Acknowledgment. We are grateful to the Natural Sciences and Engineering and Research Council for support of this work. M.G. is a holder of a National Scholarship from the Government of India.

Registry No. 1 (R = Ph; R^1 = H), 31268-20-9; 1 (R = *p*-ClC_6H_4; R^1 = H), 38325-81-4; 1 (R = $PhCH_2$; R^1 = H), 26910-36-1; 1 (R = *p*-$CH_3C_6H_4$; R^1 = H), 26910-35-0; 1 (R = β-naphthyl; R^1 = H), 87174-67-2; 1 (R = Ph; R^1 = CH_3), 26910-34-9; $Co_2(CO)_8$, 10210-68-1; Al_2O_3, 1344-28-1; α-chloromethyl phenyl sulfoxide, 7205-94-9.

Direct Acylamination of Pyridine 1-Oxide with *N*-Phenylarenimidoyl Chlorides and Fluorides

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Received April 4, 1983

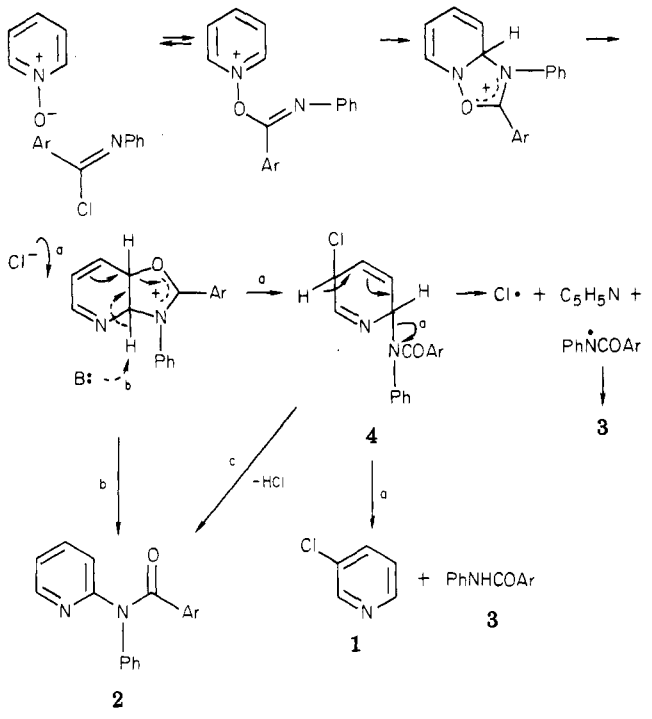
Pyridine 1-oxide reacts with *N*-phenylbenzimidoyl chloride to give 2-(*N*-benzoylanilino)pyridine (**2**) and 3-chloropyridine (**1**).[1] When substituted *N*-phenylbenzimidoyl chlorides are used, the yields of acylaminated pyridine and of **1** depend on the substituents present in both the anilide[1] and the acyl[2] moieties of the imidoyl chloride. Preliminary results[2] of the reaction of pyridine 1-oxide with some *N*-phenylarenimidoyl chlorides suggested that electron-donating substituents in the para position favored the formation of 2-(acylamino)pyridine and hindered that of 3-chloropyridine. Electron-accepting substituents suppressed both reactions.

A multistep pathway has been proposed for the reactions involved,[3] and the electrical properties of the substituents in the imidoyl chloride could influence each of these in different ways. This prompted us to study the influence of substituents in *N*-phenylarenimidoyl chlorides systematically in order to see if any regularities could be observed and to select the best reagent for the preparation of one of the two products in high yield. We also report the reaction with *N*-phenylbenzimidoyl fluoride, which was found not to produce any 3-fluoropyridine.

Results and Discussion

The products of the reactions of 16 *N*-phenylarenimidoyl chlorides with pyridine 1-oxide are summarized in Table I. It can be seen that, as anticipated, there appears to be no simple relationship between the electronic properties of the substituents and the yields of the 2-(acylanilino)-pyridine **2** and 3-chloropyridine (**1**). The highest yields of **2** are obtained by using either the *o*- or *p*-toluenimidoyl chloride. The highest yield of **1** is achieved with *N*-phenyl-*m*-nitrobenzimidoyl chloride; in this reaction, and contrary to what is reported with the *p*-nitrobenzimidoyl chloride,[2] a significant amount of 2-[*N*-(*m*-nitrobenzoyl)-anilino]pyridine is formed. Electron-withdrawing substituents in the imidoyl chloride should facilitate attack

Scheme I



by the *N*-oxide but hinder both the departure of chloride ion and nucleophilic attack by nitrogen onto the pyridine ring. It appears that these processes are delicately balanced with ortho and particularly para substituents in the aroyl portion.

