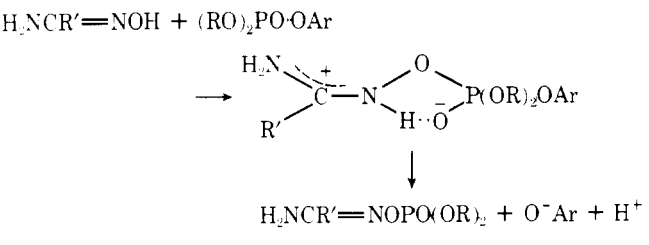
Scheme I



rate constant of ~60 M^{-1} s^{-1} estimated for reaction of the acetamidoximate ion with PNPDEP. To some extent these differences reflect the greater reactivity of PNPDPP over PNPDEP, but they suggest that amidoximate and aldoximate ions have similar reactivities toward phosphoryl groups.

The high nucleophilicity of amidoximes toward phosphoryl groups is similar to that found in deacylation, where intramolecular catalysis has been postulated.[2,5] One such reaction is shown in Scheme I. Intramolecular participation of this type has also been discussed for attack of the catechol monoanion on a phosphoryl group and in deacylation.[2,10]

Acknowledgments. Support of this work by the Army Research Office is gratefully acknowledged.

Registry No.—**1a,** 22059-22-9; **1b** HCl, 19655-67-5; acetonitrile, 75-05-8; benzonitrile, 100-47-0; hydroxylamine, 7803-49-8; *p*-nitrophenyl diethyl phosphate, 311-45-5; *p*-nitrophenyl diphenyl phosphate, 10359-36-1.

References and Notes

(1) On leave from the Centrao, C.N.R., di Studio sui Meccanismi di Reazione, Isituto di Chimica Organica, Universita di Roma, Roma, Italy.
(2) T. C. Bruice and S. J. Benkovic, "Bioorganic Mechanisms", W. A. Benjamin, New York, 1966, Chapters 5–7; W. P. Jencks, "Catalysis in Chemistry and Enzymology", McGraw-Hill, New York, 1969, Chapter 3; C. A. Bunton, *Acc. Chem. Res.*, **3**, 257 (1970).
(3) R. F. Hudson, "Structure and Mechanism in Organophosphorus Chemistry", Academic Press, New York, 1965; N. Bodor, E. Shex, and T. Higuchi, *Science*, **190**, 155 (1975); J. Epstein, J. J. Kaminski, N. Bodor, R. Enever, J. Sowa, and T. Higuchi, *J. Org. Chem.*, **43**, 2816 (1978).
(4) C. A. Bunton and Y. Ihara, *J. Org. Chem.*, **42**, 2865 (1977).
(5) (a) J. D. Aubort and R. F. Hudson, *Chem. Commun.*, 1342 (1969); (b) *ibid.*, 937, 938 (1970).
(6) For a review of amidoximes, see F. Eloy and R. Lanaers, *Chem. Rev.*, **62**, 155 (1962).
(7) R. Lenaers, F. Eloy, and C.Moussebois, *Helv. Chim. Acta*, **45**, 441 (1962).
(8) C. A. Bunton, S. J. Farber, and E. J. Fendler, *J. Org. Chem.*, **33**, 29 (1968); C. A. Bunton and S. Diaz, *ibid.*, **41**, 33 (1976).
(9) G. A. Pearse and R. T. Pflaum, *J. Am. Chem. Soc.*, **81**, 6565 (1959).
(10) J. Epstein, R. E. Plapinger, H. O. Michel, J. R. Cable, R. A. Stephani, R. J. Hester, C. Billington, and G. R. List, *J. Am. Chem. Soc.*, **86**, 3075 (1964).

Phenyl Azide from the Reaction of Phenylhydrazine with Thionyl Chloride. Preparation of *N*-Thionylbenzylhydrazine and of *N*-Thionyl-β-phenethylhydrazine

L. Bruce Pearce, M. H. Feingold, Kenneth F. Cerny, and Jean-Pierre Anselme*

Department of Chemistry, University of Massachusetts at Boston, Harbor Campus, Boston, Massachusetts 02125

