# CLXVIII.—*The Nature of the Alternating Effect in Carbon Chains. Part IV. Some Abnormal Reactions as Evidence of the Incipient Ionisation of Certain Hydrogen Atoms in Hydrocarbon Radicals.*

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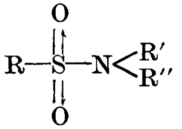
HYDROLYTIC reactions have often been utilised to diagnose the relative polarities of atoms in combination, the residue which, after fission, appears in association with hydrogen being regarded as negative in comparison with the other :

$$\overset{+}{A} - \overset{-}{B} + H_2O \longrightarrow \overset{+}{A}\cdot OH + H\cdot\overset{-}{B}.$$

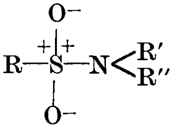
Observations are recorded in this paper which show that, in certain circumstances, the direction of fission may be changed by altering the experimental conditions even in cases in which the relative polarity of the atoms at the point of fission is fixed by the presence, according to modern theory, of a real electrical charge on one of them.

In the following formulæ for the sulphonamide group,



$$R-\overset{\overset{O}{\|\uparrow}}{\underset{\underset{O}{\|\downarrow}}{S}}-N{<}^{R'}_{R''},$$

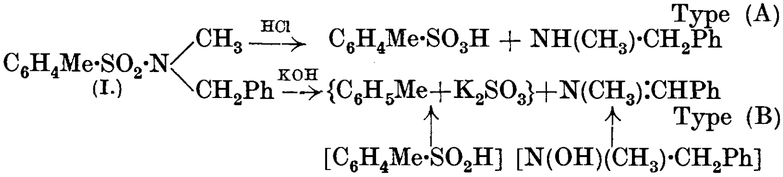
or



$$R-\overset{\overset{O^-}{|}}{\underset{\underset{O^-}{|}}{\overset{+\,+}{S}}}-N{<}^{R'}_{R''},$$

the sulphur atom is represented as carrying a double positive charge, and each of the oxygen atoms a single negative one, whilst the nitrogen atom remains neutral. That is to say, the sulphur atom is necessarily positive with respect to the nitrogen atom, and, accordingly, a sulphonic acid and an amine, $R\cdot SO_2-OH +$ $H-NR'R''$, are the expected products of fission.

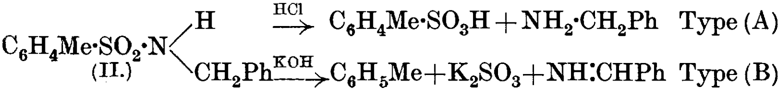
*p*-Toluenesulphonbenzylmethylamide (I) behaves in this way on treatment with mineral acids, but with concentrated alkalis it gives products equivalent, as regards state of oxidation, to a sulphinic acid and a hydroxylamine, $RSO_2-H + HO-NR'R''$. Two of the products obtained, toluene and sulphurous acid, must almost certainly have been formed from *p*-toluenesulphinic acid, which is known to undergo decomposition into these substances in the presence of strong alkalis: whilst the third, benzylidenemethylamine, is the expected dehydration product of benzylmethylhydroxylamine. The possibility of its formation from the hydroxylamine under the conditions used was controlled by subjecting the dibenzylhydroxylamine to the same conditions, when benzylidenebenzylamine was obtained.



(I.)

$$\begin{array}{l} C_6H_4Me{\cdot}SO_2{\cdot}N\begin{cases} CH_3 \xrightarrow{HCl} C_6H_4Me{\cdot}SO_3H + NH(CH_3){\cdot}CH_2Ph & \text{Type (A)} \\ CH_2Ph \xrightarrow{KOH} \{C_6H_5Me+K_2SO_3\}+N(CH_3){:}CHPh & \text{Type (B)} \end{cases} \\ \qquad\qquad\qquad\qquad\qquad\qquad \uparrow \qquad\qquad\qquad \uparrow \\ \qquad\qquad\qquad\qquad [C_6H_4Me{\cdot}SO_2H] \quad [N(OH)(CH_3){\cdot}CH_2Ph] \end{array}$$

Precisely analogous decompositions were observed in the case of *p*-toluenesulphonbenzylamide (II), only in this instance the benzylideneimine was largely hydrolysed to ammonia and benzaldehyde, which underwent further change into benzoic acid (and, probably, benzyl alcohol) under the action of the alkali.



