-carbon System. Part I. Experiments illustrating Prototropy and Anionotropy in Trialkylpropenylammonium Derivatives.*

By CHRISTOPHER KELK INGOLD and EUGENE ROTHSTEIN.

ONE of the most immediate consequences of the acceptance of the electronic theory of valency is that the double-bond displacement involved in the various phenomena grouped under the name tautomerism is to be interpreted as an electron-duplet displacement entailing a redistribution of electrical charges (the "tautomeric electron-displacement," *T*). The study of tautomerism—both of cationotropy and anionotropy—is, on this view, a study of the conditions affecting charge-distribution by the *T*-displacement; and, since some of the major reactions of Organic Chemistry, as, for example, additions to conjugated unsaturated systems, and substitutions in aromatic systems, are believed to depend largely on this type of charge-transference between *carbon* atoms, fundamental information is to be gained by an examination of prototropic and anionotropic transformations in the *true three-carbon* system.

The large accumulation of data, for which we are indebted mainly to Kon and Linstead, regarding "three-carbon" prototropy relates exclusively to systems terminated by unsaturated groups such as carbonyl: $C[H]\cdot C{:}C\cdot C{:}O \rightleftharpoons C{:}C\cdot C{:}C\cdot O[H] \rightleftharpoons C{:}C\cdot C[H]\cdot C{:}O$. The systems are, indeed, pentad (*e.g.*, pentad keto-enol); but in so far as the enolic intermediate can be neglected there is some justification for regarding them as the equivalent of three-carbon systems: the relation between the ketonic forms at equilibrium will depend *inter alia* on anionic charge-distribution in the $C\cdot C{:}C$-group (Ingold, Shoppee, and Thorpe, J, 1926, 1477). Prototropy in the *elementary* three-carbon system, that is, the $C\cdot C{:}C$-group joined to saturated radicals only, has not yet been studied, and we have therefore undertaken to repair this omission.

Amongst the saturated groups which suggest themselves as likely to fulfil the primary necessity of loosening the potentially mobile proton by the attraction of its electrons are $-NR_3^{\cdot}$, $-SR_2^{\cdot}$, $-SO_2R$, $-SO_3'$, and the work here to be described utilises the first of these. Since unsaturated diammonium bases of the type

$$\overset{\ominus}{O}H\{R_3\overset{\oplus}{N}\cdot CH_2\cdot CH{:}CH\cdot \overset{\oplus}{N}R_3\}\overset{\ominus}{O}H$$

(like glutaconic acid, except that $\cdot NR_3$ replaces $\cdot CO_2H$) have not yet been prepared, some exploratory work was necessary, and it was during the examination of a possible route to such compounds that we unexpectedly encountered evidence, not only of prototropic, but also of anionotropic, mobility * in three-carbon systems terminated by one ammonium-salt group only.

Starting from γ-chloroallyl chloride, no difficulty was experienced (see scheme below) in obtaining quaternary γ-chloroallylammonium salts of the type $\{CHCl{:}CH\cdot CH_2\cdot N(alk)_3\}^{\cdot}X'$, but the chlorovinyl chlorine atom in these could not be induced to enter into reaction with secondary or tertiary amines. This had been anticipated, and our plan was to subject the cations of these salts to the attack of an anion of high co-ordinating power; the electron-affinity of $-\overset{\oplus}{N}R_3$ might then, we supposed, induce the liberation of an α-proton with the subsequent formation of the isomeric salts

$$\{CH_2Cl\cdot CH{:}CH\cdot N(alk)_3\}^{\cdot}X',$$

which, since they are allyl chlorides, should readily react with tertiary amines to give the required diammonium compounds. The effect of treating the γ-chloroallyl salts with sodium ethoxide in warm alcohol was to produce a series of ethoxy-salts, which were at first thought to

---

* Prototropic mobility in such salts was predicted by one of us in 1926 at the meeting of the British Association in Oxford.

