

Gas-Phase Reaction of Chloramine with Olefins and Saturated Hydrocarbons

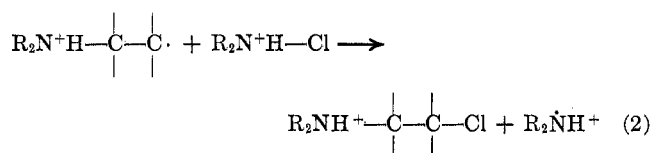
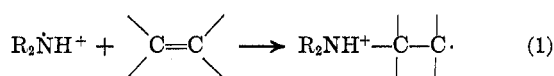
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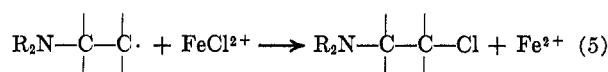
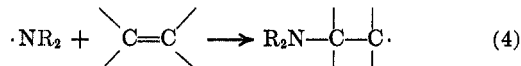
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The gas-phase reactions of chloramine with 2-methylpropene, ethylene, neopentane, and isobutane under the influence of ultraviolet radiation and heat have been shown to yield chlorinated products. Substitution as well as addition products have been isolated in the case of 2-methylpropene. The results of this study appear to support the implications in the literature that free neutral amino radicals possess a strong tendency to abstract hydrogen from olefins, rather than to add to the olefinic bond.

The dialkyl chloramines have been shown¹⁻⁵ to undergo free-radical addition to dienes, olefins, allenes, and acetylenes dissolved in a sulfuric acid-acetic acid mixture to give the corresponding β -chloroamines. All these reactions were represented as a sequence of free-radical chain reactions of the type represented by eq 1 and 2, in which the key propagation step is the addition of a protonated dialkylamino (*i.e.*, dialkylaminium) radical to a carbon-carbon multiple bond.

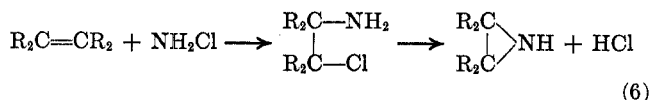


Minisci and Galli^{6,7} have recently pointed out that dialkylamino radicals, produced by the redox system, N-chloramine/ferrous or cuprous salts, easily added to the olefinic bond according to the following steps.



However, electrophilic chlorination can sometimes compete with radical addition of dialkylchloramines to allenes and olefins. Thus, chlorinated products, rather than β -chloroamines (chloraminated products), were also obtained in some cases.^{1,2,6}

We were interested in investigating the utility of chloramine with respect to the conversion of olefins to the corresponding chloroamino or imino derivatives.



There was a possibility that the direct addition of chloramine across the double bond in olefins, a source of electrons for the electrophilic chloramine, might result in a more direct route for the synthesis of β -chloroamines. No specific mode, radical or ionic, was proposed for the addition of chloramine to the olefins.

However, we believed that the electrophilic chloramine might polarize the π -electron cloud in the olefins and consequently add to the double bond, probably in an ionic manner analogous to the addition of other electrophilic reagents such as halogens and hydrogen halides.

Several olefins were exposed to chloramine in a solution phase under various reaction conditions, but no definite evidence was found for the addition of chloramine to the olefinic bond. Chloramine does not add to cyclohexene, 2-methylpropene, and 2-methyl-1-butene when ethereal solutions are exposed to either uv radiation or reacted in a strongly acidic medium such as a mixture of sulfuric acid with glacial acetic acid. Allylbenzene and 2-methyl-1-butene do not add chloramine in ether in the presence of a Fe^{2+}/Fe^{3+} redox couple. Allylbenzene, styrene, and cyclohexene do not react with chloramine in ether solutions when exposed to the emergent gases from the chloramine generator. Other unsuccessful attempts have also been made by Coleman and Patterson⁸ to add chloramine to olefins.

However, we have demonstrated that when a mixture of the gaseous chloramine and olefins is exposed to uv radiation or high temperature, chlorination of the olefin occurs. Similarly, isobutane and neopentane are chlorinated by chloramine under these conditions.

