dition for use in further reactions. Assay of the reaction mixture was made as follows: after cooling to room temperature in an atmosphere of nitrogen the solids were separated by filtration, allowed to air slake and then washed with water to remove sodium cyanide. The remaining insoluble solid was recrystallized from alcohol and yielded 19 g. (85%) of 2,2,4,6-tetraphenyldihydrotriazine, m.p. 190–191° in agreement with Lottermoser.[3] The benzene filtrate was distilled to remove the benzene and the residue was recrystallized from alcohol to yield 0.54 g. (3%) of II, m.p. 229–230° in agreement with that reported previously.[3,5]

Reaction of I *with carbon dioxide.* A portion of I was prepared (as above) from 0.23 mole of benzonitrile and 0.13 mole of sodium, using xylene as solvent. The mixture was heated to reflux and dry CO_2 was introduced through a fritted glass bubbler with stirring for 23 hr. The reaction-mixture, which contained suspended solids, was treated as in the preceding paragraph. The xylene solution yielded 2.72 g. of II, and the xylene-insoluble solids gave 1.34 g. after water washing and recrystallization from alcohol. The total yield of II was 4.06 g. (22.6%) based on the benzonitrile used. The procedures for other experiments with carbon dioxide and with sulfur dioxide differed from the above only in the solvent used and the reaction time and temperature.

Reaction of I *with benzonitrile.* A portion of I was prepared as above from 30 g. (0.26 mole +11% excess) of benzonitrile and 3 g. (0.13 mole) of sodium, using xylene as solvent. The excess of benzonitrile was added to ensure complete disappearance of the sodium in the first stage of the reaction. A further quantity of benzonitrile (0.195 mole) was then added and the mixture was refluxed with stirring for 24 hr. For this operation it appeared advantageous to partially fill the reaction vessel with glass beads, whose grinding action promotes the reaction between solid and liquid reactants. Subsequent treatment of the reaction mixture as described above yielded 4.09 g. of II (20.5%).

Methylation of I. A portion of I was prepared from benzonitrile (0.23 mole) and sodium (0.13 mole) in refluxing heptane with the aid of glass beads. After cooling the reaction mixture to 30° under nitrogen, methyl iodide (16.5 g., 0.116 mole) in 10 ml. of heptane was added over 1 hr. with stirring at 30–40°, and the stirring continued for 0.5 hr. The mixture was filtered to remove solid reaction products and the heptane filtrate was discarded. The separated solid was thoroughly washed with five 200-ml. portions of benzene and the combined benzene washes were applied to a column of 385 g. of alumina (Alcoa F-20), 1″ × 4′. The chromatogram was developed with benzene and yielded: II, m.p. 229–230°, 0.533 g. (3%); III, m.p. 191°, 0.920 g. (3.95%); IV, m.p. 210°, 3.173 g. (13.6%).

Anal. Calcd. for $C_{28}H_{23}N_3$: C, 83.8; H, 5.7; N, 10.5; mol. wt., 401. Found (III): C, 83.5; H, 5.9; N, 10.6; mol. wt., 403. (IV): C, 84.3; H, 5.3; N, 9.9; mol. wt., 401.

Active hydrogen: Calcd. for I (Na = H): 1 mole CH_4/mole subst.; found, 0.9 mole CH_4. III and IV both yielded 0.0 mole CH_4.

Mixed melting points: III–IV, 167–180°; III–I (Na = H), 155–170°; III–II, 175–205°.

Further derivatives of I. Treatment of I with other reagents under the conditions described above yielded *N*-substitution products (Table II). When heated alone or in solvents at elevated temperatures (without prior purification) these failed to yield further isolable amounts of II. The melting points and analyses shown were determined after recrystallization of the principal (probably symmetrical) isomer.

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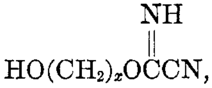
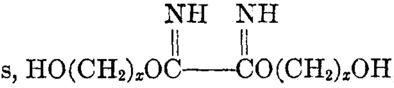
[CONTRIBUTION FROM THE GRADUATE SCHOOL OF ARTS AND SCIENCES, UNIVERSITY OF BUFFALO]

Reaction of Cyanogen with Organic Compounds. XII. Glycols and Glycol Monoethers[1]

H. M. WOODBURN, ALAN B. WHITEHOUSE,[2] AND BERNARD G. PAUTLER[3]

Received June 16, 1958

Ethylene glycol, 1,2-propanediol, 1,3-propanediol, and 2,3-butanediol, as well as the methyl, ethyl, and butyl monoethers of ethylene glycol, react with cyanogen in the presence of hydrogen chloride to yield moderately stable symmetrical oxaldiimidate dihydrochlorides. Neither 1,2-, 1,3-, nor 1,4-butanediol reacts with cyanogen under these conditions. In the presence of aqueous potassium cyanide, cyanogen and the glycol monoethers produce stable cyanoformimidates. Potassium carbonate and ammonium hydroxide are equally effective catalysts. With catalytic amounts of sodium, glycol monoethers and cyanogen produce stable oxaldiimidates. 2-Methoxyethylcyanoformimidate reacts with methyl Cellosolve to form the oxaldiimidate. Other combinations of glycol ethers and cyanoformimidates have thus far been unreactive.

