CLIX.—*The Mobility of Symmetrical Triad Prototropic Systems. Part V. A New Triad System (Methyleneazomethine).*

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THE present position relating to the study of mobile hydrogen tautomerism (prototropy) may be summarised in the statement that the ionic theory, although not directly proved, rests on a comprehensive body of indirect evidence of which the more important features are the following :

(1) *Mobility and Ionisation.*—A parallel exists between the mobility of prototropic systems and those properties, such as the alkylation, stability of alkali-metal salts to hydrolysis, alcoholysis, ammonolysis, etc., which measure the tendency to ionisation of the mobile hydrogen atom and the stability of the anion. The recognition of this principle (Part I, Ingold and Piggott, J., 1922, **121**, 2381) led to the discovery (Part II, *idem*, J., 1923, **123**, 1469) that indene, which although a hydrocarbon is peculiar in yielding relatively stable metallic " salts," is tautomeric and highly mobile.

(2) *Mobility and Constitution.*—In symmetrical triad systems a parallel exists between mobility and the facility of ionisation to be expected from the nature of the terminal atom of the system, the character of the central atom being relatively unimportant. Thus (Part I, *loc. cit.*; Part IV, Ingold and Shoppee, this vol., p. 447; this paper) systems of the types $-NH{\cdot}CR{:}N-$ and $-NH{\cdot}N{:}N-$ are highly mobile and, despite the difference in the central atom, no marked differences of mobility have been observed between them; corresponding systems of the types $-CH_2{\cdot}CR{:}CH-$ and $-CH_2{\cdot}N{:}CH-$ are relatively static, but, again, exhibit only minor differences amongst themselves. The expected order of ease of ionisation is $HC<HN(<HO<HF)$.

(3) *External Promotion of Mobility.*—In a given triad system external facilitation of prototropy could theoretically occur either directly by the attraction of a catalyst for the potentially mobile proton, or indirectly by the addition to the molecule of a catalyst in such a way as to increase the electron-restraint at the seat of ionisation; but the direct mechanism would be expected to be much the more effective. Actually, the most powerful catalysts for the promotion of mobility in intrinsically slightly mobile systems are found to be anions of high co-ordinating power, that is, entities known to have peculiarly strong proton affinity (Ingold, Shoppee, and Thorpe, J., 1926, 1480; Part IV; and this paper).

(4) *Internal Promotion of Mobility.*—In a given triad system the facilitation of prototropy by constitutional influences should correspond with the electron-affinity ($-I$), and capacity for electron-attraction ($-T$), of the groups present, and also on the degree of directness of the path for the internal transmission of their effects to the seat of ionisation. This consequence of the ionisation theory has been shown to constitute a satisfactory description of the very considerable mass of data at present available (Ingold, Shoppee, and Thorpe, *loc. cit.*; Ingold and Rothstein, this vol., p. 8; Part IV; and this paper; compare *Ann. Reports*, 1927, 106; 1928, 118).

(5) *Analogy with Reversible Additions.*—A correlation has been demonstrated between prototropic change and a large class of

reversible addition reactions (aldol, etc.) for which there is strong independent evidence of a corresponding ionic mechanism (E. H. Ingold and others, J., 1923, **123**, 1717; 1924, **125**, 435, 1319; 1925, **127**, 469; 1926, 1868, 1894; *Chem. and Ind.*, 1923, **42**, 1246).

(6) *Analogy with Anionotropy.*—An analogy has been demonstrated between the conditions for mobility in prototropic and anionotropic systems; and for the latter a corresponding ionic mechanism has been completely proved (Burton and Ingold, J., 1928, 904; Burton, *ibid.*, p. 1650).

The experimental portion of this paper records the outcome of a simple application of the above principles to aid the discovery of a new triad prototropic system, which we propose to term the "methyleneazomethine" system $>CH{\cdot}N{:}C< \rightleftharpoons >C{:}N{\cdot}CH<$. By arguments along the lines indicated (1—4, above) we reasoned that such a system, if terminated at either end by aryl groups, should be mobile in the presence of ethoxide ions in alcohol, and that for moderate concentrations the interconversion of a pair of isomerides should proceed readily at temperatures somewhat above the ordinary temperature. Accordingly, we prepared the methoxyazomethines formulated below, and found that at 85° in 1·45*N*-alcoholic sodium ethoxide each isomeride underwent rapid conversion into an identical mixture of the composition shown. The proportions are in complete agreement with the consideration referred to under (4), above:

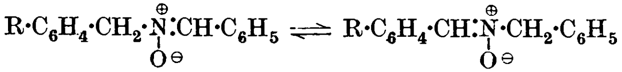
$$(21{\cdot}1\%)\ p\text{-MeO}{\cdot}C_6H_4{\cdot}CH_2{\cdot}N{:}CH{\cdot}C_6H_5 \rightleftharpoons p\text{-MeO}{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}CH_2{\cdot}C_6H_5\ (78{\cdot}9\%)$$

The experimental record also contains evidence that the methyleneazomethine system terminated by only a single phenyl group exhibits mobility in the presence of alkali at a considerably higher temperature, although in this case the change appears to be substantially unidirectional:

$$C_6H_5{\cdot}CH_2{\cdot}N{:}CH_2 \longrightarrow C_6H_5{\cdot}CH{:}N{\cdot}CH_3$$

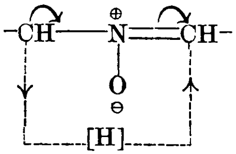
Direct demonstration, or strong presumptive evidence, of prototropic mobility was previously available for eleven out of the twelve formal triad systems constituted from the elements carbon, nitrogen, and oxygen. The outstanding case was the methyleneazomethine system, so the work now described completes a series.

Although prototropic mobility in the methyleneazomethine system has not, to our knowledge previously been demonstrated, the statement that it has not previously been under observation would require the following qualification. Behrend (*Annalen*, 1891, **265**, 238), Neubauer (*ibid.*, 1897, **298**, 187), and Wegener (*ibid.*, 1900, **314**, 231) have shown that isomeric substitution products of benzaldoxime *N*-benzyl ether undergo a reversible interconversion which may be represented thus :

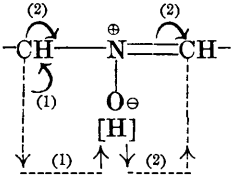


$$R\cdot C_6H_4\cdot CH_2\cdot \overset{\oplus}{\underset{O^{\ominus}}{N}}{:}CH\cdot C_6H_5 \rightleftharpoons R\cdot C_6H_4\cdot CH{:}\overset{\oplus}{\underset{O^{\ominus}}{N}}\cdot CH_2\cdot C_6H_5$$

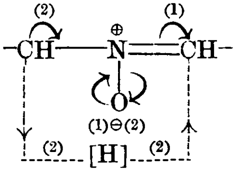
This may or may not be a methyleneazomethine triad change. The question at issue relates to the part played by the negative oxygen atom, and the possibilities are (A) that it takes no direct part, (B) that it receives and hands on the mobile proton, and (C) that, without accepting the proton, it hands on and then recovers its negative charge. In the first case the process represents simple methyleneazomethine prototropy; but in the second and third it does not, because in the former the proton-transfers, and in the latter the electron-transfers, are not those characteristic of the methyleneazomethine triad system. In short, the example is a complex one which it is impossible in the present state of knowledge definitely to assign to any recognised category.



(A.)



(B.) [(1) precedes (2)]



(C.)

EXPERIMENTAL.

p-*Methoxybenzylidenebenzylamine* was prepared by heating together *p*-anisaldehyde (1 mol.) and benzylamine (1 mol.) at 100° for 0·5 hour in an atmosphere of hydrogen. The product, dissolved in ether, was washed successively with 2% aqueous acetic acid and dilute sodium hydrogen carbonate solution, and dried with anhydrous sodium acetate; it then solidified after evaporation of the ether, and crystallised from ligroin in prisms, m. p. 42° (Found : C, 80·4; H, 6·6. $C_{15}H_{15}ON$ requires C, 80·0; H, 6·6%).

When boiled for 0·5 hour with 2*N*-sulphuric acid, the base was completely hydrolysed, the aldehydic product being pure anisaldehyde and the basic product pure benzylamine. Therefore, no isomerisation of the azomethine occurs under the conditions stated. *Benzylamine picrate* separates from alcohol in needles, m. p. 198° (decomp.) (Found : C, 46·4; H, 3·6. $C_{13}H_{12}O_7N_4$ requires C, 46·4; H, 3·6%).

Benzylidene-p-*methoxybenzylamine*, similarly prepared from *p*-

methoxybenzylamine and benzaldehyde, was a colourless oil, b. p. 217°/17 mm. (Found : C, 79·7 ; H, 6·6. $C_{15}H_{15}ON$ requires C, 80·0 ; H, 6·6%).

On hydrolysis under the conditions recorded above, it yielded pure benzaldehyde and pure *p*-methoxybenzylamine only. p-*Methoxybenzylamine picrate* separates from alcohol in prisms, m. p. 188° (decomp.) (Found : C, 46·0 ; H, 3·85. $C_{14}H_{14}O_8N_4$ requires C, 45·9 ; H, 3·85%), and the *benzoate* from chloroform–ligroin in needles, m. p. 135° (Found : C, 69·7 ; H, 6·5. $C_{15}H_{17}O_3N$ requires C, 69·5 ; H, 6·6%).