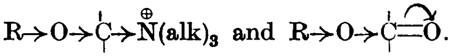
have the constitution $\{\mathrm{CH_2(OEt){\cdot}CH{:}CH{\cdot}N(alk)_3}\}^{\cdot}\mathrm{X}'$; but their properties (especially the difficulty attending the replacement of OEt by Br) aroused suspicion. Investigation then showed that these salts possessed the constitution $\{\mathrm{CH_2{:}CH{\cdot}CH(OEt){\cdot}N(alk)_3}\}^{\cdot}\mathrm{X}'$, ozonolysis yielding, in each case, formaldehyde and an ethoxyaldehydo-ammonium salt of the general formula $\{\mathrm{CHO{\cdot}CH(OEt){\cdot}N(alk)_3}\}^{\cdot}\mathrm{X}'$.

In retrospect it is obvious that such a result might have been anticipated. The potentially mobile atom being shown in square brackets, the salts, $\{\mathrm{CHCl{:}CH{\cdot}CH[H]{\cdot}N(alk)_3}\}^{\cdot}\mathrm{X}'$, contain a prototropic system only, but their tautomerides,

$$\{\mathrm{CH[H]Cl{\cdot}CH{:}CH{\cdot}N(alk)_3}\}^{\cdot}\mathrm{X}' = \{\mathrm{CH_2[Cl]{\cdot}CH{:}CH{\cdot}N(alk)_3}\}^{\cdot}\mathrm{X}',$$

have in addition an anionotropic system, which, since its mobile atom is a halogen, would be expected to function under the conditions which were established in order to effect the primary prototropic change (Burton and Ingold, J., 1928, 904). Furthermore, the proved connexion (*loc. cit.*) between the facilitation of anionotropy by groups and their orienting action in aromatic substitution, when applied to the anionotropic system $\mathrm{H}-\overbrace{\mathrm{CH{\cdot}CH{\cdot}CH}}-\overset{\oplus}{\mathrm{N}}\mathrm{R_3}$ (anion omitted), requires that the order of facilitation shall be $\mathrm{H} > \overset{\oplus}{\mathrm{N}}\mathrm{R_3}$; wherefore analogy suggests that the position of stable attachment of the mobile anion should be that adjacent to the ammonium group. But further, the production of an *isomeride* from a mobile anionotropic system depends on the absence from the medium of foreign anions having a greater co-ordinating power than that possessed by the anion derived from the system itself (Burton, J., 1928, 1650). This condition is not fulfilled in the present instance, and it is evident that the chloride ion originally eliminated would have small chance of returning to the system in the face of competition from the large concentration of ethoxide ions present in the medium. Thus, after the reaction, free chloride ions are present, ethoxide ions have disappeared, and the original chloro-salt has given place to an ethoxy-salt of the constitution $\{\mathrm{CH_2{:}CH{\cdot}CH(OEt){\cdot}N(alk)_3}\}^{\cdot}\mathrm{X}'$.

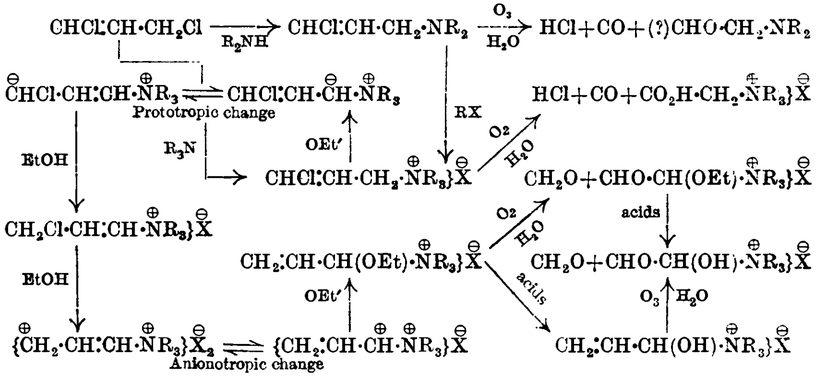
Furthermore, our failure to effect replacement of the OEt-group in these salts by Br, by methods normally successful with allyl ethers, is readily understood, for the same electron-affinity of the $\mathrm{N(alk)_3}$-group which determines the stable attachment of ethoxyl must also cause its shared electrons to be exceptionally deeply implicated in the constitution of the α-carbon atom, and must accordingly inhibit any reaction involving the separation of ethoxyl *with these electrons*. If this is correct, then, for an exactly similar reason, the ammonium group should facilitate the separation of ethyl *without* its shared electrons; in other words, the ethoxycompounds should in certain respects resemble esters rather than ethers. Of course there are limits to the analogy represented by