According to the proposed mechanism (Scheme I)[3] for the formation of 3-chloropyridine (**1**) and the corresponding *N*-aroyl anilide (ArCONHPh) (**3**), these should be formed simultaneously and, therefore, in equal yields. Table I indicates that **3** is invariably formed in higher yield than **1**. Consequently, there must be an additional pathway to **3**. By analogy with side-chain acylaminations,[4] we propose that homolysis of **4** may be taking place to give Cl· and ArCONPh. The latter can abstract hydrogen from the solvent or from another substrate or react with Cl· to give ArCON(Cl)Ph which hydrolyzes to **3** on workup. The fate of the pyridine fragment has not been determined. In support of an origin of a least some of **3** from **4** is the fact that if a strong external base is added (e.g., Et_3N or DBU), no **1** or **3** is formed from pyridine 1-oxide and *N*-phenylbenzimidoyl chloride, and the yield of **2** increases appreciably.[5] In addition, the original adduct may also undergo homolysis (for a somewhat related homolysis, see ref 5) to give ArCONPh and a pyridinyl radical, the latter eventually leading to the tars invariably observed. Similarly, two pathways can lead to **2**: base-catalyzed proton abstraction and ring opening of the 2,3-dihydropyridine derivative (path b, Scheme 1) or elimination of HCl from **4** (path c, Scheme I).

To determine whether or not 3-fluoropyridine could be prepared in this way, we studied the reaction of pyridine 1-oxides with *N*-phenylbenzimidoyl fluoride.[6] Pyridine 1-oxide gave 2-(*N*-benzoylanilino)pyridine (**2**, Ar = Ph, 40%), benzanilide (45%), and pyridine 1-oxide hydrofluoride (41%), but no 3-fluoropyridine. 3-Picoline 1-oxide

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(2) Abramovitch, R. A.; Tomasik, P. *J. Heterocycl. Chem.* **1975**, *12*, 501.
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(4) Abramovitch, R. A.; Abramovitch, D. A.; Tomasik, P. *J. Chem. Soc., Chem. Commun.* **1979**, 956.
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Table I. Yields of Products from Pyridine 1-Oxide and Substituted *N*-Phenylarenimidoyl Chlorides

substituent in benzimidoyl	% yield product: 2-C_5H_4(Ph)-COAr 1	2	3[b]	properties of new 2-(*N*-aroylanilino)pyridines: mp, °C	calcd C	calcd H	calcd N	found C	found H	found N
H[a]	28.1	57.2	36.8							
2-CH_3	17.9	58.6	39.3	117–118	79.15	5.59	9.71	79.03	5.56	9.55
3-CH_3	21.6	51.4	45.9	122	79.15	5.59	9.71	79.16	5.54	9.46
4-CH_3[c]	1.7	58.8	ND							
2,4-$(CH_3)_2$	9.8	51.5	44.8	96	79.44	6.00	9.26	79.49	6.10	9.43
3,5-$(CH_3)_2$	24.2	53.6	45.3	118	79.44	6.00	9.26	79.58	5.93	9.02
2-OCH_3	12.4	26.0	41.8	109–111	74.98	5.29	9.20	74.93	5.34	8.97
3-OCH_3	31.3	46.9	46.5	87	74.98	5.29	9.20	74.87	5.33	9.04
4-OCH_3[c]	14.7	52.5	ND							
2,4-$(OMe)_2$	10.4	45.5	54.0	130–131	71.86	5.36	8.35	71.39	5.25	8.43
3,5-$(OMe)_2$	28.8	43.7	50.9	124–125	71.86	5.36	8.35	71.95	5.49	8.28
2-Cl	29.1	46.2	48.4	145	70.02	4.24	9.07	69.41	4.52	8.88
3-Cl	32.3	45.3	48.7	120–121	70.02	4.24	9.07	69.70	4.59	8.97
2,4-Cl_2	30.5	39.5	54.9	159–160	63.36	3.53	8.16	62.86	3.61	7.93
3,4-Cl_2	22.6	48.9	39.5	95	63.36	3.53	8.16	63.48	3.60	8.23
2-NO_2	29.8	30.7	66.0	143–145	67.71	4.07	13.16	67.49	3.95	13.23
3-NO_2	41.3	30.1	62.7	114	67.71	4.07	13.16	67.49	4.00	13.33
2,4-$(NO_2)_2$	19.4	0	85.3							
3,5-$(NO_2)_2$	3.7	0	89.8							

