6-Chloropyrido[3,4-d]tetrazolo[1,5-b]pyridazine (5, R = Cl).—An ice-cold solution of compound 1 (R = Cl; R_1 = $NHNH_2$) (0.5 g) in HCl (6 ml of 2 N) was treated under stirring with a cold aqueous solution of $NaNO_2$ (0.2 g in 3 ml of water). The product which separated was crystallized from EtOH (0.32 g): mp 177°; nmr ($CDCl_3$) δ 8.20 (d, H_7), 9.28 (d, H_8), 10.1 (s, H_{10}), $J_{7,8}$ = 6.0 Hz.

Anal. Calcd for $C_7H_3ClN_6$: C, 40.69; H, 1.46; N, 40.68. Found: C, 40.79; H, 1.83; N, 40.84.

6-Chloropyrido[4,3-d]tetrazolo[1,5-b]pyridazine (4, R = Cl) was prepared as described above for 5 (R = Cl) in 75% yield: mp 184° (from EtOH); nmr ($CDCl_3$) δ 9.66 (s, H_7), 9.28 (d, H_9), 8.55 (d, H_{10}), $J_{9,10}$ = 5.7 Hz.

Anal. Calcd for $C_7H_3ClN_6$: C, 40.69; H, 1.46; N, 40.68. Found: C, 40.42; H, 1.62; N, 40.59.

6-Hydrazinopyrido[4,3-d]tetrazolo[1,5-b]pyridazine (4, R = $NHNH_2$).—A mixture of 4 (R = Cl) (0.2 g), ethanol (5 ml), and hydrazine hydrate (1 ml of 80%) was heated under reflux for 15 min. The product was recrystallized from DMF and EtOH (3:1) (0.16 g), mp 290–293° dec.

Anal. Calcd for $C_7H_6N_8$: C, 41.58; H, 2.99; N, 55.43. Found: C, 41.90; H, 3.15; N, 55.49.

6-Hydrazinopyrido[3,4-d]tetrazolo[1,5-b]pyridazine (5, R = $NHNH_2$).—The compound was prepared as described above for the isomer 4 (R = $NHNH_2$) in 66% yield, mp 286–288° dec (from DMF and EtOH, 3:1).

Anal. Calcd for $C_7H_6N_8$: C, 41.58; H, 2.99; N, 55.43. Found: C, 41.35; H, 3.09; N, 55.09.

6-Azidopyrido[4,3-d]tetrazolo[1,5-b]pyridazine (4, R = N_3). A.—Compound 4 (R = $NHNH_2$) (0.2 g) was dissolved in HCl (4 ml of 2 N) and under stirring the ice-cold solution was treated with a cold solution of aqueous $NaNO_2$ (80 mg in 1 ml) dropwise, yield 0.16 g. For recrystallization the azide was dissolved in a minimum amount of EtOH at 40°, some charcoal was added, and, after stirring a few minutes at this temperature, the obtained filtrate was cooled to about −20° and the separated product was collected: mp 146–147°; ir 2155 cm⁻¹ (N_3); nmr (DMSO-d_6) δ 9.46 (s, H_7), 9.37 (d, H_9), 8.53 (d, H_{10}), $J_{9,10}$ = 5.9 Hz.

Anal. Calcd for $C_7H_3N_9$: C, 39.44; H, 1.42; N, 59.14. Found: C, 39.31; H, 1.63; N, 59.24.

B.—A suspension of 1,4-dichloropyrido[3,4-d]pyridazine (1 g) and sodium azide (0.65 g) in ethanol (20 ml) was heated under reflux for 1 hr and evaporated then to half of the original volume. The residue was poured into ice (10 g) and the separated product (0.81 g) was collected. For analysis the compound was crystallized from ethanol, mp 146–147°. The compound was found to be identical in all respects with the product obtained as described under A.

