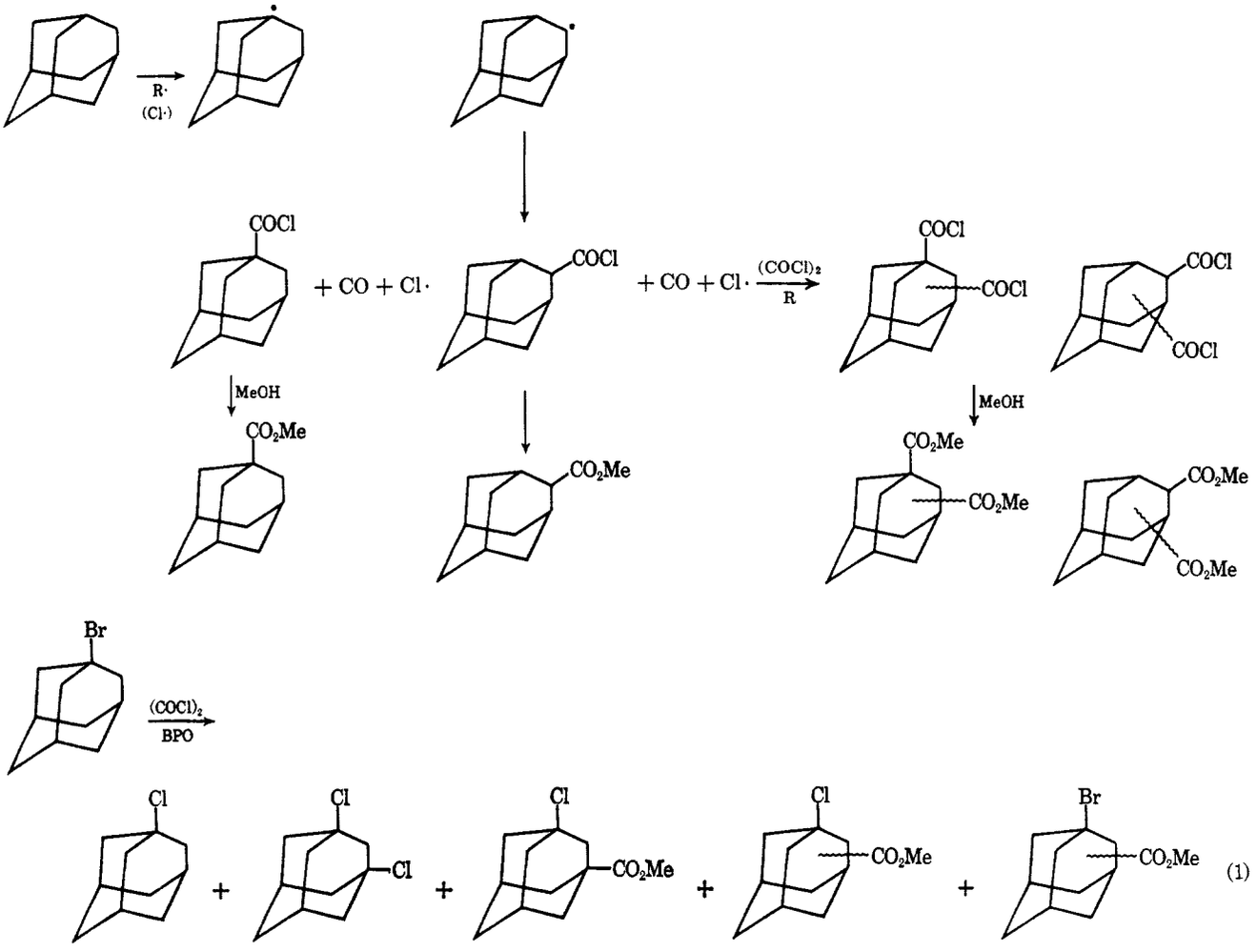
SCHEME I



anol, the combined solution was stirred for 7 hr and then volatile compounds were distilled off. The residual products were analyzed by vpc.

