was recrystallized from carbon tetrachloride–acetone (1:5) at −78° to afford sharp-melting product which was immediately utilized for physical and analytical characterization.

Octamethyl[2.2]paracyclophane (15).—After sublimation and recrystallization as described above, this dimer had m.p. 316–318°. Its infrared spectrum exhibits bands (KBr, cm.$^{-1}$) at 2985 s, 2925 s, 2880 s, 1560 m, 1480 s, 1430 s, 1385 s, 1250 m, 1192 m, 1170 m, 1057 m, 1003 m, 983 m, and 726 s; ultraviolet (isooctane, see Fig. 2), $\lambda_{\max}$ 233 (log ϵ 4.21), 257 sh (3.69), and 307.5 mμ (2.84).

Anal. Calcd. for $C_{24}H_{32}$: C, 89.94; H, 10.06; mol. wt., 320. Found: C, 89.80; H, 10.00; osmometric mol. wt., 323.

After storage at 0° for periods of weeks to months, the melting point of the dimer was gradually lowered and broadened.

Octamethyldibenzocyclooctadiene (14).—All samples of this material contained varying amounts of **15** as a contaminant (spectra); no strong efforts were made to obtain pure material. Our best sample had m.p. 184–186°. The structural assignment of this product is based on its n.m.r. (see text) and ultraviolet spectra. The latter exhibits fine structure in the normal benzenoid region with $\lambda_{\max}$ (isooctane) 255 sh, 259 sh, 263, 267, 272, 276, and 281 mμ. While the spectral data define equally well the "monomeric" hydrocarbon, tetramethylbenzocyclobutene, both the high melting point of the product and the temperature of the reaction medium[11b] in which it is formed argue against this assignment.

Dimer **14** is most readily characterized in the infrared region by bands (Nujol, cm.$^{-1}$) at 1280 m, 1240 m, and 775 s.

Pentamethylbenzyl Alcohol (16).—This alcohol, along with polymer, represents the major product of the elimination reaction. It was isolated by precipitation from the reaction filtrate in yields as high as 20%; spectral examination of unresolved reaction mixtures indicated its formation in total yields of about 30–65%. After recrystallization from benzene–isooctane (1:4) it had m.p. 160.0–160.5° (lit.[24] m.p. 160.5°).

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.77; H, 10.21.

The infrared spectrum of **16** exhibits strong bands (Nujol, cm.$^{-1}$) at 3320 and 1000 (CH_2OH), 1215, 1075, 1025 sh, 965 sh, and 805. The n.m.r. spectrum (carbon tetrachloride, 65°) has singlets at τ 5.31 (CH_2), 7.69 and 7.79 (CH_3), and 9.12 (OH).

Pentamethylbenzyl Ether (17).—This compound is a minor product (*ca.* 2–4% yield) of the reaction and had, after recrystallization from benzene–isooctane (1:4), m.p. 178–179° (lit.[25] m.p. 168°).

Anal. Calcd. for $C_{24}H_{34}O$: C, 85.15; H, 10.12. Found: C, 84.78; H, 10.06.

The infrared spectrum of **17** has bands (Nujol, cm.$^{-1}$) at 1355, 1085, 1040, and 1000 (all strong), 1580, 1510, 1235, 800, 725, and 715 (all medium). Its n.m.r. spectrum (carbon tetrachloride, 65°) has singlets at τ 5.39 (CH_2), and 7.72 and 7.79 (CH_3).

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[24] O. Jacobsen, *Ber.*, **22**, 1215 (1889).

[25] R. Willstätter and H. Kubli, *ibid.*, **42**, 4151 (1909).

Condensations at the Methyl Group of Ethyl Acetoacetate by Means of Potassium Amide or Sodium Hydride[1]

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Certain condensations at the methyl group rather than at the more acidic methylene group of ethyl acetoacetate were effected through its dicarbanion, which was prepared by means of potassium amide in liquid ammonia. The dicarbanion was condensed with benzophenone to form the δ-hydroxy-β-keto ester which could be dehydrated to give the γ,δ-unsaturated β-keto ester. The dicarbanion also underwent alkylation and benzoylation at the γ-position, but the yields were low and alkylation failed with certain halides. Terminal aroylation of ethyl acetoacetate with ethyl benzoate was achieved by means of sodium hydride, but the corresponding β-diketone acid, instead of the β-diketone ester, was obtained.