Experimental Section

Materials.—Isobutane, ethylene, 2-methylpropene, and neopentane were obtained from Matheson Company, Inc. Chloramine was produced from the gas phase reaction of ammonia with chlorine as described by Mattair and Sisler.⁹

A modified reactor design^{9a} which produces virtually quantitative yields of chloramine, even at ammonia to chlorine mole ratios almost as low as 2.0:1, was used in this study.

Nuclear Magnetic Resonance Spectra.—¹H nmr spectra were determined using a Varian Model A-60-A nuclear magnetic resonance spectrometer. The spectra of the liquids were determined as neat liquids using tetramethylsilane as an external reference.

Procedure for Gas Phase Reactions.—A typical experiment was carried out as follows: The gaseous hydrocarbon metered with the flowmeter (Tube No. 600, Tube Size R-2-15-AAA) obtained from Matheson Co., Inc., was introduced along with the effluent gases from the chloramine generator. This mixture was then passed through either a Pyrex glass tube heated to the desired temperature, or through a three-necked Pyrex glass vessel which is exposed to ultraviolet radiation (using Hanovia mercury arc lamp, 654A36, 420342). The uv source was contained in a quartz tube. The quartz tube was suspended in the Pyrex glass vessel through the middle neck. The resulting gaseous mixture was condensed in a trap chilled by a Dry Ice-acetone bath. The reaction time varied from two to several hours to obtain a sizable

(1) R. S. Neale and R. L. Hinman, *J. Amer. Chem. Soc.*, **85**, 2666 (1963).(2) R. S. Neale, *ibid.*, **86**, 5340 (1964).(3) R. S. Neale, *Tetrahedron Lett.*, 483 (1966).(4) R. S. Neale, *J. Org. Chem.*, **32**, 3263 (1967).(5) R. S. Neale and N. L. Marcus, *ibid.*, **32**, 3273 (1967).(6) F. Minisci and R. Galli, *Tetrahedron Lett.*, 167 (1964).(7) F. Minisci and R. Galli, *ibid.*, 3197 (1964).(8) G. H. Coleman and R. L. Patterson, *Proc. Iowa Acad. Sci.*, **42**, 122 (1935); *Chem. Abstr.*, **30**, 8156 (1936).(9) R. Mattair and H. H. Sisler, *J. Amer. Chem. Soc.*, **73**, 1619 (1951).(9a) NOTE ADDED IN PROOF.—H. Prakash and H. H. Sisler, *Allg. Prakt. Chem.*, **21** (4), 123 (1970).

TABLE I
 GAS PHASE REACTION OF CHLORAMINE WITH OLEFINS AND SATURATED HYDROCARBONS

Entry no.	Cl ₂ /NH ₃ /N ₂ /hydrocarbon mole ratio	Hydrocarbon	Conditions	Products	Bp, °C	% yield based on NH ₂ Cl	1H nmr data area ratios	
							Found	Calcd
1	1/2.10/5.33/0.90	CH ₂ =CH ₂	Uv	CH ₂ ClCH ₂ Cl	83.5	35.5		
2	1/2.09/3.06/0.55	(CH ₃) ₃ CH	Uv	(CH ₃) ₃ CCl	51.5	2.8		
				(CH ₃) ₂ CHCH ₂ Cl	68.5	7.6	1/2/6	1/2/6
3	1/2.09/3.13/1.35	(CH ₃) ₄ C	Uv	(CH ₃) ₃ CCH ₂ Cl	84.5-85	14.8	1/4.64	1/4.5
4	1/2.50/2.48/0.73	(CH ₃) ₄ C	Uv	(CH ₃) ₃ CCH ₂ Cl	84	10.0	1/4.6	1/4.5
5	1/3.26/2.93/1.35	(CH ₃) ₄ C	Uv	No liquid product				
6	1/2.10/9.33/0.87	(CH ₃) ₂ C=CH ₂	425°	(CH ₃) ₃ CCl		0.8		
				(CH ₃) ₂ C(Cl)CH ₂ Cl	104	5.9	1/2.91	1/3
				(CH ₃)CCH ₂ Cl	72	8.6	1/1.07/1.38	1/1/1.5
				 CH ₂				
7	1/2.07/6.62/0.87	(CH ₃) ₂ C=CH ₂	Uv	(CH ₃) ₃ CCl		0.7		
				(CH ₃) ₂ C(Cl)CH ₂ Cl	107	24.7	1/3.12	1/3
				(CH ₃)CCH ₂ Cl	71.8	6.4		
				 CH ₂				
8	1/3.15/3.09/0.92	(CH ₃) ₂ C=CH ₂	450°	No liquid product				
9	1/5.39/2.30/0.92	(CH ₃) ₂ C=CH ₂	450°	No liquid product				
10	1/2.51/3.31/0.96	(CH ₃) ₂ C=CH ₂	425°	(CH ₃) ₃ CCl ^a				
				(CH ₃) ₂ C(Cl)CH ₂ Cl ^a				
				(CH ₃)CCH ₂ Cl				
				 CH ₂ ^a				