The conversion was about 80% on the basis of recovered 1-bromoadamantane and at least eight products were formed. The main product was 1-chloroadamantane (*ca.* 41%) (identified with an authentic sample by PEG 20,000 and Silicone D.C. 550 columns) and two of the others were identified as 1,3-dichloroadamantane (*ca.* 8%) and methyl 3-chloro-admantane-1-carboxylate (24%) (identified by vpc). Structure of other minor five products were not yet determined. Presumably they were methyl halo- (chloro- and/or bromo-) adamantanecarboxylates. Methyl adamantanecarboxylate, and dimethyl adamantanedicarboxylates were not found.

Registry No.—Adamantane, 281-23-2; 1-bromoadamantane, 768-90-1.

Synthesis and Reactions of Cyclic Amidines[1-3]

EMIL J. MORICONI AND ALBERT A. CEVASCO

Department of Chemistry, Fordham University
New York, N. Y. 10458

Received November 10, 1967

In a recent article, Kwok and Pranc[4] reported the synthesis and nmr spectra of some N-substituted 2-iminopyrrolidines prepared from a variety of primary amines and 4-chlorobutyronitrile (**2c**). In this note, we summarize an independent study which supports their conclusions, corrects older literature, and expands the general reaction to include other ω-halonitriles (**2a–f**).

In 1927, Kiel reported that the reaction of excess ammonia or methylamine with **2c** in ethanol led to the hydrochlorides of 4-amino- (**3b**) and 4-methylaminobutyronitrile (**3c**), respectively.[5] Further, he structured the reduction product of his **3c** as N-methyl-1,4-diaminobutane (**5b**). Our spectral and chemical evidence, coupled with that of Kwok and Pranc,[4] decisively establish Kiel's amination product to be instead the hydrochlorides of 2-imino- (**4a**) and 1-methyl-2-methyliminopyrrolidine (**4c**), while lithium aluminum hydride or sodium in ethanol (Kiel's procedure)[5] reduction of **4c**, and the more stable hydrobromide **4d**, produces only N,N′-dimethyl-1,4-diaminobutane (**5d**). Further, mild but prolonged alkaline hydrolysis of **4c** and **4d** led to 1-methylpyrrolidone (**6a**) and methylamine.

(1) This research was supported by the Department of the Army, U. S. Army Medical Research and Development Command, Office of the Surgeon General under Contract DA-49-193-MD-2992. This is Contribution No. 327 to the Army Research Program on Malaria.

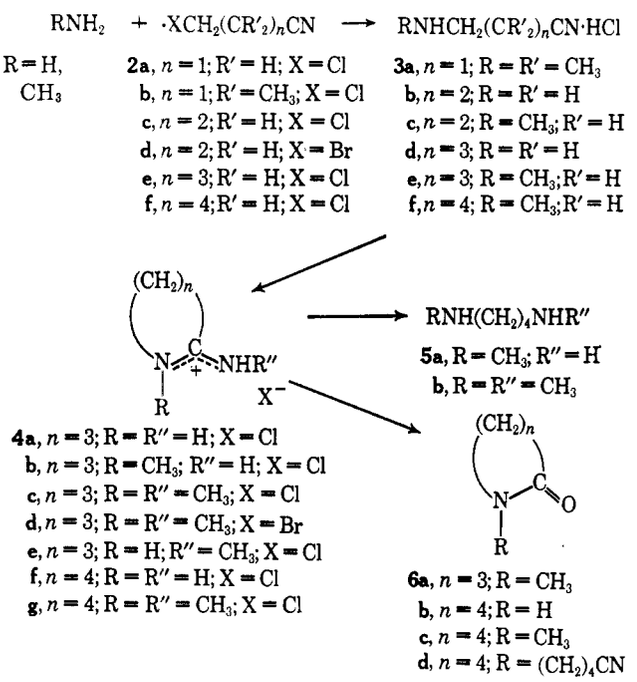
(2) Presented at the Second Middle Atlantic Regional Meeting of the American Chemical Society, New York, N. Y., Feb 7, 1967.

(3) Taken from the Ph.D. Thesis of A. A. Cevasco, 1967.

(4) R. Kwok and P. Pranc, *J. Org. Chem.*, **32**, 738 (1967).

(5) W. Kiel, *Z. Physiol. Chem.*, **171**, 242 (1927).