$$R \rightarrow O \rightarrow C \rightarrow \overset{\oplus}{N}(alk)_3 \text{ and } R \rightarrow O \rightarrow C{=}O.$$

For instance, it would not apply to *alkaline* saponification, which, in the case of carboxylic esters, depends (addition of OH′ at carbonyl) on an unsaturated linking absent from the ammonium salts. But as regards *acid* hydrolysis, in which the seat of attack (by hydrogen ions) is the unshared electrons of the singly-bound oxygen atom, the two systems should show their similarity. Experiment showed that the ethoxy-salts are in fact as readily hydrolysed by acids as are many carboxylic esters, and we confirmed our view that the presence of the vinyl group has nothing to do with the matter by showing that the ethoxyaldehydo-salts, obtained by ozonolysis, could be hydrolysed in the same way with similar facility.

Other transformations, which need no special comment, as, for instance, ozonolysis of the chloro- and hydroxy-salts to products establishing their constitutions, are included in the scheme given below, in which R represents methyl or ethyl, and X a univalent anion (chloride, acetate, picrate, etc.) or a semi-equivalent of a bivalent anion (chloroplatinate):



EXPERIMENTAL.

Diethyl-γ-chloroallylamine and its Salts.—γ-Chloroallyl chloride (10 g.) was mixed with diethylamine (14 g.) under an efficient reflux condenser. When the vigorous reaction had ceased, the product was mixed with aqueous sodium hydroxide and extracted with ether; thereafter diethyl-γ-chloroallylamine was obtained as a colourless liquid, b. p. 55°/9 mm. (yield, 75%). The hydrochloride was very soluble in water, but separated from acetone in plates, m. p. 221°. The *picrate* crystallised from water in prismatic needles,

m. p. 78° (Found : C, 41·7 ; H, 4·7. $C_{13}H_{17}O_7N_4Cl$ requires C, 41·4 ; H, 4·5%).

Triethyl-γ-chloroallylammonium Salts.—(*a*) The tertiary base (7 g.) was warmed with ethyl iodide (15 g.) in ethyl alcohol (10 c.c.) under reflux, and the quaternary iodide precipitated as a pale yellow, crystalline solid by addition of much ether. It was dissolved in alcohol, reprecipitated by the addition of ether, and crystallised from acetone, from which it separated in needles, m. p. 210°. Treatment with aqueous sodium picrate gave a *picrate*, which crystallised from water in narrow prisms, m. p. 125° (Found : C, 43·8 ; H, 5·3. $C_{15}H_{21}O_7N_4Cl$ requires C, 44·5 ; H, 5·1%).

(*b*) A mixture of γ-chloroallyl chloride (15 g.), triethylamine (15 g.), and ethyl alcohol (15 c.c.) was heated under reflux for 20 minutes with precautions against entrance of moisture. After 14 hours, ether (600 c.c.) was added and the hygroscopic chloride collected. This on treatment with sodium picrate gave the above picrate. Interconversion of the chloride and iodide has been effected through the hydroxide obtained from either with silver oxide and water.