^a Identified by vapor phase chromatography.

amount of products in order to make their separation and identification convenient. At the conclusion of the experiment, the trap was removed from the Dry Ice-acetone bath and allowed to slowly warm to room temperature. Volatile materials were evaporated from the solution. The liquid products remaining in the trap were separated into individual components on a vapor phase chromatographic preparative column packed with silicone elastomer, 20% by weight on Chromosorb P. The products were identified by their boiling points and characteristic ¹H nmr spectra.

The solid observed in almost all the cases in the receiver, in the tubes leading from the hot tube to the receiver, and in the uv reaction vessel was found to be ammonium chloride. The results of the reactions with various hydrocarbons are summarized in Table I.

Discussion and Conclusion

An examination of Table I reveals that the gas phase reaction of chloramine with ethylene and 2-methylpropene results in the chlorination of these molecules. No addition of chloramine across the double bond in ethylene to give the β-chloroamine or imine was observed. No polymeric materials were found in the cold trap. The small amounts of the solid recovered were shown by infrared spectroscopy to be principally ammonium chloride. The isolation of brown and black polymeric materials containing carbon, hydrogen, nitrogen, and chlorine in the reaction of 2-methylpropene with chloramine at 425° indicates that some addition of chloramine across the double bond may have occurred, but, if so, the resulting products probably underwent further reaction to give highly polymerized products which were not characterized. The amount of these polymeric materials was relatively very small and they were not titrated for the number of base equivalents.

The chlorination of ethylene and 2-methylpropene by chloramine raised an interesting possibility that the saturated hydrocarbons could also be chlorinated by chloramine. The experimental data (entries 2, 3, and 4) in Table I demonstrate that such is the case. These

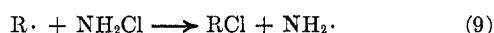
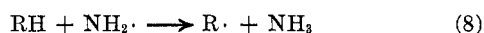
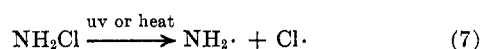
data show that chloramine reacts with isobutane to give *t*-butyl chloride and isobutyl chloride. Neopentane yields neopentyl chloride.

The fact that ammonium chloride and no liquid chlorinated product was obtained when neopentane was chloraminated at a Cl₂/NH₃/N₂/neopentane mole ratio of 1/3.26/2.93/1.35 (entry 5) was interesting to note. Similar experiments with 2-methylpropene at 450° at Cl₂/NH₃/N₂/2-methylpropene mole ratios of 1/5.39/2.30/0.92 and 1/3.15/3.09/0.92 (entries 8 and 9) yielded ammonium chloride and no chlorinated liquid product. The possibility that some unreacted chlorine coming from the generator might be responsible for giving the chlorinated products when the reactions were run at Cl₂/NH₃ mole ratio of 1/2.00 to 1/2.10 was considered. However, when neopentane was chloraminated at a Cl₂/NH₃/N₂/neopentane mole ratio of 1/2.50/2.48/0.73, a 10% yield of neopentyl chloride was again obtained (entry 4). Similarly, 2-methylpropene at a Cl₂/NH₃/N₂/2-methylpropene mole ratio of 1/2.51/3.31/0.96 (entry 10) reacts with chloramine at 425° to yield the chlorinated products. Furthermore, ultraviolet spectrophotometric measurements on the ether solutions of the emergent gases from the chloramine generator, when NH₃-Cl₂ gas phase reaction was carried out at Cl₂/NH₃ mole ratio ranging from 1.00/2.04 to 1.00/2.53, demonstrated that the only chlorine-containing product in the emergent gases was chloramine.

