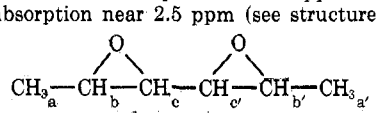
man IR-10 spectrophotometer. Nmr spectra were obtained on a Varian XL-100 spectrometer.

Reaction Procedure and Analysis. The peroxy acid was dissolved in chloroform (0.26 *M*), the solution was cooled to 0°, and the diene was added (mole ratio peroxy acid/diene, 2.2). The solution was kept at 0° and sampled directly by vpc until reaction was complete (2–3 days). Yields were determined by vpc with *p*-chlorobromobenzene as internal standard. In cases where the diepoxides were isolated, the chloroform solution was shaken with a cold sodium bisulfite–sodium bicarbonate solution and the aqueous phase was then saturated with ammonium sulfate. The phases were separated and the aqueous phase was extracted once more with ether. Vpc analysis was accomplished on the following column: 17% Carbowax 20M, 8 ft × 0.25 in., 100°, 60 ml/min. Retention times of 12, 12, 13, 14, 16, and 17 min were observed for **1a, 1c, 1b, 2a, 2c,** and **2b,** respectively. Quantitative vpc analysis was done with a Hewlett-Packard 7620A FID chromatograph.

Nmr Spectra. Spectra of all six isomers showed three regions of absorptions at approximately 1.3, 2.5, and 2.9 ppm with integrated intensities of 3:1:1, respectively. The absorption near 1.3 ppm which occurred as a sharp doublet (two doublets for the cis,trans isomers, **1c** and **2c**) is assigned to the methyl groups. The coupling constant exhibited in the absorption near 1.3 ppm can be found in the lowest field absorption, *ca.* 2.9. Also, irradiation at the frequency of the methyl proton absorptions (for isomer **2c**) caused decoupling to appear in the lowest field absorption but did not effect the absorption near 2.5 ppm. Protons H_b ($H_{b'}$) are therefore assigned to the absorption near 2.9 ppm and protons H_c ($H_{c'}$) to the absorption near 2.5 ppm (see structure below). The



low-field absorptions each show two couplings in common, due to adjacent protons, J_{bc}, and evidently the longer range coupling $J_{bc'}$. Spectra for isomers **1a, 2a, 1b,** and **2b** appear to be essentially first order, owing to equivalency of primed and nonprimed hydrogens (structure above). In isomers **1c** and **2c** the epoxide rings are cis and trans and more complex spectra result. Apparent coupling constants are reported for isomers, **1a, 2a, 1b,** and **2b** but we were not able to obtain constants for **1c** and **2c.** Summary of nmr data (100 MHz, CCl_4, parts per million downfield from TMS) follows: **1a,** 1.28 (d, CH_3, J_{ab} = 5.2 Hz), 2.36 (dd, CH_3CHCH, J = 0.9, J' = 0.7 Hz), 2.83 (dd of quartet, CH_3CH, J_{ba} = 5.2, J = 0.9, J' = 0.7 Hz); **2a,** 1.27 (d, CH_3, J_{ab} = 5.2 Hz), 2.49 (dd, CH_3CHCH, J = 1.0, J' = 0.8 Hz), 2.83 (dd of quartet, CH_3CH, J_{ba} = 5.2, J = 1.0, J' = 0.8 Hz); **1b,** 1.36 (d, CH_3, J_{ab} = 5.3 Hz), 2.62 (dd, CH_3CHCH, J = 2.5, J' = 1.5 Hz), 3.02 (dd of quartet, CH_3CH, J_{ba} = 5.3, J = 2.5, J' = 1.5 Hz); **2b,** 1.33 (d, CH_3, J_{ab} = 5.4 Hz), 2.69 (dd, CH_3CHCH, J = 2.8, J' = 1.4 Hz), 2.97 (dd of quartet, CH_3CH, J_{ba} = 5.4, J = 2.8, J' = 1.4 Hz); **1c,** 1.30 (d, CH_3), 1.35 (d, CH_3), 2.48 (m, CH_3CHCH), 2.95 (m, CH_3CH); **2c,** 1.28 (d, CH_3), 1.36 (d, CH_3), 2.51 (m, CH_3CHCH), 2.89 (m, CH_3CH).