[a] Reference 1. [b] ND = not determined. [c] Reference 2.

reacted similarly to give a mixture of 2- and 6-(*N*-benzoylanilino)-3-methylpyridine (isomer ratio roughly estimated to be 1:40) in 35% overall yield, together with benzanilide (25%). The ratio of isomers is similar to that obtained from the corresponding reaction with the imidoyl chloride (ca. 1:36).[7] Thus, either fluoride ion does not attack the intermediate complex (F^- is a harder anion than Cl^-) or it is eliminated more readily (corresponding to pathway c, Scheme I) than is benzanilide anion (path a).

Experimental Section

Aroyl Anilides. These were prepared Schotten–Baumann reactions and had the melting points described in the literature. 3,5-Dimethylbenzanilide, mp 140 °C. Anal. Calcd for $C_{15}H_{13}NO$: N, 6.28. Found: N, 6.38. 2,4-Dichlorobenzanilide, mp 152 °C. Anal. Calcd for $C_{13}H_9Cl_2NO$: N, 5.26. Found: N, 5.50. 3,4-Dichlorobenzanilide, mp 138 °C. Anal. Calcd for $C_{13}H_9Cl_2NO$: N, 5.26. Found: N, 5.33.

***N*-Phenylarenimidoyl Chlorides.** These were prepared from the anilides either with neat thionyl chloride or with PCl_5 in boiling *n*-hexane. They were purified by distillation or by recrystallization from *n*-hexane. *N*-Phenyl-2,4-dimethoxybenzimidoyl chloride was unstable and could not be purified. The crude material was used in the reaction with pyridine 1-oxide. *N*-Phenyl-*o*-nitrobenzimidoyl chloride was a brown oil which did not crystallize and exploded on heating. It was used unpurified in the reaction with pyridine 1-oxide.

***N*-Phenylarenimidoyl Fluorides.** *N*-Phenylbenzimidoyl chloride (0.05 mol), dry potassium fluoride (0.1 mol), and dibenzo-18-crown-6 (0.0012 mol) in benzene (20 mL) were stirred at 40–45 °C for 6 days. The solution was decanted from the precipitated solid, the latter was washed with benzene, the combined filtrates were evaporated, and the residue was distilled to give the imidoyl fluoride: 51%; bp 128–131 °C (4 mm); IR (film) 1690 cm^{-1} (C=N); NMR (ethylene chloride) δ 8.08–7.87 (m, 2 H), 7.56–7.06 (m, 8 H); mass spectrum, *m/e* (relative intensity) 199 (100) ($M^{+\cdot}$), 180. Anal. Calcd for $C_{13}H_{10}FN$: C, 78.39; H, 5.02; N, 7.03; F, 9.55. Found: C, 78.44; H, 5.05; N, 7.12; F, 9.80.

N-Phenyl-*p*-methoxybenzimidoyl fluoride was prepared similarly (stirring for 3–4 days until the imidoyl chloride C=N band at 1660 cm^{-1} disappeared): 70%; bp 180–186 °C (7 mm); mp 26–28 °C; IR (film) 1695 cm^{-1} (C=N); NMR (CCl_4) δ 8.27–8.10 (d, 2 H), 7.58–7.03 (m, 7 H), 4.10 (s, 3 H, CH_3). Anal. Calcd for $C_{14}H_{12}FNO$: C, 73.36; H, 5.24; N, 6.11; F, 8.30. Found: C, 73.50; H, 5.36; N, 6.21; F, 8.49.

N-Phenyl-*p*-nitrobenzimidoyl fluoride was prepared in the same way (except that only 50% of the metathesis had taken place after 3 months) but could not be obtained analytically pure: IR (CCl_4) 1700 (C=N), 1525, 1350 cm^{-1} (NO_2).

