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An Attempt to Prepare Succinaldehyde.
The Preparation and Reactions of α, α' -Dicyanosuccinaldehyde

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ABSTRACT

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Title of Thesis: An Attempt to Prepare Succinaldehyde: the
Preparation and Reactions of α, α' -Dicyanosuccin-
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Methods for preparing succinaldehyde have been reviewed. The literature has been covered through the index of Chemical Abstracts for the year 1942.

In an attempt to prepare succinaldehyde α, α' -dicyano-succinaldehyde was made by condensing ethyl formate with succinonitrile by means of sodium ethoxide. This product was obtained in thirty-nine per cent of the theoretical amount. The substance is slightly soluble in hot water, dioxan, toluene and chlorobenzene and more soluble in hot ethanol. It melts at 184-5°C. with decomposition. The compound forms an anil melting at 204-206°C., a monoxime melting at 150-150.5°C. and a 2,4-dinitrophenylhydrazone

melting at 262-4°C. with decomposition. Sodium hydroxide and benzoyl chloride converted the compound to a dibenzoate of the enol form. This product was probably a mixture of isomers as it melted after many recrystallizations at 180-215°C. A monosodium enolate of α, α' -dicyanosuccinaldehyde was prepared by partially neutralizing a cold alkaline solution of the compound.

The anil was converted to 1-phenyl-3,4-dicyanopyrrole by heating in butyl acetate. The pyrrole melted at 257.5-258°C. The anil was also converted to a compound of unknown structure by boiling alcoholic potassium hydroxide. This compound was soluble in hot alcohol, melted at 134-135.5°C. and had the same composition as the anil.

Heating with ammonium acetate converted α, α' -dicyanosuccinaldehyde to 3,4-dicyanopyrrole melting at 231.5-232.5°C. Hydrolysis of this compound gave 3,4-pyrroledicarboxylic acid, melting at 256-258°C. with decomposition.

Alkaline hydrolysis of α, α' -dicyanosuccinaldehyde gave succinic acid. The products of acid hydrolysis of the compound were not isolated, but it was shown that succinaldehyde was not one of them.

AN ATTEMPT TO PREPARE SUCCINALDEHYDE.
THE PREPARATION AND REACTIONS OF
 α, α' -DICYANOSUCCINALDEHYDE

By

Raymond I. Longley, Jr.

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the University of Maryland in Partial fulfillment of
the requirements for the degree of
Doctor of Philosophy

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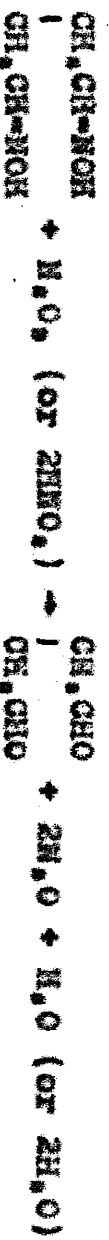


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In an attempt to improve the yield of aldehyde Harries (6) allowed nitrous acid to act on the oxime after the method used by Claisen and Knauss (5) to convert isonitrosoamphor to amphor quinone.



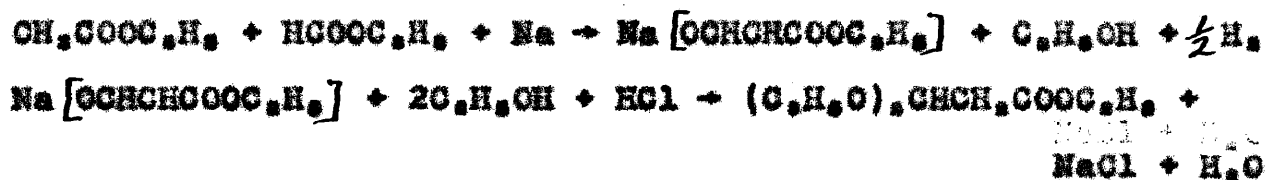
Nitrogen trioxide for the preparation was generated by arsenic and nitric acid (sp.gr.1.3, not 1.4)(17). The gas was bubbled rapidly through a well cooled suspension of the oxime in water until fumes of nitrous oxide were no longer evolved (19). The solution was treated with precipitated calcium carbonate and filtered. The filtrate was concentrated at reduced pressure in a stream of carbon dioxide at 30°C. The residue was transferred to another flask and the contents distilled rapidly at low pressure on an oil bath until the temperature reached 120°C. The fore-run contained some aldehyde which was partly recovered by repeated fractionation. Although the reaction was seventy to eighty per cent complete, the yield of aldehyde finally obtained was only about sixty per cent of the theoretical amount (13). The aldehyde thus obtained was a glassy polymer. The monomer was later obtained by fractionating the polymer at atmospheric pressure and vacuum distilling the middle fraction (16).

The yield of succinaldehyde from pyrrole was increased by Willstatter and Henner (35) and by Kammich and Budd (25). The former were able to obtain succinaldine from pyrrole in eighty per cent of the theoretical amount by increasing the

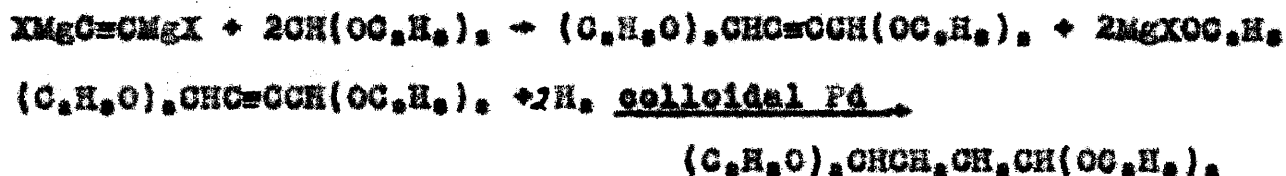
quantity of hydroxylammonium chloride to the theoretical amount; the latter obtained the aldehyde from the oxime in seventy per cent of the theoretical amount by using ethyl nitrite instead of nitrous acid.*

There are several methods of preparing the acetals of succinaldehyde. Harries (11) has presented some evidence that furan reacts with a hydrogen chloride-methanol solution to give succinaldehyde tetramethylacetal.

