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

PhN--CO ~H@ сп. ----MePhN PhN-CO θ́Сн CH ≼

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 nuclei⁵ can readily be understood.

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.

RESEARCH LABORATORIES EASTMAN KODAK COMPANY ROCHESTER, NEW YORK

Synthesis of Tertiary Carbon¹⁴-Labeled DDT^{1,2}

By D. R. BUHLER, C. H. WANG AND B. E. CHRISTENSEN **RECEIVED APRIL 22, 1953**

Although 1-C14 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 $\mu c./mM.$, 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

(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.

(3) M. Fields, J. Gibbs and D. E. Walz, Science, 112, 591 (1950).
(4) E. M. Fry, THIS JOURNAL, 71, 3238 (1949).

(5) F. A. Gunther and R. C. Blinn, J. Chem. Ed., 27, 654 (1950).

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 Fry⁴ 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

C¹⁴-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. $99.0-99.5^{\circ}$. Tertiary Carbon¹⁴-labeled *p*-Chloro- α -trichlorobenzyl Al-

cohol.—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 Carbon¹⁴-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. $104-104.5^{\circ}$ (lit. $108-108.5^{\circ}$) with a specific activity of $1.49 \times 10^{\circ}$ c.p.m./mM. The over-all chemical and radioactivity yield of purified $p_{*}p'$ -DDT based on the original BaCO₈ was approximately 10%. The redicactivity of the various compounds used deter-

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

(6) J. T. Van Bruggen, C. K. Claycomb and T. T. Hutchens, Nucleonics, 7, 45 (1950).

DEPARTMENT OF CHEMISTRY SCHOOL OF SCIENCE OREGON STATE COLLEGE CORVALLIS, OREGON

The Conversion of Veratraldehyde to Vanillin by Nitrobenzene and Alkali

BY W. J. BRICKMAN¹ 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-methyllated "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 nitro-benzene is also present. The following experiments

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

(2) F. E. Brauns, "The Chemistry of Lignin," Academic Press, Inc., New York, N. Y., 1952, Chapter XIX, pp. 552-562.

(3) B. Leopold, Acta Chem. Scand., 6, 38, 49, 55, 63, 1294 (1952); Svensk Papperstidn., 55, 816 (1952). These articles include many recent references

(4) G. H. Tomlinson and H. Hibbert, THIS JOURNAL, 58, 348 (1946).

(5) K. Kratzl and I. Keller, Monatsh., 83, 197, 205 (1952). Earlier references to the supposed "aldol" cleavage are given.

show that veratraldehyde is converted to vanillin in at least 30% yield by nitrobenzene and 2 N alkali at 160°, and this reaction therefore competes with the Cannizzaro oxidation-reduction change known to be produced by alkali alone.⁶ This observation is not inconsistent with the view that the *p*-hydroxyl group in vanillin may be present as an ether in the lignin precursor, and that cleavage of a 3-carbon side chain in the precursor may produce a para-substituted vanillin by the reverse of an aldol condensation.⁵

Experimental

The directions of Stone and Blundell⁷ were followed. Pure veratraldehyde, 10.0 mg., nitrobenzene, 0.06 cc., and 1.0 cc. of 2 N aqueous sodium hydroxide were heated together in a stainless steel micro-bomb for three hours at 160° . This bomb had a metal to metal seal with no gasket. After isolation, 0.01-cc. aliquots of the centrifuged liquor were spotted on filter paper for chromatography, the spots were made acidic with the vapor of glacial acetic acid and were then dried in the air. *n*-Butyl ether saturated with water was the developing agent, and the ascending chromatographic technique was used for 11 to 12 hr., since the descending method was inconveniently rapid. After having been located with a 2,4-dinitrophenylhydrazine spray, aldehydes were extracted with ethanol from the proper parts of the chromatogram.

The content of vanillin in the ethanol extract, 25 cc., was determined according to Lemon⁸ by adding 4 cc. of 0.2% ethanolic potassium hydroxide, diluting to 50 cc. with absolute ethanol, and examining the absorption of the solution at wave length 354 m μ . A Beckman Model DU spectrophotometer with a tungsten tube light source was used; plots were made at 5 m μ intervals over the range 320 to 400 m μ against the logarithm of the % transmission, and were assessed against calibration plots for pure vanillin at three different, known concentrations. Other control experiments showed that the recovery of vanillin by the chromatographic technique used was about 87%. Duplicate experiments gave 29.7 and 34.2% recoveries (uncorrected for the chromatographic loss) of vanillin from veratraldehyde.

