perimental results[11] (E_a = 64.2 kcal). However, we find no justification for the common assumption[4] of a large ring-closing barrier (usually assumed to be about 9 kcal[4]) for trimethylene biradical.[12] This result of no significant ring-closing barrier does not contradict experimental results[3] and is in agreement with extended Hückel calculations on trimethylene[5] and tetramethylene.[13]

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[11] B. S. Rabinovitch, E. W. Schlag, and K. B. Wiberg, *J. Chem. Phys.*, **28**, 504 (1958).

[12] In the usual calculation[4] of the ring-closing barrier of trimethylene, one starts with propane and breaks a terminal CH bond on each end. This procedure leads to a mixed spin state (neither singlet nor triplet). The singlet state is strongly bound for configurations near (90, 90) and leads to energies *below* the saddle point, which may explain the low values usually obtained.[4]

[13] R. Hoffmann, S. Swaminathan, B. G. O'Dell, and R. Gleiter, *J. Amer. Chem. Soc.*, **92**, 7091 (1970).

[14] (a) National Science Foundation Predoctoral Fellow; (b) NDEA Fellow; (c) Alfred P. Sloan Foundation Fellow.

P. J. Hay,[14a] W. J. Hunt,[14b] W. A. Goddard III*[14c]
Contribution No. 4269
Arthur Amos Noyes Laboratory of Chemical Physics
California Institute of Technology, Pasadena, California 91109

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Stabilities of the Anion Radicals of Nitrobenzyl Derivatives

Sir:

Several reports have appeared recently concerning the stabilities of the anion radicals of the nitrobenzyl halides[1-4] and thiocyanates.[5] Although all reports are in agreement that the stabilities of the halogenated anion radicals increase with increasing strength of the carbon–halogen bond, the rate constants measured or estimated recently by Mohammad, *et al.*,[2,3] are considerably smaller than the values which we reported earlier.[1,6] Because the difference in the reported stabilities of each of the anion radicals of the nitrobenzyl derivatives is so large, we undertook additional electrochemical studies to check our earlier results. During the course of these studies we also investigated the redox behavior of 4-nitrobenzyl cyanide, one of the compounds included in the report by Mohammad and coworkers.[2] In further contrast to their work, we find that the redox behavior of 4-nitrobenzyl cyanide differs significantly from that of the other nitrobenzyl derivatives.

The electrochemical reduction of 4-nitrobenzyl bromide, chloride, and thiocyanate in acetonitrile was shown in our earlier work[1,5] to be a one-electron process which initially yields the corresponding anion radical. The anion radical decomposes with loss of anion to form 4-nitrobenzyl radical which subsequently dimerizes or abstracts a hydrogen atom from the solvent system (eq 2 and 3). Both 4,4′-dinitrobibenzyl and 4-nitrotoluene are electroactive and are reduced to the dianion and anion radical, respectively, at a cyclic voltammetric peak potential of −1.23 V *vs.* sce (eq 4 and 5). The

$$\mathrm{RX} + \mathrm{e} \rightleftharpoons \mathrm{RX}\cdot^{-} \qquad (1)$$

$$\mathrm{RX}\cdot^{-} \xrightarrow{k} \mathrm{R}\cdot + \mathrm{X}^{-} \qquad (2)$$

$$\mathrm{R}\cdot \begin{cases} \xrightarrow{\mathrm{SH}} \mathrm{RH} + \mathrm{S}\cdot \\ \longrightarrow \mathrm{RR}\ (\sim 90\%\ \text{yield}) \end{cases} \qquad (3)$$

$$\mathrm{RR} \underset{-\mathrm{e}}{\overset{\mathrm{e}}{\rightleftharpoons}} \mathrm{RR}\cdot^{-} \underset{-\mathrm{e}}{\overset{\mathrm{e}}{\rightleftharpoons}} \mathrm{RR}^{2-} \qquad (4)$$

$$\mathrm{RH} + \mathrm{e} \rightleftharpoons \mathrm{RH}\cdot^{-} \qquad (5)$$

reduction of 4,4′-dinitrobibenzyl has been shown by chronoamperometric and thin-layer coulometric methods to consist of two closely spaced one-electron processes with the anion radical, RR·⁻, as an intermediate.[1,7]