Sugasawa (34) prepared potassium β,β -diethoxypropionate by the following reactions:



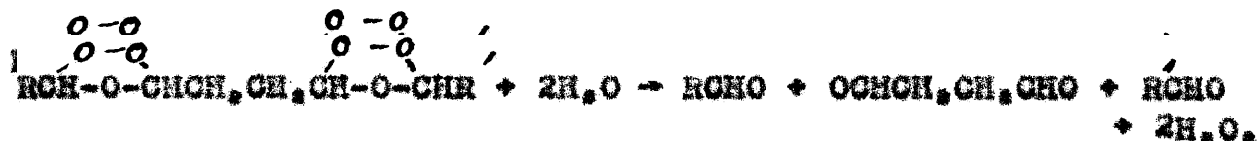
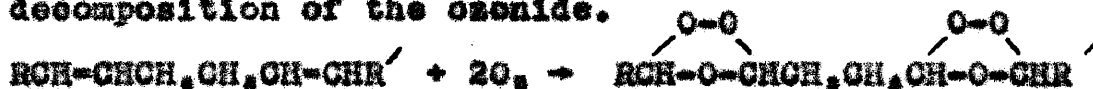
Electrolysis of this salt in water solution gave succinaldehyde tetraethylacetal. Keimatsu and Yokota (24) made the same acetal by the following method:



On hydrolysis with dilute acid the acetals give nearly the theoretical amount of succinaldehyde.

This method of preparation removes the hazard of explosions inherent in the use of nitrous acid with the oxime.

The aldehyde has also been obtained from certain dienes (14,20) and from a Buna rubber (15, 16) in the course of proof of structure by ozonization of the unsaturated compound and decomposition of the ozonide.



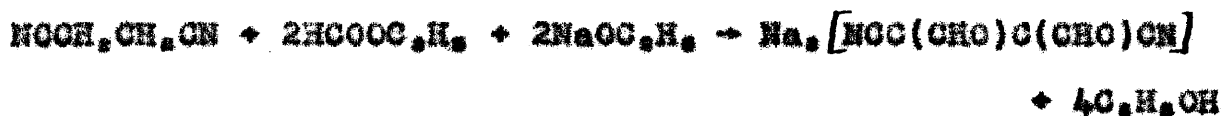
(R and R' represent alkyl groups or hydrogen atoms).

Succinaldehyde has been isolated in poor yield from the dehydrogenation products of 1,4-butandiol, but butyrolactone is the chief product of this reaction (29).

Other methods of preparing succinaldehyde might be proposed. This paper reports an unsuccessful attempt to prepare the aldehyde from succinonitrile as the starting material.

α, α' -DICYANOSUCCINALDEHYDE

The a priori reactions involved in this attempt to prepare succinaldehyde were the following:



α, α' -Dicyanesuccinaldehyde





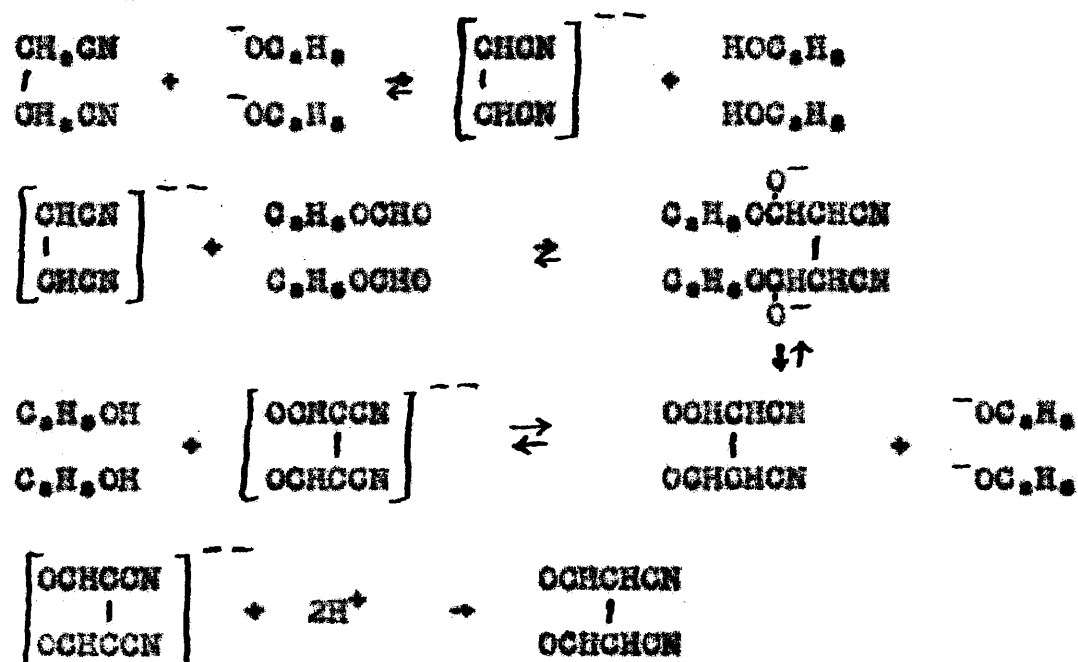
It seemed probable that the process could be simplified by combining the last three reactions in a single step.

A search of the literature revealed no account of a Claisen condensation of ethyl formate with succinonitrile or any simple aliphatic nitrile. However, analogous reactions of various sorts have been reported. In 1887 three papers were published concerning the use of ethyl formate in Claisen condensations. Ethyl formate and acetophenone were condensed to give formylacetophenone (7), and ethyl formate and ethyl acetate were condensed to form trimethyl ester (27,36). Since then ethyl formate has been used in many ester condensations, including several with esters of succinic acid (3,4,22,23,31, 37,40) to give monoformylsuccinic esters. Ethyl formate also condenses with arylsuccinonitriles to give formyl derivatives (41,43), but it has not been reported to condense with an unsubstituted aliphatic nitrile.

