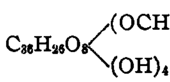
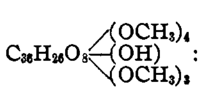
The dissected formula for this lignin fraction is therefore



$C_{36}H_{26}O_8\left<\begin{matrix}(OCH_3)_4\\(OH)_4\end{matrix}\right.$

Methylation with Diazomethane.—One-half gram of lignin was added to an ether solution containing 0.6 g. of diazomethane and allowed to remain at room temperature for three days. The methylated lignin was filtered off, air-dried and finally dried under reduced pressure at 56°.

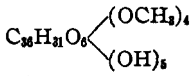
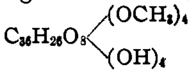
Anal. Calcd. for



$C_{36}H_{26}O_8\left<\begin{matrix}(OCH_3)_4\\(OH)\\(OCH_3)_3\end{matrix}\right.$: OCH_3, 26.46. Found: OCH_3, 26.59, 26.64.

Distillation with 12% Hydrochloric Acid.—The distillation of the lignin with the subsequent cohobation of the distillate was carried out as previously described. Formaldehyde was identified in the distillate by the dimethylcyclohexanedione method of Weinberger.

Summary

1. Two lignin fractions were isolated from barley straw by extracting it successively and exhaustively, first with a 2% alcoholic sodium hydroxide solution at room temperature and then by refluxing with 4% aqueous sodium hydroxide solution. All the data agree with the dissected formula  $C_{36}H_{31}O_6\left<\begin{matrix}(OCH_3)_4\\(OH)_5\end{matrix}\right.$ for the first lignin fraction. Of the five hydroxyl groups only three could be methylated with diazomethane, thus indicating that in all probability these three hydroxyl groups are more acidic, possibly phenolic, or enolic in character. The other two hydroxyl groups could be methylated only after repeated treatment with dimethyl sulfate and 40% potassium hydroxide solution. The results obtained in connection with the second lignin fraction agree with the dissected formula  $C_{36}H_{26}O_8\left<\begin{matrix}(OCH_3)_4\\(OH)_4\end{matrix}\right.$. Three of the hydroxyl groups could be methylated with diazomethane.

2. The alkoxyl groups present in both lignin fractions were proved definitely to be methoxyls.

3. Both lignin fractions when distilled with 12% hydrochloric acid afforded some formaldehyde. The identification of formaldehyde in the distillate is discussed from the standpoint of the probable presence of a methylene dioxide group in the lignin molecule.

WASHINGTON, D. C. RECEIVED SEPTEMBER 15, 1934

[CONTRIBUTION FROM THE WALKER CHEMICAL LABORATORY OF THE RENSSELAER POLYTECHNIC INSTITUTE]

The Synthesis of 1-Methylcyclopropanecarbonitrile from Diazomethane and Alpha-Methylacrylonitrile[1]

BY DANIEL GOTKIS AND JOHN B. CLOKE

As a part of a program on the study of certain cyclic ketimines and related compounds, it has been necessary to synthesize suitable alkyl and aryl substituted cyclopropanecarbonitriles. A previous paper by Knowles and Cloke[2] has described the preparation of 1-phenylcyclopropanecarbonitrile, $\underline{CH_2CH_2C}(C_6H_5)CN$ (I), and a related compound, which can be obtained quite readily by the condensation of phenylacetonitrile with a suitable alkylene halide by the use of sodium amide.

The synthesis of the 1-methylcyclopropanecarbonitrile, $\underline{CH_2CH_2C}(CH_3)CN$ (II), on the other hand, has presented greater difficulty. Thus, several attempts to prepare the compound (II) by the condensation of ethylene halides with propionitrile in accordance with the method for the synthesis of (I) gave no definite results. Likewise, attempts to obtain (II) by the direct methylation of cyclopropyl cyanide, $\underline{CH_2CH_2CH}CN$ (III), have also been of no avail as yet. In addition, considerable effort has been expended in endeavors to prepare the compound (II) from α-methyl-γ-halogenobutyronitriles by the same procedure that leads to the formation of (III), but to date the synthesis of the necessary amount of the pure butyronitriles has been the source of trouble. When this work is completed, it will be discussed elsewhere.

The final successful synthesis of (II) was suggested by the well-known tendency of diazomethane to add to various ethylenic compounds to give pyrazolines, which generally decompose, when suitably heated, to give cyclopropane de-

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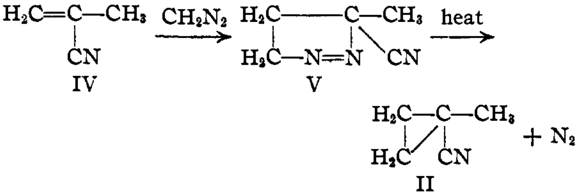
[1] This paper is an abstract of a part of a thesis presented by Daniel Gotkis to the Rensselaer Polytechnic Institute in June, 1934, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Knowles and Cloke, THIS JOURNAL, **54**, 2028 (1932).

rivatives.[3] In the case under consideration, diazomethane, CH_2N_2, was added to α-methylacrylonitrile (IV) to give an intermediate product, presumably 5-methyl-5-cyano-Δ^1-pyrazoline (V), which when heated gave the desired 1-methylcyclopropanecarbonitrile (II) and nitrogen



The structure of (V) has been assigned by analogy with that given by von Auwers and König[4] for the corresponding methyl ester. As in many of the reactions which were so carefully investigated by these authors, our reaction gave some ethylenic as well as cyclopropane derivative. The ethylenic nitrile, possibly tiglic nitrile, was removed by a permanganate oxidation.