Earlier papers have described condensations at the methyl group of such diketones as benzoylacetone and acetylacetone through their dicarbanions I, which were prepared by means of 2 mol. equiv. of potassium amide in liquid ammonia. For example, I was alkylated with benzyl chloride,[2] aroylated with methyl benzoate,[2] and condensed with benzophenone (aldol type)[3] to form terminal derivatives II, in which A is the appropriate group.

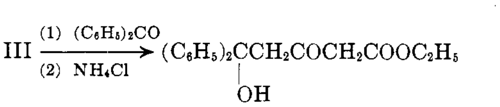
$$\underset{\text{I}}{RCO\bar{C}HCO\bar{C}H_2} \qquad \underset{\text{II}}{RCOCH_2COCH_2\text{-}A}$$

A recent paper has described similar terminal alkylations of the dicarbanions of acetoacetaldehyde and α-benzylacetoacetaldehyde.[4]

The present investigation has extended this novel mode of condensation to ethyl acetoacetate, which was converted to its dicarbanion III by treatment with 2 equiv. of potassium amide (eq. 1).

$$CH_3COCH_2COOC_2H_5 \xrightarrow[\text{liq. }NH_3]{2KNH_2} \underset{\text{III}}{\bar{C}H_2CO\bar{C}HCOOC_2H_5} \qquad (1)$$

Terminal aldol condensation of III was effected with benzophenone to form δ-hydroxy-β-keto ester IV in 50% yield (eq. 2). This reaction furnishes a good



$$\text{III} \xrightarrow[\text{(2) }NH_4Cl]{\text{(1) }(C_6H_5)_2CO} (C_6H_5)_2\underset{\substack{|\\ OH}}{C}CH_2COCH_2COOC_2H_5 \qquad (2)$$

IV

method for the synthesis of IV, which appears to be a new compound. Structure IV was supported by analysis and by absorption spectra. The spectra indicated that IV existed largely in the keto form. The infrared spectrum showed bands at 2.9, 5.75, and 5.85 μ for the hydroxyl,[5] ester,[6] and ketone[7] groups, respectively. The n.m.r. spectrum showed absorption for ten aromatic protons centered at 7.27 p.p.m., along with a triplet and a quartet centered at 1.20 and 4.10 p.p.m., respectively, characteristic of the methyl and methyl-

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[1] Supported by the National Science Foundation.

[2] C. R. Hauser and T. M. Harris, *J. Am. Chem. Soc.*, **80**, 6360 (1958).

[3] R. J. Light and C. R. Hauser, *J. Org. Chem.*, **26**, 1716 (1961).

[4] T. M. Harris, S. Boatman, and C. R. Hauser, *J. Am. Chem. Soc.*, **85**, 3273 (1963).

[5] See L. J. Bellamy, "Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 96.

[6] See ref. 5, p. 179.

[7] See ref. 5, p. 134.

ene protons of the ethoxyl group.[8] In addition there were two-proton signals at 3.21 and 3.40 p.p.m. ascribable to the α- and γ-methylene groups, but no signal for the terminal methyl group which had been observed at 2.20 p.p.m. with the original ethyl acetoacetate.

Structure IV was confirmed by dehydration with cold sulfuric acid to form γ,δ-unsaturated β-keto ester V which was isolated as its copper chelate in 57% yield.

$$(C_6H_5)_2C{=}CHCOCH_2COOC_2H_5$$

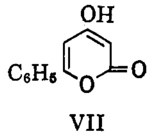
V

Structure V was supported by absorption spectra which indicated it to exist as a mixture of the keto and enol tautomers. Its infrared spectrum showed bands at 5.75 and 5.90–6.10 μ (broad) for the normal ester[6] and conjugated carbonyl system, respectively,[9] but no bands in the 3.0-μ region for the hydroxyl group. In addition to phenyl and ethoxyl absorption, the n.m.r. spectrum showed singlets at 3.08, 4.80, 6.25, and 6.60 p.p.m. The area of the first indicated 1.2 protons and the remaining three about 0.5 protons each as calculated from the phenyl absorption. Apparently the methylene and one of the vinyl absorptions arose from the keto form of V, while the other two vinyl signals were produced by the enol form.