The complete series of transformations, including ozonolysis, described below, the starting point of which was a triethyl-γ-chloroallylammonium salt, has been carried out in duplicate with material prepared by the methods (*a*) and (*b*). These salts could not be induced to react with triethylamine at temperatures up to 100°.

Trimethyl-γ-chloroallylammonium Salts.—γ-Chloroallyl chloride (20 g.) was added with cooling, under reflux, to alcoholic trimethylamine (68 c.c. of 33% solution). After the completion of the reaction the deliquescent *chloride* was precipitated with ether (600 c.c.), and crystallised from acetone, from which crystals separated, m. p. 63°, which on drying in a vacuum effloresced, leaving a microcrystalline powder, m. p. 193° (Found : Cl′, 20·5. $\{C_6H_{13}NCl\}^{\cdot}Cl'$ requires Cl′, 20·9%). The corresponding *picrate* separated from water or dilute alcohol in needles, m. p. 141° (Found: C, 39·9 ; H, 4·4. $C_{12}H_{15}O_7N_4Cl$ requires C, 39·7 ; H, 4·2%). These salts did not react with diethylamine or triethylamine at temperatures up to 100°.

Triethyl-α-ethoxyallylammonium Salts. — Triethyl-γ-chloroallylammonium chloride (or iodide) was warmed with an alcoholic solution of sodium ethoxide (2 mols.) prepared from sodium (5·5 g.) and ethyl alcohol (90 g.). When no further quantity of sodium chloride separated (or after an equal time in the case in which the iodide was used), the solution was filtered and evaporated below 60°. The residual ethoxide was converted into the *picrate* by the addition of alcoholic picric acid. The salt separated from ethyl alcohol in narrow prisms, m. p. 122—123° (Found : C, 48·9 ; H, 6·2 ; OEt, 11·3. $C_{17}H_{26}O_8N_4$ requires C, 49·3 ; H, 6·3 ; OEt, 10·9%).

Trimethyl-α-ethoxyallylammonium Salts.—The ethoxide was prepared in a similar way from trimethyl-γ-chloroallylammonium chloride, and converted into the *picrate*, which separated from ethyl alcohol in narrow prisms, m. p. 111—112° (Found : C, 45·2; H, 5·6; OEt, 12·2. $C_{14}H_{20}O_8N_4$ requires C, 45·2; H, 5·4; OEt, 12·1%).

Triethyl-α-hydroxyallylammonium Salts.—Triethyl-α-ethoxyallylammonium chloride, prepared from the ethoxide, was warmed for a short time with concentrated hydrochloric acid, and the excess of acid evaporated. The residual chloride was a viscous syrup which could not be crystallised, but the addition of aqueous sodium picrate yielded a picrate, which crystallised from water in prismatic needles, m. p. 145°, and chloroplatinic acid gave a *chloroplatinate*, which separated from water in orange needles (Found : C, 29·7; H, 5·5. $C_{18}H_{40}O_2N_2Cl_6Pt$ requires C, 29·8; H, 5·5%).

Trimethyl-α-hydroxyallylammonium Salts.—The chloride was obtained as an uncrystallisable syrup from trimethyl-α-ethoxyallylammonium chloride, as in the last experiment. The *picrate* separated from dilute alcohol in prisms, m. p. 149° (Found : C, 42·1; H, 5·0. $C_{12}H_{16}O_8N_4$ requires C, 41·9; H, 4·7%).

Fission by Ozone of Diethyl-γ-chloroallylamine : Formation of Hydrogen Chloride, Carbon Monoxide, and a Base.—A solution of the amine in ligroin was treated with ozonised oxygen for 24 hours. A deep red, liquid ozonide separated from solution as a lower layer. It was boiled with water, in which it dissolved; carbon monoxide was evolved (gas, insoluble in a solution of *p*-nitrophenylhydrazine acetate, giving blue flame on ignition in air), and chloride ions appeared in the solution, which was acid to litmus. The nonprecipitation of a *p*-nitrophenylhydrazone indicated the absence of formaldehyde. The concentrated residual solution gave a chloroplatinate, which owing to its instability was difficult to purify, but which from its properties and composition in the crude state may have been the chloroplatinate of diethylaminoacetaldehyde, although we cannot assert this definitely.