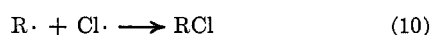
In all these chloramination reactions at a Cl₂/NH₃ mole ratios of 1/2.00 to 1/2.10, the delivery tube leading to the cold trap stayed relatively clean and little ammonium chloride was found in the cold trap. As the NH₃ to Cl₂ mole ratio was increased, more ammonium chloride was observed in the delivery tube and the cold trap. The increasing mole ratio of ammonia to chlorine resulted in a decrease in the yield of the chlorinated products. This is supported by entries 3, 4,

and 5 in Table I. It was observed that the yield of neopentyl chloride decreases from 14.8% to 0% when the Cl_2/NH_3 ratio was changed from 1/2.09 to 1/3.26. Similarly, no chlorinated product was isolated when 2-methylpropene was chloraminated at Cl_2/NH_3 mole ratios of 1/3.15 and 1/5.39. It is, thus, highly probable that the chlorinated products come from the reaction of chloramine with the hydrocarbon in the absence of excess ammonia.

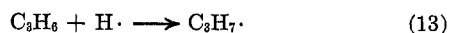
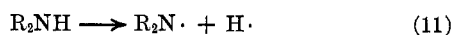
The relatively low energy of the N-Cl bond (47.7 kcal/mol)¹⁰ and the chlorinating ability of chloramine, as demonstrated in the case of isobutane and neopentane, suggests the possible initial formation of amino ($\text{NH}_2\cdot$) and chlorine ($\text{Cl}\cdot$) radicals under the influence of uv radiation or heat. If such radical formation is assumed, the chlorination of isobutane, neopentane, and 2-methylpropene could then be realized in terms of the following reactions where $\text{R} = (\text{CH}_3)_3\text{CCH}_2$ (neopen-



tyl), $(\text{CH}_3)_3\text{C}$ (*t*-butyl), $(\text{CH}_3)_2\text{CHCH}_2$ (isobutyl), and $\text{CH}_3(\text{CH}_2)\text{C}=\text{CH}_2$ (isobutenyl) groups. Equation 7 is the chain-initiating step and equations 8 and 9 are the chain-propagating steps. The proposal of chain reaction is again speculative, since no experimental evidence has been obtained. An alternative route by which the alkyl radical ($\text{R}\cdot$) could lead to the chlorinated product is to combine with the chlorine ($\text{Cl}\cdot$) radical generated in equation 7.



Equation 8 which assumes the hydrogen abstraction from the hydrocarbon by the amino radical to yield alkyl radical and ammonia, is reasonable. In many cases, the neutral amino radicals preferred to abstract hydrogen from the olefin rather than add to the olefinic bond. This strong tendency toward hydrogen abstraction by the amino radicals, and their relative inability to add to the olefinic bond, has been supported by many researchers. Cowley and Waters¹¹ carried out the liquid phase thermal decomposition of tetramethyltetrazene in the presence of 1-octene and failed to observe amination products. The postulated dimethylamino radical usually appeared as dimethylamine. This indicates hydrogen abstraction and not addition. Amino radicals from the photolyzed amines failed to add to propylene in the gas phase.¹² Propylene was converted to propane and hexane by adding hydrogen atoms resulting from the photolyzed amines according to the following reactions.



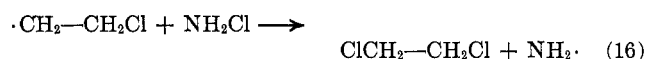
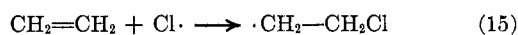
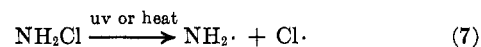
(10) L. Pauling "Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 85.

(11) B. R. Cowley and W. A. Waters, *J. Chem. Soc.*, 1228 (1961).

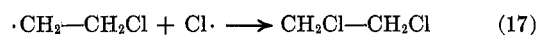
(12) C. H. Bamford, *ibid.*, 17 (1939).