This investigation is part of a series dealing with the reaction of cyanogen with bifunctional compounds. In previous papers we have described the behavior of aliphatic and aromatic diamines,[4,5] amino mercaptans,[6] and amino alcohols.[7] Although published information concerning the reaction of cyanogen with monohydroxy alcohols is scanty,[8,9] the studies referred to above indicated that glycols might logically form any of the following type products: cyanoformimidates,  $HO(CH_2)_xOC(=NH)CN$, oxaldiimidates,  $HO(CH_2)_xOC(=NH)-C(=NH)O(CH_2)_xOH$, bi-

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(1) Parts of this paper are from a thesis submitted by A. B. Whitehouse in partial fulfillment of the requirements for the Ph.D. degree, June 1957.

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(3) Postdoctoral Fellow, Mallinckrodt Chemical Works.

(4) H. M. Woodburn and R. C. O'Gee, *J. Org. Chem.*, **17**, 1235 (1952).

(5) H. M. Woodburn and J. R. Fisher, *J. Org. Chem.*, **22**, 895 (1957).

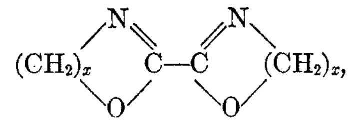
(6) H. M. Woodburn and B. G. Pautler, *J. Org. Chem.*, **19**, 863 (1954).

(7) H. M. Woodburn and E. L. Graminski, *J. Org. Chem.*, **23**, 819 (1958).

(8) J. U. Nef, *Ann.*, **287**, 274 (1895).

(9) A. Pinner and Fr. Klein, *Ber.*, **11**, 1475 (1878).

cyclic compounds,



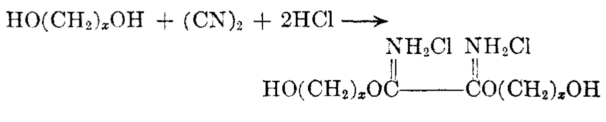
condensation polymers.

Actually only cyanoformimidates and oxaldiimidates were isolated. The absence of cyclization observed with amino alcohols was noted also with glycols.

Of the three methods reported to yield cyanogenation products from ethanol,[8,9] only that employing hydrogen chloride was applicable to glycols since either sodium or potassium cyanide caused the formation of tar from which no product could be isolated. Presumably the free oxaldiimidate is much less stable than its hydrochloride. Best yields were obtained when dry cyanogen and dry hydrogen chloride were passed into the glycol solution simultaneously. Although the presence of a solvent was not required to bring about a reaction, since pure glycols produced white precipitates when treated with cyanogen and hydrogen chloride, the high viscosity of glycols made filtration impossible and the product could not be obtained in a pure state. Dimethyl Cellosolve was found to possess high solvent action for glycols, cyanogen, and hydrogen chloride. Also, it was easily obtained in an anhydrous condition by fractionation over sodium and was preferable to diethyl ether which has poor glycol solvency.

Success in the glycol reaction often appears to depend on the purity of the glycol. For example, the practical grade of 1,3-propanediol obtained from Distillation Industries, Inc., even when distilled before use, gave a product which decomposed too rapidly for analysis. Treatment of the glycol with activated carbon followed by distillation gave a reagent which produced a stable oxaldiimidate dihydrochloride.

The following glycols, treated with cyanogen and hydrogen chloride, produced oxaldiimidate dihydrochlorides in yields of 22–74%: ethylene glycol, 1,3-propanediol, 1,2-propanediol, and 2,3-butanediol.



$$HO(CH_2)_xOH + (CN)_2 + 2HCl \longrightarrow HO(CH_2)_xO\overset{NH_2Cl}{\overset{\|}{C}}-\overset{NH_2Cl}{\overset{\|}{C}}O(CH_2)_xOH$$

1,2-Butanediol, 1,3-butanediol, and 1,4-butanediol failed to react even though it was shown that conditions were suitable since added ethylene glycol gave an immediate product.