Fission by Ozone of Trimethyl-γ-chloroallylammonium Chloride : Formation of Hydrogen Chloride, Carbon Monoxide, and Betaine.—The chloride (5 g.), dissolved in *pure* acetic acid (30 c.c.), was treated with ozonised oxygen for 48 hours, during which the crystalline ozonide-salt was precipitated. The mixture was boiled with water (100 c.c.) and the evolved gas was passed through a solution of *p*-nitrophenylhydrazine acetate contained in a bulb attached to the top of the reflux : no *p*-nitrophenylhydrazone was obtained. The solution contained free hydrochloric acid, since it contained chloride ions and was acid to Congo-red. It was evaporated and the base converted into its picrate, which had m. p. 183° and was identified as betaine picrate by analysis and direct comparison (Found: C, 38·1; H, 4·2. Calc.: C, 38·2; H, 4·1%).

Fission by Ozone of Trimethyl-α-ethoxyallylammonium Acetate: Formation of Formaldehyde and Trimethylethoxyaldehydomethylammonium Salts.—The formation and the decomposition of the ozonide were carried out in acetic acid as above. After a test portion had been distilled for the identification of formaldehyde, the liquid was evaporated and the residue treated with aqueous sodium picrate. *Trimethylethoxyaldehydomethylammonium picrate*, which was thus obtained, separated from moist ethyl alcohol in prisms, m. p. 168° (Found: C, 41·9; H, 5·0; OEt, 11·8. $C_{13}H_{18}O_9N_4$ requires C, 41·7; H, 4·9; OEt, 12·0%). We were unable to obtain a semicarbazone salt, but found that the above picrate slowly neutralised one equivalent of alkali hydroxide in dilute solution.

Trimethylhydroxyaldehydomethylammonium Salts.—The above ethoxyaldehydo-salt was warmed with concentrated hydrochloric acid, and the excess of acid evaporated. The *picrate* obtained from the residue crystallised from water in prisms, m. p. 182—184° (Found: C, 38·8; H, 4·2. $C_{11}H_{14}O_9N_4$ requires C, 38·1; H, 4·0%).

Fission by Ozone of Trimethyl-α-hydroxyallylammonium Acetate.—The experiment being carried out as in the case of the corresponding α-ethoxy-salt, the products were formaldehyde and the preceding hydroxyaldehydo-salt.

Fission by Ozone of Triethyl-α-ethoxyallylammonium Acetate.—The decomposition was conducted as described for the trimethyl analogue, and the basic fraction treated with sodium picrate; the products were formaldehyde and *triethylethoxyaldehydomethylammonium picrate*, which crystallised from absolute ethyl alcohol in long prisms, m. p. 110—111° (Found: C, 46·1; H, 5·9. $C_{16}H_{24}O_9N_4$ requires C, 46·2; H, 5·8%).

Triethylhydroxyaldehydomethylammonium Salts.—The *picrate* was obtained as prisms, m. p. 195—196°, from the corresponding ethoxy-salt by hydrolysis with hydrochloric acid, and was crystallised from dilute alcohol (Found: C, 43·7; H, 5·3. $C_{14}H_{20}O_9N_4$ requires C, 43·3; H, 5·2%). It is sparingly soluble in absolute alcohol.

Fission by Ozone of Triethyl-α-hydroxyallylammonium Acetate.—The decomposition was carried out as in the case of the ethoxyallyl-salt; the products were formaldehyde and the preceding hydroxyaldehydo-salt.

We wish to record our thanks to the Chemical Society and the Royal Society for grants from which this work received considerable assistance.

THE UNIVERSITY, LEEDS. [*Received, November* 19*th*, 1928.]