SCHEME I



Authentic **3b** (53%) and **3c** (8%) were prepared from **2c**, using, respectively, liquid ammonia[6] and methylamine in ethyl ether (Scheme I). In the latter case, 1-methyl-2-iminopyrrolidine hydrochloride (**4b**, 8%) was also isolated. When **3b** was autoclaved in ethanol, **4a** was obtained in 50% yield, while similar treatment of **4a** in ethanol with methylamine led to 2-methyliminopyrrolidine hydrochloride (**4e**).

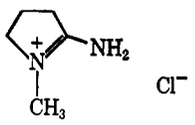
Amination of 5-chloropentanenitrile (**2e**) with ammonia and methylamine led, respectively, to the hydrochlorides of 2-iminopiperidine (**4f**, 55%) and 1-methyl-2-methyliminopiperidine (**4g**, 70%).[7] Finally, treatment of 6-chlorohexanenitrile (**2f**) and 3-chloro-2,2-dimethylpropionitrile (**2b**)[8] with methylamine produced only the hydrochlorides of 6-methylaminohexanenitrile (**3f**, 18%) and 3-methylamino-2,2-dimethylpropionitrile (**3a**, 19%).

Experimental Section[9]

Preparation of Cyclic Amidines and ω-Aminonitriles.—In general, a solution of anhydrous ammonia or methylamine in absolute ethanol and the appropriate ω-halonitrile was heated in an 800-ml stainless steel autoclave under autogenous pressure with agitation. After cooling, the autoclave contents were washed out with ethanol, treated with Norit, filtered, and concentrated *in vacuo*. The crude product was distilled or recrystallized. Specific compounds (reaction temperature and time), per cent yield, and relevant physical data are summarized.

2-Iminopyrrolidine hydrochloride (**4a**) showed the following characteristics (120°, 10 hr): 83%; mp 170–171° (from ethanol–ether), lit.[4] mp 169–171°; ir (KBr) 5.88 μ (C=N). Alternatively, the cyclization of 4-aminobutyronitrile (**3b**) in an autoclave (130°, 8 hr) led to **4a** in 50% yield.

1-Methyl-2-iminopyrrolidine hydrochloride (**4b**), mp 188–189° (lit.[4] mp 185–186°), was obtained in 8% yield in the autoclave reaction of methylamine in ethyl ether with **2c** for 24 hr at 120°: ir (KBr) 5.94 and 6.12 μ (C=N);[10] nmr (DMSO-d_6) δ 3.10 (s, 3, CH_3). The similarity of nmr signals for the 1-CH_3 group in **4b** and **4c**[4] suggest the following structure for **4b**.



Also isolated from the reaction were methylamine hydrochloride (37%), and from an aqueous extract, **4-methylaminobutyronitrile hydrochloride** (**3c**, 8%); mp 101.5–102.5°; ir (KBr) 4.48 μ (C≡N) nmr (DMSO-d_6) δ 2.49 (s, 3, CH_3).

Anal. Calcd for $C_5H_{11}N_2Cl$: C, 44.61; H, 8.24; N, 20.81. Found: C, 44.68; H, 8.37; N, 20.50.

1-Methyl-2-methyliminopyrrolidine hydrochloride (**4c**) showed the following characteristics (110°, 5 hr): 91%; mp 165–166° (from ethanol–ether), lit.[4] mp 169–170°; ir (KBr) 5.92 μ (C=N); nmr ($CDCl_3$) δ 2.10 (m, 2, 4-CH_2), 2.82 (d, 3, 2-CH_3 to which is merged a multiplet, 2, 3-CH_2), 3.08 (s, 3, 1-CH_3) and 3.52 (t, 2, 5-CH_2).[11]

1-Methyl-2-methyliminopyrrolidine hydrobromide (**4d**) showed the following characteristics (110°, 12 hr): 93%; mp 146–146.5° (from ethanol–ether); ir (KBr) 5.97 μ (C=N); nmr ($CDCl_3$) δ 3.07 (d, 3, 2-CH_3) and 3.30 (s, 3, 1-CH_3).

Anal. Calcd for $C_6H_{13}N_2Br$: C, 37.22; H, 6.78; N, 14.51; Br, 41.39. Found: C, 37.34; H, 6.83; N, 14.77; Br, 41.30.