General Procedure for Acylaminations. Freshly distilled pyridine 1-oxide (1.9 g, 0.02 mol) was added to the imidoyl chloride (0.01 mol) in dry ethylene chloride (20 mL). The solution was boiled under reflux for 24 h ($CaCl_2$ guard tube). 2-Bromopyridine (0.20 g, internal standard) was added to the cooled mixture which was then filtered from precipitated pyridine 1-oxide hydrochloride. The solid was washed with ethylene chloride, the combined filtrates were collected in a 50-mL volumetric flask, and the volume was made up to the mark with ethylene chloride. Quantitative analysis for 3-chloropyridine was carried out by gas chromatography on a 2.5 m × 3 mm column packed with 15% polyethylene glycol adipate on Chromosorb WAW at 110 °C with a H_2 carrier gas flow rate of 15 mL/min. 3-Chloropyridine had a retention time of 15 min and 2-bromopyridine one of 37 min under these conditions.

Following GLC analysis the solvent was evaporated, and the residue was chromatographed on a column of silica gel (Merck, 70–230 mesh ASTM) by using benzene and then benzene–ether (1:1) as the eluants. The products were purified by recrystallization from either methanol or aqueous methanol and compared with authentic samples.

Authentic samples of the 2-(*N*-aroylanilino)pyridines were prepared from 2-anilinopyridine and the aroyl chloride in pyridine. The known ones had the correct literature melting points. The melting points and microanalytical data for new derivatives are given in Table I.

Reaction of *N*-Phenylbenzimidoyl Fluoride with Pyridine 1-Oxide. Freshly distilled pyridine 1-oxide (0.02 mol) and *N*-phenylbenzimidoyl fluoride (0.01 mol) in ethylene chloride (40 mL) were boiled under reflux for 12 h. When the solution was cooled, pyridine 1-oxide hydrofluoride (0.051 g, 41%; mp 125–128 °C) separated and was filtered off. It decolorized a solution of ferric rhodanide.[8] The filtrate was analyzed by GLC (same conditions as used for 3-chloropyridine), but no 3-fluoropyridine was detected. Authentic 3-fluoropyridine has a retention time of 5 min under these conditions. The products were resolved on a Sephadex LH 20 column that was developed with ethylene chloride to give benzanilide (0.887 g, 45%; mp 161 °C) and 2-(*N*-benzoylanilino)pyridine (1.2 g, 40%; mp 167–169 °C) identical with an authentic sample.[1]

Reaction of *N*-Phenylbenzimidoyl Fluoride with 3-Picoline 1-Oxide. Freshly distilled 3-picoline 1-oxide (0.02 mol)

(7) Abramovitch, R. A.; Rogers, R. B. *J. Org. Chem.* **1972**, *39*, 1802.

(8) Cotton, F. A.; Wilkinson, G. "Basic Inorganic Chemistry"; Wiley: New York, 1979. Russian translation: Izdat. Mir.: Moscow, 1979, p 472.

and *N*-phenylbenzimidoyl fluoride (0.01 mol) were boiled in ethylene chloride as described for pyridine 1-oxide. 3-Picoline 1-oxide hydrofluoride separated (identified by its giving a positive color test for F_3^-[8] and by its giving 3-picoline 1-oxide on treatment with alkali). Again no ring-fluorinated product was detected by GLC. Chromatography on Sephadex LH 20 as before gave a mixture of 2- and 6-(*N*-benzoylanilino)-3-picoline [1.001 g (35%). Anal. Calcd for $C_{19}H_{16}N_2O$: N, 9.59. Found: N, 9.72] and benzanilide (0.493 g, 25%). The mixture of isomers was resolved by TLC on silica gel with benzene/ethanol (5:1 v/v) as the developer. The products were identical with authentic samples.[7] By use of a densitometer to scan the TLC plates, the 2,3-/2,5-isomer ratio was found to be approximately 1:40 (±15%).

Acknowledgment. This work was supported by grants from the DHEW (NIH GM 25242) to R.A.A. and from the National Science Foundation/Polish Fundusz Marii Sklodowskiej Curie (Grant No. OIP-75-020490 to R.A.A. and P.T.) for which we are grateful.