6-Azidopyrido[3,4-d]tetrazolo[1,5-b]pyridazine (5, R = N_3).—This compound was prepared in a similar manner as described for the isomer 4 (R = N_3) under A, yield 83%, mp 163° (crystallization was performed as described above under A). If crystallization was attempted from boiling ethanol, the isomeric azide (4, R = N_3) was obtained. Also, when melted, upon solidification the isomer 4 (R = N_3) is formed: ir 2151 cm⁻¹ (N_3); nmr (DMSO-d_6) δ 8.06 (d, H_7), 9.20 (d, H_8), 9.93 (s, H_{10}), $J_{7,8}$ = 5.7 Hz.

Anal. Calcd for $C_7H_3N_9$: C, 39.44; H, 1.42; N, 59.14. Found: C, 39.14; H, 1.68; N, 59.08.

Rate Constants and Equilibria.—For the determination of rate constants and equilibria measurements, nmr spectra of dimethyl sulfoxide-d_6 solutions were performed and the constants were calculated as described previously.[1]

For the system 5 → 4 (R = N_3) the values are as follows: ΔH = −2.2 ± 0.2 kcal/mol; rate constants, k_1 = 1.27 × 10⁻³ sec⁻¹ (at 60°), k_2 = 3.45 × 10⁻³ sec⁻¹ (at 80°); E_a = 25.2 ± 0.2 kcal/mol; ΔS = −2 eu.

For the system 6 → 7 the values are: ΔH = −1.3 ± 0.2 kcal/mol; rate constants, k_1 = 8.0 × 10⁻⁴ sec⁻¹ (at 60°), k_2 = 1.39 × 10⁻³ sec⁻¹ (at 70°), k_3 = 2.5 × 10⁻³ sec⁻¹ (at 80°); E_a = 27.8 ± 0.2 kcal/mol; ΔS^* = +7 eu.

Registry No.—1 (R = Cl; R_1 = NHN=CHPh), 31767-04-1; 1 (R = NHN=CHPh; R_1 = Cl), 31767-05-2; 2, 31767-06-3; 3, 31767-07-4; 4 (R = Cl), 31767-08-5; 4 (R = $NHNH_2$), 31767-09-6; 4 (R = N_3), 31767-10-9; 5 (R = Cl), 31821-50-8; 5 (R = $NHNH_2$), 31767-11-0; 5 (R = N_3), 31767-12-1.

A New Synthesis of Alkyl Oximinoglyoxylates and the Corresponding Acid and Hydroximoyl Chlorides

Terence W. Rave* and David S. Breslow

A number of syntheses of oximinoglyoxylate esters, $HON=CHCO_2R$, have been reported: the reaction of alkyl gloxylates[1] or the corresponding hemiacetal[2] or alkoxybromo esters[3] with hydroxylamine, the reaction of acetoacetic esters with nitrosylsulfuric acid,[4] and the alkylation of silver oximinoglyoxylate.[5] All these methods suffer from unavailability of starting materials or low overall yields.

Nitrile oxides, derived from hydroximoyl chlorides by treatment with base,[6] have been shown to be useful cross-linking agents for unsaturated polymers.[7] We have now discovered what appears to be a simple, direct synthesis of alkyl oximinoglyoxylates (I) and the corresponding hydroximoyl chlorides (II). The method involves the reaction of ketene with nitrosyl chloride, followed by treatment with excess alcohol to yield the oximino ester; chlorination then yields the hydroximoyl chloride. The conditions which ultimately

$$CH_2=C=O \xrightarrow[\text{2. ROH}]{\text{1. NOCl}} \underset{I}{HON=CHCO_2R} \xrightarrow{Cl_2} \underset{\underset{II}{|}}{\underset{Cl}{|}} HON=CCO_2R$$