2-Methyliminopyrrolidine hydrochloride (**4e**) showed the following characteristics (135°, 9 hr): 62%; mp 149–150° (from ethanol–ether), lit.[4] mp 147–148°; ir (KBr) 6.06 μ (C=N); nmr ($CDCl_3$) δ 2.97 (d, 3, CH_3) [lit.[4] $\delta_{TMS}^{CDCl_3}$ 3.16 (d, 3, CH_3)].

Anal. Calcd for $C_5H_{11}N_2Cl$: C, 44.61; H, 8.24; N, 20.81. Found: C, 44.69; H, 8.31; N, 20.80.

2-Iminopiperidine Hydrochloride (**4f**) showed the following characteristics (130–140°, 12 hr): 47%; mp 152–153°, lit.[12] mp 156–157°; ir (KBr) 5.94 μ (C=N); 31% of **2e** was recovered.

1-Methyl-2-methyliminopiperidine hydrochloride (**4g**) showed the following characteristics (130°, 10 hr): 70%; mp 175–176° (from ethanol–ether); ir (KBr) 6.04 μ (C=N); nmr ($CDCl_3$) δ 2.90 (d, 3, 2-CH_3) and 3.15 (s, 3, 1-CH_3).

Anal. Calcd for $C_7H_{15}N_2Cl$: C, 51.69; H, 9.30; N, 17.22. Found: C, 51.74; H, 9.28; N, 17.16.

Less rigorous conditions (100°, 4 hr) permitted the isolation (5%) of **5-methylaminopentanenitrile hydrochloride** (**3e**): mp 127–127.5° (from ethanol–ether); ir (KBr) 4.49 μ (C≡N); nmr (DMSO-d_6) δ 2.52 (s, 3, CH_3).

Anal. Calcd for $C_6H_{13}N_2Cl$: C, 48.49; H, 8.82; N, 18.85. Found: C, 48.78; H, 8.90; N, 18.63.

3-Methylamino-2,2-dimethylpropionitrile hydrochlorie (**3a**)[13,14] showed the following characteristics (145°, 20 hr): 20%; mp 223–224° (ethanol–ether); ir (KBr) 4.46 μ (C≡N); nmr

(6) O. W. Bauer and J. W. Teter, U. S. Patent 2,443,292 (1948).

(7) E. I. Vasiléva and R. Kh. Freidlina [*Izv. Akad. Nauk SSR, Ser. Khim.*, 263 (1966)] have reported the reactions between **2e** and liquid ammonia to yield (as a function of NH_3 concentration) **3d** and bis(4-cyanobutyl)amine (**7a**), between **2e** and alcoholic ammonia to produce piperidone (**6b**) and 1-(4-cyanobutyl)piperidone (**6d**), between **2e** and methylamine in benzene to lead to **3e** and bis(4-cyanobutyl)methylamine (**7b**), and between **2f** and methylamine in water–alcohol to yield 1-methylpiperidone (**6c**) and **3e**. In our view **6b–d** are products of alkaline hydrolysis of cyclic amidine precursors

$$RN[CH_2)_4CN]_2$$
7a, R = H
b, R = CH_3

while **7a** and **7b** are further alkylation products of **3d** and **3c**, respectively.

(8) The ease of preferential HCl elimination from 3-chloropropionitrile (**2a**) which would lead to the readily polymerizable acrylonitrile, precluded its use in the condensation.

(9) All melting points and boiling points are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 337 grating spectrophotometer. Nmr spectra were determined at 60 Mc with a Varian Model A-60 spectrometer; chemical shifts are expressed as δ values in parts per million relative to a tetramethylsilane internal standard. Microanalyses were determined by Schwarzkopf Microanalytical Laboratory.

(10) *Cf.* guanidinium bands I and II for mono- and disubstituted guanidine hydrochlorides: K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p 39.

(11) In the nmr spectrum, the C-5 methylenic protons are also characteristic of the pyrrolidine nucleus. Thus N. S. Bhacca, L. F. Johnson, and J. N. Shoolery [NMR Spectra Catalog, Vol. 1, Varian Associates, Palo Alto, Calif., 1962, Spectrum 116] report a C-5 methylene triplet at δ 3.40 for 1-methyl-2-pyrrolidone.

