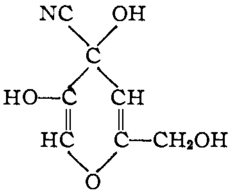
appeared[3,4] describing its reactivity and in no case were drastic conditions required.

The reaction of potassium cyanide with kojic acid takes place at the carbonyl to form the potassium salt of the cyanhydrin; which, when acidified, gives 2-(hydroxymethyl)-4-cyano-1,4-pyran-4,5-diol (I).


I

Compound I is still phenolic as indicated by a positive ferric chloride test, and has three hydroxyl groups in the molecule as shown by acetylation and phenylcarbamate formation.

The heating of 2-(chloromethyl)-4,5-dihydroxy-1,4-pyran-4-carboxylic acid with hydrochloric acid results in the regeneration of the carbonyl group and 2-(chloromethyl)-5-hydroxy-1,4-pyrone is formed.

Finally, the hydrolysis of I did not permit the isolation of the corresponding acid as did the 2-chloromethyl derivative of I, but produced a compound which is probably the lactide.

In consideration of the experimental data described no structure other than that proposed can fulfill the requirements as to the site and nature of the reaction of potassium cyanide with kojic acid.

### Experimental[5]

A mixture of 100 ml. of ice-cold absolute methanol and 6.5 g. of potassium cyanide was stirred to break up any lumps of the cyanide, and 14.2 g. of powdered kojic acid was added all at once. The resulting mixture was thoroughly shaken. The reaction was apparently complete within a few minutes; however, the material was placed in the freezer and allowed to stand overnight. The solid product was stirred with a dilute solution of glacial acetic acid in absolute ethanol, chilled, collected and air-dried. Twenty and one-half grams of pale yellow crystalline material was obtained. An analysis gave an ash content of greater than 23%. The substance was therefore recrystallized from ethanol containing 7 ml. of hydrochloric acid. The 11.3 g. of tan needles thus obtained was recrystallized twice from absolute ethanol to produce colorless needles, m.p. 160°. The compound gave an orange-red solution with a 1% solution of ferric chloride.

*Anal.* Calcd. for $C_7H_7NO_4$: C, 49.70; H, 4.14; N, 8.28. Found: C, 49.66; H, 4.21; N, 8.06.

Gentle hydrolysis of the above compound was attempted by placing a small portion of the substance in 3 volumes of water, containing a small amount of hydrochloric acid, and refluxing the mixture for 2 hours, but only the starting material was obtained. The failure of the compound to be hydrolyzed under the conditions described diminished the likelihood that compound I was an aldimine.

The trisphenylcarbamate derivative was formed by refluxing a mixture of 1 g. I, 2.2 g. of phenyl isocyanate, 70 ml. of benzene and 1 ml. of pyridine for 30 minutes. The mixture was filtered and allowed to stand overnight, giving 2.5 g. of colorless crystals. Recrystallization from hot benzene produced a white amorphous material which progressively decomposed above 208°.

*Anal.* Calcd. for $C_{23}H_{22}N_4O_7$: N, 10.64. Found: N, 10.50.

When 5 g. of I was allowed to react with an excess of thionyl chloride and then recrystallized from hot water 3.6 g. of yellow prisms was obtained which was sublimed to yield colorless needles, m.p. 166. Only the 2-chloromethyl derivative was obtained. This was to be expected, since a chlorine replacing the hydroxyl on the carbon in position 4 is 1,3 from unsaturated groupings in three directions and is easily displaced by water.

*Anal.* Calcd. for $C_7H_6ClNO_3$: C, 44.81; H, 3.22. Found: C, 44.85; H, 3.07.

Hydrolysis of the nitrile group of the 2-chloromethyl derivative of I was effected by using the procedure of Cheronis and Entrikin.[6] The acid was recrystallized several times from absolute ethanol to give colorless needles, m.p. 167–168°.

*Anal.* Calcd. for $C_7H_7ClO_5$: C, 40.68; H, 3.39. Found: C, 40.44; H, 3.12.

The above acid was decarboxylated by slowly heating 1 g. of the compound with 10 ml. of concentrated hydrochloric acid over a steam-bath to dryness. The resulting tan solid weighed 0.8 g. The analytical sample was obtained by subliming the substance to a white powder, m.p. 166–167°, which is the accepted value for the melting point of 2-(chloromethyl)-5-hydroxy-1,4-pyrone.[7]

*Anal.* Calcd. for $C_6H_5ClO_3$: C, 44.85; H, 3.11. Found: C, 44.78; H, 3.40.