(II.)

$$C_6H_4Me{\cdot}SO_2{\cdot}N\begin{cases} H \xrightarrow{HCl} C_6H_4Me{\cdot}SO_3H+NH_2{\cdot}CH_2Ph & \text{Type (A)} \\ CH_2Ph \xrightarrow{KOH} C_6H_5Me+K_2SO_3+NH{:}CHPh & \text{Type (B)} \end{cases}$$

In attempting to account for these remarkable reactions (Type B), we have formed the view that the decomposition with alkali, essentially an attack by negative hydroxyl ions, commences not at the sulphur atom (in spite of its positive polarity), but at a carbon–hydrogen linking in an alkyl group attached to the nitrogen atom. Owing to the diminished additive power of the ionised double linkings in the sulphonic acid group (they are single linkings from the standpoint of co-valency), we regard the sulphur atom as largely protected from the direct attack of hydroxyl ions by the additive mechanism discussed by Gane and Ingold (this vol., p. 10) in connexion with the alkaline hydrolysis of carboxylic esters. The attack therefore commences, in the above instances, at the $CH_2$ group in which, we believe, the hydrogen atoms are in a condition of incipient ionisation, ready to give up their nuclei (but not their electrons) to a hydroxyl ion to form undissociated water (compare Goss and Ingold, J., 1925, **127**, 2777). As the extraction of a hydrogen ion from the benzyl group proceeds, a charged unsaturated residue is left, which in rearrangement necessarily gives a Schiff's base and splits off the ion of a sulphinic acid :

$$Ph\underset{\underset{H\,+\,OH'}{|}}{C}H{\cdot}NMe{\cdot}SO_2{\cdot}C_7H_7 \longrightarrow Ph\underset{|}{C}H{\cdot}NMe{\cdot}SO_2{\cdot}C_7H_7{}' \longrightarrow PhCH{:}NMe + SO_2{\cdot}C_7H_7{}'$$

The changes here represented as taking place in steps are regarded as being actually continuous and simultaneous. According to this view, the hydroxylamine does not intervene in the formation of the Schiff's base, but the ready dehydration of hydroxylamines to

Schiff's bases under the action of alkali can be explained by a somewhat similar mechanism.

In order to test the view that the attack by hydroxyl ions commences at the benzyl group, the sulphonamides $C_6H_4Me{\cdot}SO_2{\cdot}NMePh$ (III) and $C_6H_4Me{\cdot}SO_2{\cdot}NHPh$ (IV) were treated with potash under the same conditions.

In case (III), an opportunity still remains for the suggested mechanism to function if the attack could begin at one of the hydrogen atoms of the methyl group : the initial products would be toluenesulphinic acid and methyleneaniline, and the formation of these would be shown by the identification of toluene, sulphite, formaldehyde, and aniline. However, for reasons indicated below, the extraction of a hydrogen nucleus (ion) from the methyl group would be expected to offer much greater difficulty than its extraction from the benzyl group in examples (I) and (II). Consequently fission of Type (B) should occur only to a small extent or not at all. Actually a reaction of Type (B) can be detected, but the principal change is that which corresponds with Type (A).*

In case (IV), the mechanism by which reaction (B) has been explained cannot operate at all, and actually there is no evidence of fission to form a sulphinic acid, the observed decomposition being wholly of type (A). The occurrence of reaction (A) in the last two cases and, under the influence of acids (hydrogen ions), in all four cases, we attribute to the direct ionic fission of the sulphur–nitrogen bond, a process which occurs only when more facile modes of decomposition are impossible.

In our opinion, then, the remarkable action of alkalis on the sulphonamides (I) and (II) provides clear evidence of the occurrence of the benzyl hydrogen atoms in a state of incipient ionisation. The cause of this condition we attribute to general polarity (Lewis), the inherent tendency of hydrogen to function as a positive ion (separate as a proton) being augmented by the presence of a group such as phenyl, which is assumed to be capable of drawing electrons towards itself, thus leaving the hydrogen nuclei in a loosely-combined, active state. This condition obtains in all ψ-acids, and bears on the questions of hydrogen-tautomerism and meta-substitution (next paper). The opposite condition, in which a group, by allowing electrons to be withdrawn from it, increases a pre-existing, inherent tendency for an atom or group (*e.g.*, hydroxyl) to separate as a negative ion, is similarly illustrated in ψ-bases, mobile hydroxyl tautomerism, and ortho-para-substitution (see next paper). In the first case, the activating group may be said to act as an "electron-

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* Excepting that, of course, *p*-cresol and potassium sulphite are obtained in place of *p*-toluenesulphonic acid.

sink," and in the second as an "electron-source," towards the rest of the molecule :

$$\overset{+}{H}\longrightarrow C\longrightarrow X \qquad\qquad H\overset{-}{O}\longleftarrow C\longleftarrow Y$$

(*ψ-acid*) (*ψ-base*)