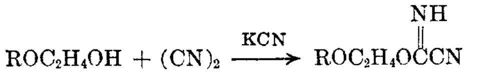
Ethylene glycol, 1,3-propanediol, and 2,3-butanediol are symmetrical compounds; hence there can be no doubt concerning the structure of the diimidate product. 1,2-Propanediol, however, contains both a primary and a secondary hydroxy group and should, theoretically, form an oxaldiimidate in three ways. To throw light on this question a mixture of ethylene glycol (which contains only primary hydroxy groups) and 2,3-butanediol (which contains only secondary hydroxy groups) was cyanogenated using a quantity of cyanogen such that each of the glycols was present in excess. Hence the cyanogen should react only with that glycol offering the faster reaction. The product from the mixture was the oxaldiimidate dihydrochloride of ethylene glycol. It was concluded that the primary hydroxy group of 1,2-propanediol should have reacted more rapidly than the secondary and that the principal product of its cyanogenation should be *sym*-bis(2-hydroxypropyl)oxaldiimidate.

This result makes it difficult to understand the behavior of the butanediols since the one which reacted contains only a secondary hydroxy group whereas all the others contain at least one primary hydroxy group.

The monomethyl-, monoethyl-, and monobutyl ethers of ethylene glycol reacted with cyanogen and hydrogen chloride in dimethyl Cellosolve solution but the products which were obtained were too unstable for analysis. Therefore other methods of cyanogenation were investigated.

In the presence of sodium, the pure monoethers gave fair yields of oxaldiimidates. Because of their rather high boiling points, these liquids decomposed appreciably upon distillation even under reduced pressure. Their hydrochloride, made by passing anhydrous hydrogen chloride into a dimethyl Cellosolve solution of the free base, corresponded in instability and decomposition temperatures to those prepared directly from monoether, cyanogen, and hydrogen chloride.

Under conditions similar to those used on ethanol by Nef,[8] we treated the monoethers with cyanogen in the presence of aqueous potassium cyanide. In this case the products were cyanoformimidates,

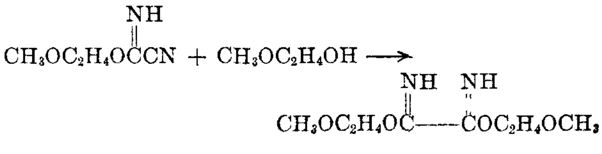


$$ROC_2H_4OH + (CN)_2 \xrightarrow{KCN} ROC_2H_4O\overset{NH}{\overset{\|}{C}}CN$$

They were unstable liquids, turning yellow and finally brown at room temperature but easily purified by vacuum distillation.

Potassium carbonate was an equally effective catalyst for the reaction, and even better yields were obtained when diethyl ether was used as solvent and ammonium hydroxide as catalyst.

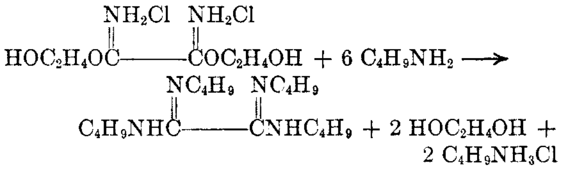
Because sodium as catalyst caused both nitrile groups of cyanogen to react, we attempted to catalyze the reaction of cyanoformimidates with Cellosolves to yield oxaldiimidates. This was actually accomplished with the reaction pair 2-methoxyethyl cyanoformimidate and methyl Cellosolve,



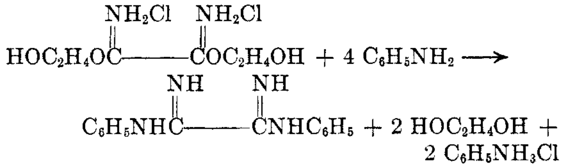
$$CH_3OC_2H_4O\overset{NH}{\overset{\|}{C}}CN + CH_3OC_2H_4OH \longrightarrow CH_3OC_2H_4O\overset{NH}{\overset{\|}{C}}-\overset{NH}{\overset{\|}{C}}OC_2H_4OCH_3$$

However, no other combinations were successful whether the ether portions were identical or not. Thus the attractive possibility of producing an unsymmetrical oxaldiimidate was not realized. After more than 10 years of effort we have not yet succeeded in making an unsymmetrical oxamidine or oxaldiimidate.