One gram of 2-(hydroxymethyl)-4-cyano-1,4-pyran-4,5-diol (I) was hydrolyzed exactly as previously described in the case of the 2-chloromethyl derivative of I. However, upon diluting the mixture with the requisite amount of water no crystals were obtained. Storage in the freezer for three days produced 0.4 g. of needles of the lactide, which were recrystallized twice from ethanol, m.p. 156°.

*Anal.* Calcd. for $C_{14}H_{12}O_{10}$: C, 49.41; H, 3.52. Found: C, 49.59; H, 3.68.

Acetylation of I was carried out in the usual manner with acetic anhydride, the reaction mixture was diluted with water, neutralized with sodium bicarbonate, and the precipitate was collected and air-dried. The sample was taken up in hot benzene, decolorized with Norit and allowed to crystallize. Colorless needles of the triacetyl derivative melting at 99–100° were formed.

*Anal.* Calcd. for $C_{13}H_{13}NO_7$: C, 52.88; H, 4.40. Found: C, 52.44; H, 4.30.

The phenacyl ether of I was prepared by allowing a mixture of 2 g. of phenacyl bromide, 1 g. of sodium bicarbonate, 2 g. of I and 40 ml. of ethanol to reflux for two hours. Isolation of the phenacyl derivative was accomplished by diluting the mixture with 120 ml. of water and collecting the precipitate. The resulting tan solid was purified by recrystallization first from ethanol, then from benzene to give colorless crystals, m.p. 150°.

*Anal.* Calcd. for $C_{15}H_{13}NO_5$: C, 62.71; H, 4.52. Found: C, 62.38; H, 4.30.

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[3] H. N. Barham and B. L. Smits, *Trans. Kansas Acad. Sci.*, **37**, 112 (1934).

[4] D. N. Bedekar, *et al.*, *J. Indian Chem. Soc.*, **12**, 465 (1935) [*C. A.*, **30**, 459 (1936)].

[5] All analyses were performed by Dr. Carl Tiedcke. All melting points were determined on a Fisher–Johns melting point assembly.

[6] N. D. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis," Thomas Y. Crowell Co., New York, N. Y., 1947, p. 296.

[7] T. Yabuta, *J. Chem. Soc.*, **125**, 575 (1924).

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## The Structure of Quaternary Salts from 1-Alkyl-1,2,3-triazoles

BY RICHARD H. WILEY AND JAMES MOFFAT

RECEIVED NOVEMBER 19, 1954

The commonly encountered[1] problem of assigning the proper isomeric structure to N-substituted 1,2,3-triazoles which involve 1- and 2-alkyl isomerism is one for which no satisfactory attack has been devised. An unavailable type of basic information needed for such studies is that establishing the

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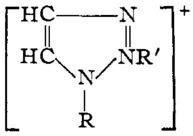
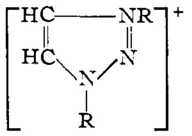
[1] R. H. Wiley, N. R. Smith, D. M. Johnson and James Moffat, THIS JOURNAL, **76**, 4933 (1954).

structure of quaternary salts obtained by alkylation of 1-alkyl-1,2,3-triazoles. This quaternization can result in two structural possibilities—the 1,2-dialkyl I and 1,3-dialkyl II types. The formation of quaternary salts of known structure from triazoles which may be of either the 1- or 2-alkyl type can be coupled with other information and alternative routes of synthesis to establish or exclude structural possibilities. The only previous study of the alkylation of a 1-alkyl-1,2,3-triazole is that of Wolff[2] who treated methyl iodide with 1,5-dimethyl-1,2,3-triazole and obtained a quaternary salt but offered no evidence as to its structure. We wish to record data which eliminate the formation of the 1,2-structure in the quaternization of 1-alkyl-1,2,3-triazoles.



I



II

1-Benzyl-1,2,3-triazole[3] has been methylated with methyl iodide in 70% yield, and 1-methyl-1,2,3-triazole has been benzylated with benzyl iodide in 83% yield. The 1-methyl-1,2,3-triazole was prepared by decarboxylation of 1-methyl-1,2,3-triazole-4,5-dicarboxylic acid in turn prepared from methyl azide and acetylenedicarboxylic acid.[4] The two quaternary salts thus prepared were homogeneous and identical on the basis of direct comparison. This is conclusive proof that the alkylation did not occur on the 2-nitrogen in each reaction and that the product is probably 1(3)-benzyl-3(1)-methyl-1,2,3-triazole. It is likely that this behavior is general.