That diazomethane adds primarily to the double bond of α,β-ethylenic nitriles and not to the nitrile group, which appeared to be possible when we first carried out our reaction, may also be inferred from some recent work of von Auwers and Ungemach.[5] These authors state that diazomethane adds to nitriles of the type of cinnamonitrile, $C_6H_5CH{=}CHCN$, to give unstable cyanopyrazolines which decompose easily into hydrogen cyanide and a pyrazole.

Experimental Part

Acetone Cyanohydrin.—The acetone cyanohydrin was prepared by the method of Welsh and Clemo,[6] with the exception that ten-fold quantities of materials were employed and the cyanohydrin was removed by a continuous extraction apparatus.

α-Methylacrylonitrile.—The α-methylacrylonitrile was prepared by the dehydration of acetone cyanohydrin in accordance with the reaction recorded by Henry,[7] who, however, gave no experimental details. In our work several lots of the compound were prepared as follows.

A weight of 75 g. of phosphorus pentoxide was rapidly weighed into a 500 cc. flask which was immediately provided with a stopper bearing a dropping funnel and a long reflux condenser whose open end was attached to a drying tube. The body of the flask was then immersed in water at 10–15°, and 42.5 g. of acetone cyanohydrin was added through the funnel during the course of half an hour while the mixture was occasionally agitated. The nitrile was finally separated from the viscous mass by distillation on an oil-bath. Redistillation of the product gave 11.5 g. of nitrile of b. p. 89–91°, a 34.3% yield. Smaller yields were obtained at temperatures higher than 10–15° and also when larger quantities of reactants were employed.

1-Methylcyclopropanecarbonitrile. (1) The α-Methylacrylonitrile–Diazomethane Addition.—An ice-cold ether solution of diazomethane,[8] prepared from 33.8 g. of nitrosomethylurea, 66 cc. of 70% potassium hydroxide and 165 cc. of ether, was added slowly over a period of two hours to a solution of 16.75 g. of α-methylacrylonitrile in an equal volume of anhydrous ether. The addition was carried out at such a rate that the color of the diazomethane almost disappeared before an additional amount was added. Whether this rather slow addition is advantageous has not yet been ascertained. After all of the diazomethane had been added, the reaction flask was provided with a drying tube and allowed to remain in a refrigerator overnight.

(2) **Decomposition of the Intermediate.**—The removal of the ether under diminished pressure from a solution of the diazomethane addition product, such as that just described, gave in one run 21 g. of residue, presumably 5-methyl-5-cyano-Δ^1-pyrazoline (V). Several lots of this compound were collected before it was subjected to pyrolytic decomposition, which was carried out on small quantities on account of the difficulty of controlling the reaction, which may become quite violent.

Approximately 15-g. portions of the intermediate were decomposed in a 500-cc. round-bottomed flask which was provided with a long reflux condenser. The flask at first was heated carefully and intermittently with a free flame, and as soon as the evolution of nitrogen began, which takes place at approximately steam-bath temperature, the flask was immersed from time to time in cold water in order to prevent the reaction from becoming too violent. After the greater part of the product had been decomposed, it was possible to heat the contents more constantly with the burner. The termination of the reaction was readily recognized by the retardation of activity within the flask upon the removal of the flame.

(3) **Purification of the Nitrile.**—The reddish product obtained by the pyrolysis of a total weight of 65.5 g. of the intermediate (V) as described above was fractionated twice through a 1 × 60 Hempel column with the following results at 761 mm.: fraction (a) 125.5–126.5° (corr.), 1 g.; (b) 126.5–127.5°, 28 g.; (c) 127.5–128°, 7.5 g.; (d) residue about 10 g.

Anal. (b). Calcd. for C_5H_7N: N, 17.28. Found: N, 17.68, 17.24.

In view of the fact that fraction (b) reduced alkaline potassium permanganate, whereas neither the methyl ester of 1-methylcyclopropane carboxylic acid[9] nor cyclopropanecarbonitrile reacts significantly, the presence of an isomeric ethylenic nitrile was indicated. Accordingly a known amount of nitrile was allowed to react in sunlight for two minutes with a known amount of the bromine–carbon disulfide reagent of von Auwers and König,[4] when the excess bromine was titrated. This analysis indicated the presence of about 4% of ethylenic nitrile.

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(3) Von Pechmann, *Ber.*, **27**, 1888 (1894), etc.

(4) Von Auwers and König, *Ann.*, **496**, 252–282 (1932).

(5) Von Auwers and Ungemach, *Ber.*, **66**, 1201 (1933).

(6) Welsh and Clemo, *J. Chem. Soc.*, **131**, 2629 (1928).