The above oxidation of veratraldehyde with alkaline nitrobenzene was repeated on a 100-fold scale in another bomb. After being centrifuged, the alkaline liquors were extracted with ether to remove impurities, were acidified, and again extracted with ether to remove phenolic and acidic substances. Phenolic aldehydes were recovered from this extract in a saturated solution of sodium bisulfite, which was then acidified and extracted with ether. The residue left on evaporation of the ether was dissolved in ethanol and was used to prepare a crystalline 2,4-dinitrophenylhydrazone.⁹ After recrystallization (yield 0.276 g. or 14%), the product had the correct m.p. 270-271°, not depressed by admixture with a sample of the same m.p. made from pure vanillin.

(8) H. W. Lemon, ibid., 19, 846 (1947).

(9) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 171.

DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY

MCGILL UNIVERSITY AND PULP AND PAPER RESEARCH INSTITUTE OF CANADA

MONTREAL. P.Q., CANADA

Reaction of Acetoin and Hydroxyacetaldehyde with Cyclohexylamine¹

By J. F. CARSON

RECEIVED APRIL 14, 1953

The non-enzymatic browning of vegetables which is generally attributed to reaction of amino groups (1) Presented at 123rd National Meeting of American Chemical Society, Los Angeles, March. 1953. of amino acids or proteins with reducing sugars is being investigated by the use of simple α -hydroxycarbonyl compounds and aliphatic amines as models for sugars and amino acids. In particular the reactions of acetoin and hydroxyacetaldehyde with primary aliphatic amines have been studied with the idea that α -hydroxyimino compounds might be isolated which would be analogous to the open chain formulas of the 1-amino-1-desoxy sugars.²

When acetoin is dissolved in anhydrous primary aliphatic amines at room temperature in the absence of air and allowed to stand several days, removal of excess amine by distillation yields colorless oils generally soluble in hydrocarbons. Short exposure to dry air produces darkening and precipitation of resin. With cyclohexylamine, however, two oxidative products could be isolated, crystalline cyclohexylamine salt of acetic acid and the new crystalline diimine, diacetyldicyclohexylimine I (R = CH₃). The mechanism whereby the primary condensation product of acetoin and amine is split to acetic acid and also oxidized to a derivative of diacetyl has not been investigated. Hydroxyacetaldehyde and cyclohexylamine in a similar way yield small quantities of the crystalline glyoxaldicyclohexylimine II (R = H). No acid has been isolated from this reaction.

$$\begin{array}{ccc} R-C-C-R & I, R = CH_3 & II, R = H \\ \parallel & \parallel \\ C_6H_{11}N & NC_6H_{11} \end{array}$$

The structures of the two diimines were established by ultimate analysis and by acid hydrolysis to yield diacetyl or glyoxal and cyclohexylamine. The diimines, on catalytic hydrogenation with platinum oxide, each absorb two moles of hydrogen to yield oily diamines. In the ultraviolet in methanol solution, diacetyldicyclohexylimine shows a strong absorption maximum at 213 m μ and a weak, broad inflection in the range 245–260 m μ . Glyoxaldicyclohexylimine has a maximum at 218 m μ and a second weak maximum at 267 m μ . The principal maxima are near the range where conjugated dienes absorb.

Reaction of diacetyl with cyclohexylamine yields only small quantities of the diimine, the bulk of product being of a different nature.⁸ Glyoxaldicyclohexylimine, however, could be prepared in good yield by reaction of 30% aqueous glyoxal solution with cyclohexylamine in alcoholic or aqueous solution.⁴ Simple crystalline aliphatic 1,2-diimines have not heretofore been described.

Acknowledgment.—The author gratefully acknowledges the assistance of L. M. White and G. E. Secor for analyses and G. Bailey for ultraviolet absorption spectra.

(2) The importance of 1-amino-1-desoxy sugars as possible intermediates in Maillard browning reactions has been emphasized by J. Hodge and C. Rist (THIS JOURNAL, **74**, 1494 (1952); **7**, 316 (1952)) and A. Gottschalk and S. M. Partridge (*Nature*, **165**, 684 (1950)).

(3) J. F. Carson, THIS JOURNAL, 75, 4300 (1953).

(4) K. Maurer and E. H. Woltersdorf (Z. physiol. Chem., 254, 18 (1938)) have shown that the reaction of glyoxal bisulfite with aliphatic amines in alcohol yields the corresponding N-alkyl-a-amino acid-N-alkylamide. In our experience, the diimine is obtained in quantity only with free glyoxal. Reaction of glyoxal bisulfite with cyclohexyl-amine in refluxing ethanol yielded only traces of the diimine and resinous material; no amide was isolated.

⁽⁶⁾ H. Decker and R. Pschorr, Ber., 87, 3403 (1904).

⁽⁷⁾ J. E. Stone and M. J. Blundell, Anal. Chem., 23, 771 (1951).