## EXPERIMENTAL.

(1) *Hydrolysis of* p-*Toluenesulphonbenzylmethylamide* (I).—The amide (8 g.) was cautiously warmed with moist fused potassium hydroxide (20 g.) during about 0·5 hour, the volatile decomposition products being distilled towards the end of that period. The distillate, on being dried and redistilled, gave two fractions, b. p. 110—120° (*a*) and b. p. 180—190° (*b*). Fraction (*a*) (2·5 g.) had the odour of toluene, on redistillation boiled close to 110° and on nitration yielded 2 : 4-dinitrotoluene (m. p. 71°), which was identified by comparison with an authentic specimen. Fraction (*b*) (3·75 g.) consisted essentially of benzylidenemethylamine (Found : C, 80·4; H, 7·6. Calc. : C, 80·7; H, 7·0%). On treatment with dilute hydrochloric or nitric acid, an oil separated, which was identified as benzaldehyde by its odour, and semicarbazone (m. p. 224°, which is the correct m. p., not 214° as stated in the literature). The hydrochloric acid solution on evaporation gave methylamine hydrochloride (m. p. 226°; mixed m. p. with genuine specimen 226°. Found : Cl, 52·0. Calc. : Cl, 52·6%), and similarly, the nitric acid solution yielded methylamine nitrate (m. p. 99—101°; mixed m. p. with genuine specimen 99—101°. Found : C, 13·0; H, 7·0. Calc. : C, 12·8; H, 6·7%). An authentic specimen of benzylidenemethylamine prepared as described by Zaunschirm (*Annalen*, 1888, **245**, 281) behaved in the same way. The residual alkali on dilution and acidification evolved sulphur dioxide.

(II) *Hydrolysis of* p-*Toluenesulphonbenzylamide* (II).—The hydrolysis of 8 g. of this amide was carried out as in the previous case, but a considerable amount of ammonia was evolved. The volatile liquid products were shaken with dilute acid, and the undissolved portion was distilled; 0·9 g. of pure toluene was then obtained. The acid extract deposited benzaldehyde and gave ammonia on being made alkaline, so that the presence of benzalimine in the original distillate may be inferred. The residual alkali was extracted with ether to remove any neutral or basic products (which, however, were absent) and then acidified. The solution was boiled to expel most of the sulphur dioxide and then extracted with ether. The solid residue (1·5 g.) from the ether consisted largely of benzoic acid contaminated by some substance or substances which instantaneously decolorised permanganate and could only be removed by distillation (b. p. 240—245°/750 mm.) followed by several crystallisations from carbon disulphide and ligroin. (Found : C, 68·6; H, 5·0; *M*, 120. Calc. : C, 68·9; H, 4·9%; *M*, 122). *p*-Cresol was searched for, but could not be detected.

(III) *Hydrolysis of* p-*Toluenesulphonphenylmethylamide* (III).—This *amide*, m. p. 93°, was prepared by the action of *p*-toluenesulphonyl chloride on a sample of Kahlbaum's methylaniline which qualitative tests showed to contain no trace of a primary base. The hydrolysis of 8 g. was carried out as before, the gas evolved being passed through Schiff's reagent acidified with dilute sulphuric acid, when a permanent red colour was produced. The volatile liquid products were separated into neutral and basic portions. The former was small in amount, had the odour of toluene, and yielded a solid which was identified as unchanged amide. The basic portion (2·9 g.) had b. p. 185—190°, and gave the qualitative reactions both of a primary and of a secondary base, and both aniline and methylaniline were identified as their *p*-toluenesulphonyl derivatives (Hinsberg's method of separation). The alkaline residue on acidification evolved sulphur dioxide, and extraction with ether yielded a dark oil which slowly deposited a small quantity of crystals, m. p. 190—200° (0·1 g.). After crystallising twice from water, these yielded prisms, m. p. 210°, which were identified as *p*-hydroxybenzoic acid by analysis (Found : C, 60·5; H, 5·0. Calc. : C, 60·8; H, 4·4%) and comparison with a genuine specimen. The oil from which the crystals separated was distilled (b. p. 190—195°) and was identified as *p*-cresol by conversion into its benzoyl derivative. *p*-Hydroxybenzoic acid is known (Barth, *Annalen*, 1870, **154**, 359) to be formed by the action of potassium hydroxide on *p*-cresol.

(IV) *Hydrolysis of* p-*Toluenesulphonanilide* (IV).—This amide (8 g., m. p. 99°) was treated as in the previous cases and the products were separated similarly. The volatile portion of the hydrolysis products (3·7 g.) consisted of aniline, whilst the alkaline residue yielded *p*-cresol (3·0 g.) and *p*-hydroxybenzoic acid (0·1 g.).

(V) *Action of Potassium Hydroxide on Dibenzylhydroxylamine.*—Dibenzylhydroxylamine (5 g.), prepared as described by Schramm (*Ber.*, 1883, **16**, 2104), was treated in the usual way, and the volatile products were isolated by distillation at 5 mm. Redistilled at 2 mm., these gave a small fraction (*a*) boiling up to 160°, and a main fraction (*b*), b. p. 160°. Fraction (*b*) consisted of benzylidenebenzylamine (Found : C, 85·8; H, 7·2. Calc. : C, 86·1; H, 6·7%), since on treatment with dilute hydrochloric acid it gave benzaldehyde (identified as its semicarbazone) and benzylamine (identified as hydrochloride). Fraction (*a*), although too small to purify, must have contained much of the same azomethine, since the same amine and aldehyde were obtained from it.

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