Terminal aroylation of dicarbanion III was evidently realized with methyl benzoate to form β-diketone ester VI, since, on treatment of the crude reaction product with sulfuric acid, lactone VII was obtained in 11% yield.

$$C_6H_5COCH_2COCH_2COOC_2H_5$$

VI



VII

Terminal alkylations of dicarbanion III were effected with methyl iodide and ethyl bromide to form VIIIa and VIIIb in yields of 37 and 27%, respectively (eq. 3). The yields of these products were determined by

$$III \xrightarrow[(2)\ NH_4Cl]{(1)\ RX} RCH_2COCH_2COOC_2H_5 \qquad (3)$$

$$VIIIa,\ R = CH_3$$
$$b,\ R = C_2H_5$$

v.p.c. Samples were isolated by v.p.c. and identified as their copper chelates. No improvement in yields of VIIIa and b was observed on variation of the time of preparation of III or the time of alkylation (Table I).

TABLE I

ALKYLATIONS OF DICARBANION III

Prepn. time of III, min.	Alkyl halide	Alkylation period, min.	Alkyl deriv.	Yield, %
1	CH_3I	5	VIIIa	36[a]
60	CH_3I	60	VIIIa	37[a]
5	C_2H_5Br	5	VIIIb	27[b]
60	C_2H_5Br	60	VIIIb	29[b]

[a] Determined by v.p.c. using acetophenone as an internal standard. [b] Determined by v.p.c. using propiophenone as an internal standard.

Attempted alkylations of III with *n*-butyl bromide and benzyl chloride were unsuccessful. The latter halide underwent self-condensation to form stilbene (see below).

The realization of the three types of terminal condensations of dicarbanion III described above is significant even though the yields of the products were considerably lower than those obtained in corresponding condensations of dicarbanion I.[2,3] Since III was shown not to decompose appreciably under the conditions employed (see Experimental), the relatively low yields of condensation products appear ascribable to incomplete conversion of the β-keto ester to III (eq. 1), leaving appreciable amide ion in the equilibrium to compete for the electrophilic compound. This was strikingly demonstrated in the reaction with benzyl chloride, with which the amide ion competed favorably to effect the self-condensation of the halide, accompanied by the appearance of the characteristic purple color,[10] to form stilbene (Scheme I).

SCHEME I

$$\bar{N}H_2 + CH_3CO\bar{C}HCOOC_2H_5 \rightleftarrows NH_3 + III$$

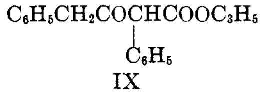
$$\downarrow C_6H_5CH_2Cl$$

$$C_6H_5\bar{C}HCl \xrightarrow{C_6H_5CH_2Cl} C_6H_5CH_2CHClC_6H_5 \xrightarrow{-HCl} C_6H_5CH{=}CHC_6H_5$$

It seems unlikely that dicarbanion III effected this self-condensation of the benzyl chloride, which is initiated by ionization of an α-hydrogen of the halide (see Scheme I), since the closely related dicarbanions I do not effect this reaction. Instead I, with which there is presumably less amide ion in equilibrium, undergoes alkylation with benzyl chloride to form the terminal benzyl derivative in 73% yield.[2]

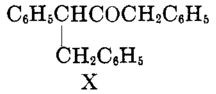
The less extensive conversion of the monoanion of ethyl acetoacetate to dianion III (see Scheme I) than of the monoanion of benzoylacetone or acetylacetone to dianion I by amide ion is not surprising, since the methyl hydrogen of the former monoanion should be less acidic than that of the latter monoanion.