Esters, other than those of formic acid, are known to condense with nitriles of the fatty acid series. In 1893 Pletschauer reported that sodium methoxide caused condensation of acetonitrile with ethyl oxalate, and phenylacetoneitrile with ethyl succinate (9). Sodium methoxide did not bring about condensation of propionitrile with ethyl oxalate, nor acetonitrile with ethyl succinate. Mislowius and Silberstein (44), however, obtained eighty-three per cent of the theoretical quantity of the potassium derivative of ethenylpropionitrile by using potassium ethoxide as the condensing agent. Other

ester-nitrile condensations are reported, but only two need be mentioned here. Ethyl oxalate, which behaves like ethyl formate in the Claisen condensation, reacts both with esters of succinic acid and with succinonitrile to form α, α' -diethoxy-allyl derivatives in good yields (26,38,39,42).

The mechanism by which an ester condenses with a nitrile would be expected to parallel that by which an ester condenses with itself or with another ester (40). If that is the case, ethyl formate would condense with succinonitrile in the following manner:



This formulation is a simplified one in two respects. Actually the ionizations and reactions would take place in steps, and the last reaction shown would occur through formation and rearrangement of an intermediate enol.

In the first attempt to prepare α, α' -diacyanosuccinaldehyde the procedure for the preparation of acetylacetone described in Organic Syntheses (2) was used as a guide. One mole of sodium

ethoxide was made as described. A large excess of ethyl formate was added to the ethoxide solution while the latter was stirred and cooled. Considerable ethyl formate was swept from the reaction flask and out the reflux condenser by the carbon monoxide formed. One half mole of solid succinonitrile was added immediately with stirring. The mixture became viscous at first, then more fluid as stirring was continued for one hour. The resulting suspension was then left to stand overnight. A large volume of ice and water was next added and the flask was shaken to dissolve all the material. The resulting solution was extracted with ether to remove unreacted material, and the aqueous layer was neutralized with the calculated quantity of cold dilute sulfuric acid and extracted with three one hundred ml. portions of ether.

The ether extract was dried with sodium sulfate and the ether removed by distillation on a water bath at 80°C. On standing red-brown crystals precipitated and were filtered off and dried. The crude material weighed only twenty grams (twenty-six per cent of the theoretical amount).

An attempt was made to distill the mother liquor, but no distillate was obtained although the mixture was heated to 220°C. on the oil bath and the pressure was reduced to three mm. of mercury. At this high temperature the liquid decomposed to a black carbonaceous mass.

The crude product obtained above was partially purified by recrystallization from toluene. Light yellow crystals thus obtained melted with decomposition at 180-186°C. The

compound reacted with 2,4-dinitrophenylhydrazine, gave a positive test with Tollens' reagent and evolved ammonia when heated with dilute aqueous sodium hydroxide. It was insoluble in cold water, but soluble in cold dilute sodium hydroxide solution, and gave a weak positive test for an enol with ferric chloride solution. These properties might have been expected for an α,β -ketonitrile. The results of an elementary analysis indicated that the compound was α,α' -dicyanosuccinaldehyde.

On repeating the preparation of the substance using three times the quantities only twenty-seven per cent of the theoretical amount of pure product was obtained. A search of the literature was then made in an effort to find an explanation for the poor results of the first experiments. Geuther (10) had shown long ago that ethyl formate decomposed in the presence of sodium ethoxide to form ethanol and carbon monoxide. Adickes and Schäfer (1) had studied the velocity of the decomposition in ethanol solution, and had found that the rate of decomposition increased with the temperature and with the concentration of sodium ethoxide. Stähler (33) had investigated the reverse reaction, and had synthesized formate esters from alcohols and carbon monoxide under pressure at room temperature using sodium alkoxide catalysts. Under the conditions used by the above investigators the reactions had been slow at room temperature. The decomposition of ethyl formate would be even slower at zero degrees Centigrade. An attempt was made to carry out the condensation at this temperature to determine whether any improvement in the yield of α,α' -dicyanosuccinaldehyde could be noted.

This preparation was carried out as before, except that the reaction flask was immersed in a bath of ice and water for two-thirds of its height, and the ethyl formate was cooled to 6°C. before it was added. By this method little gas was evolved and ethyl formate was not swept from the flask. After two hours of stirring the reaction mixture, the temperature of the bath was allowed to rise slowly. It was left standing overnight, and the product was isolated later as in the previous preparation. The crude material was recrystallized once from alcohol. The dried product amounted to thirty-nine per cent of the theoretical quantity. The mother liquor deposited some additional crystalline material contaminated with tarry material on standing.

The mother liquor from the preparation of α, α' -dicyano-succinaldehyde was a dark red-brown liquid. It always amounted to at least one-third of the total quantity of crude product. Monoformylsuccinonitrile was probably present in this liquid and may have formed a large part of it. A crystalline product was formed by cooling the liquid in a bath of dry ice and alcohol, but the mass melted when filtered off on a Büchner funnel. It was never isolated as a pure liquid or solid and was not further investigated.

Before the physical properties of α, α' -dicyanosuccinaldehyde could be determined it was necessary to purify the substance further. The crude material was recrystallized from various solvents repeatedly. The most suitable solvents found were toluene, chlorobenzene, water and ethanol. The

compound was only slightly soluble in the first three mentioned. Norite best removed the colored impurities from the hot solutions, but from every solvent the product was obtained as yellow, iridescent needle crystals. However, the compound was obtained as a white powder by subliming the yellow material at 100°C. at very low pressure. The white powder melted at 184-185°C. The yellow product, after two recrystallizations from water, followed by drying at 100°C. for one hour in an Abderhalden pistol, melted at the same temperature.