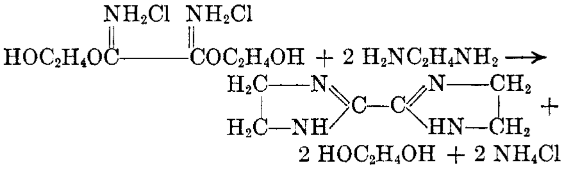
Incidental to this work was the study of certain reactions such as (a), (b), and (c) which proved the structure of the oxaldiimidates and demonstrated the chemical similarity of oxaldiimidates and oxamidines.[10]

(a)


$$\mathrm{HOC_2H_4O\overset{NH_2Cl}{\overset{\|}{C}}\text{———}\overset{NH_2Cl}{\overset{\|}{C}}OC_2H_4OH + 6\,C_4H_9NH_2 \longrightarrow C_4H_9NH\overset{NC_4H_9}{\overset{\|}{C}}\text{———}\overset{NC_4H_9}{\overset{\|}{C}}NHC_4H_9 + 2\,HOC_2H_4OH + 2\,C_4H_9NH_3Cl}$$

(b)


$$\mathrm{HOC_2H_4O\overset{NH_2Cl}{\overset{\|}{C}}\text{———}\overset{NH_2Cl}{\overset{\|}{C}}OC_2H_4OH + 4\,C_6H_5NH_2 \longrightarrow C_6H_5NH\overset{NH}{\overset{\|}{C}}\text{———}\overset{NH}{\overset{\|}{C}}NHC_6H_5 + 2\,HOC_2H_4OH + 2\,C_6H_5NH_3Cl}$$

(c)


$$\mathrm{HOC_2H_4O\overset{NH_2Cl}{\overset{\|}{C}}\text{———}\overset{NH_2Cl}{\overset{\|}{C}}OC_2H_4OH + 2\,H_2NC_2H_4NH_2 \longrightarrow \quad + 2\,HOC_2H_4OH + 2\,NH_4Cl}$$

The three products (a) tetrabutyloxamidine, (b) diphenyloxamidine, and (c) bis(Δ^2-2-imidazolinyl) have been prepared independently by the action of cyanogen on butyl amine,[11] aniline,[12] and ethylenediamine.[4]

EXPERIMENTAL

Reagents. Cyanogen was prepared and purified essentially by the method of Janz.[13] We found it expedient, however, to add 100 ml. of water to the initial pot charge of copper sulfate. The resulting slurry could be stirred more readily than dry copper sulfate at the beginning of the reaction, and it reduced local heating and polymerization of the cyanogen.

After purification, the cyanogen was frozen in a Dry Ice–acetone trap at −80°. This allowed its weight to be easily determined. Removal of the freezing bath caused the cyanogen to distill quietly into the reaction vessel.

Glycols and glycol ethers were commercially available with the exception of 1,2-butanediol. This was synthesized according to a method used by Gattermann for ethylene glycol.[14] One mole (160 g.) of bromine was dissolved in 50 ml. of carbon tetrachloride, cooled by means of an ice bath, and C.P. butene-1 admitted. When the bromine was used up, as shown by the discharge of the red color, the mixture was washed with aqueous sodium carbonate, then water, and dried over calcium chloride. Fractionation through a 20-in. column packed with glass helices yielded 207 g. (92%) of 1,2-dibromobutane; b.p. 78.0–78.5°/45 mm.

A mixture of 0.47 mole (103 g.) of 1,2-dibromobutane, 30 g. of glacial acetic acid, and 0.9 mole (90 g.) of fused potassium acetate was refluxed for 2 hr. The crude mixture was distilled and to the distillate was added 103 g. of the dibromide and 1.35 moles (132 g.) of potassium acetate. This was in turn refluxed for 8 hr. and the crude mixture again distilled. The distillate was fractionated, yielding 30 g. (30%) of 1,2-butanediol diacetate; b.p. 74°/3 mm.

Dry methanol was prepared by distillation from magnesium methoxide. Dry hydrogen chloride was passed in until a 2.5% by weight solution was obtained. A mixture of 50 g. of the methanol solution and 50 g. of the butanediol diacetate was then refluxed for 1 hr., and fractionated. Methyl acetate was drawn from the head of the column very slowly at 58°. The temperature gradually rose to 64°, yielding a mixture of methyl acetate and methanol. The remaining liquid was distilled under reduced pressure over calcium sulfate, yielding 24 g. (92%) of pure 1,2-butanediol. Sodium was avoided in drying butanediols since it caused dehydration and polymerization during distillation.