### Experimental[5]

**Methylation of 1-Benzyl-1,2,3-triazole.**—From a mixture of 1.59 g. (0.010 mole) of 1-benzyl-1,2,3-triazole, 1 ml. of methyl iodide (*ca.* 2.5 g., 0.018 mole), 10 ml. of acetone and 5 ml. of ether there precipitated 2.2 g., 74%, of large, colorless, transparent crystals after five days at room temperature. Recrystallization from acetone and ether gave a product, m.p. 135–136°, unchanged on further recrystallizations.

*Anal.* Calcd. for $C_{10}H_{12}N_3I$: C, 39.88; H, 4.02. Found: C, 39.96, 40.06; H, 3.99, 4.23.

**Benzylation of 1-Methyl-1,2,3-triazole.**—To the 1-methyl-1,2,3-triazole prepared by the dry distillation of 5.40 g. (0.0316 mole) of 1-methyl-1,2,3-triazole-4,5-dicarboxylic acid[4] was added 10 ml. of acetone, 10 ml. of ether and 6 ml. (10.4 g., 0.048 mole) of benzyl iodide. After eight days at room temperature during which time the mixture separated into two liquid layers, the lower of which solidified, there was obtained 7.9 g., 83%, of ether-washed crystals. Recrystallization from acetone gave a product, m.p. 130–132°, mixed m.p. with a sample from the preceding experiment (m.p. 132–134°), 130–134°.

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[2] L. Wolff, *Ann.*, **394**, 53 (1912).

[3] T. Curtius and K. Raschig, *J. prakt. Chem.*, **125**, 466 (1930).

[4] R. H. Wiley and D. M. Johnson, unpublished work.

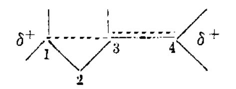
[5] Analyses by Micro Tech Laboratories.

## The Reaction of Cyclohexadiene-1,4 with Electrophilic Reagents

BY EUGENE E. VAN TAMELEN

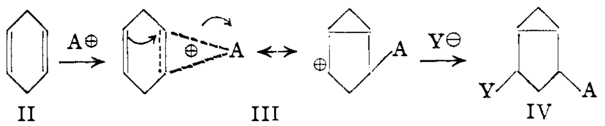
RECEIVED SEPTEMBER 13, 1954

During recent years considerable attention has been paid to the phenomenon of "homoallylic resonance,"[1] which may be defined as the interaction of an electron-deficient center with a suitably oriented $\pi$-electron source in the 3,4-position, thereby involving a mesomeric cation of the type I.[1,2]



I

Interaction at C-4 with a nucleophilic reagent can lead to the formation of a cyclopropyl compound.[3,4] In an attempt to detect the "*i*-steroid" effect in simpler systems, we have had occasion to investigate the reactions of cyclohexadiene-1,4 (II), which might be expected, on electrophilic attack, to form a mesomeric cation III and then be converted to IV by subsequent attachment of the nucleophile.



II III IV

This proposed course of reaction is thus the *homo*-allyl counterpart of the familiar 1,4-addition to a 1,3-diene. Now, several instances of addition reactions of cyclohexadiene-1,4 have appeared in the literature and, in fact, the characteristics of the product resulting from one of these has led us to suspect that III may in reality play a decisive role in determining the course of reaction. Cyclohexadiene-1,4 has been subjected to the Prévost reaction with a controlled amount of silver benzoate and iodine,[5] and the product obtained was assigned the structure cyclohexenediol-4,5 dibenzoate. This dibenzoate was said not to decolorize an acetone solution of potassium permanganate, and neither the diester nor the diol obtained by saponification was attacked by bromine in carbon tetrachloride.[6] These properties—hardly in keeping with olefinic structures—can be construed to favor bicyclo-(0,1,3)hexanediol-2,4 (VI) and its dibenzoate V as the true structures, which would result from a II → III → IV mechanistic sequence.[7] Further study of

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[1] M. Simonetta and S. Winstein, THIS JOURNAL, **76**, 18 (1954).

[2] C. W. Shoppee, *Bull. soc. chim.*, **18**, 120 C (1951).

[3] T. Wagner-Jauregg and L. Werner, *Z. physiol. Chem.*, **213**, 119 (1932).

[4] J. D. Roberts, E. R. Trumbull, Jr., W. Bennett and R. Armstrong, THIS JOURNAL, **72**, 3116 (1950).

[5] G. E. McCasland and E. C. Horswill, *ibid.*, **76**, 1654 (1954).

[6] Bromine water did, however, react positively with both the dibenzoate and the diol. This behavior does not necessarily exclude structures V and VI, since ring opening of the cyclopropyl group could occur with the hydrobromic acid always present (along with hypobromous acid) in equilibrium with bromine and water.

[7] The stereochemistry indicated in formula V follows from considerations already applied in the *i*-steroid system.[2]

V

VI