proved to be most successful for the preparation of oximinoglyoxylates consisted of first condensing a measured quantity of ketene in the desired solvent at −78°. One equivalent of nitrosyl chloride then was added slowly to the cold solution followed by an excess of alcohol. The reaction mixture was warmed to room temperature and stirred for several hours. Yields of 65–78% of methyl, ethyl, and n-butyl oximinoglyoxylates were obtained with this procedure. Both cis and trans isomers of the oximino esters were detected by gas chromatographic analysis. By-products in the ethyl system, which was studied most thoroughly, included diethyl oxalate, ethyl diethoxyacetate, hydrazine hydrochloride, and, probably, ethyl chloroacetate. All identifications except that of ethyl chloroacetate were firm and were made by comparison of purified samples with authentic materials, either commercially available or prepared by an independent route.

In order to obtain good yields of oximinoglyoxylates from the reaction of ketene, NOCl, and alcohols, several variables must be controlled carefully. First, the reaction temperature must be kept low, not only to prevent decomposition of the ketene–NOCl adduct but also to prevent ketene dimerization. Second, nitrosyl chloride

(1) L. J. Simon and G. Chavanne, *C. R. Acad. Sci.*, **143**, 904 (1906).
(2) L. W. Kissinger and H. E. Ungnade, *J. Org. Chem.*, **23**, 1517 (1958).
(3) L. A. Carpino, *ibid.*, **29**, 2820 (1964).
(4) L. Bouveault and A. Wahl, *Bull. Soc. Chim. Fr.*, **31** [3], 675 (1904).
(5) C. Cramer, *Ber.*, **25**, 713 (1892).
(6) H. Wieland, *ibid.*, **40**, 1667 (1907).
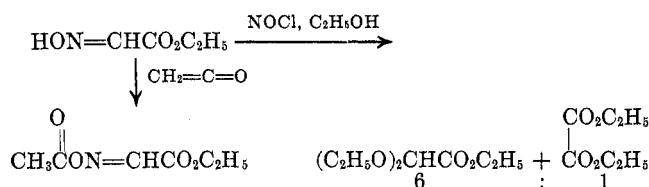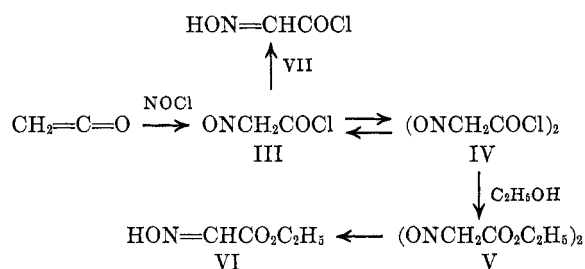(7) D. S. Breslow, U. S. Patent 3,390,204 (1968).

must be added to ketene rather than *vice versa*. When addition was carried out in the reverse fashion, the yields of oximino esters decreased to less than 20% and the quantities of diethyl oxalate and ethyl diethoxyacetate increased markedly; several new by-products also appeared. Third, a 1:1 stoichiometry of ketene and nitrosyl chloride should be maintained as closely as possible, since both reactants have been demonstrated to react with the product. An excess of ketene is less harmful than an excess of NOCl, because it acylates the oxime rather slowly and will react with

$$HON{=}CHCO_2C_2H_5 \xrightarrow{\text{NOCl, } C_2H_5OH}$$

$$\Big\downarrow CH_2{=}C{=}O$$

$$\overset{O}{\overset{\|}{CH_3CON}}{=}CHCO_2C_2H_5 \qquad (C_2H_5O)_2CHCO_2C_2H_5 + \overset{CO_2C_2H_5}{\overset{|}{CO_2C_2H_5}}$$
$$6 \qquad : \qquad 1$$

the alcohol. Finally, an excess of alcohol is required; when a single equivalent was used, yields dropped to below 25%. Attempts to make the reaction stoichiometric in alcohol by the addition of an HCl acceptor (triethylamine, 2,6-lutidine, acrylonitrile,[8] Mg, Zn, or basic Al_2O_3) or to add the ketene–NOCl adduct to an equivalent of alcohol plus base did not improve the yields.