In contrast to ethyl acetoacetate, β-keto ester IX, which has relatively acidic α- and γ-hydrogens, evidently underwent γ-benzylation through its dicarbanion on treatment with 2 mol. equiv. of potassium amide in liquid ammonia, followed by benzyl chloride. Thus, no purple color was observed, and, on subsequent hydrolysis and decarboxylation of the product, ketone X was obtained in 44% over-all yield. No stilbene was isolated.



$$C_6H_5CH_2CO\underset{\displaystyle C_6H_5}{\underset{|}{C}}HCOOC_3H_5$$

IX



$$C_6H_5\underset{\displaystyle CH_2C_6H_5}{\underset{|}{C}}HCOCH_2C_6H_5$$

X

Although α-alkylation would also have led to the formation of X, this mode of alkylation of the intermediate dicarbanion seems unlikely in view of the present and earlier results.[2,4]

Benzoylation by Means of Sodium Hydride.—Since sodium hydride has recently been observed to produce better yields than potassium amide in aroylation of

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[8] N.m.r. spectra were obtained from carbon tetrachloride solutions with tetramethylsilane as internal standard using a Varian A-60 spectrometer.

[9] See ref. 5, pp. 136 and 184.

[10] C. R. Hauser, W. R. Brasen, P. S. Skell, S. W. Kantor, and A. E. Brodhag, *J. Am. Chem. Soc.*, **78**, 1653 (1956).

β-diketones,[11] this reagent seemed likely to do so also in the benzoylation of ethyl acetoacetate with ethyl benzoate. This was evidently realized, although the β-diketone ester VI was not isolated. Instead, the corresponding β-diketone acid XI was obtained in 39% yield (eq. 4).

$$C_6H_5COOC_2H_5 + CH_3COCH_2COOC_2H_5 \xrightarrow[\text{(2) acid}]{\text{(1) NaH}} \underset{\text{XI}}{C_6H_5COCH_2COCH_2COOH} \quad (4)$$

Acid XI was identified by decarboxylation to form benzoylacetone, by cyclization to give lactone VII, and by independent synthesis involving carbonation of the dicarbanion of benzoylacetone.[2] The manner of formation of acid XI from the intermediate ester VI was not determined.

Experimental[12]

Dicarbanion of Ethyl Acetoacetate (III).—In a typical experiment, 13.0 g. (0.1 mole) of ethyl acetoacetate in 30 ml. of anhydrous ether was added to 0.2 mole of potassium amide in 500 ml. of commercial anhydrous ammonia. After stirring for 1 hr. the olive green reaction mixture was considered to contain 0.1 mole of III, and was used in the experiments described below. In certain cases the time of formation of dicarbanion III was varied.

To show that III was relatively stable, the above preparation was repeated and the reaction mixture was neutralized with excess ammonium chloride. After 1 hr. there was recovered 8.6 g. (66%) of ethyl acetoacetate, which was identified by its v.p.c. retention time and infrared spectrum.

In another experiment the monocarbanion of ethyl acetoacetate was prepared from 0.1 mole of ester and 0.1 mole of potassium amide in 500 ml. of liquid ammonia. After 1 hr. the reaction mixture was acidified to regenerate 73% of the β-keto ester.

Condensation of III with Benzophenone.—To a stirred suspension of dicarbanion III (0.1 mole) was added 18.2 g. (0.1 mole) of benzophenone in 80 ml. of anhydrous ether. After 2 hr., the reaction mixture was neutralized inversely[3] with excess ammonium chloride. The ammonia was evaporated rapidly (steam bath) as 300 ml. of ether was added. The resulting suspension was shaken with a mixture of 200 g. of crushed ice and 25 ml. of concentrated hydrochloric acid. The ethereal layer was combined with an ethereal extract of the aqueous layer. The solution was washed with sodium bicarbonate solution and dried over sodium sulfate. Concentration of the solution yielded a viscous red oil which was dissolved in 30 ml. of methanol. The methanolic solution was cooled at 0° overnight to precipitate 15.8 g. (50%) of ethyl 3-oxo-5-hydroxy-5,5-diphenylpentanoate (IV), m.p. 63–67°. The product was recrystallized from cyclohexane containing a trace of methanol to give 13.3 g. (42%) of analytically pure IV, m.p. 68.5–69.5°.

