Table I. Reaction of *p*-Chloronitrobenzene (0.03 M) with Potassium Alkoxides (0.24 M)[a]

ROH	atmosphere	*t*, h[b]	% ArOR[c]	% ArOH[c]	% azoxy[c]	% azo[c]	% amine[c]
EtOH	air	20	>95				
2-PrOH	air	20	9	5	33	23	28
t-BuOH	air	300		15	13	31	
2-PrOH	helium	1.3			65		13
2-PrOH	oxygen	45	40	12			

[a] At 75 °C, under the atmosphere described. [b] This is the time required for the disappearance of *p*-chloronitrobenzene. [c] The reaction products are the following: ArOR, *p*-nitrophenyl alkyl ether, where the alkyl group is ethyl or 2-propyl; ArOH, *p*-nitrophenol; azoxy, *p,p'*-dichloroazoxybenzene; azo, *p,p'*-dichloroazobenzene; amine, *p*-chloroaniline. The yields reported have been evaluated by gas chromatography.

whose constant has been shown to be greater than 10^{8}.[10]

Direct reaction of potassium alkoxide with *p*-chloronitrobenzene yields the aryl ether through the normal S_NAr mechanism (eq 5). In principle, the phenoxide could be formed via a base-catalyzed elimination from the aryl ether. Under our conditions ([*i*-PrOK] = 0.24 M, 75 °C, under oxygen), this reaction is, however, slower (only 5% of the starting ether reacted after 50 h) than the one leading to the phenol from chloronitrobenzene (12% formed after 50 h). Also, addition of water does not appreciably change the relative yields of ether and phenol.

The results presented call for caution in generalizing the behavior of nitro aromatics toward alkoxides and for a detailed reexamination of these reactions, now in progress in our laboratory.

Experimental Section

Materials and Solvents. Ethanol, 2-propanol, and *tert*-butyl alcohol were purified by distillation from magnesium turnings. *p*-Chloronitrobenzene, *p*-chloroaniline, and *p*-nitrophenol were commercial products recrystallized until pure by GLC. *p,p'*-Dichloroazoxybenzene, mp 154–155 °C,[11] *p,p'*-dichloroazobenzene, mp 186–187 °C,[12] *p*-chloronitrobenzene, mp 85–87 °C,[13] *p*-nitrophenyl ethyl ether, mp 59–60 °C,[14] *p*-nitrophenyl 2-propyl ether, mp 32–33 °C,[14] and *p*-nitrophenyl *tert*-butyl ether, bp 123–125 °C (0.5 mmHg),[15] were prepared according to published procedures.

General Reaction Procedures. Typical procedures for the reactions under helium or under oxygen were as follows:

Under Helium. Solutions of *p*-chloronitrobenzene (0.157 g) and tetracosane (0.053 g) in 2-propanol (20 mL) and of potassium 2-propoxide in 2-propanol (10 mL of a 0.72 M solution), in the side arms of an inverted Y-shaped tube, were carefully and repeatedly deaerated under helium by using the thaw–freeze procedure and thermostatted at 75 °C. At zero time the solutions were mixed by inverting the Y-tube. Aliquots were withdrawn at appropriate time intervals, diluted with a mixture of 95% ethanol and ethyl ether, quenched with solid CO_2, and analyzed by GLC and/or UV.

Under Oxygen. A solution of *p*-chloronitrobenzene (0.237 g) and tetracosane (0.075 g) in 2-propanol (25 mL) in a three-necked flask equipped with a reflux condenser, a gas inlet tube, and a rubber septum was deaerated by bubbling oxygen through for 15 min at 75 °C. A solution of potassium 2-propoxide in 2-propanol (25 mL of a 0.48 M solution) was injected at zero time and the reaction solution was kept in a thermostat at 75 °C under a continuous flow of oxygen. Aliquots withdrawn by a syringe at appropriate time intervals were analyzed by GLC (*p*-chloronitrobenzene and *p*-nitrophenyl 2-propyl ether) and UV (*p*-nitrophenol).

Analytical Procedures. GLC analyses were performed on a Varian 3700 gas chromatograph coupled to a Varian CDS 111 Digital Integrator with a 150 cm × 2 mm 10% UCW 982 on 80/100 Chromosorb WAW DMCS column. Concentrations were determined by calibration curves with tetracosane as internal standard. UV analyses were made on appropriate aliquots (2 mL) of the reacting solutions diluted with 2-propanol and examined at 416 nm on a Cary 219 instrument for the amount of potassium *p*-nitrophenoxide (ϵ 2.37 × 10^4 in 2-propanol at 416 nm and 25 °C).