Reaction of cyanogen with glycols. sym-Bis(2-hydroxyethyl)-oxaldiimidate dihydrochloride from ethylene glycol. Sixty-two g. (1.0 mole) of ethylene glycol was mixed with 50–75 ml. of dry diethyl ether in an absorption bottle protected from the atmosphere by a calcium chloride drying tube and cooled in an ice salt bath. Dry hydrogen chloride was passed through the mixture for a few minutes, after which cyanogen and hydrogen chloride were passed in *simultaneously.* The reaction mixture was treated in this manner with an estimated half mole of cyanogen, causing the mixture to become turbid. After standing overnight in the ice box, a white solid precipitated, which was filtered off, washed well with ethanol, and placed in a desiccator containing both sulfuric acid and sodium hydroxide to dry. The yield based on glycol was 34%.

Anal. Calcd. for $C_6H_{14}N_2O_4Cl_2$: C, 28.9; H, 5.6; N, 11.2; Cl, 28.5. Found: C, 28.8; H, 5.7; N, 11.0; Cl, 28.6.

Although yields of more than 70% could be obtained by the substitution of dimethyl Cellosolve for diethyl ether, the purity of the product was not as high as that obtained above and much time was required for recrystallization.

sym-Bis(2-hydroxypropyl)oxaldiimidate dihydrochloride from 1,2-propanediol. A mixture of 24 g. (0.32 mole) of dry 1,2-propanediol and 90 g. of dry dimethyl Cellosolve was cooled to 0° in an ice bath. Hydrogen chloride and cyanogen (15.3 g.; 0.29 mole), both anhydrous, were admitted to the solution simultaneously. The mixture was protected from moisture by a calcium chloride tube and, after a short time, became turbid. It was allowed to stand for 0.5 hr. after the reagents had been added, was then filtered by suction, and was washed with dry dimethyl Cellosolve. The product was dried under vacuum in the presence of sulfuric acid and sodium hydroxide. The yield was 32 g. (74% based on glycol) of white solid melting at 168–170° (dec.).

Anal. Calcd. for $C_8H_{18}O_4N_2Cl_2$: C, 34.7; H, 6.6; N, 10.1; Cl, 25.6. Found: C, 34.4; H, 6.8; N, 10.0; Cl, 25.9.

sym-Bis(3-hydroxypropyl)oxaldiimidate dihydrochloride from 1,3-propanediol. A pure and relatively stable product could be obtained in this case only if the glycol as purchased had been purified by shaking with activated carbon, filtering, and vacuum-distilling over calcium sulfate. A solution of 15.4 g. (0.2 mole) of this specially purified 1,3-propanediol, dissolved in 90 g. of dry dimethyl Cellosolve, was cooled to 0°. Dry hydrogen chloride and dry cyanogen (10.0 g.; 0.19 mole) were passed in simultaneously. The product, worked up as described above, was a white solid weighing 10.3 g. (37% yield based on glycol); m.p. 87–88°.

Anal. Calcd. for $C_8H_{18}O_4N_2Cl_2$: C, 34.7; H, 6.6; N, 10.1; Cl, 25.6. Found: C, 34.3; H, 6.4; N, 10.0; Cl, 25.9.

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[10] H. M. Woodburn and W. E. Hoffman, *J. Org. Chem.*, **23**, 262 (1958).

[11] H. M. Woodburn, B. Morehead, and M. C. Chen, *J. Org. Chem.*, **15**, 535 (1950).

[12] A. W. Hofmann, *Ber.*, **20**, 2252 (1887).

[13] G. J. Janz, *Inorg. Syntheses*, **5**, 43 (1957).

[14] L. Gattermann, *Laboratory Methods of Organic Chemistry.* The Macmillan Company, New York, N. Y., 1932, p. 102.

sym-Bis(1-methyl-2-hydroxypropyl)oxaldiimidate dihydrochloride from 2,3-butanediol. A solution containing 14.4 g. (0.16 mole) of anhydrous 2,3-butanediol and 90 g. of dry dimethyl Cellosolve was cooled to 0° and treated simultaneously with dry hydrogen chloride and cyanogen (13.9 g.; 0.27 mole). After 2 hr., precipitation appeared to be complete, and the white, crystalline solid was filtered by suction and worked up as described above. The yield was 5.4 g. (22% based on glycol); m.p. 148–152° (dec.).

Anal. Calcd. for $C_{10}H_{22}O_4N_2Cl_2$: C, 39.4; H, 7.3; N, 9.2; Cl, 23.2. Found: C, 39.1; H, 7.6; N, 9.1; Cl, 23.5.

