contrast to **7**, a necessary degree of order for participation is achieved already in the ground state. Extended participation would therefore be favored since there is no requirement for the loss of many degrees of freedom in the transition state.

Having in mind that in biomimetic cyclization of **1** tricyclic products were isolated, and according to our kinetic measurements, it is possible that even concerted tricyclization is operative in reactions of some squalene derivatives in highly polar solvents.

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Registry No. 1, 7200-26-2; **3**, 131974-28-2; **3** alcohol, 14031-38-0; **3-*D***, 132017-39-1; **3-*D*** alcohol, 131974-32-8; **4**, 102736-14-1; **4** alcohol, 131974-31-7; **4-*D***, 131974-34-0; **4-*D*** alcohol, 131974-33-9; **5a**, 118599-19-2; **5b**, 132017-40-4; **6**, 131974-29-3; **6-*D***, 131974-35-1; **7**, 131974-30-6; **7-*D***, 131974-36-2; acetone, 67-64-1; acetone-d_6, 666-52-4.

Supplementary Material Available: IR and ^{13}C NMR spectra of the alcohols corresponding to **3**, **3**-D, and **4**, ^1H NMR spectra of the alcohols corresponding to **3**, **3**-D, **4**, and **4**-D, and mass spectra of the alcohols corresponding to **3**, **3**-D, and **4**-D (13 pages). Ordering information is given on any current masthead page.

N-Nitrosoaziridinium Ion Isomerization: Dihydrodiazete *N*-Oxides and Azoxyalkenes from Aziridine Nitrosation

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N-Nitrosoaziridines are unstable compounds which readily lose N_2O to give an alkene.[1] Some years ago we sought to determine whether *N*-nitrosoaziridinium ions produced from the nitrosation of 1-substituted aziridines would undergo a similar chelotropic loss of $[RNNO]^{+}$.[2] The nitrosation of *cis*-1-butyl-2,3-diphenylaziridine (**1**, R = nBu) in glacial HOAc at 60 °C gives among other products a compound whose structure was assigned as (*Z*)-1-(*N*-butylnitrosamino)-1,2-diphenylethene.[2] While this structure was consistent with an extensive body of spectroscopic data, its failure to give a positive *N*-nitroso test created uncertainty about its structural assignment. A recent X-ray crystallographic diffraction analysis showed this substance to be an α,β-unsaturated azoxy compound[3] (Figure 1). 1-Azoxyalkenes constitute a growing class of antibiotic agents,[4-7] and this reaction represents a new synthetic route to these compounds and a highly novel course for an amine nitrosation. We show here that the azoxyalkene **3** is produced by the electrocyclic ring opening of a novel dihydrodiazete *N*-oxide produced from the isomerization of a *N*-nitrosoaziridinium ion, and we discuss our experimental and theoretical probing of this process.

In order to shed light on the mechanism of azoxyalkene formation, we have undertaken a reinvestigation of the aziridine nitrosation and independently synthesized the nitrosenamine[8] by

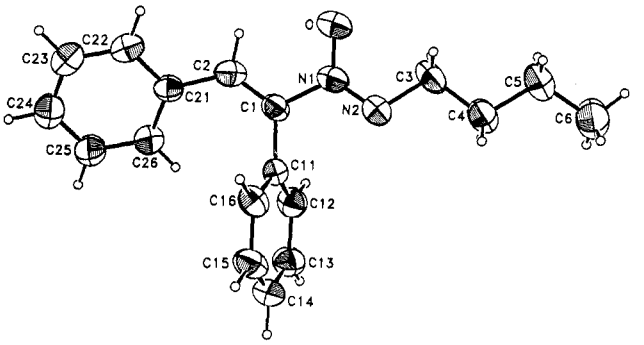


Figure 1. The X-ray crystal structure of the azoxyalkene **3**, R = nBu.