Registry No. *p*-Chloronitrobenzene, 100-00-5; potassium ethoxide, 917-58-8; potassium isopropoxide, 6831-82-9; potassium *tert*-butoxide, 865-47-4; *p*-nitrophenyl ethyl ether, 100-29-8; *p*-nitrophenyl 2-propyl ether, 26455-31-2; *p*-nitrophenol, 100-02-7; *p,p'*-dichloroazoxybenzene, 614-26-6; *p,p'*-dichloroazobenzene, 1602-00-2; *p*-chloroaniline, 106-47-8.

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N-Nitroaziridines: Structure Confirmed[1a]

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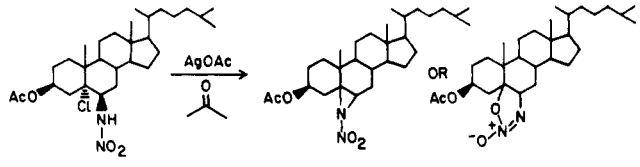
The first synthesis of *N*-nitroaziridine **2** was reported



1 **2** **3**

recently by Haire and Boswell.[2] The unique substitution of a nitro group on an aziridine nitrogen afforded a structure which was of interest both chemically and biologically. This class of compounds showed interesting thermal reactivity, reported earlier,[2] but none of the *N*-nitroaziridines tested have shown biological activity.

N-Nitrosoaziridines are known to decompose spontaneously at −15 °C.[3] Thus, it was surprising that the *N*-nitroaziridines appear to be quite stable at room temperature. In fact, rearrangement of **2** occurs at 180 °C. Support for structure **2** rested solely on spectroscopic and solvolytic data which were consistent but not conclusive for the *N*-nitroaziridine. The oxadiazole oxide structure **3** was suggested as an alternative to fit the experimental results.[4]

We now report on the X-ray crystal study which confirms the originally proposed structure **2**. The important bond distances and angles are given in Table I (Supple-

(1) (a) Contribution No. 2688. (b) Chevron Research, Ortho, Richmond, CA 94802.
(2) M. J. Haire and G. A. Boswell, *J. Org. Chem.*, **42**, 4251 (1977).
(3) (a) W. Rundel and E. Muller, *Chem. Ber.*, **96**, 2528 (1963); (b) R. D. Clark and G. K. Helmkamp, *J. Org. Chem.*, **29**, 1316 (1964).
(4) J. P. Freeman (University of Notre Dame), private communication.

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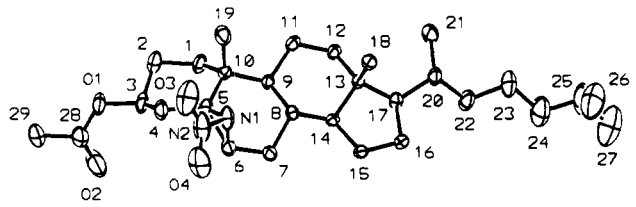

Figure 1. ORTEP drawing of 3β-acetoxy-5β,6β-*N*-nitroaziridinylcholestene.

mentary Material). The aziridine ring is asymmetric with one C–N bond being significantly longer than the other. The longer C–N bond is associated with the more sterically hindered C(5) atom. The two *N*-nitroaziridines reported earlier[2] were found to undergo different thermal rearrangements; the steroid-fused compound gave an epoxide on heating while the decalin-fused *N*-nitroaziridine gave an olefinic nitramine. This difference was thought to be due to steric interactions encountered by the aziridine ring. This study, however, shows no steric interactions either between the aziridine and acetoxy moieties or between the aziridine and the steroidal C ring. The reason for the divergent thermal reactivities remains obscure.

Experimental Section

Crystal Data: monoclinic, space group $P2_1$; at −98 °C a = 19.290 (3), b = 6.037 (2), c = 12.145 (2) Å, β = 92.33 (1)°, V = 1413 Å, Z = 2.

Intensity Data: Syntex P3 diffractometer, graphite monochromator, Mo Kα radiation, λ = 0.71069 Å, omega scans of 1.0°, 4° < 2θ <55°, 3547 reflections.

Structure Solution and Refinement. The structure was solved by direct methods (QTAN). Hydrogen-atom positions were calculated but not refined. The structure was refined by full-matrix, least-squares techniques, 2983 reflections with $I > 2\sigma(I)$, 315 variables, R = 0.061, R_w = 0.058. The largest peak in the final difference Fourier had a magnitude of 0.36 e Å^{-3} and was located near O(2). The mathematical and computational details may be found elsewhere.[5]

Registry No. 2, 63866-33-1.