α, α' -dicyanosuccinaldehyde was found to be soluble in boiling methanol and ethanol, and slightly soluble in boiling acetone, acetic acid, water, toluene and chlorobenzene. It is insoluble in all of these solvents at zero degrees Centigrade, and it is also insoluble in boiling ether and benzene.

Some of the chemical properties of α, α' -dicyanosuccinaldehyde have already been mentioned. It readily dissolves in ten per cent aqueous sodium hydroxide, and it also dissolves in warm sodium bicarbonate, with evolution of carbon dioxide. In alkaline solution the compound reacts with benzoyl chloride to form a dibenzoate. This ester was obtained as a white powder melting over a long range, 150-215°C., even after many recrystallizations from toluene or ethyl acetate. Probably the product is a mixture of the three isomers made possible by the two carbon-carbon double bonds:



If an alkaline solution of α, α' -dicyanosuccinaldehyde is acidified with cold dilute nitric acid and then treated

with a solution of silver nitrate, a white precipitate of silver enolate forms. A mono-sodium enolate was obtained by treating an alkaline solution of α, α' -dicyanosuccinaldehyde with one equivalent of cold hydrochloric acid. A copper derivative of the compound was also prepared.

Derivatives of the aldehyde group of α, α' -dicyanosuccinaldehyde were also obtained. The monoxime was prepared from the dialdehyde, hydroxylammonium chloride and precipitated calcium carbonate in dioxan solution at 80°C. It is soluble in hot water, but decomposes quite rapidly if the solution is boiled. A dioxime was never obtained although the hydroxylammonium chloride was added in large excess when making the mono derivative. A mono-2,4-dinitrophenylhydrazone was prepared in butanol. This product precipitated as a dark red-brown microcrystalline material which was extremely insoluble in all the common organic solvents.

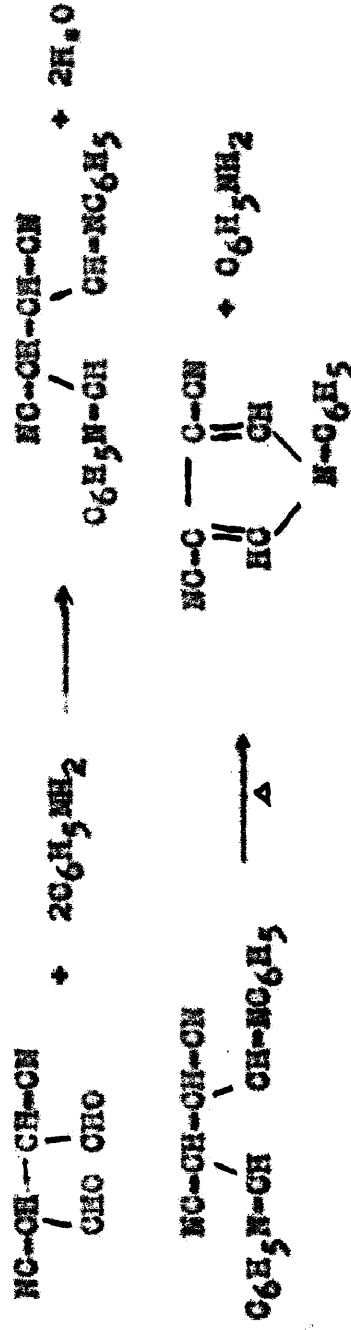
Derivatives of α, α' -dicyanosuccinaldehyde and derivatives of its enol have been mentioned. The compound itself has been isolated only as the aldehyde. The asymmetric carbon atoms in the aldehyde make possible the existence of isomers, but no attempt was made to resolve the material into the d,l and meso forms. Several attempts were made to isolate the enol form of the compound. In the preparation of the aldehyde the enol was first formed, but it changed spontaneously to the aldehyde during the isolation of the compound. In an attempt to prepare the enol, the aldehyde

was dissolved in sodium hydroxide solution forming the sodium enolate. Acidification of this solution by cold acid gave an aqueous solution of enol. Attempts to extract the enol with ether gave the aldehyde instead, as the enol tautomerized during the process. Nevertheless certain properties of the enol are apparent from the method of preparation of the aldehyde: the enol is soluble in water and ether and changes spontaneously to the aldehyde at room temperature.

Wislicenus and coworkers (36,39) isolated both keto and enol forms of ethoxalylsuccinonitrile and of α, α' -diethoxalylsuccinonitrile. These compounds behaved very much like α, α' -dicyanosuccinaldehyde. It seems likely that the enol form of this latter compound might be isolated at sufficiently low temperatures by a similar method.

Several reactions involving α, α' -dicyanosuccinaldehyde have not been mentioned. First, the compound yielded a dianil when heated with aniline in boiling ethanol. The product precipitated as a pink amorphous material, rather insoluble in all the solvents tested. It was recrystallized from butyl acetate, but much of the material was lost in the process. The compound melted at 203-205°C. after one recrystallization. It was somewhat soluble in boiling chloroform, cellosolve and dioxan. If the boiling was only momentary and the solution was immediately cooled, the dianil precipitated, but if boiling was prolonged no precipitate formed on cooling. Evidently a reaction occurred during the boiling.

On concentrating the butyl acetate used in a recrystallization of the dianil a new product was obtained. It was recrystallized from aqueous dioxan, and was found to have a melting point of 257.5-259°C. An analysis indicated an empirical formula $C_{12}H_7N_3$. The reactions involved in preparing the dianil and the new compound, 1-phenyl-3,4-dicyanopyrrole, are the following:



The dianil formed another compound when treated with a boiling aqueous ethanol solution of potassium hydroxide. This new substance was soluble in hot ethanol and insoluble in water and aqueous alkali. It melted at 135°C., but it had the same empirical formula as the dianil. Lacking any other explanation, it is suggested that this compound may be 1,4-dianilino-2,3-dicyanobutadiene-1,3.,



Rearrangement of the dianil to this compound would resemble the enolization of α, α' -dicyanosuccinaldehyde effected by aqueous alkali.