Evidence suggests that the reaction takes the following course.

$$HON{=}CHCOCl$$
$$\Big\uparrow VII$$
$$\overset{NOCl}{CH_2{=}C{=}O \longrightarrow ONCH_2COCl} \rightleftharpoons (ONCH_2COCl)_2$$
$$\qquad\qquad\qquad III \qquad\qquad\qquad IV$$
$$\qquad\qquad\qquad\qquad\qquad\qquad \Big\downarrow C_2H_5OH$$
$$HON{=}CHCO_2C_2H_5 \longleftarrow (ONCH_2CO_2C_2H_5)_2$$
$$\qquad VI \qquad\qquad\qquad V$$

Thus, when ketene and nitrosyl chloride are combined in methylene chloride at −80°, a blue solution, presumably due to monomeric nitrosoacetyl chloride (III), is first formed. The color fades rapidly and a white solid, postulated to be the dimeric nitrosoacetyl chloride (IV), precipitates.[9] Efforts to isolate IV failed owing to its instability at room temperature; an attempt at filtration resulted in ignition of the filter paper. Addition of ethanol to the solid, when formed in the absence of solvent, gave a second white solid which was relatively stable. Both the infrared and nmr spectra were consistent with the latter's formulation as the dimeric nitroso ester (V). The infrared spectrum showed neither –OH nor –C=N– absorption, but did exhibit carbonyl absorption at 5.68 μ. The nmr spectrum displayed resonances typical of an ethyl group and a sharp singlet (relative area 2.0) at δ 4.99 attributable to the methy-

(8) N. K. Bliznyuk, P. S. Khokhlov, R. V. Strel'tsov, Z. N. Kvasha, and A. F. Kolomiets, *J. Gen. Chem. USSR,* **37**, 1061 (1967).

(9) Monomeric nitroso compounds are reported to dimerize at −80° in preference to isomerization to oxime.[10]

(10) B. G. Gowenlock and W. Lüttke, *Quart. Rev. (London),* **12**, 333 (1958).

lene protons between the nitroso and carbonyl moieties. Even more significantly, when the solid was allowed to stand at temperatures above about −25°, it was slowly transformed into the oxime (VI). The half-life for this transformation was estimated to be several hours at 30° from an nmr experiment in which the rate of disappearance of the singlet at δ 4.99 and appearance of a singlet at δ 7.58, characteristic of the "vinylic" oxime C–H, was determined. Excess alcohol is necessary to favor esterification of nitrosoacetyl chloride (III or IV) over isomerization to oximinoglyoxylyl chloride (VII); VII never has been isolated, and probably polymerizes to [–ON=CHCO–]$_n$.[11]

Substitution of water for the alcohol gave oximinoglyoxylic acid in good yield. However, attempts to prepare the corresponding phenyl ester or di-*n*-butyl amide by substituting phenol or di-*n*-butylamine for the alcohol were unsuccessful.

Since aliphatic oximes can be converted into hydroximoyl chlorides by low-temperature chlorination in ether,[13] we attempted the one-step synthesis of ethyl 2-chlorooximinoglyoxylate (II, R = C_2H_5). Indeed, it was isolated in 60% yield when ketene, NOCl, ethanol, and chlorine were mixed at low temperature in the order given and in a ratio of 1:1:2:2. Although ethyl oximinoglyoxylate (I, R = C_2H_5) has been chlorinated with nitrosyl chloride in methylene chloride,[2] the excess alcohol required here interferes with the reaction, as already mentioned.

Experimental Section[14]

Ketene Generation and Measurement.—Ketene was generated by thermal cracking of acetone using a typical ketene lamp.[15] The resulting stream of ketene and by-product methane was passed through first a water condenser and then a cold trap maintained at −35° to remove entrained acetone. The amount of ketene produced per unit time was determined by passing the resulting gas stream into sodium hydroxide for 5.0 min and then titrating residual base. Above a ketene rate of *ca.* 1.5 mmol/min, significant quantities of ketene escaped from the sodium hydroxide solution.