Neale and Hinman¹ found that strong irradiation of carbon tetrachloride solutions of alkyl substituted chloramines containing butadiene failed to result in the addition of the chloramine to the unsaturated substrate. This is in contrast with the smooth addition occurring with aminium radicals (R_2NH^+). The conclusion was reached that either the neutral amino radicals do not form, or if they do form, they do not add to the diene. Paquette and Farley¹³ did not observe any chlorinated or chloraminated product of 1-octene when an ethereal solution of chloramine was added to solutions of various phenols in 1-octene. The phenols were dimerized. These reactions are believed to be initiated *via* the aminium radical formation ($\cdot\text{NH}_3^+$). In fact the observation that in our studies, in the presence of a considerable excess of ammonia, chlorination of the hydrocarbons by chloramine did not occur would be understandable if a mechanism involving NH_3Cl^+ and its breaking into NH_3^+ and $\cdot\text{Cl}$ radicals is assumed. It is, however, not readily apparent where the protons to form the NH_3Cl^+ would come from. Furthermore, Paquette's and Farley's results were obtained in a highly acidic liquid phase molten phenols or solutions of phenols in hydrocarbons.

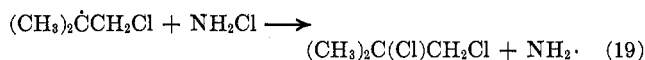
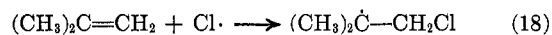
The suggestion in the literature that amino radicals have little tendency to add to the olefinic bond is in accord with the experimental results obtained in this study. The formation of 1,2-dichloroethane from ethylene and chloramine (entry 1) and 1,2-dichloro-2-methylpropane from 2-methylpropene and chloramine (entries 6, 7, and 10) can be accounted according to the following sequence of reactions.



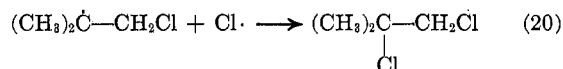
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Similarly, with 2-methylpropene



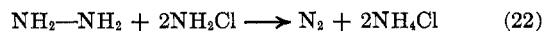
or



The amino radicals produced in equations 7, 9, 16, and 19 may couple to produce hydrazine.



Any hydrazine formed would probably react with chloramine to yield nitrogen and ammonium chloride.



(13) L. A. Paquette and W. C. Farley, *J. Org. Chem.*, **32**, 2718 (1967).

Reaction 22, which is the important yield reducing reaction in the synthesis of hydrazine, has been postulated to proceed *via* a free radical mechanism,¹⁴ indicating that chloramine is capable of undergoing this type of reaction.

(14) F. N. Collier, Jr., H. H. Sisler, J. G. Calvert, and F. R. Hurley, *J. Amer. Chem. Soc.*, **81**, 6177 (1959).

Registry No.—Chloramine, 55-86-7; 2-methylpropene, 115-11-7; ethylene, 74-85-1; neopentane, 463-82-1; isobutane, 75-28-5.

Acknowledgments.—We gratefully acknowledge the generous support of the research reported in this paper by W. R. Grace and Company through a contract with the University of Florida.

Heterocyclic Synthesis with 2-Benzimidazoleacetic Acid Derivatives

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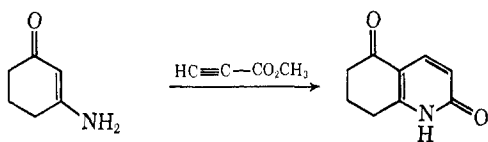
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Received February 2, 1970

Ethyl 2-benzimidazoleacetic ester (2) reacted with diethyl azodicarboxylate and oxidative cyclization of the adduct yielded ethyl 1-hydroxy-*as*-triazino[4,5,*a*]benzimidazole-4-carboxylate (13). The chemistry of this new heterocycle and the mechanism of its formation are discussed. Reactions of 2 and 2-benzimidazoleacetonitrile (1) with dimethyl acetylenedicarboxylate are described.

One of the most commonly employed procedures for the construction of new heterocyclic systems is cycloaddition.¹ This process has been well investigated mechanistically, and the factors determining the orientation of addition and the stereochemistry of the product are relatively well understood.