(12) T. B. Grave, *J. Amer. Chem. Soc.*, **46**, 1460 (1924).

(13) The nitrile precursor, **3-chloro-2,2-dimethylpropionitrile** (**2b**), bp 175–176° [lit.[14] bp 175° (745 mm)], was prepared in 41% yield by the reaction between pivalonitrile and sulfuryl chloride catalyzed with benzoyl peroxide. The nmr of **2b** (DMSO-d_6) displayed resonances at δ 1.40 (s, 6, CH_3) and 3.41 (s, 2, CH_2).

(14) O. W. Cass, U. S. Patent 2,425,029 (1947).

(DMSO-d_6) δ 1.49 (s, 6, CH_3), 2.60 (s, 3, N-CH_3) and 3.23 (s, 2, CH_2).

Anal. Calcd for $C_6H_{13}N_2Cl$: C, 48.49; H, 8.82; N, 18.85. Found: C, 48.69; H, 8.90; N, 18.61.

4-Aminobutyronitrile hydrochloride (3b) showed the following characteristics (liquid ammonia, no solvent; ambient temperature, 40 hr): 53%; mp 144–145° (from ethanol–ether); infrared (KBr) 4.44 μ (C≡N); nmr (DMSO-d_6) δ 3.47 (s, 3, $-^+NH_3$).

Anal. Calcd for $C_4H_9N_2Cl$: C, 39.84; H, 7.52; N, 23.23. Found: C, 39.99; H, 7.49; N, 23.04.

6-Methylaminohexanenitrile hydrochloride (3f) showed the following characteristics (155°, 25 hr): 18%; mp 97–98° (from ethanol–ether; filtered under N_2 in a drybox); ir (KBr) 4.47 μ (C≡N); nmr (DMSO-d_6) δ 2.50 (broad singlet, 3, CH_3).

Anal. Calcd for $C_7H_{15}N_2Cl$: C, 51.69; H, 9.30; N, 17.22. Found: C, 51.55; H, 9.51; N, 17.05.

N,N'-Dimethyl-1,4-diaminobutane (5b).—$LiAlH_4$ (33.0 g, 0.08 mol in 125 ml of THF) reduction of 8.0 g (0.07 mol) of the free base of **4c** in 25 ml of the same solvent gave 4.0 g (50%) of **5b**, bp 71–72° (15 mm); **5b dihydrochloride** (ethanol–ether), mp 273–275° dec, lit.[15] mp 265° dec; **N,N'-dimethyl-N,N'-dibenzoyl-1,4-diaminobutane**, mp 116.5–117° (methylene chloride–hexane).

Anal. Calcd for $C_{20}H_{24}N_2O_2$: C, 74.05; H, 7.46; N, 8.63. Found: C, 74.26; H, 7.40; N, 8.36.

Registry No.—**3a**, 16011-89-5; **3b**, 16011-90-8; **3c**, 16011-91-9; **3e**, 16011-92-0; **3f**, 16011-93-1; **4a**, 7544-75-4; **4b**, 16011-95-3; **4c**, 7544-84-5; **4d**, 16012-00-3; **4e**, 7544-87-8; **4f**, 16011-96-4; **4g**, 16012-02-5; **5b**, 16011-97-5; **5b**·2HCl, 16011-98-6; N,N'-dimethyl-N,N'-dibenzoyl-1,4-diaminobutane, 16012-03-6.

(15) W. R. Boon, *J. Chem. Soc.*, 311 (1947).

β-Chloroalkylsulfenamides. The Addition of Dimethylaminosulfenyl Chloride to Unsaturated Hydrocarbons

WOLFGANG H. MUELLER[1] AND PETER E. BUTLER[2]

Central Basic Research Laboratory, Esso Research and Engineering Co., Linden, New Jersey