Harris (6) prepared pyrrole by heating succinaldehyde with a mixture of ammonium hydroxide and acetic acid. By

a similar method, α, α' -dicyanosuccinaldehyde was converted to 3,4-dicyanopyrrole. This compound was recrystallized readily from water. After drying it melted at 231.5-232.5°C. Various 3,4-substituted pyrroles, which are difficult to prepare by the usual pyrrole syntheses, should be capable of preparation from 3,4-dicyanopyrrole.

Alkaline hydrolysis of the above compound liberated ammonia, and on acidifying the solution a white, microcrystalline precipitate of 3,4-pyrroledicarboxylic acid was obtained. This is the only pyrroledicarboxylic acid which has not been described previously. It is less soluble in water than the parent compound, but it may be recrystallized from water containing some dioxan. The purified product melts at 256-258° with decomposition.

It was hoped that hydrolysis of α, α' -dicyanosuccinaldehyde would yield α, α' -diformylsuccinic acid, but this compound was never isolated. Hydrolysis by aqueous sodium hydroxide gave sodium succinate and, presumably, sodium formate. α, α' -Diethoxalylsuccinonitrile by a similar reaction gives sodium succinate and sodium oxalate (36).

Acid hydrolysis of α, α' -dicyanosuccinaldehyde gave carbon dioxide in poor yield, but no other products were isolated. By a similar reaction α, α' -diethoxalylsuccinonitrile gives succinic acid and oxalic acid (36). This fact suggests that succinic acid and formic acid may be the principle products of the acid hydrolysis of dicyanosuccinaldehyde. Harries (6) found that succinaldehyde was very

unstable to alkali, and unstable to hot dilute acid. It seems unlikely that the aldehyde could be obtained in appreciable yield either by acid or alkaline hydrolysis of the dienyosuccinaldehyde.

EXPERIMENTAL

PREPARATION OF α, α' -DICYANODIBENZYLIDENE

Sixty-nine grams of freshly cut sodium was weighed into a dry three liter three-necked flask containing 500 ml. of dry xylene. The flask was heated on a sand bath until the sodium was melted. The mixture was shaken gently to remove the excess air in the flask, then clean, dry rubber stoppers were tightly inserted. The hot flask was wrapped in two thicknesses of cloth and vigorously shaken for about five seconds, then set aside to cool.* The xylene was decanted, the sodium powder was washed with two one hundred ml. portions of absolute ether and nine hundred ml. of absolute ether was added.

The flask was supported on an unheated steam cone. A Hershberg stirrer, reflux condenser and a 500 ml. separatory funnel were attached. The stirrer was sealed by a piece of rubber tubing moistened with glycerin, and the openings in the tops of the funnel and the condenser were fitted with calcium chloride tubes loosely filled with dry cotton. One hundred and seventy-four ml. of absolute ethanol was poured into the separatory funnel.

*The sodium thus treated was sometimes quite finely divided, other times it was more coarse and had to be reworked.

The stirrer was started, and the alcohol was run into the mixture slowly so that the ether was not lost through the condenser. The complete addition required two to three hours. The mixture was stirred and kept at the boiling point for six more hours until almost all of the sodium had reacted.

The condenser was changed to allow distillation, and the ether was distilled off completely on the steam bath. The product was always tinged with yellow, although it should be white. The flask containing the sodium ethoxide was then supported in a large bath. The reflux condenser was replaced making the apparatus the same as for the preparation of the ethoxide. The bath was filled with crushed ice and water to two-thirds the height of the flask. Nine hundred ml. of ethyl formate, dried over potassium carbonate and distilled from excess phosphorus pentoxide, had been cooled to 6°C. in the refrigerator. The formate was added to the flask very rapidly with mechanical stirring. During the addition the mixture became so viscous that stirring had to be stopped temporarily. A little ethyl formate was swept out by the carbon monoxide evolved at this time. After all the ethyl formate had been added the stirrer was restarted. A mixture of 120 g. of redistilled succinonitrile* and fifty ml. of dry ethyl formate was

*The succinonitrile was prepared by the method described in Organic Syntheses** for the preparation of trimethylene cyanide except that two 400 ml. portions of ethyl acetate were used to extract the product. The compound distilled at 140-145° at 13 mm. of mercury pressure and weighed 162 g. (seventy per cent of the theoretical amount).

**Marvel and McCollm, Org. Syntheses, Coll. Vol. I, 536 (1941).

added through the separatory funnel during five minutes. The mixture was stirred for four hours as the bath temperature rose to room temperature, then the stirrer was stopped and the mixture was left to stand overnight.

About 1600 ml. of ice and water was added to dissolve the creamy precipitate. The orange colored solution obtained was extracted with two one hundred ml. portions of ether in a three liter separatory funnel. The ether extracts were discarded. To the aqueous layer, a solution of eighty-six ml. of concentrated sulfuric acid poured over 400 g. of ice was slowly added. Two layers formed. The top layer was separated, and the bottom layer was saturated with sodium chloride. Again two layers were formed, and the top layer was again separated. The aqueous solution remaining was extracted by four 250 ml. portions of ether. The water insoluble layers and the ether extracts were combined, amounting to about two liters of light orange solution. The ether layer was dried over 200 g. of sodium sulfate at 10°C. for twelve hours.

