came crystalline; m.p. 116–117° after recrystallization from acetone. This material was found to be the acid amide.

Anal. Calcd. for $C_{18}H_{31}ON_3$: N, 13.77. Found: N, 13.58.

The amide was refluxed with 150 cc. of 70% sulfuric acid for 48 hours. The mixture was poured onto ice, the solution was decolorized with Norite, filtered and the filtrate made alkaline with sodium hydroxide (*p*H 8–9). After the precipitated oil had been warmed under 16 mm. pressure, it became crystalline. The product was dissolved in absolute alcohol, the solution was filtered and the filtrate evaporated to dryness. The acid melted at 197–198° after recrystallization from dioxane.

Anal. Calcd. for $C_{18}H_{30}O_2N_2$: N, 9.15. Found: N, 8.96.

1-Methyl-3-phenyl-3-(γ-dimethylaminopropyl)-2-piperidone.—A mixture of 24.5 g. of the acid and 75 cc. of thionyl chloride was refluxed for 1.5 hours. The excess thionyl chloride was removed and the solid residue was heated in an oil-bath (200–205°) for 40 minutes when the evolution of gas practically stopped. The cold residue was dissolved in water, the solution was made alkaline and extracted with ether. Upon fractionation 12.5 g. (57%) of product was obtained, b.p. 148–150° (0.01 mm.).

The hydrochloride, obtained by the use of hydrogen chloride, melted at 182–183° after recrystallization from methyl ethyl ketone.

Anal. Calcd. for $C_{17}H_{27}ON_2Cl$: N, 9.02; Cl, 11.40. Found: N, 9.06; Cl, 11.61.

1-Methyl-3-phenyl-3-(γ-dimethylaminopropyl)-piperidine.—The piperidone (9.6 g.), dissolved in 30 cc. of ether, was reduced with 1.4 g. of lithium aluminum hydride dissolved in 70 cc. of ether. The mixture was stirred and refluxed for 5 hours, 3 cc. of water was added and the product was isolated in the usual manner; b.p. 122–124° (0.5 mm.), yield 7.8 g. (86%).

Since both the hydrochloride and the methobromide were hygroscopic, the methiodide was prepared. One gram of the base, dissolved in ether was treated with 2 g. of methyl iodide. After 2 hours the precipitated methiodide was recrystallized from methyl ethyl ketone; m.p. 172–173°.

Anal. Calcd. for $C_{18}H_{31}N_2I$: N, 6.97; I, 31.58. Found: N, 6.93; I, 31.50.

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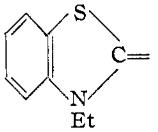
The Significance of Basicity and Acidity of Nuclei in Cyanine Type Condensations

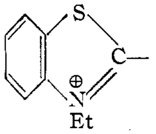
By L. G. S. Brooker, S. G. Dent, Jr., D. W. Heseltine and E. Van Lare

Received June 6, 1953

The gain in stabilization in passing from the net-uncharged form to the positively charged form of certain heterocyclic rings (*e.g.*, from I to II) is a quantity (the "basicity") that has considerable



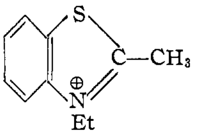
I



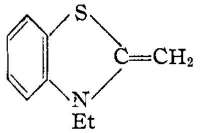
II

significance for the absorptions of cyanine and related dyes containing these nuclei.[1] It is now suggested that this "basicity" has an equal significance in reactions leading to these dyes.

These reactions commonly employ quaternary salts of heterocyclic bases containing a reactive methyl group (III is a typical cation), the cations losing a proton to give methylene bases (*e.g.*, IV)



III



IV

which are the reactive intermediates.[2] The formulas show that the formation of methylene base by the process III → IV involves the same loss of ring stabilization as in II → I, and, as a general proposition, a methylene base will be liberated from the corresponding cation the more readily, the lower the basicity of the nucleus in the sequence established by the "deviation" and similar procedures.[1] The *availability* of methylene base in a given reaction (which will in large measure determine whether that reaction will take place or not) therefore depends partly on the basicity of the particular nucleus and partly on the basic nature of the reaction medium.

By this reasoning it becomes possible to correlate a great many hitherto unrelated empirical observations and to account for many seeming anomalies, of which the following examples are illustrative.

Salts of a number of the less basic cations in the sequence[1] referred to react directly with *p*-dimethylaminobenzaldehyde in ethanol solution to give high yields of styryl dyes, whereas salts of more basic cations require piperidine as catalyst. For the first group, the aldehyde is itself sufficiently basic to liberate methylene base, but not for the second group. Again, salts of highly basic nuclei, such as α-picoline ethiodide, fail completely to give carbocyanine by the pyridine–ethyl orthoformate method. Here the nucleus is so basic that an insufficient concentration of methylene base is reached under the conditions of the experiment. Similarly, the low yields of carbocyanines given by salts of certain thiazoles (*e.g.*, 2,4-dimethylthiazole ethiodide)[3] are a consequence of the high basicity of these nuclei.[1] Introduction of a negative substituent (as in 5-ethoxycarbonyl-2,4-dimethylthiazole ethiodide) increases the apparent reactivity of the 2-methyl group[4] (*i.e.*, the yields of certain dyes are higher) by lowering the basicity of the nucleus and increasing the availability of the methylene base.

Less is known about the actual reactivity of a methylene base, as distinct from its availability. It is possible that the reactivity increases with increasing basicity of the ring, though this is still uncertain.

