four 30-mL portions of dichloromethane. The combined extracts were dried (Na_2SO_4) and evaporated to give a colorless semisolid. The NMR spectrum indicated it to be a polymer similar to the one obtained above by the selenide oxidation route for **2** (R = R′ = CH_3).

Michael Addition of Sulfinate and Mercaptide Ions to Alkyl α-(Alkylsulfonyl)acrylates. The following represent typical preparative procedures.

***tert*-Butyl 2-(*tert*-Butylsulfonyl)-3-(methylsulfonyl)-propionate.** A solution of sodium methylsulfinate (0.7 g, 14.5 mmol) in ethyl alcohol (10 mL) buffered with acetic acid (1 mL) was added dropwise to *tert*-butyl α-(*tert*-butylsulfonyl)acrylate (1.3 g, 5.2 mmol) in ethyl alcohol (10 mL) at 25 °C, and the mixture was stirred for 20 h. Water (30 mL) was added, and the mixture was extracted with two 25-mL portions of chloroform. The combined organic layers were washed with saturated aqueous $NaHCO_3$ (25 mL), dried over $MgSO_4$, and concentrated to give a viscous oil: 1.5 g (90%); ^1H NMR ($CDCl_3$) τ 8.62 (9 H, s, CO_2-*t*-Bu), 8.51 (9 H, s, SO_2-*t*-Bu), 7.18 (3 H, s, SO_2CH_3), 6.64–6.00 (1 H, m, CH), 5.61–5.46 (2 H, q, CH_2).

***tert*-Butyl 2-(*tert*-Butylsulfonyl)-3-(*tert*-butylthio)-propionate.** To a solution of *tert*-butyl α-(*tert*-butylsulfonyl)-acrylate (1.3 g, 5.2 mmol) in methylene chloride (20 mL) were added *tert*-butyl mercaptan (1.3 g, 14.5 mmol) and a trace of potassium *tert*-butoxide (~10 mg), and the mixture was stirred for 20 h. Workup as above furnished the desired adduct as a colorless oil which crystallized to give 1.6 g (95%) of white needles: mp 68.5–69.5 °C; ^1H NMR ($CDCl_3$) τ 8.79 (9 H, s, S-*t*-Bu), 8.67 (9 H, s, CO_2-*t*-Bu), 8.41 (9 H, s, SO_2-*t*-Bu), 7.68–6.73 (1 H, m, CH), 6.21–6.02 (2 H, q, CH_2). Oxidation of the sulfide to the corresponding sulfone proceeded quantitatively with 2.5 equiv of *m*-chloroperbenzoic acid in methylene chloride at 0 °C for 24 h.

