

Fig. 2. Infrared spectrum of 2-methylpyrrole

TABLE I
ABSORPTION BANDS IN INFRARED SPECTRA OF
3-METHYLPYRROLE AND 2-METHYLPYRROLE^a

3-Methyl- pyrrole	2-Methyl- pyrrole	3-Methyl- pyrrole	2-Methyl- pyrrole
3462 vs	3441 vs	1390 vw	1386 vw
3390 vs	3362 vs	1375 vw	1375
3080 sh	3072 w	1259 m	1259
2981 vs	2971 vs	1218 ^b m	1230 ^b s
2915 s	2904 m	1139 m	1130 s
2862 m	2850 w (sh)	1097 ^b	1097 ^b vs
2730 vw	2730	1061 vs	1061
2550 vw	2550	1030 ^b	1030 ^b vs
1700	1700 vw	980 w	980 w
1672 vw	1672	956 m	951 m
1635	1635 vw	889 m	889 m
1570 ^b w	1577 ^b s-vs	879	879 sh
1556 ^b w-m	1550 ^b	790 ^b	790 ^b m
1490 ^b m-s	1490 ^b	700 s	704 vs
1463 m	1463 m	660	660 sh
1432 m-s	1418 m-s	633	633 w

^a Values are frequencies in cm.⁻¹; s = strong, m = medium, w = weak, vs = very strong, sh = shoulder. ^b Principal differences.

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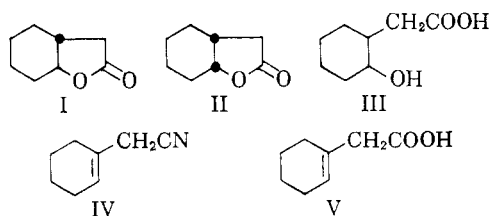
Preparation of *cis*-2-Hydrocyclohexane-acetic Acid Lactone

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The *trans*-lactone (I) of 2-hydroxycyclohexane-acetic acid is easily obtainable from diethyl sodiomalonate and cyclohexene oxide. However, the *cis*-lactone (II) has only been obtained indirectly by hydrolysis of I to the *trans*-acid (III), followed by oxidation to the corresponding ketoacid and catalytic hydrogenation to a mixture of the acids III, containing 84% of the *cis*-isomer. The latter lactonized spontaneously to II. The over-all yield of II, based on cyclohexene oxide, was 38%.¹

It has now been found that II is obtained in about 30% yield by one-step reaction of the readily accessible 1-cyclohexene-1-acetonitrile² (IV) with concentrated hydrochloric or hydrobromic acid in boiling glacial acetic acid. The determination of the



composition of the lactone obtained was based on the fact observed by Newman and Vanderwerf¹ that I yields on dissolution in aqueous sodium hydroxide and subsequent acidification the *trans*-acid III, while the *cis*-acid III, obtained under these conditions from II, cyclizes spontaneously again to II.

The mechanism of this stereospecific reaction very probably does not consist of initial hydration of the double bond and subsequent attack of the hydroxy group on the nitrile triple bond. In this case it would have to lead to a mixture of I and II and should not markedly depend on the nature of the acid employed. In fact sulfuric acid, for example, does not bring about the conversion of IV to II. The first step in the production of the lactone II is the formation of the unsaturated acid (V); it can be isolated when the reaction is interrupted after a shorter time than that required for the formation of the lactone. The hydrolysis of the nitrile function is obviously not a simple acid-catalyzed reaction, but is brought about by an addition of the acid to the C≡N bond and is influenced also by the anion of the acid. Therefore, the order of the rates of the reaction of IV with the acids employed is: hydrobromic > hydrochloric > sulfuric acid; this is also the order of the nucleophilicities of the anions.

The cyclization step, which follows the formation of the acid V, is not the rate controlling one, since the acid V is cyclized smoothly in the presence of either hydrobromic or sulfuric acid.

EXPERIMENTAL

Reaction of hydrobromic acid with 1-cyclohexene-1-acetonitrile IV. General procedure. To 20 g. of IV in 80 ml. of glacial acetic acid, 140 ml. of concentrated hydrobromic acid was added and the mixture was refluxed for the desired period of time, after which water was added and the product extracted with benzene. The benzene layer was washed with 5% aqueous sodium carbonate solution. The acidic products, obtained by acidification of the washings, were extracted with benzene and distilled. 1-Cyclohexene-1-acetic acid (V) distills at 155–158° (20 mm.) and melts at 37°.³ Some bromine-containing acids were also observed after longer reaction periods. They boiled at 170–190° (20 mm.), but have not been obtained in pure form.

The neutral products remaining in the benzene layer can be separated by fractionation. The nitrile IV distills at 120° (20 mm.); the lactone II boils at 145–148° (20 mm.).

The obtained lactone consisted of the *cis*-product II. In one case only was a small amount of the *trans*-isomer I found.