By somewhat similar reasoning, the yields of dyes of the merocyanine and oxonol types may be correlated with the "acidity" of the ketomethylene compounds that give them.[5] Such condensations also take place under basic conditions, and it is reasonable to suppose that the first step is the loss

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(4) J. Götze and H. Socher, *Beihefte Z. ver. deut. Chem.*, No. 40, 1 (1940).

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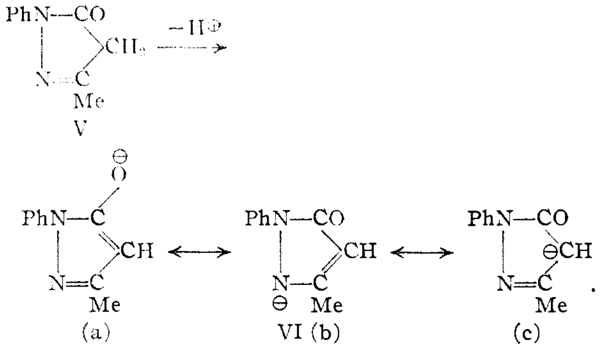
of a proton from the ketomethylene compound (*e.g.*, V) to give an enolate anion (*e.g.*, VI) which is the reactive intermediate. Ions such as VI are the more stabilized by resonance, the higher the electron-attracting power (or "acidity") of the nucleus in the sequence recently established.[5] Under given basic conditions, the availability of an enolate anion is therefore greater, the higher the "acidity" of the nucleus, and on the assumption that the presence of enolate ion is necessary for the ensuing reaction, the, in general, greater ease of reaction of ketomethylene compounds derived from the more highly acidic nuclei[5] can readily be understood.



V

(a) VI (b) (c)

The actual reactivity of an enolate ion is clearly distinct from its availability. This reactivity is very possibly dependent upon high electron density at the methylene carbon, as shown in VI(c). But the contribution of this structure will be relatively less, the greater the attraction for the electron shown by oxygen and nitrogen in the competing structures VI(a) and VI(b). By this argument the actual reactivity of an enolate ion would be expected to be reduced by the attraction of the electron to atoms in the nucleus other than the methylene carbon, but this again is uncertain.

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Synthesis of Tertiary Carbon^{14}-Labeled DDT[1,2]

BY D. R. BUHLER, C. H. WANG AND B. E. CHRISTENSEN

RECEIVED APRIL 22, 1953

Although 1-C^{14} ring labeled 2,2-bis-(*p*-chlorophenyl)-1,1,1-trichloroethane has been synthesized by Fields,[3] *et al.*, with a specific activity of 54 μc./mM., recent studies on the mode of action and detoxification mechanism of DDT have made it imperative to synthesize uniquely labeled DDT with a higher specific activity on the millimole scale.

Several proposed schemes[4,5] based on known reactions which could be used for the preparation of chain labeled DDT have appeared in the literature; however, none are supported by experimental procedures which would give the necessary information regarding the feasibility on a millimole scale such as demanded for isotopic preparations.

One of the most ingenious of these is that of Fry[4] for labeling DDT in the tertiary position; unfortunately Fry discontinued his work. The method which was devised in this Laboratory is a microscale adaptation of Fry's original suggestion. The over-all yield for this procedure was found to be 10%.

Experimental

C^{14}-Carbonyl Labeled *p*,α-Dichloroacetophenone.—Prepared according to the method of Van Bruggen,[6] *et al.*, and then diluted with ordinary *p*-chlorobenzoic acid and converted to the acid chloride. The acid chloride was converted to crude dichloroacetophenone with diazomethane and dry hydrogen chloride; yield 44.5%, m.p. 99.0–99.5°.

Tertiary Carbon^{14}-labeled *p*-Chloro-α-trichlorobenzyl Alcohol.—The *p*,α-dichloroacetophenone was chlorinated in a trichloroacetic acid solvent using chlorine gas. This product was reduced to the alcohol with aluminum isopropoxide; yield 70.0%, m.p. of the acetate 123–124°.

Tertiary Carbon^{14}-labeled 2,2-Bis-*p*-(chlorophenyl)-1,1,1-trichloroethane.—The crude carbinol was condensed with dry chlorobenzene in a sulfuric acid medium. The isolated product DDT gave m.p. 104–104.5° (lit. 108–108.5°) with a specific activity of 1.49×10^8 c.p.m./mM. The over-all chemical and radioactivity yield of purified *p*,*p*'-DDT based on the original $BaCO_3$ was approximately 10%.

The radioactivity of the various compounds was determined as barium carbonate in the conventional manner; counting data were corrected for background and self-absorption.

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(1) Published with the approval of the Monograph Publication Committee as Research Paper No. 228, School of Science, Department of Chemistry.

(2) A more detailed form of this paper has been deposited as Document 3990 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35 mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

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The Conversion of Veratraldehyde to Vanillin by Nitrobenzene and Alkali

BY W. J. BRICKMAN[1] AND C. B. PURVES

RECEIVED APRIL 11, 1953

One method of studying the structure of wood lignins and lignosulfonic acids is to determine the amounts of vanillin they yield when oxidized with nitrobenzene and aqueous caustic soda under pressure. Parallel experiments are also carried out with samples previously methylated by various reagents, and also with methylated and non-methylated "model" substances of the guaiacyl propyl type.[2,3] Veratraldehyde has been obtained by heating methylated lignosulfonic acids with aqueous alkali,[4,5] but apparently not when nitrobenzene is also present. The following experiments

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(1) Holder of an Allied Chemical and Dye Corporation Fellowship, 1952–1953.

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