Anal. Calcd. for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45. Found: C, 72.98; H, 6.39.

When the time allowed for formation of dicarbanion III was reduced to 5 min. and the benzophenone was allowed to react for only 5 min. before neutralization, the yield of pure IV was 34%.

Dehydration of IV.—A 5.0-g. (0.016-mole) sample of hydroxy keto ester IV was added in small portions to 50 ml. of concentrated sulfuric acid at 0°. The resulting dark red solution was stirred occasionally for 1 hr., and then poured into 200 ml. of ice–water. The mixture was extracted with ether. The ethereal extracts were washed with sodium bicarbonate solution, dried over sodium sulfate, and evaporated to yield 4.6 g. of crude ethyl 5,5-diphenyl-3-oxo-4-pentenoate (V) as a light yellow oil. This product was dissolved in 30 ml. of ether, and the ethereal solution was added to 200 ml. of saturated, aqueous copper acetate solution. After evaporation of the ether, the suspended chelate was separated by filtration and recrystallized from cyclohexane to give 3.0 g. (57% based on IV) of the copper chelate of V, m.p. 190–191.5° dec.

Anal. Calcd. for $C_{38}H_{34}CuO_6$: C, 70.19; H, 5.27; Cu, 9.77. Found: C, 70.25; H, 5.38; Cu, 9.41.

Benzoylation of III.—To a stirred suspension of 0.2 mole of dicarbanion III in 800 ml. of liquid ammonia was added 15.0 g. (0.11 mole) of methyl benzoate. After 2 hr., excess ammonium chloride was added, and the reaction mixture was processed in the usual manner. The ethereal solution of the product was concentrated and the residue was freed of ethyl acetoacetate under vacuum on the steam bath. The residue was treated with an equal volume of concentrated sulfuric acid at room temperature for 2 hr. to afford, after pouring onto crushed ice, 2.0 g. (11%) of 6-phenyl-4-hydroxy-2-pyrone (VII), m.p. 258–259° dec., the infrared spectrum of which was identical with that of an authentic sample of VII.[2]

Alkylations of Dicarbanion III.—To a stirred suspension of dicarbanion III (0.1 mole) in liquid ammonia was added 0.10–0.15 mole of alkyl halide in 30 ml. of anhydrous ether. After an appropriate time, the reaction mixture was neutralized, and the ammonia was replaced by ether. The suspension was shaken with cold acid, and the layers were separated. The ethereal solution was washed with saturated sodium bicarbonate solution and dried over sodium sulfate. The solvent was removed carefully at atmospheric pressure. The crude alkylation products, which contained much unchanged ethyl acetoacetate, were analyzed by v.p.c. The results are summarized in Table I.

The terminal alkylation products were collected from the v.p.c. column and converted to their copper chelates. The copper chelate of VIIIa melted at 145–146° (lit.[13] m.p. 144–145°), and that of VIIIb at 124–125° (lit.[13] m.p. 124–125°). Mixture melting points of VIIIa and b with authentic samples[13] were undepressed. The infrared spectra of chelates VIIIa and b were identical with spectra of authentic samples.

In similar experiments with *n*-butyl bromide and benzyl chloride, none of the desired terminal alkylation products could be detected. In the reaction with the latter halide a purple color[10] persisted during the addition period. Analysis of the crude product mixture by v.p.c. revealed the presence of starting β-keto ester, stilbene, and stilbene dimer. The latter two products were isolated and identified.