Alternative procedures involving construction of heterocycles by condensation processes have been subject to less mechanistic scrutiny. One such process is the reaction of an electrophilic multiple bond with enamino ketones and esters, where the amine is not fully substituted, followed by acylation of the amine by a substituent on the multiple bond, *e.g.*²



Many examples of this type of process are extant and they have usually been described as Michael additions by the nucleophilic carbon atom of the enamino carbonyl compound.³ There is however a high degree of selectivity in the orientation of the electrophilic multiple bond. While addition by the nitrogen atom is in principle reversible, this requires more vigorous conditions than are normally employed in such processes.⁴ This suggests that there is an additional factor operating which favors addition of the olefin to carbon rather than nitrogen. We would like to consider this to be the intramolecular transfer of a proton from nitrogen, *i.e.*, a hetero example of the ene reaction,⁵ which may be represented by the sequence shown in Scheme I. The exclusive carbon alkylation of enamines by electrophilic olefins, where this mechanism cannot operate, is due to the more facile reversibility of N-alkylation in such cases.⁶

(1) R. Gompper, *Angew. Chem., Int. Ed. Engl.*, **8**, 312 (1969).

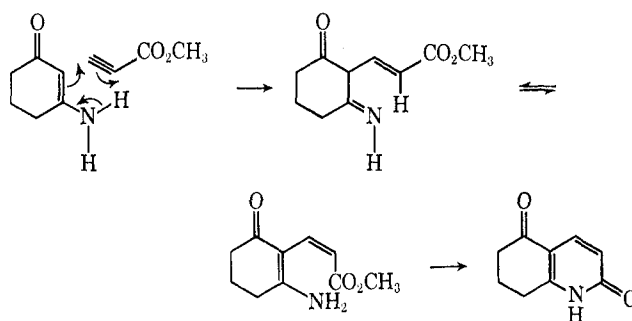
(2) M. A. T. Sluyter, U. K. Pandit, W. N. Speckamp, and H. O. Huisman, *Tetrahedron Lett.*, 87 (1966).

(3) L. Paquette "Principles of Modern Heterocyclic Chemistry," W. A. Benjamin, New York, N. Y. 1968, p 354.

(4) Z. Horii, C. Iwata, Y. Tamura, N. A. Nelson, and G. H. Rasmussen, *J. Org. Chem.*, **29**, 2768 (1964).

(5) H. M. R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 556 (1969).

SCHEME I



2-Benzimidazoleacetonitrile (1) is readily accessible by condensation of *o*-phenylenediamine with cyanoacetic ester.⁷ Ethyl 2-benzimidazoleacetic ester (2) is available by ethanolysis of this nitrile (1).⁷ The chemistry of neither substance has been well investigated but it might be anticipated that they would react with electrophilic multiple bonds to give new heterocycles. In particular with diethyl azodicarboxylate they might react to give an *as*-triazinobenzimidazole system reminiscent of the *as*-triazinoindoles for which good antiviral properties have been claimed.⁸

The reaction may be envisioned as proceeding *via* the tautomers 5 and 6 (Scheme II).

Equimolar mixtures of diethyl azodicarboxylate with 2 and with 4 in refluxing methylene chloride rapidly gave good yields of the adducts 9 and 8, respectively. The interesting observation that the position of tautomeric equilibrium between 9 and 7, and between 10 and 8, was sensitive to substitution on the imidazole nitrogen atom has been commented on previously.⁹ There was, however, no evidence to suggest that the cyclized forms were present to any extent. (The three O-ethyl resonances in the nmr spectra were very similar in both compounds.) This was not unexpected; however, it was hoped that oxidation would yield a cyclized product as

(6) G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkowicz, and R. Terrell, *J. Amer. Chem. Soc.*, **85**, 207 (1963).

(7) R. A. B. Copeland and A. R. Day, *ibid.*, **65**, 1072 (1943).

(8) J. M. Z. Gladysck, J. H. Hunt, D. Jack, R. F. Hagg, J. J. Boyle, R. C. Stewart, and R. J. Ferlanto, *Nature*, **221**, 286 (1969).

(9) In a preliminary report of some of this work: N. Finch and C. W. Gemenden, *Tetrahedron Lett.*, 1203 (1969).