Chronoamperometry was used here to set a lower limit on the rate constant for decomposition of the 4-nitrobenzyl chloride anion radical. In this technique the potential of the working electrode is changed abruptly from a value which is insufficiently negative (−0.6 V) to cause reduction of the 4-nitrobenzyl derivative to a value sufficiently cathodic (−1.5 V) so as to cause concurrent reduction of the 4-nitrobenzyl halide ($E_{1/2}$ = −1.09 V) and the products of the radical decomposition, 4,4′-dinitrobibenzyl and 4-nitrotoluene (both $E_{1/2}$ = −1.20 V). Theory predicts[8,9] for this sequence of electrochemical and chemical reactions that the apparent value of n (n_{app}) should vary from a lower limit of 1.0 when kt is small (*i.e.*, the only reaction which occurs is the one-electron reduction of the nitrobenzyl halide to its anion radical) to a limit of 2.0 when kt is large (*i.e.*, reactions 1–5 proceed to completion). We find experimentally that the electrochemical reduction of 4-nitrobenzyl chloride at −1.5 V is diffusion controlled for all values of t greater than 200 μsec and that all chemical reactions (eq 2 and 3) must occur rapidly since n_{app} equals 2 (Figure 1). If it is arbitrarily assumed that a value of 1.8 or smaller is required for n_{app} before kinetic control can be detected, then a lower limit of 10^4 sec^{-1} can be set for the decomposition rate constant of the anion radical of 4-nitrobenzyl chloride.[9] The value of 2 × 10^4 sec^{-1} measured earlier by us by another procedure[1,10] must

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[1] J. G. Lawless, D. E. Bartak, and M. D. Hawley, *J. Amer. Chem. Soc.*, **91**, 7121 (1969).

[2] M. Mohammad, J. Hajdu, and E. M. Kosower, *ibid.*, **93**, 1792 (1971).

[3] M. Mohammad and E. M. Kosower, *ibid.*, **93**, 2713 (1971).

[4] P. Peterson, A. K. Carpenter, and R. F. Nelson, *J. Electroanal. Chem. Interfacial Electrochem.*, **27**, 1 (1970).

[5] D. E. Bartak, T. M. Shields, and M. D. Hawley, *ibid.*, **30**, 289 (1971).

[6] Our measured values of 6 × 10^8 and 2 × 10^4 sec^{-1} for the decomposition rate constants of 4-nitrobenzyl bromide and chloride anion radicals, respectively, may be compared with their estimated value (footnote 14 of ref 2) of 10^3 sec^{-1} for 4-nitrobenzyl bromide anion radical and their reported value of 10–20 sec^{-1} for 4-nitrobenzyl chloride anion radical.

[7] J. E. Harriman and A. H. Maki, *J. Chem. Phys.*, **34**, 778 (1963).

[8] G. S. Alberts and I. Shain, *Anal. Chem.*, **35**, 1859 (1963).

[9] M. D. Hawley and S. W. Feldberg, *J. Phys. Chem.*, **70**, 3459 (1966).

[10] The decomposition rate constants reported earlier by us[1,5] were calculated from the anodic shifts which occur in the cyclic voltammetric peak reduction potentials when the anion radicals decompose. This procedure[11] requires an estimate of the half-wave reduction potential of the nitrobenzyl halide in the absence of a follow-up chemical reaction and is obtained from a plot of $E_{1/2}$ *vs.* σ for a series of substituted nitrobenzenes which form stable anion radicals. Since ρ is a function of the supporting electrolyte and the solvent, the value was determined under our experimental conditions. Our value of ρ = 0.33 V is consistent with previously reported values (ρ = 0.22 to 0.42 V) for the reduction of substituted nitrobenzenes in dipolar aprotic solvents.[12,13]

[11] R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).

[12] W. C. Danen, T. T. Kensler, J. G. Lawless, M. F. Marcus, and and M. D. Hawley, *J. Phys. Chem.*, **73**, 4389 (1969).

[13] P. Zuman, "Substituent Effects in Organic Polarography," Plenum Press, New York, N. Y., 1967, p 102.