Registry No. **1** (R = R′ = CH_3), 62020-09-1; **1** (R = *t*-Bu, R′ = CH_3), 63864-29-9; **2** (R = R′ = CH_3) monomer, 73017-61-5; **2** (R = R′ = CH_3) polymer, 73017-62-6; **2** (R = CH_3, R′ = *t*-Bu) monomer, 73017-59-1; **2** (R = CH_3, R′ = *t*-Bu) polymer, 73017-60-4; **2** (R = *t*-Bu, R′ = CH_3) monomer, 73017-57-9; **2** (R = *t*-Bu, R′ = CH_3) polymer, 73017-58-0; **2** (R = R′ = *t*-Bu), 73017-80-8; **3** (R = R′ = CH_3), 73017-81-9; **3** (R = CH_3, R′ = C_2H_5), 73017-82-0; **3** (R = CH_3, R′ = *t*-Bu), 73017-83-1; **3** (R = *t*-Bu, R′ = CH_3), 73017-84-2; **3** (R = R′ = *t*-Bu), 73017-85-3; **4** (R = CH_3), 20277-69-4; **4** (R = C_6H_5), 873-55-2; **4** (R = *p*-ClC_6H_4), 14752-66-0; **4** (R = *t*-Bu), 69152-35-8; **5** (R′ = CH_3), 17639-93-9; **5** (R′ = C_2H_5), 535-13-7; **5** (R′ = *t*-Bu), 40058-88-6; **7** (R = R′ = CH_3), 73017-86-4; **7** (R = CH_3, R′ = C_2H_5), 73017-63-7; **7** (R = CH_3, R′ = *t*-Bu), 73017-64-8; **7** (R = *t*-Bu, R′ = CH_3), 73017-65-9; **7** (R = R′ = *t*-Bu), 73017-66-0; **9**, 3708-04-1; **10**, 65020-08-8; methyl chloroacetate, 96-34-4; methyl α-(*tert*-butylthio)acetate, 49827-06-7; *tert*-butyl α-(*tert*-butylthio)propionate, 64041-97-0; phenylselenyl chloride, 5707-04-0; methyl chloroformate, 79-22-1; *tert*-butyl 2-(*tert*-butylsulfonyl)-3-(methylsulfonyl)propionate, 73017-67-1; *tert*-butyl 2-(*tert*-butylsulfonyl)-3-(*tert*-butylthio)-propionate, 73017-68-2; *tert*-butyl mercaptan, 75-66-1; *p*-chlorobenzenethiol, 106-54-7; *tert*-butyl 2-(*tert*-butylsulfonyl)-3-(phenylsulfonyl)propionate, 73017-69-3; methyl 2-(*tert*-butylsulfonyl)-3-(*p*-chlorobenzylthio)propionate, 73017-70-6; methyl 2-(*tert*-butylsulfonyl)-3-(*p*-chlorobenzenesulfonyl)propionate, 73017-71-7; *tert*-butyl 2-(*tert*-butylsulfonyl)-3-(*tert*-butylsulfonyl)propionate, 73017-72-8.

Reactions of (*E*)-2-*tert*-Butyl-3-phenyloxaziridine with Lithium Amide Bases

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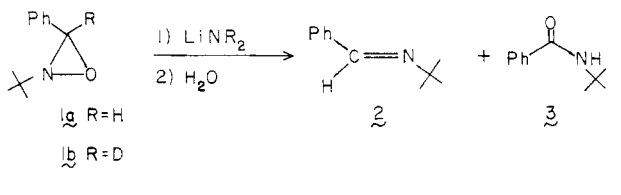
The reactions of (*E*)-2-*tert*-butyl-3-phenyloxaziridine (**1a**) with lithium amide bases in tetrahydrofuran have been studied. In competing reactions, **1a** is reduced to *N*-*tert*-butylbenzaldimine (**2**) and isomerized to *N*-*tert*-butylbenzamide (**3**). The former reaction proceeds through an intermediate which accumulates and slowly decomposes to **2**; the reaction apparently occurs via an initial electron transfer from the base to the oxaziridine. The latter reaction occurs by simultaneous deprotonation and ring opening of the oxaziridine to give the anion of **3**.

The reactions of oxaziridines with strong bases have not been studied extensively, but limited studies have been reported which suggest that various reaction pathways exist. Deprotonation at an α position to the ring carbon or nitrogen and concomitant ring opening occurs when oxaziridines are treated with alkoxide or hydroxide.[1,2] However, when no protons are available at these positions [e.g., (*E*)-2-*tert*-butyl-3-phenyloxaziridine (**1a**)], the oxaziridine is stable in the presence of alkoxides.[1] Rubottom reported that 2-*tert*-butyl-3-(*p*-nitrophenyl)oxaziridine reacted with sodium hydride in hexamethylphosphoramide to give *N*-*tert*-butyl-*p*-nitrobenzamide,[3] and Watt and Dinizo have found that a pyridine-substituted oxaziridine containing a proton on the carbon adjacent to the ring nitrogen produced the corresponding amide in 0–68% yield in reactions with various bases.[2] Recently, Davis et al.[4] have reported that oxaziridines react with lithium and Grignard reagents in ether to give coupling and/or hydroxylation products of the organometallic reagent; they postulated that mechanisms involving electron transfer and initial nucleophilic attack at oxygen occurred, respectively. We report here the results of our studies of the reaction of **1a** with lithium amide bases in tetrahydrofuran (THF); under these conditions the oxaziridine is both reduced to *N*-*tert*-butylbenzaldimine (**2**) and isomerized to *N*-*tert*-butylbenzamide (**3**) in competitive reactions.