In the experiments described below, the total amount of ketene used in a given experiment was determined by first measuring its rate of formation and then passing the gas stream into cold (−78°) solvent for a measured length of time. The ketene rate was usually redetermined after 0.5 or 1 hr; when it differed from the original rate, average values were used for the computation of the total amount of ketene. The gas stream exiting from the cold solvent was always conducted past a Dry Ice–acetone trap in an attempt to ensure that all of the ketene which passed into the flask would remain there. Measurements on the exit gas showed that no ketene escaped as long as the ketene input rate was less than *ca.* 1.5 mmol/min.

Preparation of Alkyl Oximinoglyoxylates (I) from Ketene, Nitrosyl Chloride, and Alcohol.—In a 250-ml, round-bottomed, three-necked flask equipped with a rubber septum, an adapter connected to a nitrogen manifold, and a Dry Ice–acetone condenser with a gas exit tube were placed a stir bar and 250 ml of methylene chloride. The flask was flushed with nitrogen and

(11) Oglobin and Kunovskaya[12] reacted ketene diethyl acetal with NOCl in ether and obtained a yellow solid without observing an intermediate blue solution. Although they postulated the formation of VI after hydrolysis, they isolated only the corresponding phenylhydrazone in low yield.

(12) K. A. Oglobin and D. M. Kunovskaya, *J. Org. Chem. USSR,* **1**, 1741 (1965).

(13) G. Casnati and A. Ricca, *Tetrahedron Lett.,* 327 (1967).

(14) Infrared spectra were recorded using a Perkin-Elmer Model 137 Infracord. Proton nmr spectra were obtained using a Varian HA-60 spectrometer and were measured in deuteriochloroform solution using tetramethylsilane as an internal standard. Microanalyses were carried out by the Analytical Division of the Hercules Research Center.

(15) J. W. Williams and C. D. Hurd, *J. Org. Chem.,* **5**, 122 (1940).

cooled in a Dry Ice-acetone bath. The stopcock in the adapter was closed, and ketene gas was bubbled into the cold solvent for 90 min at a rate of 0.80 mmol/min using a needle inserted through the rubber septum. The total ketene input was 72 mmol. Nitrosyl chloride (1780 ml at 756 mm and 25°, 72 mmol, Matheson) was added to the cold solution in portions *via* a syringe during a 5-min interval; a green-blue color appeared, which gave way to a white solid. After a tenfold excess of anhydrous alcohol was added, the mixture was opened to nitrogen and stirred for 2 hr in the cold, then overnight at room temperature.

The methyl ester was isolated in 66% yield as a yellow solid by sublimation at 70° (0.2 mm). Resublimation gave a white solid, mp 53-55° (lit.[4] mp 55°), whose nmr spectrum agreed with the assigned structure (two singlets in a 3:1 ratio, the methyl protons at δ 3.87, and the oxime C-H at δ 7.58); it is rather surprising that only one of the two possible stereoisomers was observed.

The ethyl ester was isolated as a yellow oil by evaporation of the solvent. Analysis by gas chromatography on a 10-ft SE-30 column maintained at 130° (He flow 1.0 cc/sec, detector temperature 205°, injector temperature 220°) showed two peaks with retention times of 3.2 and 6.3 min; these were identical with those assigned to authentic cis and trans isomers, respectively, of ethyl oximinoglyoxylate. The material with the longer retention time was trapped; its infrared spectrum was identical with that of an authentic sample of ethyl oximinoglyoxylate prepared as described below. The yield was calculated to be 67% from the combined areas under the peaks of the two isomers. Two isomers of the *n*-butyl ester were isolated and identified in the same manner; the yield was calculated to be 70%.