(7) Henry, *Bull. acad. roy. Belg.*, [3] **36**, 31–50 (1898).

(8) Werner, *J. Chem. Soc.*, **115**, 1093 (1919); Arndt and Amende, *Z. angew. Chem.*, **43**, 444 (1930).

(9) Kohn und Mendelewitsch, *Monatsh.*, **42**, 227 (1921).

In order to remove the ethylenic compound, a mixture of 19 g. of fraction (b), 2 cc. of 10% sodium carbonate and 50 cc. of water was shaken with successive quantities of aqueous potassium permanganate until the permanganate color persisted, which required the addition of about 7.3 g. of the salt. The aqueous mixture was then extracted several times with low-boiling petroleum ether, the extract was dried over anhydrous sodium sulfate and fractionated through the 1 × 60 cm. Hempel, whereby 10 g. of distillate of b. p. 127–127.5° (corr.) at 761.5 mm. was obtained. This compound, the 1-methylcyclopropanecarbonitrile, which is stable to permanganate, is a colorless, very mobile liquid, with a penetrating odor somewhat similar to α-methylacrylonitrile or acetone. The compound possessed a density d_4^{20} of 0.8554 and a refractive index n_D^{20} of 1.41407, which correspond to a molecular refractivity MR_D, of 23.67, whereas the calculated MR_D is 23.61, which includes Östling's[10] value of 0.7 for the exaltation produced by the cyclopropane ring.

1-Methylcyclopropanecarbonamide.—A weight of 1.03 g. of 1-methylcyclopropanecarbonitrile was saponified by the McMaster–Langreck modification of the Radziszewiski[11] method. Two recrystallizations of the amide from benzene gave a compound which began to contract at 138° and melted at 143–145° (corr.).

Anal. Calcd. for C_5H_9ON: N, 14.14. Found: N, 14.01, 14.17.

The same amide was obtained by the procedure of Bruylants and Castille[12] for the saponification of nitriles. In this case 2.58 g. of concd. sulfuric acid was heated to 66° in a flask and to this was added 2 g. of the nitrile, whereupon the flask was plunged immediately into cold water. At the end of six days the brown, solid, vitreous mass was dissolved in water, neutralized with sodium carbonate, and the solution extracted with ether. The amide obtained from the ether solution was recrystallized from benzene.

Anal. Calcd. for C_5H_9ON: N, 14.14. Found: N, 14.16, 14.17.

The identity of the two amides was also established by a mixed melting point. The sulfuric acid reaction throws some light on the stability of the cyclopropane ring in the compound under consideration.

At the suggestion of Dr. C. F. H. Allen the same reaction was applied to 1-phenyl-1-cyanocyclopropane,[2] which gave 1-phenylcyclopropanecarbonamide.

The Rupture of the Ring by the Action of Hot Phosphoric Acid on 1-Methylcyclopropanecarbonitrile.—By the procedure of Berger and Olivier[13] for the saponification of nitriles, 3.01 g. of the nitrile was heated for four hours at 140–155° with 30 g. of 100% phosphoric acid. The mixture was then poured into water, the aqueous mixture extracted with ether, the ether extract extracted with 10% sodium hydroxide, which when acidified gave a precipitate. Recrystallization of this precipitate gave white glistening crystals of m. p. 64–64.5°, which corresponds to the melting point of tiglic acid. No amide was obtained from the ether extract.

1-Methylcyclopropyl Phenyl Ketimine Hydrochloride.—Phenylmagnesium bromide was added to 8.1 g. (0.1 mole) of 1-methylcyclopropanecarbonitrile and the addition product decomposed in liquid ammonia. The ketimine was extracted with ether and the evaporation of the extract gave 10.6 g. of the impure ketimine. An attempt to determine the stability of the ring by the method employed by one of us[14] for the cyclopropyl phenyl ketimine failed. However, the substance gave a hydrochloride of m. p. 103–106°, which rearranged to give a pyrroline, whose formation was indicated by the fact that it gave a picrate of m. p. 150–151° with some decomposition, and a chloroplatinate.

Anal. of chloroplatinate. Calcd. for $C_{22}H_{28}N_2PtCl_6$: Pt, 26.8. Found: Pt, 27.3.

The rates of reaction of several 1-methylcyclopropyl ketimines with water will be studied in the future.

Summary

1-Methylcyclopropanecarbonitrile may be obtained by the action of diazomethane on α-methylacrylonitrile. The ethylenic isomer or isomers which are also formed may be removed by a permanganate oxidation. Some of the properties of the cyclic nitrile are discussed.

TROY, N. Y. RECEIVED SEPTEMBER 17, 1934

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[10] Östling, *J. Chem. Soc.*, **101**, 457 (1912).

[11] Radziszewiski, *Ber.*, **18**, 355 (1885); McMaster and Langreck, THIS JOURNAL, **39**, 103 (1917).

[12] Bruylants and Castille, *Bull. sci. acad. roy. Belg.*, [5] **13**, 767 (1927).

[13] Berger and Olivier, *Rec. trav. chim.*, **46**, 600 (1927).

[14] Cloke, THIS JOURNAL, **51**, 1174 (1929).