Results and Discussion

We have investigated the reactions of **1a** with lithium diethylamide (LDEA), lithium diisopropylamide (LDA), and lithium 2,2,6,6-tetramethylpiperidide (LTMP) in THF under nitrogen. At 0 °C in the presence of excess base, **1a** was converted after protonation of the reaction mixture to imine **2** and amide **3**. Although imine **2** was isolated



1a R=H
1b R=D
2
3

(1) W. D. Emmons, *J. Am. Chem. Soc.*, **79**, 5739 (1957).
(2) S. E. Dinizo and D. S. Watt, *J. Am. Chem. Soc.*, **97**, 6900 (1975).
(3) G. M. Rubottom, *Tetrahedron Lett.*, 3887 (1969).
(4) F. A. Davis, P. A. Mancinelli, K. Balasubramanian, and U. K. Nadir, *J. Am. Chem. Soc.*, **101**, 1044 (1979).

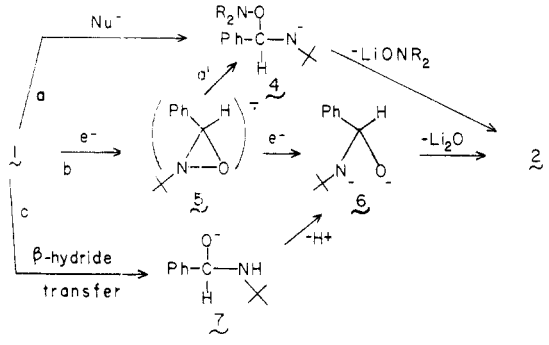
0022-3263/80/1945-1489$01.00/0

Table I. Product Yields from the Reactions of Oxaziridine 1a with Excess Lithium Amide Bases at 0 °C

base	concn, M[a]	% yield[b] 2	3
LDEA	0.05	73.4 ± 0.6[c]	23.3 ± 1.2
	0.10	75.2 ± 1.4	21.8 ± 0.3
	0.20	77.5 ± 0.8	19.7 ± 0.2
LDA	0.05	58.1 ± 0.4	38.9 ± 0.2
	0.10	64.0 ± 1.2	33.2 ± 0.5
	0.20	72.8 ± 0.7	24.1 ± 1.0
LTMP	0.05	88 ± 1	13.6 ± 0.5
	0.10	89 ± 3	10 ± 2
	0.20	86 ± 6	11 ± 2

[a] ±10%. [b] Absolute yield; see Experimental Section. [c] Error limits represent the range of three GC determinations.

Scheme I



when the reaction was quenched with a slight excess of water, it was hydrolyzed to benzaldehyde when the reaction mixture was treated with aqueous hydrochloric acid solution. Imine 2 and the anion of 3 arise from reactions of 1a with the lithium amide bases since control experiments established that 1a is stable to the workup conditions and 2 and 3 are unchanged by treatment with excess LDA at 0 °C. As shown in Table I, the yields of 2 and 3 vary with the identity and the concentration of amide base. We observed no correlation in the distribution of 2 and 3 as a function of monomeric base size.[5] For LDEA and LDA, as base concentration was increased, the yield of 2 increased at the expense of 3. When 1a (ca. 0.4 M) was allowed to react with ca. 1.7 M amide base in reactions monitored by ^{13}C NMR spectroscopy, signals from imine 2 were observed (vide infra). These results and others discussed below show that 2 and 3 arise from competing reactions of the base with oxaziridine. The variation in relative yields of 2 and 3 as a function of LDEA and LDA concentration suggests that the competing reactions may occur with different aggregates of base or different molecularity.