Preparation of Authentic Samples of Ethyl and *n*-Butyl Oximinoglyoxylates.—A mixture of 5.0 g (54.4 mmol) of glyoxylic acid monohydrate (Aldrich), 25.0 ml of dry ethanol, and molecular sieves 4-A contained in a 100-ml round-bottomed flask equipped with a water condenser connected to a nitrogen manifold was refluxed under nitrogen for 16 hr. The mixture was cooled and, after 20 ml of additional ethanol was added, filtered. Evaporation of the filtrate gave 1.35 g of colorless liquid; this was redissolved in 30 ml of ethanol and treated with 920 mg (13.2 mmol) of hydroxylamine hydrochloride (Eastman) and 1.85 ml (13.2 mmol) of triethylamine (Eastman). The resulting mixture was stirred under nitrogen for 3 days at room temperature and filtered, and the filtrate was evaporated *in vacuo* to give a gummy solid. This was dissolved in 30 ml of water and the aqueous solution was extracted three times with 30-ml portions of ether. Evaporation of the combined, dried (Na₂SO₄) extracts gave a pale brown liquid which slowly crystallized. One recrystallization from an ether-hexane mixture gave 455 mg of white crystals, mp 34-35° (lit.[1] mp 35°). The nmr spectrum showed a singlet (relative area 1.00) at δ 7.58 assigned to the oxime C-H. A quartet (relative area 2.2) centered at δ 4.32 and a triplet (relative area 3.3) centered at δ 1.34 were attributed to the ethyl group protons.

n-Butyl glyoxylate[16] was reacted with hydroxylamine in a similar manner. Distillation gave a 56% yield of oximino ester, bp 77-82° (0.1 mm). The nmr spectrum showed a singlet (relative area 1.00) at δ 7.53 assigned to the oxime C-H. The remainder of the spectrum was comprised of a triplet (relative area 2.2) centered at δ 4.20, a multiplet (relative area 4.3) centered at *ca.* δ 1.5, and another triplet (relative area 3.2) centered at δ 0.87. These resonances were assigned to the methylene protons adjacent to oxygen, the internal methylene protons, and the methyl protons, respectively, of the butyl group.

Anal. Calcd for C₆H₁₁NO₃: C, 49.70; H, 7.64. Found: C, 49.86; H, 8.05.

Preparation of Oximinoglyoxylic Acid from Ketene, Nitrosyl Chloride, and Water.—Ketene (79.2 mmol) and nitrosyl chloride (79.2 mmol) were combined in 250 ml of dry tetrahydrofuran using a method similar to that described above. After water (1.0 mol) was added to the resulting black reaction mixture, it was stirred under nitrogen for 1 hr in the cold and then overnight at room temperature. Evaporation of the solvent using a rotary evaporator gave a black liquid which was placed on a watch glass and allowed to stand overnight while a nitrogen stream was directed onto it. The resulting orange solid was extracted four times with 100-ml portions of ether; evaporation of the combined,

dried (Na₂SO₄) extracts gave 5.67 g of an orange solid. This was recrystallized once from an ether-hexane mixture to yield 4.73 g (67%) of light tan crystals, mp 137-140° (lit.[5] mp 140°). A mixture melting point of a sample prepared similarly and authentic HON=CHCO₂H prepared using the procedure of Cramer[5] was undepressed. The X-ray powder diagrams of the two samples were identical.

Preparation of Ethyl Chlorooximinoglyoxylate from Ketene, Nitrosyl Chloride, Ethanol, and Chlorine.—In 120 ml of methylene chloride at −78° were combined 39.9 mmol of ketene and 38.0 mmol of nitrosyl chloride. After ethanol (76 mmol) was added and the resulting mixture was stirred for 15 min, chlorine gas [80 mmol = 1950 ml at 23° (760 mm)] was added *via* a syringe over a 10-min period. This mixture was stirred for 1 hr in the cold and then overnight at room temperature. Evaporation of the solvent gave 5.90 g of yellow solid which was recrystallized once from a 1:1 benzene-hexane mixture to give 2.94 g (52%) of while solid, mp 76-79° (lit.[17] mp 80°). The recrystallization filtrates yielded an additional 460 mg (8%) of ethyl chlorooximinoglyoxylate. The infrared spectrum of this material was identical with that of authentic ethyl chlorooximinoglyoxylate prepared by chlorination of ethyl oximinoglyoxylate. A mixture melting point of the two was undepressed.