Cyanogenation of a mixture of ethylene glycol and 2,3-butanediol. A mixture of 0.1 mole (6.2 g.) of dry ethylene glycol and 0.1 mole (9.0 g.) of dry 2,3-butanediol was dissolved in 30 g. of anhydrous dimethyl Cellosolve and cooled to 0°. Dry hydrogen chloride and dry cyanogen (2.1 g.; 0.04 mole) were admitted simultaneously. The mixture, protected from moisture by a calcium chloride tube, formed a white precipitate, which was filtered by suction, washed with dry solvent and dried under vacuum in the presence of sulfuric acid and sodium hydroxide. The solid melted at 183–185° and contained 28.8% chlorine, which obviously indicated that the product was the *dihydrochloride of sym-bis-(2-hydroxyethyl)-oxaldiimidate.* See above.

Reaction of cyanogen with the monoethers of ethylene glycol. 2-Methoxyethyl cyanoformimidate from methyl Cellosolve. (a) *Potassium cyanide present.* A solution containing 23.1 g. (0.3 mole) of methyl Cellosolve, 7 g. of potassium cyanide, and 100 ml. of distilled water was cooled to 0°. Cyanogen (12.0 g.; 0.23 mole) was passed in and the solution was immediately extracted with ether. After 24 hr., the solution was extracted a second time, and the ethereal solutions were combined and dried over calcium chloride. The oil remaining after evaporation of the ether was distilled under vacuum giving 7.5 g. (25% yield based on cyanogen) of colorless liquid; b.p. 54–55°/1.5 mm; n_D^{26} 1.4362; d_4^{26} 1.0719.

Anal. Calcd. for $C_5H_8O_2N_2$: C, 46.9; H, 6.29; N, 21.9; mol. wt. 128. Found: C, 46.6; H, 6.6; N, 22.1; mol. wt. 138.

(b) *Ammonia and ether present.* A solution of 45 g. (0.59 mole) of methyl Cellosolve dissolved in 150 ml. of ethanol-free ether was cooled to 0°. One-half ml. of concentrated ammonium hydroxide was added and 30 g. (0.58 mole) of cyanogen was passed in. The mixture was filtered to remove a solid presumed to be oxamide, and the ether was evaporated from the filtrate. Distillation of the residue produced methyl Cellosolve and a product having a boiling range of 53–55°/1.5 mm. The yield was 25.0 g. or 34% based on cyanogen.

2-Ethoxyethyl cyanoformimidate from ethyl Cellosolve. A solution containing 50 g. (0.55 mole) of ethyl Cellosolve, 7 g. of potassium cyanide, and 100 ml. of distilled water was cooled to 0° and treated with 13 g. (0.25 mole) of cyanogen. The brown solution was extracted with ether, dried with calcium chloride, and distilled. The product was a colorless liquid boiling at 48°/1.5 mm. Yield 8.0 g., 23% based on cyanogen.

Anal. Calcd. for $C_6H_{10}O_2N_2$: C, 50.7; H, 7.1; N, 19.7; mol. wt., 142. Found: C, 50.5; H, 6.9; N, 19.5; mol. wt. 134.

2-Butoxyethyl cyanoformidate from butyl Cellosolve. A cold solution of 60 g. (0.51 mole) of butyl Cellosolve and 7 g. of potassium cyanide in 150 ml. of distilled water was treated with 16.1 g. (0.31 mole) of cyanogen. The mixture became turbid, then brown. It was extracted with ether; the extracts being dried over calcium chloride and distilled. A colorless liquid weighing 15.2 g. (28.7% yield based on cyanogen) resulted; b.p. 75–77°/1.5 mm.

Anal. Calcd. for $C_8H_{14}O_2N_2$: C, 56.5; H, 8.3; N, 16.5; mol. wt. 170. Found: C, 56.2; H, 8.2; N, 16.8; mol. wt. 158.

sym-Bis(2-methoxyethyl)oxaldiimidate from methyl Cellosolve. A solution of 6 g. (0.26 mole) of freshly cut sodium in 54.8 g. (0.72 mole) of anhydrous methyl Cellosolve was cooled to 0° and treated with 13.8 g. (0.27 mole) of dry cyanogen. One hundred ml. of water was then added and the mixture extracted with ether. After drying over calcium chloride, the extract was distilled, yielding 9.3 g. (6.5% based on Cellosolve) of liquid boiling at 115°/1.5 mm; m.p. 41–43°.

Anal. Calcd. for $C_8H_{16}O_4N_2$: C, 47.0; H, 7.9; N, 13.7; mol. wt. 204. Found: C, 47.0; H, 8.0; N, 13.5; mol. wt. 190.

The *dihydrochloride* was prepared by saturating an ether solution of the oxaldiimidate with anhydrous hydrogen chloride. The resulting white solid melted at 95° but was too unstable to analyze.