Registry No. 1, 626-60-8; 2 (Ar = Ph), 20107-78-2; 2 (Ar = 2-$CH_3C_6H_4$), 87281-82-1; 2 (Ar = 3-$CH_3C_6H_4$), 87281-83-2; 2 (Ar = 4-$CH_3C_6H_4$), 56969-75-6; 2 (Ar = 2,4-$(CH_3)_2C_6H_3$), 87281-84-3; 2 (Ar = 3,5-$(CH_3)_2C_6H_3$), 87281-85-4; 2 (Ar = 2-$OCH_3C_6H_4$), 87319-90-2; 2 (Ar = 3-$OCH_3C_6H_4$), 87281-86-5; 2 (Ar = 4-$OCH_3C_6H_4$), 56969-76-7; 2 (Ar = 2,4-$(OMe)_2C_6H_3$), 87308-16-5; 2 (Ar = 3,5-$(OMe)_2C_6H_3$), 87281-87-6; 2 (Ar = 2-ClC_6H_4), 87281-88-7; 2 (Ar = 3-ClC_6H_4), 87281-89-8; 2 (Ar = 2,4-$Cl_2C_6H_3$), 87281-90-1; 2 (Ar = 3,4-$Cl_2C_6H_3$), 87281-91-2; 2 (Ar = 2-$NO_2C_6H_4$), 87281-92-3; 2 (Ar = 3-$NO_2C_6H_4$), 87281-93-4; 3 (Ar = 3,4-$Cl_2C_6H_3$), 6043-42-1; 3 (Ar = Ph), 93-98-1; 3 (Ar = 2-$CH_3C_6H_4$), 7055-03-0; 3 (Ar = 3-$CH_3C_6H_4$), 23099-05-0; 3 (Ar = 4-$CH_3C_6H_4$), 6833-18-7; 3 (Ar = 2,4-$(CH_3)_2C_6H_3$), 5180-83-6; 3 (Ar = 2-$OCH_3C_6H_4$), 6833-21-2; 3 (Ar = 3-$OCH_3C_6H_4$), 6833-23-4; 3 (Ar = 4-$OCH_3C_6H_4$), 7465-88-5; 3 (Ar = 2,4-$(OMe)_2C_6H_3$), 1718-94-1; 3 (Ar = 3,5-$(OMe)_3C_6H_3$), 87282-04-0; 3 (Ar = 2-ClC_6H_4), 6833-13-2; 3 (Ar = 3-ClC_6H_4), 6832-92-4; 3 (Ar = 2-$NO_2C_6H_4$), 2385-27-5; 3 (Ar = 3-$NO_2C_6H_4$), 2243-73-4; 3 (Ar = 2,4-$(NO_2)_2C_6H_3$), 22978-56-9; 3 (Ar = 3,5-$(NO_2)_2C_6H_3$), 7461-51-0; 3 (Ar = 3,5-$Me_2C_6H_3$), 87282-03-9; 3 (Ar = 2,4-$Cl_2C_6H_3$), 6043-39-6; PhCCl=NPh, 4903-36-0; 2-$CH_3C_6H_4CCl$=NPh, 51619-51-3; 3-$CH_3C_6H_4CCl$=NPh, 87281-94-5; 4-$CH_3C_6H_4CCl$=NPh, 34916-13-7; 2,4-$(CH_3)_2C_6H_3CCl$=NPh, 87281-95-6; 3,5-$(CH_3)_2C_6H_3CCl$=NPh, 87281-96-7; 2-$OCH_3C_6H_4CCl$=NPh, 59386-97-9; 3-$OCH_3C_6H_4CCl$=NPh, 87281-97-8; 4-$OCH_3C_6H_4CCl$=NPh, 38968-72-8; 2,4-$(OMe)_2C_6H_3CCl$=NPh, 87281-98-9; 3,5-$(OMe)_2C_6H_3CCl$=NPh, 87281-99-0; 2-ClC_6H_4CCl=NPh, 59387-00-7; 3-ClC_6H_4CCl=NPh, 55832-04-7; 2,4-$Cl_2C_6H_3CCl$=NPh, 87282-00-6; 3,4-$Cl_2C_6H_3CCl$=NPh, 87282-01-7; 2-$NO_2C_6H_4CCl$=NPh, 57761-80-5; 3-$NO_2C_6H_4CCl$=NPh, 5509-90-0; 2,4-$(NO_2)_2C_6H_3CCl$=NPh, 87282-02-8; 3,5-$(NO_2)_2C_6H_3CCl$=NPh, 29955-47-3; pyridine oxide, 694-59-7.