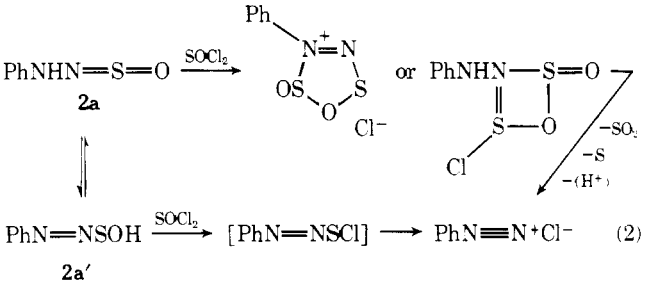
Received July 31, 1978

Despite the pioneering investigations of Michaelis and his group[1,2] at the turn of the century, *N*-thionylhydrazines, >NN=S=O, remain a relatively little studied class of compounds. *N*-Thionylphenylhydrazine (**2a**), first prepared (no yield given) in 1889 by Michaelis,[1a] was reported to be formed in ~82% yield from the reaction of phenylhydrazine with thionyl chloride by Klamann and his group[3,4] more than 70 years later. Our repeated failures to duplicate the reported yield of **2a** prompted a closer examination of this reaction.

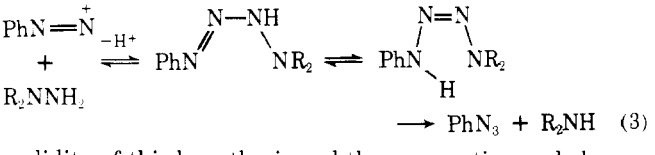
$$\underset{\mathbf{1}}{RNHNH_2} + SOCl_2 \xrightarrow[\text{pyridine}]{CHCl_3} \underset{\mathbf{2}}{RNHN{=}S{=}O} + [2HCl] \quad (1)$$

a, R = Ph; **b**, R = $PhCH_2$; **c**, R = $PhCH_2CH_2$

The best yield of crystallized **2a** obtained by Klamann's procedure was 34%. Distillation or extraction of the reddish brown residue left from the isolation of **2a** gave a 16% yield of phenyl azide. Klamann and co-workers[3] reported without experimental details the isolation of an azo dye during the preparation of **2a.** Michaelis and Ruhl[1c] had demonstrated the formation of phenyldiazonium chloride from the reaction of **2a** with thionyl chloride. This early report suggested a possible rationalization for the formation of phenyl azide during the preparation of **2a.** As shown in eq 2, phenyldiazo-

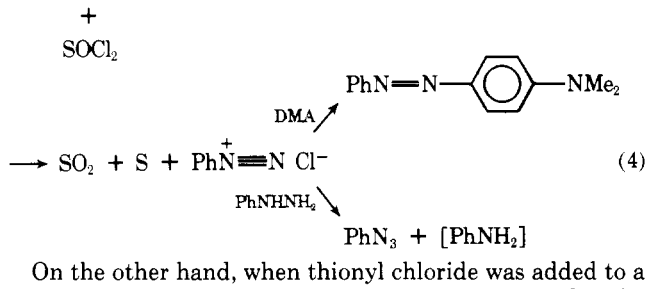


nium chloride could arise by reaction of thionyl chloride with **2a** directly or via the tautomeric phenylazosulfenic acid **2a′**.[1] The subsequent conversion of aryldiazonium salts to aryl azides with hydrazines is an old and well-known reaction (eq 3).[5,6] This note describes experiments which establish the



validity of this hypothesis and the preparation and characterization of the novel *monosubstituted N*-thionylalkylhydrazines (**2b** and **2c**).

Treatment of **2a** with thionyl chloride in pyridine at 0 °C resulted in the evolution of sulfur dioxide and the precipitation of elemental sulfur. The addition of *N,N*-dimethylaniline (DMA) to the solution gave *p*-(dimethylamino)azobenzene. In a separate experiment, when the solution obtained above was treated with 1 equiv of phenylhydrazine instead of DMA, a 25% yield of phenyl azide was obtained (eq 4).



On the other hand, when thionyl chloride was added to a twofold excess of phenylhydrazine in chloroform at 0 °C in the presence of pyridine, very little phenyl azide was formed and the yield of **2a** increased to 40%. *p*-(Dimethylamino)azobenzene was detected from the reaction of phenylhydrazine with thionyl chloride in chloroform[3] using DMA as the base instead of pyridine. Additional support for the mechanism of the generation of phenyl azide was the preparation of **2a** in 89%

0022-3263/79/1944-1881$01.00/0

yield from *transthionylation* of phenylhyrazine with *N*-thionylaniline; no phenyl azide could be detected. In contrast, when phenylhydrazine was slowly added to thionyl chloride at 0 °C, essentially pure phenyl azide was obtained.