The dry material was decanted from the sodium sulfate, filtered and the solution was distilled on a water bath until the bath temperature reached 60°C.. The residue, about one liter, was distilled on the water bath at reduced pressure and at a bath temperature of 60°C.. About 250 ml. of distillate collected while yellow crystals formed slowly in the residue. The contents of the distilling flask was cooled to about 10°C.. The crystals were filtered off on a

Schneer funnel and washed on the funnel with two one hundred ml. portions of ether. On concentrating the dark mother liquor red-brown crystals separated. This material was recrystallized from 400 ml. of water containing five grams of Norite. The yellow crystalline material obtained was combined with the first isolated product, and the mixture was dried at 120°C.. Eighty grams (thirty-nine per cent of the theoretical quantity) of rather pure product was thus obtained. By recrystallization from one liter of boiling ethanol containing ten grams of Norite the yield was decreased to only sixty grams without materially increasing the purity. The compound was purified for analysis by recrystallizing it twice from water containing Norite. The light yellow crystals were dried at 100°C. in an Abderhalden pistol for one hour. The material darkens in a capillary tube at 179° and melts from 184-185°C. with decomposition.

Analysis. Calculated for $C_6H_4O_2N_2$: C, 53.0; H, 2.96; N, 20.6. Found: C, 52.8; H, 3.11; N, 21.0.

DETERMINATION OF THE MOLECULAR WEIGHT OF α, α' -DICYANOSUCCIN-ALDEHYDE

The boiling point of one hundred grams of glacial acetic acid was determined in a Davis Molecular weight apparatus protected from moisture by a calcium chloride tube. The boiling point, measured by a Beckmann thermometer, dropped slowly as shown:*

*The decrease in boiling point of the acetic acid is difficult to explain. It may be that some water was originally present on the walls of the apparatus. In any case the decrease varied directly with time.

Time (minutes)	0	2	4	6	11
Temperature	1.930	1.930	1.925	1.918	1.905

1.00 grams of compound was added at the end of eleven minutes of boiling. After six minutes more of boiling the solution had become dark red and boiled at 2.100°. The boiling point of the acetic acid was graphically extrapolated along a straight line to the value 1.857° after seventeen minutes. The boiling point elevation was therefore .213°C. The constant for acetic acid is 29.9°C. per mole per one hundred grams of solvent. The actual molecular weight is 136 and that found experimentally was 140.

PREPARATION OF THE DIBENZOATE OF THE ENOL FORM OF

α, α' -DICYANOSUCCINALDEHYDE

In a 125 ml. Erlenmeyer flask three grams of the aldehyde was dissolved in fifty ml. of five per cent aqueous sodium hydroxide. Six ml. of benzoyl chloride was added, and the flask was stoppered. The mixture was vigorously shaken for about ten minutes while cooled in running water. A gray precipitate formed and was filtered on a small Büchner funnel and washed in succession on the funnel with fifty ml. portions of five per cent sodium hydroxide solution, water and ether. The product was dried at 60°C. in a vacuum oven for two hours. It was recrystallized three times from eighty ml. portions of toluene containing two grams of Norite. The white material was washed three times with fifty ml. portions of ether and after drying for two hours at 100°C. in an Abderhalden pistol weighed only 2.55

grams (thirty-four per cent of the theoretical amount). The material melted from 185°C. to over 205°C. with some decomposition. It was sublimed at very low pressure at 130-150°C.; the sublimate melted at 180-185°C. and the residue melted at 185-193°C. with decomposition. Analyses were made on the unsublimed product.

Analysis. Calculated for $C_{20}H_{12}O_4N_2$: C, 69.8; H, 3.48.
Found: C, 69.8; H, 3.53.

PREPARATION OF THE MONOSODIUM ENOLATE OF α, α' -DICYANOSUCCINALDEHYDE

In a fifty ml. Erlenmeyer flask, two grams of α, α' -dicyanosuccinaldehyde was dissolved in a mixture of twenty ml. of water and eleven ml. of ten per cent sodium hydroxide solution. Ten grams of sodium chloride was added to the solution, and the mixture was filtered into another flask. This solution was cooled and one ml. of cold concentrated hydrochloric acid was added producing a dense precipitate immediately. The product was filtered on a small Büchner funnel. The flask was rinsed with two five ml. portions of cold water, and the washings were added to the funnel. The pale yellow product was dried at 100°C. for two hours in an Abderhalden pistol. The yield was 2.2 grams (ninety-four per cent of the theoretical amount). In a capillary tube the compound discolored and gradually decomposed above 210°C. Combustion analyses were run without modifying the usual method, so one-half atom of carbon

was left combined as sodium carbonate.

Analysis. Calculated for $C_6H_3O_2N_2Na$: C, 45.6; H, 1.90.
Found: (including carbon combined with sodium as sodium carbonate) C, 46.4; H, 1.86.

PREPARATION OF α, α' -DICYANOSUCCINALDEHYDE MONOXIME

A mixture of one gram of the aldehyde, two grams of hydroxylammonium chloride, two grams of precipitated calcium carbonate and forty ml. of dioxan in a 125 ml. Erlenmeyer flask was warmed to 80°C. on a steam bath. The flask was shaken frequently and more calcium carbonate was added from time to time during thirty minutes heating. The mixture was filtered yielding a red brown solution. The solvent was evaporated in a stream of air. The oxime was recrystallized three times from sixty ml. portions of toluene containing two grams of Norite. The light brown crystals were dried for an hour at 100°C. in an Abderhalden pistol and then melted at 149.5-150.5°C. with decomposition. The oxime was further purified by sublimation at 100°C. and very low pressure. This product melted at 150-150.5°C. with decomposition.

Analysis. Calculated for $C_6H_5O_2N_3$: C, 47.7; H, 3.30.
Found: C, 48.2; H, 3.40.

PREPARATION OF α, α' -DICYANOSUCCINALDEHYDE MONO-2,4-DI-NITROPHENYLHYDRAZONE

A mixture of two grams of aldehyde, five grams of 2,4-dinitrophenylhydrazine, two ml. of glacial acetic acid

and 200 ml. of 1-butanol was heated in a 500 ml. flask fitted with a reflux condenser. The mixture must be boiled for a long time to complete the reaction; twelve hours is sufficient. The dark red-brown product was filtered from the hot mixture, suspended in 400 ml. of boiling ethanol and again filtered from the liquid. It was dried for one hour at 100°C. in an Abderhalden pistol, and then melted at 262-264°C. with decomposition. The yield was 4.12 grams (ninety per cent of the theoretical amount).

