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				Hydrochloric Acid after			Sulfuric Acid after	
	2 hr.	4 hr.	7 hr.	13 hr.	2 hr.	4 hr.	10 hr.	4 hr.	10 hr.
Lactones[a]			23	24			22	2	5
cis-Lactone (II)	15	30			8	24			
trans-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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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-cyclohexanedionedioxime was prepared in this Laboratory.

The synthesis of 4-carboxy-1,2-cyclohexanedionedioxime 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-cyclohexanedionedioxime, and hydrolysis of this dioxime to the desired compound, 4-carboxy-1,2-cyclohexanedionedioxime.

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

The pK values were determined for the three acidic hydrogens of 4-carboxy-1,2-cyclohexanedionedioxime 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 catalyst[15] on a strontium car-

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(1) No. XX in a series on "Chemistry of the *vic*-Dioximes." Previous paper in this series is No. XIX, *J. Org. Chem.*, **21**, 815 (1956).

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

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bonate support were suspended in 150 ml. of purified dioxane, and the material was reduced at a hydrogen pressure of 1800 p.s.i. at 150° for 4 hr. in a Parr high-pressure apparatus. The reaction mixture was filtered, the dioxane removed by distillation and the 4-ethoxycarbonylcyclohexanol was vacuum-distilled through a 50-cm. Vigreux column. Yield of 4-ethoxycarbonylcyclohexanol, 80%; b.p. 115–123° (4 mm.); n_D^{20} 1.4635.

4-Ethoxycarbonylcyclohexanone. 4-Ethoxycarbonylcyclohexanol was oxidized by the acid-dichromate method,[16] but because of possible hydrolysis of the ester grouping, the usual procedure was slightly modified in that the temperature was not allowed to rise above 35°. The crude 4-ethoxycarbonylcyclohexanone was vacuum-distilled through a 50-cm. Vigreux column and the product was collected. Yield of 4-ethoxycarbonylcyclohexanone, 65%; b.p. 112–118° (4 mm.); n_D^{25} 1.4594.

4-Ethoxycarbonyl-1,2-cyclohexanedione. The 4-ethoxycarbonylcyclohexanone was oxidized with alcoholic selenium dioxide to give the corresponding diketone. The method reported by Riley, Morley, and Friend[17] as modified by Hach, Banks, and Diehl[18] was employed. The reaction mixture was filtered and fractionated through a 50-cm. Vigreux column under reduced pressure. The dione is very unstable towards prolonged heating and the distillation should be completed as rapidly as possible. Yield of 4-ethoxycarbonyl-1,2-cyclohexanedione, 48%; b.p. 120–135° (2 mm.); n_D^{20} 1.4862.

4-Ethoxycarbonyl-1,2-cyclohexanedionedioxime. 4-Ethoxycarbonyl-1,2-cyclohexanedione was oximated by a method very similar to that of Bachmann and Boatner.[19] One-half mole of the dione, 2 moles of hydroxylammonium chloride, 4 moles of pyridine, and 600 ml. of absolute alcohol were refluxed for 35 min. on a steam bath. After most of the pyridine had evaporated, the oily mixture was poured into an equal volume of cold water to precipitate the crude 4-ethoxycarbonyl-1,2-cyclohexanedionedioxime. This material was dried and recrystallized twice from ethyl acetate. Yield of 4-ethoxycarbonyl-1,2-cyclohexanedionedioxime, 55%; m.p. 167°.

Analytical samples were obtained by dissolving 1 g. of the ester in 50 ml. of absolute ethanol and passing the solution through a column 10 cm. in length and 2.5 cm. in diameter packed with Woelm basic alumina. Ethanol was used as the eluant. The 4-ethoxycarbonyl-1,2-cyclohexanedionedioxime was precipitated from the ethanol by the addition of petroleum ether, filtered, and dried at 110° for 1 hr.

Anal. Calcd. for $C_9H_{14}N_2O_4$: N, 13.08%. Found: N, 12.97%; 13.15%.

4-Hydroxyaminocarbonyl-1,2-cyclohexanedionedioxime. 4-Hydroxyaminocarbonyl-1,2-cyclohexanedionedioxime can be prepared from 4-ethoxycarbonyl-1,2-cyclohexanedionedioxime by using the synthesis given for benzohydroxamic acid.[20] This compound gave a red precipitate with nickel while cupric acetate produced a greenish-blue color characteristic of hydroxamic acids. It was observed that this hydroxamic acid was hydrolyzed readily by aqueous acid solution, which is in agreement with the information reported in the review paper by Yale.[21] Yield of 4-hydroxyaminocarbonyl-1,2-cyclohexanedionedioxime 60%; m.p. 152°.

Anal. Calcd. for $C_7H_{11}N_3O_4$: N, 21.00%. Found: N, 21.10%; 20.81%.

4-Carboxy-1,2-cyclohexanedionedioxime. 4-Carboxy-1,2-cyclohexanedionedioxime was obtained by hydrolysis of 4-ethoxycarbonyl-1,2-cyclohexanedionedioxime. This was accomplished by heating on a steam bath for 1 hr. a mixture of 0.1 mole of the ester, 0.15 mole of potassium hydroxide, and 125 ml. of water. After cooling, the reaction mixture was acidified to pH 1–2. The precipitated acid was filtered and dried. More acid can be obtained by extraction of the hydrolysis mixture with diethyl ether. The acid was recrystallized by dissolving in a minimum amount of hot dioxane, adding petroleum ether to incipient cloudiness, cooling, and filtering. The acid had a purity of 95% based on micro Dumas nitrogen determinations and titration of the carboxy hydrogen.

Further purification can be obtained by dissolving approximately 2 g. of the acid in 50 ml. of dioxane and passing the solution, while hot, through a column 10 cm. in length and 2.5 cm. in diameter which was packed with a 1:1 mixture of acidic and basic Woelm alumina. This procedure was repeated twice and a very pure compound was obtained, as indicated by titration of the acid which gave a molecular weight of 186.16; theoretical is 186.17. Yield of 4-carboxy-1,2-cyclohexanedionedioxime, 50%; m.p. 218–220° with decomposition.

Anal. Calcd. for $C_7H_{10}N_2O_4$: N, 15.05%. Found: N, 15.08%; 15.04%.

pK Determinations. The molar dissociation constants for 4-carboxy-1,2-cyclohexanedionedioxime were determined by the following methods. The pK_1' for the carboxy hydrogen was determined by direct titration with 0.1*N* potassium hydroxide after having added a known excess of standardized 0.1*N* hydrochloric acid. A value of 4.75 ($\mu = 0.100$) was found. Conversion to the thermodynamic constant, pK_1, by application of the Debye and Hückel theory, gave a value of 4.85.

The method of Banks and Carlson[22] was used to determine the pK values of the oxime hydrogens. The average value found for four determinations of pK_2' was 10.44 ($\mu = 0.01$) and for two determinations of pK_3' was 12.31 ($\mu = 0.06$). Conversion to the thermodynamic constants gave 10.45 for pK_2 and 12.37 for pK_3.

Due to the hydrolysis of 4-hydroxyaminocarbonyl-1,2-cyclohexanedionedioxime the pK values were not determined.

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Reactivity Ratios of Trifluoromethyl-substituted Styrenes with Methyl Methacrylate and Styrene

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To find the effect of substitution of the trifluoromethyl group on the polymerization reactivity of styrene, the reactivity ratios of 3-

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