The low melting points of *N*-thionylbenzylhydrazine (**2b**) and *N*-thionyl-β-phenethylhydrazine (**2c**) coupled with the side reaction of monosubstituted *N*-thionylhydrazines just discussed may explain our initial difficulties in obtaining **2b** and **2c** in pure form. A further complication in this context appears to be their sensitivity (at least of **2b**)[7] to heat. These novel monosubstituted alkyl *N*-thionylhydrazines (**2b** and **2c**) were finally obtained pure by the addition of thionyl chloride to a *twofold* excess of the corresponding hydrazines. *N*-Thionylbenzylhydrazine (**2b**) was isolated as a colorless solid, mp 30–35 °C; its infrared spectrum displayed a sharp NH band at ~3150 cm^{-1} and two broad peaks at 1270 and 1080 cm^{-1} (N=S=O) while its ^1H NMR spectrum ($CDCl_3$) displayed a very broad NH (D_2O exchangeable) at δ 9.1, a sharp aromatic peak at δ 7.2, and doublet for the benzylic hydrogens at δ 4.6 (singlet after D_2O exchange). *N*-Thionyl-β-phenethylhydrazine (**2c**) was obtained as a nearly colorless solid, mp 27.5–29 °C. Its infrared spectrum was remarkably similar to that of **2b**, and its ^1H NMR spectrum ($CDCl_3$) was in complete agreement with the assignment, exhibiting an NH peak at δ 9.1 (D_2O exchangeable), a fairly sharp aromatic peak at δ 7.15, a triplet for the benzylic hydrogens at δ 2.8, and a sextet (CH_2NH) at δ 3.6 (triplet after D_2O exchange). As expected, there was no evidence for the presence of the corresponding alkyl azides from the reaction of thionyl chloride with a twofold excess of **1b** and **1c**. Indeed, the putative alkyldiazonium ions would not be expected to survive long enough to be converted to azides and could undergo nucleophilic displacement to give a myriad of products. To our knowledge, these are the first monosubstituted *N*-thionylalkylhydrazines reported.[2]

Experimental Section

All melting points are uncorrected. All infrared spectra were obtained on a Perkin-Elmer 137 spectrophotometer. NMR spectra were carried out in deuteriochloroform on a Hitachi Perkin-Elmer R-24 spectrometer, using Me_4Si as an internal standard.

***N*-Thionylphenylhydrazine.** In a 1000-mL, three-neck, round-bottom flask equipped with an addition funnel, a mechanical stirrer, and a reflux condenser with a drying tube were placed 90 g (0.83 mol) of phenylhydrazine and 137 g (1.7 mol) of pyridine in 400 mL of chloroform. To this cold (ice–salt bath) rapidly stirred mixture was added dropwise a solution of 64 mL (0.84 mol) of thionyl chloride in 100 mL of chloroform over a period of 3 h. With continued cooling, the reaction mixture was stirred for an additional hour and then the temperature was allowed to become ambient. The reaction mixture was washed with three 200-mL portions of water, three 200-mL portions of 5% HCl, and three 200-mL portions of water and then dried over a 50:50 mixture of anhydrous sodium sulfate and magnesium sulfate. Evaporation of the solution gave 96.1 g of crude product which upon recrystallization from absolute ethanol gave a first crop of 32.4 g, mp 103–104.5 °C (lit.[3] mp 105 °C), and a second crop of 10.9 g, mp 101–104 °C (total yield 34%). Workup of the filtrate gave phenyl azide as described below.

Phenyl Azide from the Reaction of Phenylhydrazine with Thionyl Chloride. When the combined filtrate from the recrystallization of *N*-thionylphenylhydrazine from another preparation using 67.1 g (0.62 mol) of phenylhydrazine, 100 mL of pyridine, 150 mL of chloroform, and 52 mL (0.69 mol) of thionyl chloride in 75 mL of chloroform was evaporated and the reddish oily residue was distilled in vacuo into a receiver cooled in a dry ice–isoamyl alcohol bath, 5.8 g (16%) of phenyl azide [bp 35 °C (0.7 mm)] was isolated and identified. Alternatively, extraction of the thick reddish residue with three 50-mL portions of cyclohexane afforded, after evaporation of the cyclohexane, a residue which was distilled to give phenyl azide in 7% yield.