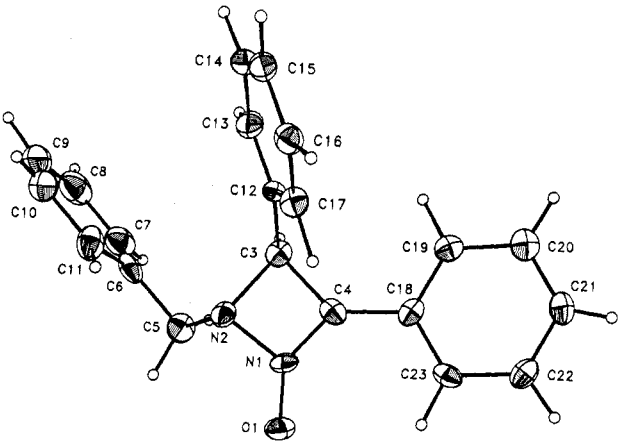
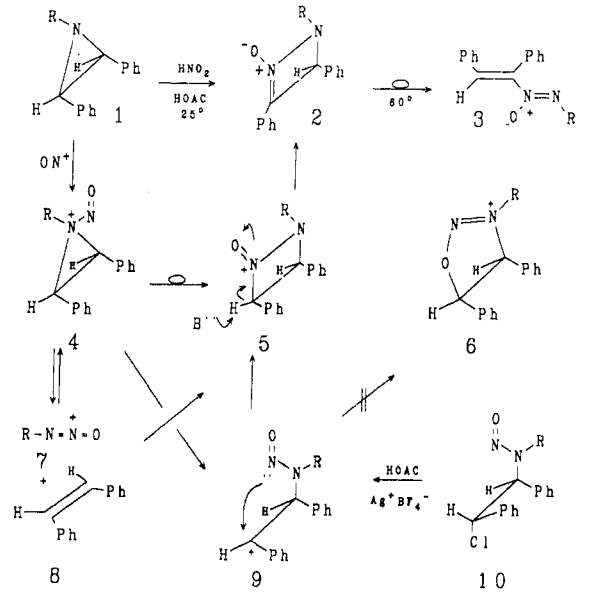


Figure 2. The X-ray crystal structure of the dihydrodiazete *N*-oxide **2**, R = Bn.

Scheme I



a modification of the procedure of Seebach and Enders.[9] HPLC analysis of the reaction mixture from the nitrosation (25 °C, HOAc) of *cis*-1-alkyl-2,3-diphenylaziridine (alkyl = butyl or benzyl) reveals, in addition to those products reported previously and the respective azoxyalkene, the generation of a major product whose GCMS characteristics (retention time and mass spectrum) are identical with those of the azoxyalkene, but whose ^1H NMR spectrum is significantly different.[8,10] The presence of a singlet at δ 4.7, the MS, and the origin of the substance suggest the

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(10) The vinyl proton of **3** appears at δ 7.85 while the ring C-H singlet of **2** occurs at δ 4.7.

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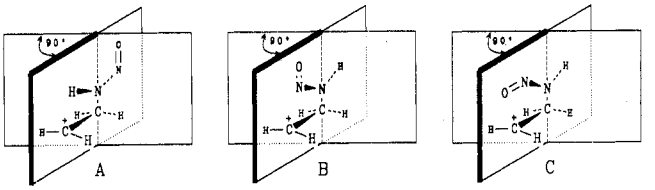
structure of the isomeric 1-alkyl-1,4-dihydro-3,4-diphenyl-1,2-diazete 2-oxide **2**, which was confirmed by X-ray analysis of the benzyl analogue[3] (Figure 2).

We believe the two dihydrodiazete *N*-oxides to be the first examples of these types of compounds. They are hydrazone *N*-oxides which are likewise unknown. The dihydrodiazete *N*-oxides easily isomerize to the corresponding azoxyalkenes upon heating by a conrotatory electrocyclic ring opening, and the latter compounds are coproducts of the nitrosation if care is not taken to control the temperature. Control experiments showed that the nitrosenamine cannot be a major product or intermediate in the aziridine nitrosation.

The dihydrodiazete *N*-oxide is perceived to arise from an isomerization of the *N*-nitrosoaziridinium ion by one of the pathways shown in Scheme I. At least two chemically novel features attend this process. Nitrosamines exhibit little chemistry emanating from reactions of the nitroso N unshared pair. Secondly, isomerization to a four-membered ring is surprising since, a priori, a pathway to the five-membered 3-alkyl-1,2,3-oxadiazolinium ion is open! We have demonstrated that protonation of the α-nitrosamino aldehyde carbonyl results in cyclization to the oxadiazolinium cation,[11] and Michejda and co-workers have shown that solvolysis of *N*-methyl-2-(tosyloxy)ethylnitrosamine occurs with neighboring-group participation to generate this heterocyclic cation.[12]