Ir Spectra. The medium to strong absorptions for each hexadiene diepoxide isomer are shown below. These absorptions allow the six isomers to be readily distinguished from each other. Bands near 1250, 945, and 825 cm^{-1} which have been previously assigned to the epoxide function[6] are observed in these compounds. Also (as observed previously for the *cis*- and *trans*-2-butene oxides[6]) the absorption near 940 cm^{-1} is essentially constant but the 800-cm^{-1} absorption is higher for the all-trans isomers **1a** and **2a** than for the all-cis isomers **1b** and **2b;** isomers **1c** and **2c,** which contain both cis and trans epoxide rings, show two absorptions each, in the 810–845-cm^{-1} region. Summary of ir spectra (CCl_4 solvent, except CS_2 solvent for 900–700-cm^{-1} region) follows: **1a,** 2990, 2920, 1420, 1445, 1375, 950, 830, 745 cm^{-1}; **2a,** 2990, 2920, 1446, 1380, 1240, 1010, 945, 835, 748 cm^{-1}; **1b,** 2990, 2920, 1440, 1402, 1375, 1255, 1125, 1042, 990, 940, 820, 740 cm^{-1}; **2b,** 2990, 2920, 1445, 1390, 1379, 1260, 1128, 1042, 1090, 940, 810, 740 cm^{-1}; **1c,** 2990, 2920, 1450, 1415, 1395, 1260, 1100, 950, 810, 840, 740 cm^{-1}; **2c,** 2990, 2920, 1446, 1385, 1250, 1142, 1100, 945, 922, 817, 845, 740 cm^{-1}.

Acknowledgment. Financial support for this work was provided by the Research Corporation. We wish to thank Dr. K. D. Berlin and Oklahoma State University for providing the use of the nmr spectrometer.

Registry No.—**1a,** 51065-35-1; **1b,** 51153-42-5; **1c,** 51153-43-6; **2a,** 51153-44-7; **2b,** 51153-45-8; **2c,** 51153-46-9; *trans,trans*-2,4-hexadiene, 5194-51-4; *cis,cis*-2,4-hexadiene, 6108-61-8; *cis,trans*-2,4-hexadiene, 5194-50-3.

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dibromide $\xrightarrow{KMnO_4}$ dibromo glycol $\xrightarrow{base}$ diepoxide

Isomer **2c** is obtained from the dibromide assigned the meso structure and a mixture of **2a** and **2b** is obtained from the dibromide assigned the racemic structure.
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A Novel Reaction of Alkyl 3-Chloropropionimidate Hydrochlorides

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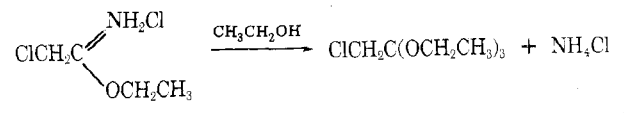
Received June 5, 1973

The treatment of imino ester hydrochlorides with excess alcohol is a general reaction for the preparation of ortho esters.[1] The reaction of ethyl chloroacetimidate hydrochloride with ethanol, for example, yields triethyl orthochloroacetate (70–73% yield) and ammonium chloride.[2] Treatment of the corresponding methyl or ethyl 3-chloropropionimidate hydrochlorides with methanol or ethanol, respectively, however, does not yield the expected trimethyl or triethyl ortho-3-chloropropionates. Unexpectedly high yields of alkyl 3-alkoxypropionates are obtained instead.



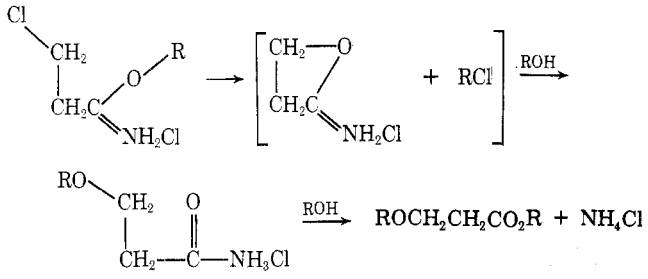
$R = CH_3, CH_3CH_2$

This simple reaction seems remarkable in view of known reactions of 3-halo-substituted imidate hydrochlorides, nitriles, or acids, wherein the halide substituent is retained under reaction conditions similar to those of the present work. For example, 3-chloro- or 3-bromopropionimidate hydrochlorides react with water to form the corresponding esters and ammonium chloride.[3-5] 3-Halo-substituted nitriles are converted to the corresponding 3-halo esters or amides in reactions where imidates are presumably intermediates.[6,7] Similar results are observed for 4-halo-substituted nitriles,[8,9] and 3-halo-substituted propionic acids can be esterified without displacement of the halide group.[8]

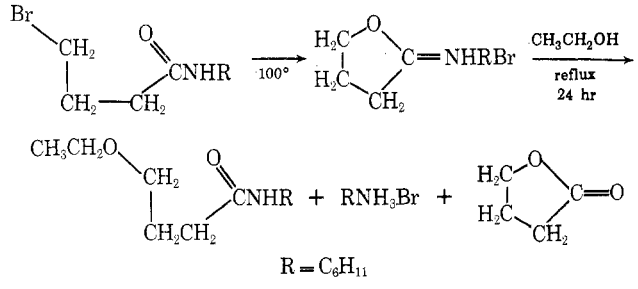
3-Chloropropionamide is not an intermediate leading to the observed products, since it does not yield any ethyl 3-ethoxypropionate under reaction conditions (refluxing ethanol in the presence of equimolar ammonium chloride). The 3-chloropropionamide which is isolated no doubt arises from the known thermal decomposition of imidate

hydrochlorides.[10] The 3-chloropropionate esters, also observed as by-products in this work, would be expected based on the work of McElvain.[11]