***p*-(Dimethylamino)azobenzene.** To an ice-cold solution of 15 g (0.1 mol) of **2a** and 7.8 g (0.1 mol) of pyridine in 200 mL of chloroform was added dropwise with rapid stirring a solution of 11.55 g (0.1 mol) of thionyl chloride in 100 mL of chloroform over a period of 1.5 h. This was followed by the addition of a solution of 12.2 g (0.1 mol) of DMA in 100 mL of chloroform over a 1-h period. The reaction mixture was evaporated in vacuo, and the semisolid residue was dissolved in hot ethanol. The ethanol solution was then stirred over 3–4 g of sodium hydroxide, upon which the solution turned to an orange-red color. The solution was filtered and evaporated, and the residue was again dissolved in hot ethanol. Recrystallization gave a light orange solid, mp 114–115 °C, identical with an authentic sample.

Phenyl Azide from *N*-Thionylphenylhydrazine, Thionyl Chloride, and Phenylhydrazine. To a 125-mL round-bottom flask cooled in an ice bath were added 5 g (0.032 mol) of *N*-thionylphenylhydrazine and 2.7 mL (0.034 mol) of pyridine in 30 mL of chloroform. A solution of 6.0 mL (0.084 mol) of thionyl chloride in 30 mL of chloroform was added dropwise with continuous stirring. After about 5 min, 3.4 mL (0.035 mol) of phenylhydrazine was added dropwise. A vigorous reaction ensued, and the brownish slurry which was formed was stirred for an additional 30 min and then poured into 200 mL of ice water and stirred for 15 min. The organic phase was separated and dried over a 50:50 mixture of anhydrous sodium sulfate and magnesium sulfate. Evaporation of the solvent left a viscous liquid which was chromatographed on Florisil with hexane as the eluent to yield 1.0 g (26%) of phenyl azide.

Reaction of Excess Phenylhydrazine with Thionyl Chloride. To a mixture of 86.5 g (0.8 mol) of phenylhydrazine and 63.3 g (0.8 mol) of pyridine in 400 mL of chloroform in a 1-L, three-neck, round-bottom flask fitted with a mechanical stirrer, a calcium chloride drying tube, and an addition funnel, cooled in an ice bath, was added over a period of 3.5 h a solution of 47.6 g (0.4 mol) of thionyl chloride in 50 mL of chloroform. The reaction mixture was stirred for an additional 0.5 h and then extracted three times with 100-mL portions of water, three times with 100-mL portions of 5% hydrochloric acid, and finally with water (3 × 100 mL). The organic layer, after drying (sodium sulfate, 24 h) and upon removal of the solvent, gave 25 g (40%) of **2a**, mp 104–105 °C (from ethanol).

***N*-Thionylphenylhydrazine by Transthionylation with *N*-Thionylaniline.** To 50 mL of anhydrous ether in a 250-mL, three-neck, round-bottom flask fitted with a drying tube and two addition funnels were added simultaneously 21.6 g (0.2 mol) of phenylhydrazine and 27.8 g (0.2 mol) of *N*-thionylaniline each in 25 mL of anhydrous ether with stirring. Stirring was continued for 1 h at 0 °C, and the precipitated yellow solid was collected from the cold solution, washed with ether, and recrystallized from ethanol to give 24.8 g (89%) of **2a**, mp 103.5–105.5 °C. An infrared spectrum of the residue from evaporation of the filtrate did not indicate the presence of phenyl azide.

Phenyl Azide from the Addition of Phenylhydrazine to Thionyl Chloride. To a solution of 47.6 g (0.4 mol) of thionyl chloride in 50 mL of chloroform in a 500-mL three-neck, round-bottom flask fitted with a drying tube and an addition funnel was added over a period of 2 h a solution of 43.3 g (0.4 mol) of phenylhydrazine and 63.2 g (0.8 mol) of pyridine in 200 mL of chloroform with stirring and cooling (ice bath). After workup with water and 5% HCl (see above), the solution was dried at 0 °C over sodium sulfate. Evaporation of the solution gave a pale amber liquid, whose infrared spectrum showed it to be phenyl azide probably contaminated with some chloroform.