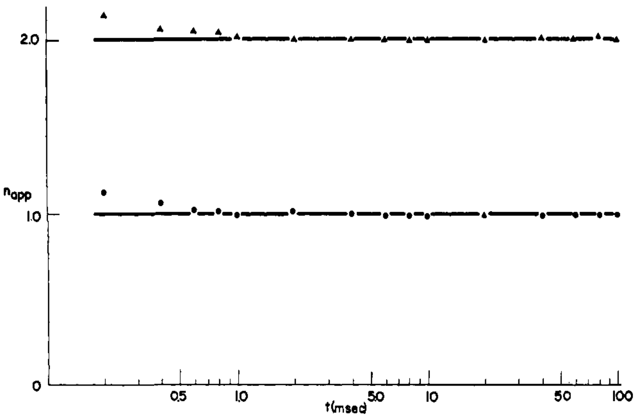

Figure 1. Plots of the chronoamperometric data obtained for 4-nitrobenzyl chloride (▲) and 4-nitrotoluene (●) on a planar platinum electrode at an applied potential of -1.5 V *vs.* sce in 0.1 *M* tetraethylammonium perchlorate-acetonitrile. The electrochemical reduction of 4-nitrotoluene under these conditions is a known one-electron process which gives the corresponding anion radical. The experiments were performed with a three-electrode potentiostat with electronic compensation of ohmic potential loss. All electrochemical experiments were performed on a vacuum line according to previously described procedures: J. L. Sadler and A. J. Bard, *J. Amer. Chem. Soc.*, **90**, 1979 (1968).

therefore be considered to be a more accurate value of the decomposition rate constant than the value of 10–20 sec^{-1} reported by Mohammad.[2]

Since the results reported by Mohammad, *et al.*,[2,3] were obtained on a mercury surface rather than on platinum, several, brief studies were undertaken with a hanging mercury drop working electrode at scan rates comparable to those employed by Mohammad, *et al.*[3] In contrast to the report of Mohammad,[3] cyclic voltammograms of 4-nitrobenzyl chloride show no anodic current for the oxidation of the anion radical at scan rates up to 50 V/sec. If we again arbitrarily assume that the ratio of the anodic peak current to the cathodic peak current must be 0.1 before the anion radical can be detected, we then estimate from the working curve given by Nicholson and Shain[11] for a follow-up chemical reaction that the lower limit for the rate constant must be at least 4×10^3 sec^{-1}. Thus, data obtained on both platinum and mercury electrode surfaces indicate that the anion radical is very unstable and suggest that our values measured previously for the other nitrobenzyl halide anion radicals are also valid.[14,20]