In order to determine the content of I and II in the lactone, the neutral products obtained after evaporating

(1) M. S. Newman and C. A. Vanderwerf, *J. Am. Chem. Soc.*, **67**, 233 (1945).

(2) A. C. Cope, *et al.*, *Org. Syntheses*, **31**, 25 (1951).

(3) O. Wallach, *Ann.*, **343**, 51 (1905).

the benzene solution were stirred with warm 10% aqueous sodium hydroxide solution for 15 min. and extracted with benzene, which removed the unchanged nitrile IV. The alkaline solution was acidified with cooling, and the oil which separated extracted with benzene. From the extract, the *trans*-acid could be removed by means of 5% aqueous sodium carbonate solution, while the *cis*-lactone II was obtained by distillation of the benzene solution. B.p. 145–148° (20 mm.).

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.6; H, 8.6. Found: C, 68.6; H, 8.7.

The *trans*-acid, eventually obtained by acidification melts at 106°.¹

The results of the experiments are summarized in Table I.

TABLE I
ACID HYDROLYSIS OF THE NITRILE IV

Product (in % of theory)	Hydrobromic Acid after				Hydro- chloric Acid after			Sul- furic Acid after	
	2	4	7	13	2	4	10	4	10
	hr.	hr.	hr.	hr.	hr.	hr.	hr.	hr.	hr.
Lactones ^a			23	24			22	2	5
<i>cis</i> -Lactone (II)	15	30			8	24			
<i>trans</i> -III		4							
V	26		10		30	15			
Acid m.p. 117°								1	8
Starting material (IV)	5				30	8		73	
Unsaturated amides ^b									
Acids containing bromine			13	15					

^a Total amount of lactones, when no separation of the isomers was carried out. ^b See text.

Reaction of sulfuric acid with IV. To 20 g. of IV in 150 ml. of acetic acid, 100 ml. of 10% sulfuric acid was added and the reaction mixture was treated as above. In this case, the neutral product had m.p. 135–152° and showed the same elementary analysis as the amide of V.⁴

In the acidic fraction a product m.p. 117° was found.

Reaction of 1-cyclohexene-1-acetic acid (V) with sulfuric acid. To 4.5 g. of the acid V in 35 ml. of glacial acetic acid, 25 ml. of 50% sulfuric acid was added and the mixture was refluxed for 4 hr. Water was added and the product worked up as usual. Distillation of the benzene layer gave 2.5 g. (55%) of the *cis*-lactone II, b.p. 140–150° (20 mm.). An unidentified acidic product (1 g.), b.p. 180–200° (20 mm.), was also found.

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(4) O. Wallach, *Ann.*, **353**, 292 (1907), m.p. 153°.

Preparation of 4-Carboxy-1,2-cyclohexanedione Dioxime^{1,2}

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In an effort to find a *vic*-dioxime which was water soluble and still possessed the desired properties

which would make it useful as an analytical reagent for nickel and palladium,³ and for the study of the complexes formed between nickel and the *vic*-dioxime in basic solution,^{4–13} 4-carboxy-1,2-cyclohexanedione dioxime was prepared in this Laboratory.

The synthesis of 4-carboxy-1,2-cyclohexanedione dioxime involves the following steps: the high pressure hydrogenation of ethyl-4-hydroxybenzoate to 4-ethoxycarbonylcyclohexanol, the oxidation of this alcohol by the acid-chromate method to 4-ethoxycarbonylcyclohexanone, the selenium dioxide oxidation of the monoketone to 4-ethoxycarbonyl-1,2-cyclohexanedione, the oximation of the dione to 4-ethoxycarbonyl-1,2-cyclohexanedione dioxime, and hydrolysis of this dioxime to the desired compound, 4-carboxy-1,2-cyclohexanedione dioxime.

Aqueous oximation of 4-ethoxycarbonyl-1,2-cyclohexanedione using potassium hydroxide and hydroxylammonium chloride gave as the major product 4-hydroxyaminocarbonyl-1,2-cyclohexanedione dioxime rather than 4-ethoxycarbonyl-1,2-cyclohexanedione dioxime. 4-Hydroxyaminocarbonyl-1,2-cyclohexanedione dioxime can also be conveniently prepared from 4-ethoxycarbonyl-1,2-cyclohexanedione dioxime.

The *pK* values were determined for the three acidic hydrogens of 4-carboxy-1,2-cyclohexanedione dioxime and the following results were obtained: $pK_1 = 4.85$, $pK_2 = 10.45$ and $pK_3 = 12.37$.

EXPERIMENTAL

4-Ethoxycarbonylcyclohexanol. 4-Ethoxycarbonylcyclohexanol has been prepared by Ungnade and Morriss.¹⁴ Equally satisfactory results were obtained by the following procedure. One hundred grams of ethyl-4-hydroxybenzoate and 15 g. of a 2% palladium catalyst¹⁵ on a strontium car-

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(2) Contribution No. 583; work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

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