Isolation of Ethyl Nitrosoacetate Dimer from Ketene, Nitrosyl Chloride, and Ethanol.—A 100-ml, round-bottomed, three-necked flask equipped with a rubber septum, an adapter connected to a nitrogen manifold, and a Dry Ice-acetone condenser with a gas exit tube was flushed with nitrogen and cooled in a Dry Ice-acetone bath. The stopcock on the adapter was closed, and ketene gas was bubbled into the empty flask for 45 min at a rate of 0.2 mmol/min using a needle inserted through the rubber septum. A small amount of ketene probably was not condensed, because its characteristic odor was noticed at the gas exit tube. Nitrosyl chloride [226 ml at 24° (754 mm)] was then added to the flask and a yellow solid deposited on the walls. After 10 min, 20 ml of dry ethanol was added, and a white solid rapidly replaced the yellow one. The resulting mixture was stored at −20° overnight and then filtered under nitrogen to give 401 mg of a white solid formulated as the dimeric nitroso ester (V). The infrared spectrum showed absorptions at 5.68, 6.99, 7.41, 8.01, 8.19, 8.60, 9.14, 9.70, 10.28, 11.27, 11.42, 12.60, and 13.30 μ.

The white solid was transformed into ethyl oximinoglyoxylate (identified by spectral comparison with an authentic sample) immediately upon addition of triethylamine and over a 3-day period upon standing at room temperature.

Reaction of Ethyl Oximinoglyoxylate with Nitrosyl Chloride in Ethanol.—In a 25-ml, round-bottomed, two-necked flask equipped with an adapter connected to a nitrogen manifold and a rubber septum were placed 154 mg (1.34 mmol) of ethyl oximinoglyoxylate and 10 ml of ethanol. To this solution cooled to *ca.* 0° in an ice-salt bath was added 1.34 mmol [33.0 ml at 26° (750 mm)] of nitrosyl chloride. The resulting mixture was stirred for 1 hr in the cold and then analyzed by gas chromatography on a 10-ft SE-30 column maintained at 124° (He flow 1 cc/sec, injector temperature 230°, detector temperature 250°). The peaks corresponding to the cis and trans isomers of ethyl oximinoglyoxylate had practically disappeared and were replaced by peaks in a 1:6 ratio with retention times of 5.4 and 9.4 min, respectively. The retention time of the former peak corresponded to that of authentic diethyl oxalate and that of the latter to ethyl diethoxyacetate. The latter identification was confirmed by trapping the material corresponding to this peak and comparing its infrared and nmr spectra with those of an authentic sample prepared as described by Bloch.[18] In another experiment, the material corresponding to the 5.4-min retention time peak was trapped and identified as ethyl oxalate by comparing its infrared and nmr spectra with those of a commercial sample.

Registry No.—I (R = Me), 31767-13-2; *cis*-I (R = Et), 31767-14-3; *trans*-I (R = Et), 31767-15-4; *cis*-I (R = Bu), 31767-16-5; *trans*-I (R = Bu), 31767-17-6; I (R = H), 3545-80-0; II (R = Et), 14337-43-0; V, 31760-16-4; ketene, 463-51-4; nitrosyl chloride, 2696-92-6.

(16) F. J. Wolf and J. Weijlard, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 124.

(17) G. S. Skinner, *J. Amer. Chem. Soc.*, **46**, 731 (1924).
(18) R. Bloch, *Ann. Chim. (Paris)*, [13] **10**, 583 (1965).