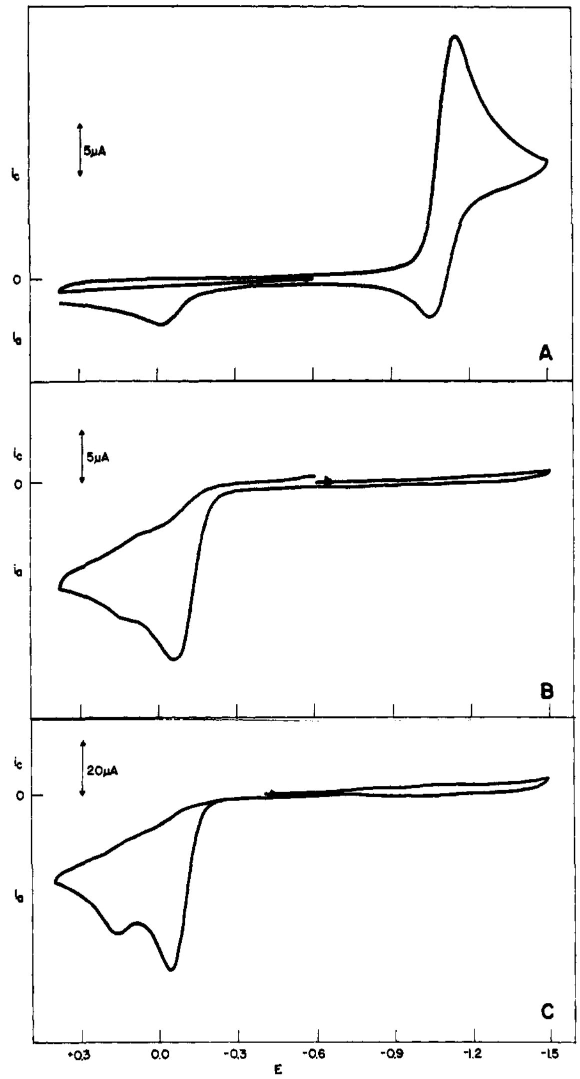

Figure 2. Cyclic voltammograms in 0.1 *M* tetraethylammonium perchlorate-acetonitrile at a scan rate of 100 mV/sec: (A) 1.15×10^{-3} *M* 4-nitrobenzyl cyanide on a platinum bead electrode; (B) 1.15×10^{-3} *M* 4-nitrobenzyl cyanide, after exhaustive electrolysis at -1.5 V *vs.* sce, on a platinum bead electrode; (C) 1.27×10^{-3} *M* 4-nitrobenzyl cyanide on a planar platinum electrode after the addition of a slight excess (1.48×10^{-3} *M*) of tetraethylammonium hydroxide.

The redox behavior of 4-nitrobenzyl cyanide was also found to differ distinctly from the behavior reported by Mohammad, *et al.*[2] In contrast to the nitrobenzyl halides, we find that the reduction of 4-nitrobenzyl cyanide near -1.14 V is not followed by the reduction of either 4-nitrotoluene or 4,4′-dinitrobibenzyl at -1.23 V (Figure 2). After reversal of the direction of the potential scan at -1.50 V, two oxidation processes are seen on the anodic sweep, the more negative of which corresponds to the oxidation of the unreacted anion radical back to starting material while the anodic peak

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(14) The report of the recording of the esr spectrum of 4-nitrobenzyl chloride anion radical in aqueous media[15] has been cited[2,3] as evidence for the stability of the anion radical. However, it should be noted that water is frequently added to dipolar aprotic solvents to stabilize highly reactive, halogenated nitro aromatic anion radicals.[16] The addition of water apparently stabilizes the anion radical to anion expulsion much more effectively than it increases the rate of an alternate decomposition pathway[17] involving protonation of the nitro aromatic anion radical and further reduction. As an example of the extreme stabilizing effect of a large quantity of water, the esr spectrum of the sterically hindered 2,6-dibromonitrobenzene anion radical has been successfully recorded in 50% aqueous dimethylformamide.[18] It should also be noted that neither Nelson[4] nor Danen and Russell[19] were able to observe the anion radical in their studies of the reduction of 4-nitrobenzyl chloride in either dipolar aprotic solvents or ethanol.

(15) W. A. Waters and L. Kolker, *Proc. Chem. Soc., London*, 55 (1963).

(16) R. N. Adams, *J. Electroanal. Chem. Interfacial Electrochem.*, **8**, 141 (1964).

(17) C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems," Marcel Dekker, New York, N. Y., 1970, p 371.

(18) T. Kitagawa and R. Nakashima, *Rev. Polarogr.*, **13**, 115 (1966).

(19) W. C. Danen and G. A. Russell, *J. Amer. Chem. Soc.*, **90**, 347 (1968).

(20) Although we have never observed an anodic wave for the oxidation of 4-nitrobenzyl chloride anion radical on either platinum or mercury electrode surfaces at scan rates up to 50 V/sec, we do note that the surface of the mercury electrode is altered irreversibly by the electroreduction of 4-nitrobenzyl chloride. Modification of the electrode surface is indicated by a very marked change which occurs in both the shape and the magnitude of the cathodic wave for 4,4′-dinitrobibenzyl when the experiment is repeated a second time on the same electrode surface. If repeated runs are made on the same electrode surface, we observe a continued decrease in 4,4′-dinitrobibenzyl peak current, a cathodic shift in the peak potential for 4-nitrobenzyl chloride, and eventually, merger of the two peaks.