The dihydrochloride was prepared directly by the following method: A solution containing 30.4 g. (0.4 mole) of anhydrous methyl Cellosolve and 50 g. of anhydrous dimethyl Cellosolve was cooled to 0° and treated with 15.4 g. (0.3 mole) of cyanogen. Dry hydrogen chloride was then passed into the mixture and the resulting white, crystalline precipitate was filtered. It was washed three times with solvent and dried in vacuum over sulfuric acid and sodium hydroxide. The yield was 5.2 g. (9.4% based on Cellosolve) of product melting at 95°. It was too unstable for analysis.

sym-Bis(2-ethoxyethyl)oxaldiimidate from ethyl Cellosolve. From a solution of 5 g. (0.22 mole) of freshly cut sodium in 45 g. (0.5 mole) of anhydrous ethyl Cellosolve, treated at 0° with 15 g. (0.29 mole) of cyanogen, was obtained 9.8 g. (8.5% yield, based on Cellosolve) of product boiling at 117°/1.5 mm. and melting at 30–32°. The product was recovered as described under methyl Cellosolve.

Anal. Calcd. for $C_{10}H_{20}O_4N_2$: C, 51.7; H, 8.7; N, 12.1; Mol. wt. 232. Found: C, 51.6; H, 8.7; N, 12.1; Mol. wt., 211.

The *dihydrochloride* prepared by saturating an ether solution of the oxaldiimidate with hydrogen chloride, or directly from ethyl Cellosolve, cyanogen, and hydrogen chloride as described above, melted at 95° but was too unstable to analyze.

sym-Bis(2-butoxyethyl)oxaldiimidate from butyl Cellosolve. From 4 g. (0.17 mole) of freshly cut sodium in 60 g. (0.51 mole) of butyl Cellosolve treated with 16.3 g. (0.31 mole) of cyanogen was obtained 19.3 g. (26.8% yield based on Cellosolve) of liquid boiling at 137–140°/1.5 mm.

Anal. Calcd. for $C_{14}H_{28}O_4N_2$: C, 58.3; H, 9.8; N, 9.7; mol. wt. 288. Found: C, 58.4; H, 9.9; N, 10.0; mol. wt. 252.

The *dihydrochloride* prepared by saturating an ether solution of the oxaldiimidate with hydrogen chloride, or directly from butyl Cellosolve, cyanogen, and hydrogen chloride, melted at 85° but was too unstable to analyze.

Associated reactions: sym-Bis(2-methoxyethyl)oxaldiimidate from 2-methoxyethyl cyanoformimidate and methyl Cellosolve. A small piece of sodium was dissolved in 3 g. (0.04 mole) of anhydrous methyl Cellosolve in a clean, dry flask fitted with a calcium chloride tube. When the solution had cooled, 5.2 g. (0.04 mole) of freshly distilled 2-methoxyethyl cyanoformimidate was added slowly, with continued cooling. The mixture was allowed to stand for 0.5 hr. at room temperature. The red solution was extracted with petroleum ether, and the extract was treated with decolorizing carbon and evaporated, leaving 1.6 g. (19.6% yield) of *sym-bis(2-methoxyethyl)oxaldiimidate* melting at 41–43°.

The same procedure was employed with all combinations of the cyanoformimidates prepared above and methyl, ethyl, and butyl Cellosolve. Only tars and starting materials were recovered. In no case was an oxaldiimidate isolated.

Tetra-n-butyloxamidine from sym-bis(2-hydroxyethyl)-oxaldiimidate and butylamine. One gram of *sym*-bis(2-hydroxyethyl)oxaldiimidate dihydrochloride was dissolved in 15 ml. of *n*-butyl amine. There was considerable evolution of heat accompanying the mixing. The solution was refluxed for 1 hr., after which 50 ml. of distilled water was added, forming a white precipitate. This was filtered and recrystallized from petroleum ether (activated carbon present), producing a white, silky product melting at 84–86°. Admixture of tetra-*n*-butyloxamidine[15] resulted in a melting point of 84–85°.

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[15] H. M. Woodburn, B. Morehead, and M. C. Chen, *J. Org. Chem.*, **15**, 541 (1950).