Benzylation of Ethyl α,γ-Diphenylacetoacetate (IX).—The dicarbanion of IX was prepared from 7.1 g. (0.025 mole) of the ester[14] and 0.5 mole of potassium amide in 300 ml. of liquid ammonia (stirred 45 min.) and treated with 3.5 g. (0.028 mole) of benzyl chloride. After 1 hr., the reaction mixture was processed to give 9.3 g. of a dark oil, which presumably contained starting material and the diastereoisomers of the γ-alkylation product. This mixture was subjected to acidic hydrolysis and decarboxylation[15] to afford, after two recrystallizations from absolute ethanol, 3.4 g. (44% based on IX) of 1,3,4-triphenyl-2-butanone (X), m.p. 75–76.5° (lit.[16] m.p. 73–74.5°), which was identified by mixture melting point and infrared spectra employing an authentic sample.[16]

Benzoylation of Ethyl Acetoacetate by Sodium Hydride.—To a slurry of 10.6 g. of finely divided sodium hydride in 200 ml. of refluxing 1,2-dimethoxyethane was added, during 20 min., a mixture of 13.0 g. (0.1 mole) of ethyl acetoacetate and 24.0 g. (0.16 mole) of ethyl benzoate in 100 ml. of 1,2-dimethoxyethane. The reaction mixture was refluxed for 8 hr. under a nitrogen atmosphere, and the solvent was removed under reduced pressure. The residual paste was cooled, and 200 ml. of ether was added followed by cautious dropwise addition of 150 ml. of ice–water. The layers were separated and the aqueous layer was acidified with ice-cold 3 *N* hydrochloric acid. The resulting red oil was quickly extracted into ether. The ethereal extract was washed thoroughly with 5% sodium bicarbonate solution until the aqueous washings were basic. The combined aqueous extracts were cooled in an ice bath, and acidified with cold 3 *N* hydrochloric acid to precipitate 10.0 g. (48%) of crude 5-phenyl-3,5-dioxopentanoic acid, m.p. 87–92° dec. Two recrystallizations from ether–petroleum ether (b.p. 30–60°) afforded 8.1 g. (39%) of

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[11] See M. L. Miles, T. M. Harris, and C. R. Hauser, *J. Am. Chem. Soc.* **85**, 3884 (1963).

[12] Melting points were taken on a Thomas–Hoover melting point apparatus in open capillary tubes and are corrected. Analyses were by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were taken on a Perkin-Elmer Model 137 Infracord using the potassium bromide pellet method for solids, and the neat liquid between sodium chloride plates for liquids. Vapor phase chromatograms were obtained on an F and M Model 500 gas chromatograph using either a 5-ft. Apiezon L or a 2-ft. silicone gum rubber column.

[13] R. Levine and C. R. Hauser, *J. Am. Chem. Soc.*, **66**, 1768 (1944).

[14] J. C. Shivers, M. L. Dillon, and C. R. Hauser, *ibid.*, **69**, 119 (1947).

[15] B. E. Hudson and C. R. Hauser, *ibid.*, **63**, 3163 (1941).

[16] C. R. Hauser and T. M. Harris, *ibid.*, **81**, 1154 (1959).

pure acid XI, m.p. 94–96° dec. A mixture melting point with an authentic sample of XI (lit.[2] m.p. 94–96°) was not depressed. The infrared spectra of the two samples were identical.

Acid XI (2.1 g., 0.01 mole) was heated in an oil bath at 110–115° until carbon dioxide evolution had ceased, to give 1.6 g. (98%) of benzoylacetone, m.p. 58–60°.

Acid XI (2.1 g., 0.01 mole) was heated on the steam bath with 20 g. of polyphosphoric for 1.5 hr. The resulting dark red mixture was poured onto 200 g. of crushed ice to precipitate a solid which was collected by filtration and digested with hot absolute ethanol. There was obtained 1.7 g. (90%) of lactone VII, m.p. 258–259° dec., which was identified by mixture melting point and by comparison of infrared spectra with an authentic sample of VII, m.p. 254–256° dec.[17]

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[17] Melting of lactone VII was accompanied by considerable decomposition which evidently resulted in the lower melting point (241–244°) reported in ref. 2.