near −0.04 V must arise from the product of anion radical decomposition. Exhaustive, controlled-potential electrolysis of 4-nitrobenzyl cyanide at a potential of −1.5 V *vs.* sce gives an n value of 1 ($n_{\text{expt}} = 1.01$) and a dark, reddish purple solution that contains neither 4,4′-dinitrobibenzyl nor 4-nitrotoluene. Since a solution with electrochemical and spectroscopic properties identical with those of the exhaustively electrolyzed solution is obtained by the addition of an equivalent amount of tetraethylammonium hydroxide to a solution of 4-nitrobenzyl cyanide, we conclude that 4-nitrobenzyl cyanide anion radical decomposes with loss of hydrogen to form the stable α-cyano-4-nitrobenzyl anion (eq 6).[21] Although current reversal

$$4\text{-}O_2NC_6H_4CH_2CN + e \rightleftharpoons [4\text{-}O_2NC_6H_4CH_2CN]\cdot^{-} \xrightarrow{-[^1/_2H_2]} 4\text{-}O_2NC_6H_4\bar{C}HCN \quad (6)$$

chronopotentiometric and double potential step chronoamperometric studies of the anion radical reveal that decomposition of the anion radical is not a first-order process, neither the decomposition process nor the oxidation of the anion was investigated in greater detail.

Acknowledgment. Support of this work by the National Science Foundation (GP-21316) is gratefully acknowledged.

[21] A. R. Metcalfe and W. A. Waters, *J. Chem. Soc. B*, 918 (1969), also report that 4-nitrobenzyl cyanide behaves as an acid and gives its magenta-colored anion upon electroreduction.

D. E. Bartak, M. D. Hawley*
Department of Chemistry, Kansas State University
Manhattan, Kansas 66502

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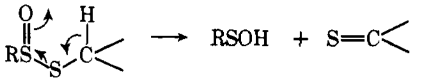
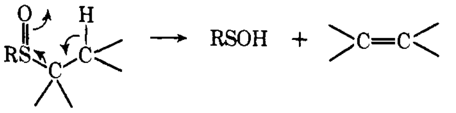
The Chemistry of Alkyl Thiolsulfinate Esters. II. Sulfenic Acids from Dialkyl Thiolsulfinate Esters[1]

Sir:

Alkanesulfenic acids represent a fundamental yet elusive class of organic sulfur compounds. Postulated as key intermediates in a variety of organic transformations,[2] the simplest alkanesulfenic acids have not been studied primarily because of difficulty of preparation.[3] We wish to report a method of generating and trapping these compounds under relatively mild conditions and present evidence that alkanesulfenic acids play a key role in the chemistry of alkyl thiolsulfinate esters.

In view of the unusual weakness of the thiolsulfinate S–S bond[4] together with the enhanced acidity of hydrogen on carbon bonded to sulfur, it seemed possible that the elimination reaction depicted in eq 1 might occur under conditions considerably milder than those required for the analogous transformation of alkyl sulfoxides (eq 2).[5,6] In accord with the reaction


(1)


(2)

proposed in eq 1, the mass spectra of alkyl thiolsulfinate esters were found to display prominent peaks corresponding to elimination of RSOH, with metastable peaks supporting a direct elimination process.[8,10]

The intermediacy of alkanesulfenic acids in the pyrolysis of alkyl thiolsulfinates was demonstrated by trapping experiments. Thus a mixture of a thiolsulfinate ester and various alkenes or alkynes (in excess), on heating at 96° for 8–16 hr, gave good yields of the sulfenic acid adducts as summarized in Table I. In the case of reactions with methyl alkanethiolsulfinates, RS(O)SCH$_3$, a white, highly insoluble solid was also formed, presumably polythioformaldehyde. Depolymerization of this substance in a sublimation apparatus at 200–210° gave a sublimate whose infrared spectrum was indistinguishable from that of authentic 1,3,5-trithiane in the region 3–25 μ. As would be predicted on the basis of the mechanism of eq 1, *tert*-butyl methanethiolsulfinate, CH$_3$S(O)SC$_4$H$_9$-*t*,[11] failed to react under the above conditions. The stereospecific preparation of α,β-unsaturated sulfoxides utilizing thiolsulfinate esters would appear to be of some synthetic value in view of the relative inaccessibility of the former class of compounds[12] and the ready availability of the latter.[13] The addition of

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[1] Paper I in this series: R. W. Murray, R. D. Smetana, and E. Block, *Tetrahedron Lett.*, 299 (1971).