Ring opening of the *N*-nitrosoaziridinium ion **4** to the benzylic carbocation **9** followed by attack of the N lone pair produces **5**, which loses H^+ to give the dihydrodiazete *N*-oxide **2**. Alternatively, **5** can either result from the direct isomerization of **4** or involve a chelotropic ring opening (**4** → **7** + **8**) followed by a $2\pi_s + 2\pi_a$ cycloaddition. The latter pathways are reminiscent of proposals made by Greene to explain phenyltriazolinedione–alkene chemistry, which is proposed to proceed through an aziridinium imide.[13] The various mechanistic pathways shown in Scheme I have been probed by both experiment and theory. Treatment of the *threo*-β-chloro nitrosamine **10** with $AgBF_4$/HOAc gives the same product profile (HPLC and GCMS) as does the aziridine nitrosation although the yield of **3** exceeds that of **2** and more of the presumed carbocation intermediate **9** is captured by solvent.[8] Ab initio calculations[14] of the carbocation rotamers A–C (models for **9**) and the related cations **4**–**6**, where all carbon substituents have been replaced by H, show the carbocations A–C to be "unstable"[15] and to spontaneously close to **4**, **5**, or **6** depending upon the stereochemical arrangement of the RNNO group. Carbocation A undergoes a 90° C–N bond rotation and regenerates **4**, while B closes to **5**. The same carbocation with the opposite R, N=O arrangement C collapses to **6**. While N–N bond rotation in the carbocations A–C (**9**) is likely to be significantly restricted, this should not be the case in the *N*-nitrosoaziridinium ion **4**. The 180° N–N rotamer (anti) of that shown for **4** (syn) in Scheme I is only 0.6 kcal/mol more stable than the syn form. Replacement of the H atoms of the theoretical model with phenyl substituents (at the carbons) is likely to result in a distinct energetic preference for the syn conformer which is predisposed to give **5**.

The relative energies (MP2/6-31G*//RHF/3-21G) calculated for **4**, **5**, and **6** are 23.7, 14.0, and 0 kcal/mol, respectively, while the relative energy of the isolated **7** and **8** combined is 46.8 kcal/mol. Interaction between **7** and **8** is likely to lower the energy of the ensemble, but theory predicts the production of **5** by this route to be disfavored compared to the **4** → **5** isomerization for kinetic reasons. The chemical properties of **6** in our system are



unknown, and we cannot rule out its formation at this time. If it is formed it must be a minor product since the combined yield of **2** and **3** is 62%. This suggests that **4** represents the preferred conformation of this *N*-nitrosoaziridinium ion, and the course of the rearrangement to the less stable four-membered ring is determined by this stereochemical arrangement through either the carbocation **B** (**9**) or a transition state like it.

In addition to the novel chemical features of this work and the promise of new synthetic routes to unusual compounds, this research has relevance in the area of nitrosamine carcinogenesis.[11,12] Amine nitrosation usually produces nitrosamines, 90% of which are animal carcinogens. This pathway gives other compounds as the major products and suggests means of subverting nitrosamine formation. Carbocations such as **9** have been suggested as intermediates in the carcinogenic activation of β-hydroxy nitrosamines.[12] The chemistry shown here introduces alternative pathways and merits further investigation from numerous perspectives.

Acknowledgment. The support of this research by Grant No. R37 CA 26914 from the National Cancer Institute, NIH, DHHS, is gratefully acknowledged.

Supplementary Material Available: Experimental summaries, including spectroscopic data for the synthesis of the nitrosenamine, the aziridine nitrosation, and the $AgBF_4$ reaction, details of the calculations, and tables of positional parameters, thermal parameters, interatomic distances, and interatomic angles for **2** and **3** (12 pages); listings of observed and calculated structure factors for **2** and **3** (13 pages). Ordering information is given on any current masthead page.

Facile Li/HMPA-Promoted Polymerization Method for the Synthesis of Soluble Poly(phenylenes)

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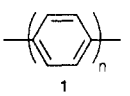
Poly(*p*-phenylene) (PPP) (**1**) has attracted much interest since it can act as an excellent organic conductor upon doping.[2] The conductivity of doped PPP has reached beyond the semiconducting



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and into the conducting region with values of 500 Ω^{-1} cm^{-1} being reported for the pressed pellets (films could not be formed due to the insolubility). There have been numerous syntheses of PPP; however, in nearly all cases, the materials are insoluble and intractable in organic solvents.[3-10] The most widely used methods

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(14) See supplementary material for details of ab initio calculations.
(15) While the calculations do not reveal an independent existence for A–C, the phenyl substituents of **9** could produce sufficient stabilization to allow its existence on the reaction coordinate.

(1) Recipient of an Office of Naval Research Young Investigator Award (1989-1992).
(2) For several reviews on the topic, see: (a) Kovacic, P.; Jones, M. B. *Chem. Rev.* **1987**, *87*, 357. (b) Noren, G. K.; Stille, J. K. *Macromol. Rev.* **1971**, *5*, 385. (c) Tourillion, G. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Dekker: New York, 1986. (d) Elsenbaumer, R. L.; Schacklette, L. W., in ref 2c. (e) Baughman, R. H.; Bredas, J. L.; Chance, R. R.; Elsenbaumer, R. L.; Shacklette, L. W. *Chem. Rev.* **1982**, *82*, 209.
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