An Unusual Reaction Product from Epichlorohydrin and Sodium Cyanide

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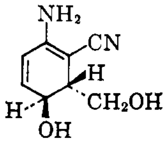
The major product arising from the reaction of epichlorohydrin and unbuffered potassium cyanide solution, aside from water-soluble polymers, is shown, largely by physical means, to be *trans*-3,4-dihydro-2-cyano-3-hydroxymethyl-4-hydroxyaniline (I). A seven-step mechanism for its formation is proposed.

The reaction of potassium cyanide in aqueous solution with epichlorohydrin was first investigated by Pazschke[1] in 1870, although undoubtedly this same system was under study indirectly, when Simpson[2] treated 1,3-dichloropropanol-2 with 2 equiv. of this salt, exactly a century ago.

In the interim other investigators have examined this reaction and have shown that the nature of the products is dependent on the pH at which the system is maintained. At neutral pH the chief product is 4-chloro-3-hydroxybutyronitrile,[3] whereas at pH 9–9.5 the major component is 3-hydroxyglutaronitrile[4] accompanied by small amounts of 4-chloro-3-hydroxybutyronitrile and 4-hydroxycrotononitrile. With an unbuffered potassium cyanide solution (pH 11.5–12.5) small amounts of the two latter substances were isolated[3] together with 2,5-biscyanomethyl-1,4-dioxane[3,5,6] in yields of 10% or less.

However, under the latter conditions, the material (I) which is produced in greatest amount, apart from water-soluble polymer, appears to have been missed by previous workers. Failure to observe it, can be traced to the fact that it is water soluble and can only be isolated from the reaction mixture by prolonged continuous extraction with ethyl acetate. Obtained in this manner I crystallized from ethanol as cubic, lemon yellow crystals, m.p. 154°, having a molecular weight of 166 and the empirical formula, $C_8H_{10}N_2O_2$. Acetylation was trouble free and gave a pale yellow diacetate (II). Catalytic reduction, equally facile, led to a colorless dihydro derivative (III) and acetylation of this substance or hydrogenation of II led to the same dihydrodiacetate (IV). In an attempt to deduce the structure of I by chemical means a number of other reactions, including acid hydrolysis, various oxidations, and diazotization, were tried, but quite consistently, if starting material were not recovered, irresolvable syrups or tars were obtained. Rather than persist with chemical failure we turned to a study of the spectroscopic properties of the compounds I–IV in the hope that this would provide an answer. The data, presented below, has permitted the assignment of the structure *trans*-3,4-dihydro-2-cyano-3-hydroxymethyl-4-hydroxyaniline to I.



I

Infrared Evidence.—The infrared spectrum[7] of I showed bands at 2.90, 2.99 (sharp), and 3.09 μ, indicative of both hydroxyl and amino groups, while a strong absorption at 4.56 μ characterized a highly unsaturated nitrile. Bands at 6.01, 6.11, and 6.34–6.35 μ could be ascribed to double bond and/or imine functions whereas those at 9.40, 9.65, and 9.90 μ were characteristic of C–O stretching vibrations. Lastly a weak absorption at 12.85 μ suggested *cis* ethylenic hydrogens but its unusual sharpness mitigated against this geometry.

In the spectrum of the diacetate (II) a triplet of sharp bands at 2.91, 2.99, and 3.08 μ, highly characteristic of an unsaturated amino group in the solid state, confirmed the presence of this function. A number of the bands already observed for I were apparent in the spectrum of II but in the latter the appearance of two peaks at 5.76 and 5.80 μ indicated the presence of two different types of acetate groups.

The spectra of the dihydro derivatives (III and IV) were interesting in that they showed the nitrile group absorption to be unchanged at 4.55 μ despite the fact the band for *cis*-ethylenic hydrogen atoms at 12.85 μ was now absent. The high position of absorption of the nitrile group in all these compounds, together with the fact that the amine group did not acetylate under the mild conditions used, indicated the presence of a Ziegler–Thorpe system, while the loss of color on hydrogenation suggested that the latter group in I was conjugated with a double bond. Taken as a whole then, the above information permitted the partial formulas,

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[1] F. O. Pazschke, *J. prakt. Chem.*, [2] **1**, 97 (1870).

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