[2] See, for example, (a) J. R. Shelton and K. E. Davis, *J. Amer. Chem. Soc.*, **89**, 718 (1967), *tert*-butylsulfenic acid; (b) J. E. Baldwin, G. Höfle, and S. C. Choi, *ibid.*, **93**, 2810 (1971), allylsulfenic acid; (c) B. C. Pal, M. Uziel, D. G. Doherty, and W. E. Cohn, *ibid.*, **91**, 3634 (1969), pyrimidinesulfenic acids; (d) R. D. G. Cooper, *ibid.*, **92**, 5010 (1970), and D. H. R. Barton, *et al.*, *Chem. Commun.*, 1683 (1970), penicillinsulfenic acids; (e) D. N. Jones, E. Helmy, and A. C. F. Edmonds, *J. Chem. Soc. C*, 833 (1970), D. W. Emerson and T. J. Korniski, *J. Org. Chem.*, 34, 4115 (1969), and references therein, pyrolysis of sulfoxides.

[3] *tert*-Butylsulfenic acid has been reported.[2a]

[4] By mass spectrometric appearance potential measurements we have determined the strength of the methyl methanethiolsulfinate S–S bond to be 45 kcal. The similarly determined value for the S–S bond in dimethyl disulfide is 70 kcal: T. F. Palmer and F. P. Lossing, *J. Amer. Chem. Soc.*, 84, 4661 (1962).

[5] For a recent discussion of α elimination in disulfides, see U. Miotti, U. Tonellato, and A. Ceccon, *J. Chem. Soc. B*, 325 (1970).

[6] The thiolsulfinate oxygen is slightly less basic than sulfoxide oxygen as measured by the hydrogen bond strength method.[7] Thus, the frequency shift of the phenol OH stretching vibration band in the presence of methyl methanethiolsulfinate and ethyl ethanethiolsulfinate is, respectively, 278 and 308 cm^{-1} compared to 360 and 243 cm^{-1} for dimethyl sulfoxide[7] and methyl methanesulfinate,[7] respectively.

[7] J. B. F. N. Engberts and G. Zuidema, *Recl. Trav. Chim. Pays-Bas*, **89**, 1202 (1970).

[8] The mass spectra of alkyl sulfoxides reveal a similar fragmentation process. However, recent mass spectral studies with deuterated sulfoxides[9] indicate a lack of site specificity for hydrogen transfer which contrasts with the well-documented[2e] thermal β elimination process.

[9] R. Smakman and Th. J. de Boer, *Org. Mass Spectrom.*, 3, 1561 (1970).

[10] In the mass spectra of CH$_3$S(O)SCH$_3$, CH$_3$S(O)SC$_2$H$_5$,[11] C$_2$H$_5$S(O)SCH$_3$,[11] and C$_2$H$_5$S(O)SC$_2$H$_5$, the intensities (relative to the base peak) of the sulfenic acid fragments (CH$_3$SOH from the first two and C$_2$H$_5$SOH from the last two thiolsulfinates) are 91, 91, 70, and 42%, respectively. The mass spectrum of CH$_3$S(O)SCH$_3$ reveals a significant metastable peak at mass number 37.3, as calculated for a direct mass 110 → 64 fragmentation. A detailed discussion of the mass spectra of alkyl thiolsulfinates will be presented elsewhere.

[11] All new compounds have been fully characterized by spectroscopic methods and, except in the case of the thermally labile alkyl thiolsulfinate esters, by elemental analysis. Details will be given in the full report.

[12] For recent syntheses of α,β-unsaturated sulfoxides, see G. A. Russell, E. Sobourin, and G. J. Mikol, *J. Org. Chem.*, 31, 2854 (1966), and G. A. Russell and L. A. Ochrymowycz, *ibid.*, 34, 3624 (1969).

[13] See ref 1 and also R. W. Murray and S. L. Jindal, *Prepr., Div. Petrol. Chem., Amer. Chem. Soc.*, 16 (4), A72 (1971); T. L. Moore and D. E. O'Connor, *J. Org. Chem.*, 31, 3587 (1966); G. Zinner and W. Ritter, *Arch. Pharm.*, 296, 681 (1963); P. Allen, Jr., and J. W. Brook, *J. Org. Chem.*, 27, 1019 (1962), and references therein.