Supplementary Material Available: Bond distances and angles and positional and thermal parameters of **2** (7 pages). Ordering information is given on any current masthead page.

(5) W. A. Nugent and R. L. Harlow, *Inorg. Chem.*, 8, 2030 (1979).

Reactions of α-Azido Sulfones with Bases

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In a previous series of publications,[1] we reported our investigations of the reactions of α-halo sulfones with nucleophiles. On the basis of this chemistry, we anticipated that sulfones possessing a pseudohalogen atom in the α-position would exhibit useful and interesting properties. Herein, we report the reactions of α-azido sulfones with bases, reactions which take a course much different from that observed with α-halo sulfones.

The α-azido sulfones were prepared as shown in eq 1. The intermediate α-azido sulfides could be isolated, but

$$\underset{\mathbf{1}}{\mathrm{PhSCH_2R}} \xrightarrow[2.\ NaN_3/Me_2SO\text{–}DMF]{1.\ SO_2Cl_2/CCl_4} \underset{\mathbf{2}}{\mathrm{PhSCH(N_3)R}} \xrightarrow{MCPBA} \underset{\mathbf{3}}{\mathrm{PhSO_2CH(N_3)R}} \quad (1)$$

it was often more convenient to oxidize the crude sulfides with *m*-chloroperoxybenzoic acid (MCPBA) to the more crystalline sulfones.

The syntheses of α-azidobenzyl phenyl sulfones (**3**, R = Ar) failed in those cases where the ring of the benzyl group possessed either a strong electron-donating group (e.g., *p*-methoxy) or a very strong electron-withdrawing group (e.g., *p*-nitro). Treatment of *p*-methoxybenzyl phenyl sulfide with sulfuryl chloride under a variety of conditions gave *p*-methoxybenzyl chloride, the result of carbon–sulfur bond cleavage. This type of halogenolysis reaction has been observed previously[2] with benzyl sulfides which contain electron-donating groups. *p*-Nitrobenzyl phenyl sulfide appeared to undergo α-chlorination with sulfuryl chloride smoothly to give α-chloro-*p*-nitrobenzyl phenyl sulfide (monitored by NMR spectroscopy). However, treatment of this α-chloro sulfide in the same manner as the other α-chlorobenzyl sulfides (sodium azide in Me_2SO–DMF) resulted in the formation of *p*-nitrobenzonitrile (eq 2). It was, in fact, this reaction which suggested

$$p\text{-}NO_2C_6H_4CH_2SPh \xrightarrow[2.\ NaN_3]{1.\ SO_2Cl_2} [p\text{-}NO_2C_6H_4CH(N_3)SPh] \xrightarrow{N_3^-} p\text{-}NO_2C_6H_4CN + PhSO_2^- + N_2 \quad (2)$$

to us that α-azido sulfones would react with bases to give nitriles (infra vide).[3]

The α-azidobenzyl phenyl sulfones (**3**, R = Ar) reacted with 0.25 M piperidine in 95% ethanol (reaction time 3–5 h at 55 °C) to give benzonitriles in 85–100% yield (by GLC analysis). Nitrogen gas also was evolved and liberated benzene sulfinate was trapped with methyl iodide to give methyl phenyl sulfone. Equation 3 outlines a likely

$$PhSO_2CH(N_3)Ar + B^- \rightarrow PhSO_2\bar{C}(N_3)Ar \xrightarrow{-N_2} PhSO_2C(Ar)\text{=}N^- \rightarrow ArCN + PhSO_2^- \quad (3)$$

mechanism for these reactions. Precedent for this reaction can be found in several isolated examples of the reactions of α-azido ketones with bases which yield α-imino ketones (or α-diketones after hydrolysis).[4]

Extention of this reaction to the synthesis of alkyl nitriles was generally unsuccessful. Since the α-azidoalkyl phenyl sulfones are significantly weaker carbon acids than the α-azidobenzyl phenyl sulfones, it was necessary to use stronger base systems. Both α-azidoisobutyl phenyl sulfone [**3**, R = $CH(CH_3)_2$] and α-azidoneopentyl phenyl sulfone [**3**, R = $C(CH_3)_3$] reacted with potassium *tert*-butoxide in THF at 25 °C and with sodium methoxide in methanol at 60 °C but gave no isolable nitriles. Control experiments showed that both isobutyronitrile and pivalonitrile do not survive under these reaction conditions. However, α-azido-β-phenethyl phenyl sulfone (**3**, R = CH_2Ph) reacted with sodium methoxide in methonol at 60 °C to give phenylacetonitrile, and α-azido-1-

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