Analysis. Calculated for $C_{12}H_8O_5N_6$: C, 45.6; H, 2.53. Found: C, 45.3; H, 2.54.

ATTEMPTED PREPARATION OF THE ENOL FORM OF α, α' -DICYANO-SUCCINALDEHYDE

Two grams of aldehyde was dissolved in ten ml. of water and ten ml. of ten per cent aqueous sodium hydroxide. The orange-yellow solution was exactly neutralized by thirty-one ml. of approximately normal hydrochloric acid. This solution was continuously extracted by 200 ml. of warm ether for two days. Orange crystals and a water layer collected in the ether boiling flask. The ether was distilled off and the residue filtered. The crystals were recrystallized from eighty ml. of water containing two grams of Norite. The product was dried in an Abderhalden pistol and melted at 182-185°C. with decomposition. The crystals had the same appearance, the same melting point and the same solubility in water as the original material. The product

also gave a test with ferric chloride solution just like that given by the starting material.

PREPARATION OF α, α' -DICYANOSUSCINALDEHYDE ANIL

Five grams of aldehyde was dissolved in fifty ml. of boiling ethanol contained in a 125 ml. Erlenmeyer flask on a steam bath. Ten ml. of aniline was added. The mixture was boiled for ten minutes before any precipitate formed, but thereafter precipitation was rapid. After thirty minutes of boiling the mixture was allowed to cool. It was treated with a solution of thirty ml. of concentrated hydrochloric acid in 120 ml. of water with stirring. The pink precipitate was filtered on a small Büchner funnel and washed on the funnel with one hundred ml. of water in several portions. The dried material weighed 7.6 grams (seventy-two per cent of the theoretical amount). Five grams of the crude product was recrystallized from 250 ml. of boiling butyl acetate containing five grams of Norite. The yield of light yellow crystals was only about two grams. After drying for thirty minutes at 100°C. in an Abderhalden drying pistol the product melted at 204-206°C. It was sufficiently pure for analysis.

Analysis. Calculated for $C_{18}H_{14}N_4$: C, 75.4; H, 4.89.
Found: C, 75.5; H, 5.04.

ISOLATION OF 1-PHENYL-3,4-DICYANOPYRROLE

Five hundred ml. of butyl acetate used in recrystallizations of the anil was concentrated by distillation until

the residue amounted to only 150 ml. The latter was cooled in a refrigerator whereupon needle crystals formed. These were filtered off and twice recrystallized from mixtures of twenty ml. of dioxan, ten ml. of water and one gram of Norite. The asbestos-like crystals obtained were dried for one hour at 100°C. in an Abderhalden pistol. They melted at 257.5-258°C.

Analysis. Calculated for $C_{11}H_7N_3$: C, 74.5; H, 3.63.
Found: C, 74.2; H, 3.66.

REACTION OF THE ANIL WITH ALCOHOLIC POTASSIUM HYDROXIDE SOLUTION

Three grams of potassium hydroxide was dissolved in fifty ml. of ninety-five per cent ethanol in a one hundred ml. flask. Two grams of anil was added to the solution, a reflux condenser was attached and the mixture was heated at the boiling point for about twenty minutes. About twenty ml. of water was added, and the mixture was again heated to boiling. A small quantity of insoluble material was filtered from the hot solution, which was then cooled slowly. A light yellow crystalline product formed. The compound was filtered off and air dried for four hours. It weighed about 1.6 grams (seventy-five per cent of the theoretical amount, assuming the reaction was only a rearrangement). One gram of the substance was dissolved in forty ml. of hot ethanol in a 125 ml. Erlenmeyer flask. Water was added in small portions to incipient precipitation at the boiling point. This hot solution was filtered and cooled. The

crystals formed were filtered off and after drying for one hour at 100°C. in an Abderhalden pistol the substance melted at 134-135.5°C. It was evidently not very pure, but analyses were made nevertheless.

Analysis. Calculated for $C_{18}H_{14}N_4$: C, 75.4; H, 4.89.
Found: C, 74.5; H, 5.00.

PREPARATION OF 3,4-DICYANOPYRROLE

Five grams of α, α' -dicyanosuccinaldehyde, fifteen grams of ammonium acetate and fifty ml. of concentrated ammonium hydroxide were mixed in a two hundred ml. evaporating dish. The mixture was heated nearly to dryness in a hood while stirring with a thermometer. The highest temperature recorded was 180°C., but because of the small quantity of material left when this temperature was attained the thermometer must have registered far too low. The black material thus formed was scraped and washed into a beaker. It was extracted with four one hundred ml. portions of boiling water to dissolve the pyrrole. The hot extracts were individually filtered and cooled to 0°C. The first two gave light brown precipitates which were filtered off together. This material was recrystallized from one hundred ml. of water containing two grams of Norite. The white crystalline product was recrystallized from fifty ml. of water. This product was dried as before. The yield was small. The compound melted at 231.5-232.5°C. forming a red liquid.

Analysis. Calculated $C_6H_3N_3$: C, 61.6; H, 2.56.
Found: C, 62.1; H, 2.50.