Tetra-n-butyloxamidine from sym-bis(2-methoxyethyl)oxaldiimidate and butylamine. A mixture of 3.0 g. (0.11 mole) of *sym*-bis(2-methoxyethyl)oxaldiimidate dihydrochloride and 12.0 g. (1.64 moles) of *n*-butylamine was refluxed for 3 hr. The solution was poured into 300 ml. of water and the precipitate filtered by suction. Recrystallization from petroleum ether gave white crystals melting at 85–86°. Admixture with tetra-*n*-butyloxamidine[15] resulted in a melting point of 85–86°.

sym-Di-n-butyloxamidine dihydrochloride from sym-bis-(2-hydroxypropyl)oxaldiimidate dihydrochloride and butylamine. A solution of 1.0 g. (0.004 mole) of *sym*-bis(2-hydroxypropyl)oxaldiimidate dihydrochloride dissolved in 0.6 g. (0.008 mole) of *n*-butylamine was mixed with 25 ml. of dimethyl Cellosolve and refluxed for 5 min. Petroleum ether was added to the cooled mixture until it turned turbid. An oil separated, which was frozen solid by the use of Dry Ice. The solvent was then decanted and the residue dissolved in ethanol. Dry hydrogen chloride was passed into the solution and the white precipitate filtered by suction. It melted at 270°. When mixed with pure di-*n*-butyloxamidine dihydrochloride,[11] it melted at 268–269°.

sym-Diphenyloxamidine from sym-bis(2-hydroxyethyl)oxaldiimidate and aniline. By dissolving the diimidate dihydrochloride in aniline and allowing the solution to stand at room temperature for several hours, a 32% yield of *sym*-diphenyloxamidine[16] was obtained. Recrystallized from benzene, the product melted at 208–212°; mixed with diphenyloxamidine at 210–214°.

Bis(Δ^2-2-imidazolinyl) from sym-bis(2-hydroxyethyl)oxaldiimidate and ethylenediamine. Two grams of the diimidate was dissolved in 15 ml. of 95% ethylenediamine solution and heated in a hot water bath for 5 min. On cooling, a white solid precipitated. The mixture was diluted with water and the solid filtered off and recrystallized from alcohol. Melting point (sealed tube) 289–292°; mixed with bis-(Δ^2-2-imidazolinyl),[4] 286–290°.

BUFFALO 14, N. Y.

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(16) A. W. Hofmann, *Ann.*, **66**, 130 (1848).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

Acenaphthene Chemistry. IV.[1] The Aluminum Chloride Catalyzed Diacylation of Acenaphthene

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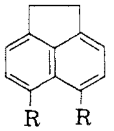
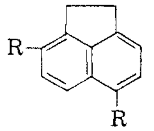
3,6-Dibenzoylacenaphthene is formed by the direct acylation of acenaphthene in the Friedel-Crafts reaction. It was converted into the dioxime which was rearranged to the dibenzamide and then hydrolyzed to 3,6-diaminoacenaphthene. The diacetylacenaphthene formed by direct acetylation was shown to be 3,6-isomer and not the 5,6-diacetyl compound as reported.

The literature gives numerous examples of electrophilic substitution in the acenaphthene nucleus. Reactions such as nitration, sulfonation, halogenation, and acylation with aluminum chloride give predominately 5-substituted acenaphthenes.[3] It has been established that monoacetylation will produce a small amount of the 3-isomer.[4,5] If these mono substituted derivatives are subjected to further electrophilic attack the entering group shows a strong preference for the 6 position.[6–9] Disubstituted derivatives have been prepared by the Friedel-Crafts reaction. Thus Dziewonski and Spirer[10] prepared a diacetyl derivative m.p. 149° which they described as the 5,6-isomer I since the dioxime is reported to rearrange to the diacetamide II which was hydrolyzed to the known 5,6-diaminoacenaphthene III. Similar reactions were used to characterize a dipropionyl derivative.[11] The formation of 4,7-di-*t*-butylacenaphthene by means of the Friedel-Crafts reaction has been definitely established.[3]





I. R = $COCH_3$
II. R = $NHCOCH_3$
III. R = NH_2
IV. R = COC_6H_5
V. R = $NHCOC_6H_5$
VI. R = COOH

VII. R = NH_2
VIII. R = $NHCOC_6H_5$
IX. R = COC_6H_5
X. R = $COCH_3$
XI. R = $NHCOCH_3$
XII. R = COOH

In our work the 5,6-dibenzoylacenaphthene (IV) was desired. The patent literature[12] describes a dibenzoylacenaphthene, m.p. 143°, and a diacetyl

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[1] For paper III see H. J. Richter and B. C. Weberg, *J. Am. Chem. Soc.*, **80**, 6446 (1958). The support of this work by an Ohio Oil Co. Fellowship and a grant from the National Institute of Health (Cy-2997-Cy) is respectfully acknowledged.

[2] A portion of the dissertation submitted to the Graduate School of the University of Colorado in partial fulfillment of the requirements for the Ph.D. degree.

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