***N*-Thionylbenzylhydrazine (2b).** To a solution of 48.8 g (0.4 mol) of benzylhydrazine and 31.6 g (0.4 mol) of pyridine in 100 mL of chloroform (ice bath) was added a solution of 23.8 g (0.2 mol) of thionyl chloride in 60 mL of chloroform with stirring. The reaction mixture was stirred for an hour after the addition at 0 °C and filtered to remove the precipitated salts. The filtrate was washed successively with three 50-mL portions of water, three 50-mL portions of 5% hydrochloric acid, and finally three 50-mL portions of water and dried at 0 °C over sodium sulfate. Removal of the solvent left 16.9 g of crude product which was chromatographed over 20 g of silical gel using a 97:3 mixture of petroleum ether–ether (125 mL) to give a pale yellow solution. Ether was used as eluent thereafter until the pale yellow band had eluted. From the initial 125 mL of eluent was obtained 8 g of fairly pure **2b**; an additional 6 g of less pure product was obtained from the elution with ether. The total yield amounted to 14 g (41%). Very careful crystallization from ethanol gave an analytically pure sample, mp 30–30.5 °C.

Anal. Calcd for $C_7H_8N_2SO$: C, 49.98; H, 4.79; N, 16.65; S, 19.06. Found: C, 49.73; H, 5.06; N, 16.83; S, 19.21.

***N*-Thionyl-β-phenethylhydrazine (2c).** From 0.8 mol of β-phenethylhydrazine, using the ratio and separation procedure described above, was obtained 33.8 g of crude product. Chromatography on 50 g of silica gel gave 31 g (42%) of relatively pure material. Careful crystallization from ethanol gave an analytical sample, mp 27.5–29 °C.

Anal. Calcd for $C_8H_{10}N_2SO$: C, 52.74; H, 5.53; N, 15.38; S, 17.56. Found: C, 52.44; H, 5.79; N, 15.08; S, 17.65.

Acknowledgment. The authors gratefully acknowledge the assistance of Messrs. Edward Orton and Michael E. Newman in performing some of the experiments.

Registry No.—**1a,** 100-63-0; **1b,** 555-96-4; **1c,** 51-71-8; **2a,** 17420-03-0; **2b,** 69517-45-9; **2c,** 69517-46-0; thionyl chloride, 7719-09-7; phenyl azide, 622-37-7; *p*-(dimethylamino)azobenzene, 60-11-7; *N,N*-dimethylaniline, 121-69-7; *N*-thionylaniline, 1122-83-4.

References and Notes

(1) (a) A. Michaelis, *Ber.*, **22,** 2228 (1889); (b) A. Michaelis and J. Ruhl, *ibid.*, **23,** 474 (1890); (c) *Justus Liebigs Ann. Chem.*, **270,** 114 (1892); A. Michaelis and R. Herz, *Ber.*, **23,** 3480 (1890).
(2) G. Kresze, A. Maschke, R. Albrecht, K. Bederke, H. P. Patzske, H. Smalla, and A. Trede, *Angew. Chem., Int. Ed. Engl.*, **1,** 89 (1962).
(3) D. Klamann, U. Kramer, and P. Weyerstahl, *Chem. Ber.*, **95,** 2695 (1962).
(4) Professor Klamann has informed us that the 82% yield reported[3] was obtained once and that the exact experimental conditions were not determined. We thank him for providing this information to us.
(5) C. Grundmann, *Methoden Org. Chem. (Houben-Weyl), 4th Ed., 1965,* **10,** Part 3, 806 (1965).
(6) No attempt was made to determine the presence of aniline as it would be expected to react with the diazonium ion.
(7) Benzonitrile and benzaldehyde have been identified from the neat pyrolysis of **2b.** Details of these investigations will be reported in a future publication.

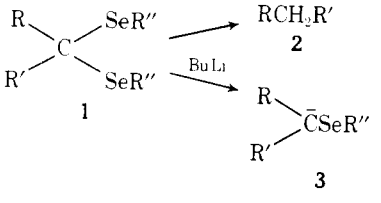
New Route to Selenoacetals: Exchange Reaction between Acetals and Tris(phenylseleno)borane

Derrick L. J. Clive* and Steven M. Menchen

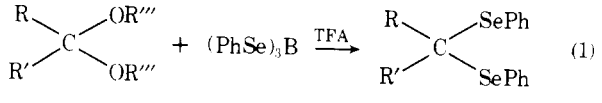
Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Received October 31, 1978