HYDROLYSIS OF 3,4-DICYANOPYRROLE (3,4-PYRROLEDICARBOXYLIC
ACID)

About one gram of crude 3,4-dicyanopyrrole was heated with twenty-five ml. of ten per cent aqueous sodium hydroxide under a reflux condenser for one hour. Ammonia was evolved. The resulting solution was acidified with twenty ml. of concentrated hydrochloric acid, stirred and cooled. A light yellow-brown microcrystalline precipitate was filtered off on a small Büchner funnel. The product was heated with one hundred ml. of water, and just enough dioxan was added to dissolve it at the boiling point of the mixture. Two grams of Norite was added to the solution, which was then boiled for five minutes and filtered. The filtrate was cooled to 0°C. and allowed to stand for several hours. The white precipitate formed was filtered off on a small Büchner funnel, washed once with fifty ml. of water, then dried for an hour at 100°C. in an Abderhalden pistol. The product melted at 256-258°C. with decomposition.

Analysis. Calculated for $C_6H_5O_4N$: C, 46.5; H, 3.23.
Found: C, 46.2; H, 3.31.

HYDROLYSIS OF α, α' -DICYANOSUCCINALDEHYDE BY AQUEOUS
SODIUM HYDROXIDE

One half gram of α, α' -dicyanosuccinaldehyde was dissolved in ten ml. of ten per cent aqueous sodium hydroxide solution in a fifty ml. Erlenmeyer flask. The solution was heated on the steam bath for two hours. A small amount of insoluble material was filtered off, and the filtrate

was acidified with concentrated hydrochloric acid. This solution was cooled in a mixture of ice and hydrochloric acid. Light gray crystals separated and were filtered off immediately. The yield was only four tenths of a gram (forty-six per cent of the theoretical amount). The material was recrystallized from six ml. of water containing a little Norite. The purified product melted at 184-6°C. A mixture of this substance with an equal quantity of succinic acid melted at 185-7°C. Both the unknown material and succinic acid form white insoluble silver salts when their aqueous solutions are treated with silver nitrate solution.

HYDROLYSIS OF α, α' -DICYANOSUCCINALDEHYDE BY DILUTE HYDROCHLORIC ACID

To a one liter flask supported on a steam cone was added fifteen grams of α, α' -dicyanosuccinaldehyde, five hundred ml. of distilled water and forty ml. of concentrated hydrochloric acid. A reflux condenser was attached to the flask, and a tube was fitted to the top of the condenser to conduct any gas evolved through a bubble counter. The flask was heated by steam for three hours. At first the evolution of gas was rapid, but after an hour it had slowed very much and at the end of three hours it was negligible. Meanwhile the color of the solution had changed through yellow, orange and red to red-black. The acid solution was extracted continuously for sixteen hours with two hundred ml. of ether. During the extraction a water layer collected in the flask. The ether layer was distilled off leaving about forty ml. of

an aqueous solution.

Eight ml. of the solution was added to one hundred ml. of ethanol and three grams of 2,4-dinitrophenylhydrazine in a two hundred ml. flask. The mixture was heated to boiling and two ml. of concentrated hydrochloric acid was added. The solution was boiled for fifteen minutes, then allowed to cool. Large yellow crystals separated. They were filtered off and recrystallized from one hundred ml. of ethanol containing two grams of Norite. The product was filtered off, washed with thirty ml. of ethanol and dried at 78°C. for one hour in an Abderhalden pistol. The material softened at 93°C. and melted from 102°C. to about 125°C. Recrystallizations from ethanol and butanol failed to purify the material at all. The solubility is too high and the melting range is too low for the 2,4-dinitrophenylhydrazone of succinaldehyde.

In an attempt to prepare an oxime, ten ml. of the aqueous solution extracted from the hydrolysis mixture, five grams of hydroxylammonium chloride, three grams of sodium hydroxide and twenty ml. of water were heated in a 125 ml. Erlenmeyer flask for ten minutes. The solution was then cooled in a mixture of ice and water. The side of the flask was scratched, but no precipitate formed.

The remaining aqueous solution was shaken with precipitated calcium carbonate and filtered. The filtrate was concentrated to about four ml. in a twenty-five ml. distilling flask with a ten inch Vigreux column. The concen-

trate was distilled in a ten ml. distilling flask. The distillate gave a negative test with Schiff's reagent, but the residue of less than one half ml. gave a strong positive test. The residue formed no 2,4-dinitrophenylhydrazone, however.

In a separate experiment 7.5 grams of α, α' -dicyano-succinaldehyde was hydrolyzed by one hundred ml. of 2N. hydrochloric acid in a side-arm flask equipped with a reflux condenser. Nitrogen was passed in through the side arm, and swept the evolved gases out the condenser through a dry ice trap and into a U tube filled with Ascarite. After three hours of boiling the reaction was complete, but only 1.3 grams of carbon dioxide had been adsorbed. This is a yield of only twenty-seven per cent of the theoretical amount. The hydrolysis mixture was saturated with sodium bisulfite, but no precipitate formed. On adding thirty ml. of ethanol a precipitate formed which was very soluble in water. This material charred slightly in a flame, but seemed to consist essentially of sodium bisulfite.

SUMMARY

1. Methods for preparing succinaldehyde have been reviewed. The literature has been covered through the index of Chemical Abstracts for 1942.

2. α, α' -dicyanosuccinaldehyde has been prepared, and its physical and chemical properties have been partially studied.

3. Three derivatives of the aldehyde form of α, α' -dicyanosuccinaldehyde have been prepared: the anil, the monoxime and the mono-2,4-dinitrophenylhydrazone.

4. Although the enol form of α, α' -dicyanosuccinaldehyde was not isolated, a mono sodium enolate and a dibenzoate of the enol form were obtained.

5. With ammonium acetate, the aldehyde was converted to 3,4-dicyanopyrrole, and this compound was hydrolyzed to the corresponding acid.

6. The anil gave 1-phenyl-3,4-dicyanopyrrole in boiling butyl acetate, and alcoholic potassium hydroxide converted the anil to a neutral compound of unknown structure which had the same empirical formula as the anil and which melted at 135°C.

7. Hydrolysis of α, α' -dicyanosuccinaldehyde with acid gave no succinaldehyde. Hydrolysis with alkali, followed by acidification, gave succinic acid.

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