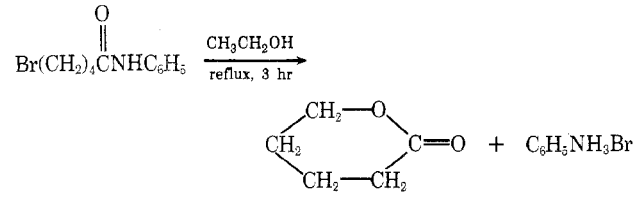
The high yields and mild conditions suggest a cyclic intermediate of the type shown. We have not attempted to define the mechanism other than by product identification; the following is postulation based on published isolations of alkyl β-alkoxypropionates from treatment of β-propiolactone with alcohols.[12,13]



There are mechanistic similarities to the work of Stirling,[14] wherein 4-bromo-*N*-cyclohexylbutyramide is cyclized to a stable, isolable five-membered cyclic imino ether, either thermally (100°) or in refluxing ethanol.



Ethanolysis of the imino ether hydrobromide, however, yields mainly 4-ethoxy-*N*-cyclohexylbutyramide, plus cyclohexylammonium bromide and butyrolactone. Also, the ethanolysis of 5-bromopentananilide is reported to yield valerolactone and anilinium bromide.[14] Differences in reactivity between four-, five-, and six-membered imino ether intermediates may account for the product differences.



Experimental Section

All chemicals were reagent grade, used as received. Nmr spectra were recorded on a Varian A-60A spectrometer by Dr. J. H. Fager, whose assistance is gratefully acknowledged. Melting points and boiling points are uncorrected.

Methyl 3-Methoxypropionate. Methyl 3-chloropropionimidate hydrochloride[15] (252 g, 1.6 mol) was combined with 1150 ml of dry ethyl ether and 320 g (10 mol) of methanol in a 2-l. 1NRB flask fitted with mantle, magnetic stirrer, thermometer, and condenser. The reaction mixture was heated at reflux for 6 hr. After standing for 2 days in the refrigerator, NH_4Cl was removed by filtration and the solution was stripped to remove solvents. Distillation yielded 102.8 g (53%) of methyl-3-methoxypropionate. A portion of the solid residue was recrystallized twice from ethyl ether containing a few drops of methanol, and the solid was identified as 3-chloropropionamide, mp 98.5–99.5° (lit.[16] mp 96–98°). The ester boiled at 45–48° (18 mm) [lit.[17] bp 55° (21 mm)], $n^{25}D$ 1.4035 (lit.[18] $n^{20}D$ 1.4030). Methyl chloride was detected in the reaction solution by vpc before work-up but was not isolated.

Ethyl 3-Ethoxypropionate. Ethyl 3-chloropropionimidate hydrochloride (88.2 g, 0.5 mol) was dissolved in 204 g (5.8 mol) of absolute ethanol and heated slowly to 40° over 5 hr with stirring. Product formation was complete by vpc. After standing overnight, the reaction was heated to reflux to distil out ethyl chloride, of which 14 g (43% of theory) was collected in a Dry Ice trap and identified. After cooling, NH_4Cl was removed by filtration and the remainder of ethyl chloride and ethanol was stripped. The residual oil was vacuum distilled, yielding a single cut, bp 65–67° (17 mm), 68.8 g (92% [lit.[17] bp 75–77° (20 mm)], $n^{26}D$ 1.4066 (lit.[18] $n^{20}D$ 1.4071). The product contained about 5% ethyl 3-chloropropionate by nmr.

Registry No.—Methyl 3-methoxypropionate, 3852-09-3; methyl 3-chloropropionimidate hydrochloride, 21367-88-4; ethyl 3-ethoxypropionate, 793-69-9; ethyl 3-chloropropionimidate hydrochloride, 21367-89-5.

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Concerning Anionic Nucleophilic Attack upon a Carboxyl Anion

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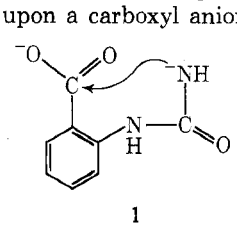
Received January 29, 1974

The rate of cyclization of *N*-(*o*-carboxyphenyl)urea in strongly basic solutions is first order in hydroxide ion concentration.[2,3] This observation was presented as evidence for anionic attack upon a carboxyl anion (1).[2,3] If mechanisms 2 or 3 were valid, then the rates would respectively decrease or remain constant with increasing hydroxide ion.[2,3] The base dependency of the ring closure could also be explained by a mechanism (Scheme I) in which rate-determining *collapse* of a tetrahedral intermediate is assisted by hydroxide ion. The rate law governing this mechanism (eq 1) shows first-order dependence on hydroxide ion if $k_{-1} \gg k_2K[OH^-]$. Therefore, anionic nucleophilic attack upon a carboxyl anion need not be in-



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