Interconversion. Either isomeride was heated for 2 hours at 85° with 30 parts of 1·45*N*-alcoholic sodium ethoxide, and the product isolated by pouring the mixture into water and extracting it with ether. That from *p*-methoxybenzylidenebenzylamine (Found : C, 79·0 ; H, 6·8%), on hydrolysis as already described, gave a basic fraction which yielded mainly benzylamine picrate together with a small amount of *p*-methoxybenzylamine picrate, and a neutral (aldehydic) fraction, which on oxidation with cold 3% permanganate gave *p*-anisic acid, from which a little benzoic acid was separated by sublimation. The product from benzylidene-*p*-methoxybenzylamine (Found : C, 80·1 ; H, 6·8%) behaved similarly.

Determination of the Equilibrium.—Preliminary experiments with artificial mixtures of the azomethines led to two methods by which their proportions could be estimated with fair accuracy. The first depends essentially on an estimation of the methoxyl content of the mixture of acids obtained as described above. After hydrolysis of the original mixture of azomethines, the aldehydes are isolated by extraction with ether and, after partial removal of the solvent under a long column, oxidised to the acids, which are extracted from the acidified solution with ether after dissolution of the oxides of manganese by the passage of sulphur dioxide. The second method (which on the whole is to be preferred, since it avoids the difficulty of freeing from solvent without loss mixtures containing so volatile a substance as benzoic acid) consists in converting the mixed aldehydes into their semicarbazones and estimating the methoxyl content in the latter, due correction being applied for the solubilities of the semicarbazones in the medium (100 c.c. of 2·5% aqueous ethyl alcohol containing 0·05 g. of free semicarbazide carbonate) from which they are precipitated. (The medium referred to was found to contain 0·0615 g. of benzaldehydesemicarbazone and 0·1102 g. of *p*-anisaldehydesemicarbazone unprecipitated.) A third method employing the mixed bases was found to be less expeditious and accurate than either of the above processes, and was therefore not developed. The following results relate to products of interconversion obtained under the conditions specified in the preceding paragraph (*p*-methoxybenzylidenebenzylamine = I, benzylidene-*p*-methoxybenzylamine = II) :

Isomeride used.	Substances analysed.	Conversion (%).	MeO-Compound by Zeisel.			Percentage of I.
			Wt. %, uncorr.	Wt. %, corr.	Mols. %.	
I	Semicarbazones	98·6	81·1	82·3	79·7	79·7
II	,,	96·6	79·1	80·4	77·7	78·0
II	,,	97·2	78·0	79·4	76·5	
II	Acids	98·2	83·1		79·8	

The mean percentage of I, namely 78·9%, is recorded in the introduction as the percentage at equilibrium. The equilibrium ratio $k_{(I \rightarrow II)}/k_{(II \rightarrow I)}$ is 21·1/78·9 = 0·268.

Action of Alkali on Methylenebenzylamine and Benzylidenemethylamine.—Methylenebenzylamine, obtained by dehydration of benzylaminomethyl alcohol (Henry, *Ber.*, 1895, **28**, 924) over sulphuric acid in a vacuum and crystallised from ligroin, had m. p. 48° (Henry, *loc. cit.*, records 43°). It was stable to boiling aqueous alkali and boiling 1·46*N*- and 2·92*N*-alcoholic sodium ethoxide, and was hydrolysed by hot 2*N*-sulphuric acid to formaldehyde and benzylamine but no benzaldehyde. Fusion with potassium hydroxide at 300°, and heating with 1·45*N*-alcoholic sodium ethoxide at 190° for 7 hours, yielded nearly colourless oils which on hydrolysis with mineral acids gave formaldehyde (qualitative tests), benzaldehyde (about 10% of semicarbazone), benzylamine (picrate, chloroplatinate), and a very volatile base (small quantity). These results indicate a partial conversion into benzylidenemethylamine by potassium hydroxide and sodium ethoxide at the temperatures employed.

Benzylidenemethylamine prepared by Zaunschirm's method (*Annalen*, 1888, **245**, 281) contained benzaldehyde which could not be removed by distillation. Since treatment with aqueous semicarbazide acetate and sodium hydrogen sulphite brought about hydrolysis of the azomethine, the crude product was treated with an excess of hydroxylamine in 10% aqueous sodium hydroxide. Distillation of the residue from the ethereal extract yielded the pure azomethine as a colourless oil, b. p. 90—91°/30 mm. Experiments parallel with those indicated in the preceding paragraph yielded no evidence of conversion into methylenebenzylamine in the presence of hot alkali.

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