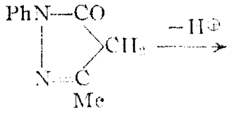
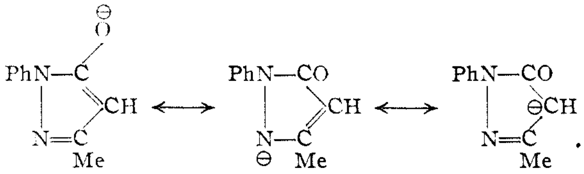
of a proton from the ketomethylene compound (*e.g.*, V) to give an enolate anion (*e.g.*, VI) which is the reactive intermediate. Ions such as VI are the more stabilized by resonance, the higher the electron-attracting power (or "acidity") of the nucleus in the sequence recently established.[5] Under 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

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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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[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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