We report a new method for preparing selenoacetals (**1,** R″ = Ph), a class of compounds that promises to be very useful in organic synthesis.[1] These substances are reduced smoothly by triphenyltin hydride (**1** → **2**), and this process, taken together with the conversion of a carbonyl compound into a selenoacetal, constitutes an alternative to the classical Wolf–Kishner reduction.[2] Selenoacetals are converted by the action of butyllithium into selenium-stabilized carbanions[1,3] (**1** → **3**) which can be used, inter alia, for making carbon–carbon bonds[1,3] and for preparing sulfur-stabilized carbanions that are *not* available by deprotonation.[3b,4,5]

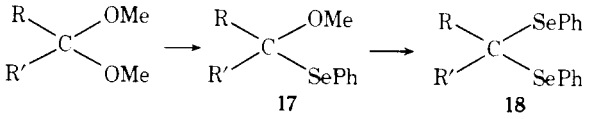


These reactions have established a need for simple methods of preparing selenoacetals from a variety of readily accessible precursors.[6] The crystalline reagent, $(PhSe)_3B$,[7] is convenient in this respect as it is easy to handle,[8] and it reacts[9] with ketones and aldehydes to generate diphenyl diselenoacetals.[10] In the case of acetophenone and 2′-acetylnaphthalene the performance of the boron reagent is unsatisfactory,[11] but we have found that oxygen acetals undergo an exchange reaction (eq 1) which constitutes an efficient alternative route to the phenylseleno analogues. The following procedure gives the results shown in Table I. The acetal is added to a stirred mixture of $(PhSe)_3B$ (1.1 equiv) and an inert solvent, usually $CHCl_3$. Trifluoroacetic acid [ca. 3–20 mol % (based on acetal)] is injected at 0–25 °C, and the product **1** (R″ = Ph) can be isolated by chromatography after an appropriate time at room temperature. Under these standard conditions the dithioacetal **10** is inert.[12]



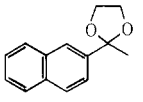
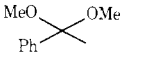
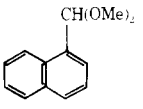
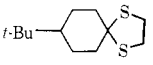
(1)

The presence of trifluoroacetic acid is essential.[13] When the reactions are monitored by NMR, the two stages of the process (eq 2) can be observed. For example, in an experiment with



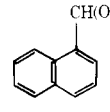
(2)

Table I

starting material	mol % TFA	conditions: time, temp., solvent	diphenyl diselenoacetal compd no.	diphenyl diselenoacetal yield, %
$C_{10}H_{21}CH(OMe)_2$ **4**	19	0.5 h at 0 °C, then 1 h at 25 °C, $CHCl_3$	**11**	85
 **5**	1	0.5 h at 0 °C, then 1.5 h at 25 °C, CH_2Cl_2	**12**	71
 **6**	10	3 h at 25 °C, $CHCl_3$	**13**	80
 **7**	4	3 h at 25 °C, $CHCl_3$	**14**	89
$Bu_2C(OMe)_2$ **8**	17	0.5 h at 0 °C, then 1 h at 25 °C, $CHCl_3$	**15**	83
$HC(OEt)_3$ **9**	3	13 h at 25 °C, $CHCl_3$	$HC(SePh)_3$ **(16)**	76[a]
 **10**	7	24 h at 25 °C, $CHCl_3$		*b*

[a] The corresponding reaction with $CH_3C(OMe)_3$ to give $CH_3C(SePh)_3$ is very sluggish. [b] No reaction (TLC control).

Table II

starting material	conditions:[a] time (h), solvent	mixed acetal compd no.	mixed acetal yield, %
$C_{10}H_{21}CH(OMe)_2$  **7**	6, toluene[b]	**19**	87[c]
	7.5, $CHCl_3$	**20**	78[d]
$Bu_2C(OMe)_2$ **8**	1, toluene[b]	**21**	80[e]

[a] Reactions were conducted at room temperature. For workup the mixture was diluted with MeOH, decolorized with $NaBH_4$, and partitioned between water and pentane. Further purification was not necessary for the first two entries. [b] Reaction in toluene was cleaner than that in chloroform. [c] δ ($CDCl_3$) 4.88 (t, J = 6 Hz). [d] Isolated by crystallization from hexane: mp 60–63 °C; δ ($CDCl_3$) 6.54 (s). [e] A satisfactory oxygen analysis could not be obtained for this compound, the value being 0.33% too high.

0022-3263/79/1944-1883$01.00/0