Received December 5, 1967

The ability of a variety of sulfenamides to act as vulcanization accelerators has been recognized for a number of years. More recently, a nematocidal activity has been ascribed to the R_2NS function.[3] Therefore, the addition of dialkylaminosulfenyl chlorides to unsaturates as a synthetic route to β-chloroalkylsulfenamides is of interest. To our knowledge, the only prior work on this subject has been disclosed in the patent literature[4] and was limited to the aluminum chloride catalyzed addition of dialkyaminosulfenyl chlorides to propylene and cyclohexene. The observed exclusive Markovnikov orientation (I), *e.g.*

$$R_2NSCl + CH_2{=}CHCH_3 \longrightarrow \underset{\text{I}}{R_2NSCH_2\overset{Cl}{\overset{|}{C}}HCH_3} + \underset{\text{II}}{ClCH_2\overset{SNR_2}{\overset{|}{C}}HCH_3}$$

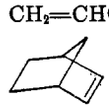
was in contrast to our recent work on the mechanism of sulfenyl chloride additions to terminal olefins.[5–7] With several sulfenyl chlorides and a variety of terminal alkenes, it had been found that sterically controlled ring opening of the episulfonium ion intermediate by the chloride ion takes place to afford predominantly the anti-Markovnikov adduct II. Postisomerization of the initial adducts led to I. Thus, it was of interest to establish a possible deviation from this mechanistic picture by aminosulfenyl chlorides, and to explore concurrently the synthetic scope of this addition reaction. For simplification of the important nmr analyses, the readily accessible dimethylaminosulfenyl chloride was chosen as a model reagent.[8]

Addition to Olefins.—Propylene, isobutylene, 3-methylbutene, 3,3-dimethylbutene, and norbornene were chosen as model systems. Dimethylaminosulfenyl chloride was added to a cold methylene chloride solution of the olefin. The reaction temperature employed was dependent on the reactivity of the olefin. The solution contained a small amount of calcium carbonate to prevent possible postisomerization.[5] In general, the reaction is quite sluggish in contrast to the previously experienced spontaneous reaction of methane-, benzene-, and acetylthiosulfenyl chloride with unsaturates.

The isomer distribution of the adducts obtained from the above olefins is summarized in Table I. The relative amounts of isomeric adducts could be deduced from nmr analyses of the crude product mixtures. A considerable amount of spectral data obtained during the previous studies in this area[5–7] aided the structure assignments. In general, protons α to chlorine are considerably deshielded relative to those α to sulfur.[7,9] A detailed compilation of the nmr parameters is given in Table II.

TABLE I

DIMETHYLAMINOSULFENYL CHLORIDE–OLEFIN ADDUCTS

Olefin	Mole % adduct ratio		
	CH_2—C<		CH_2—C<
$CH_2{=}C<$	Cl	$SN(CH_3)_2$	$SN(CH_3)_2$ Cl
$CH_2{=}CHCH_3$		78[a]	22
$CH_3{=}C(CH_3)_2$		71	29
$CH_2{=}CHCH(CH_3)_2$		>90	<10[b]
$CH_2{=}CHC(CH_3)_3$		~95	~5[b]
		>98 (*trans*)	...

[a] Registry no. in descending order are 16133-66-7, 16133-67-8, 16133-68-9, 16133-69-0, and 16133-72-5. [b] The adduct ratio was approximated due to partly overlapping nmr signals.

With the exception of the 3,3-dimethylbutene adduct, analytical samples were obtained by fractional distillation *in vacuo*.

An analysis of the data given in Table I shows that dimethylaminosulfenyl chloride additions to olefins follow the previously proposed mechanism.[5] The *trans* stereospecificity observed with norbornene supports the intervention of an episulfonium ion intermediate in the addition process.

(1) To whom inquiries should be directed.
(2) Analytical Research Division.
(3) H. R. Williams, Canadian Patent 737,941 (1966).
(4) G. Weiss, German Patent 1,153,744 (1963).
(5) W. H. Mueller and P. E. Butler, *J. Amer. Chem. Soc.*, **88**, 2866 (1966); *ibid.*, **90**, 000 (1968).
(6) W. H. Mueller, R. M. Rubin, and P. E. Butler, *J. Org. Chem.*, **31**, 3537 (1966).
(7) W. H. Mueller and P. E. Butler, *ibid.*, **32**, 2925 (1967).
(8) G. Weiss and G. Schulze, German Patent 1,131,222 (1962).
(9) P. E. Butler and W. H. Mueller, *Tetrahedron Lett.*, **19**, 2179 (1966).