An Intramolecular Bromonium to Thiiranium Ion Rearrangement

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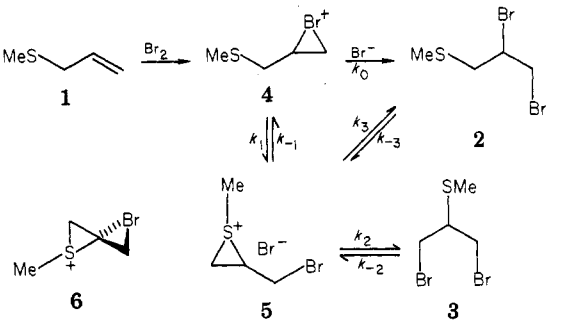
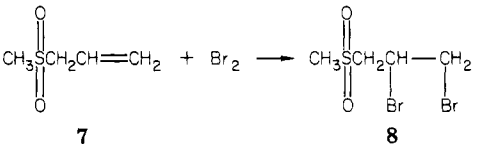
Received March 1, 1983

In connection with our synthetic program, we had occasion to carry out the bromination of methyl allyl sulfide (1) at 0 °C in CCl_4 solution with the intention of obtaining the unsymmetrical dibromide 2. It was immediately clear from the ^1H NMR spectrum of the product that 2 was not formed and that the symmetrical structure 3 best accommodated the spectroscopic evidence. A ^{13}C spectrum of the product showed only three peaks (Table I), while four peaks were expected for the unsymmetrical compound 2. When 3 was heated in refluxing $CDCl_3$, four new peaks appeared in the ^{13}C spectrum corresponding to structure 2. The equilibrium mixture (after 5 h) contained approximately 82% of 2 according to direct measurement of the methyl peak heights in the ^{13}C spectrum at room temperature.



The explanation for this behavior must lie in the tremendous ease with which the "mustard" type of structure can form thiiranium ions.[1] The fact that the symmetrical compound 3 is the kinetic product while the expected product 2 is the thermodynamic one requires that an intermediate thiiranium ion (5) be formed directly from the bromonium ion (4). To our knowledge there is no known case that invokes the rapid intramolecular conversion of a bromonium ion into a thiiranium ion. The transition state for such a rearrangement requires a spiro[2.2]pentane structure (6) which has the two three-membered rings in an orthogonal arrangement. This phenomenon (4 ⇌ 5) is, however, required to explain the formation of 3 in this case, because it is not energetically feasible that the thermodynamically more stable product 2 is intermediate in the formation of 3 from 4. Quantitatively speaking, $k_1 > k_0$ and $k_2 > k_3$, but since $K_3 > K_2$, k_{-2} must be considerably greater than k_{-3}. For this reason, at temperatures greater than 25 °C, we expect bromination of 1 to give a mixture of 2 and 3. The rapid opening of the thiirane ring at the primary carbon of 5 giving 3 is consistent with what is known[2] about these reactions in nonpolar solvents such as CCl_4.

Since the proposed mechanism requires participation of the sulfur atom, we investigated bromination of allyl methyl sulfone[3] (7) in which the sulfur atom should be unable to participate in the reaction. Four signals in both the ^1H and ^{13}C NMR spectra of the product indicated that the sole bromo compound formed at room temperature was the unsymmetrical dibromo sulfone 8 (Table II). The



7 8

spectra of 8 were unchanged after a week at ambient temperature, indicating no tendency to rearrange. This result strengthens the proposed hypothesis that a bro-

(1) (a) Streitweiser, A., Jr. "Solvolytic Displacement Reactions"; McGraw-Hill: New York, 1962; pp 16–18, 108–110. (b) Gundermann, K.-D. *Angew. Chem.* **1963**, *75*, 1194. (c) Capon, B. *Q. Rev.* **1964**, *18*, 45. (d) Ohishi, J.; Ikegami, S. *Chem. Pharm. Bull.* **1978**, *26*, 3211. (e) Sammes, P. G. *Chem. Rev.* **1976**, *76*, 115–117.

(2) See Bolster, J.; Kellog, R. M. *J. Chem. Soc., Chem. Commun.* **1978**, 630 and references therein.

(3) Attempts to use methyl allyl *sulfoxide* led to mixtures containing 2 and 3 formed, apparently, from 1 produced by bromine reduction (see Aida, T.; Furukawa, N.; Oae, S. *Tetrahedron Lett.* **1973**, 3853) of the starting sulfoxide.

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