Oxaziridine Reduction Reaction. We can envision three reaction pathways for the reduction of oxaziridine 1a by an amide base (Scheme I). Initial nucleophilic attack at the oxygen atom of oxaziridine (path a) to give intermediate 4 which then forms imine 2 in an elimination step is a mechanism similar to that proposed by Davis[4] to account for hydroxylation of lithium and Grignard reagents by oxaziridines. Alternatively, electron transfer from the amide base to 1a to give 5 followed by radical–radical anion collapse to intermediate 4 would be an equivalent process

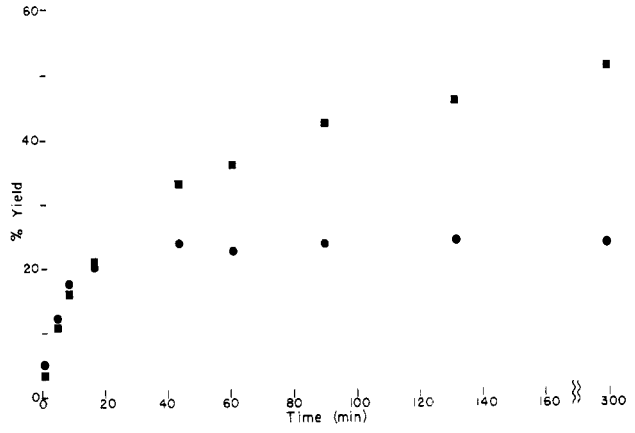


Figure 1. Percent yield of 2 (■) and 3 (●) as a function of time from the reaction of 1a with LDA at −32 °C.

(path b, a'). An electron-transfer pathway (b) which does not lead to intermediate 4 is also possible. Further reduction of 5 to dianion 6 or a radical–radical coupling (not shown) could give an intermediate which leads ultimately to imine. Electron transfer from lithium amide bases has been demonstrated by Scott[7] in the reduction of benzophenone by LTMP and LDA in the presence of hexamethylphosphoramide. Finally, β-hydride transfer (path c) from amide base to 1a to give reduced intermediate 7 which eventually dehydrates or eliminates lithium oxide to give imine 2 is possible; such β-hydride transfer from LDA to enolizable ketones has been reported by Creary,[8] but this pathway is doubtful for the oxaziridine reduction since ketones reduced by β-hydride transfer from LDA are not reduced by LTMP,[8] whereas we find the highest yields of reduction when LTMP is the base.

By studying the product composition as a function of time, we concluded that the reaction of 1a with LDA to give imine 2 proceeds through an intermediate with a finite lifetime. Oxaziridine 1a was treated with 0.10 M LDA in THF at −32 °C, and the reaction was monitored for products at various times by GC analysis of workup aliquots. Figure 1 shows the percent yield of 2 and 3 as a function of time. Although initially amide 3 was formed faster than imine 2, ultimately the yield of 2 was higher. After 44 min the percentage of 3 was constant, but the yield of 2 continued to increase over 5 h. Oxaziridine 1a was partially pyrolyzed under our GC conditions, preventing quantitative measurements of unreacted material; however, we saw a regular decrease in the amount of 1a up to 18 min and no evidence of 1a at or beyond 44 min. This behavior is consistent with formation of an intermediate in the pathway for production of 2 which accumulates in significant quantities and cannot revert to 1a. In addition, the results shown in Figure 1 verify that distinct pathways for the production of 2 and 3 exist.

^{13}C NMR spectroscopic studies confirmed the existence of a long-lived intermediate in the conversion of oxaziridine 1a to imine 2 by all three amide bases. For these studies highly concentrated solutions of amide base (LDEA or LDA) in THF were made by distilling the solvent from a solution of base and then dissolving the residue in THF. LTMP decomposed partially when treated in this manner, and we used a less concentrated solution of LTMP in THF/hexane. Oxaziridine 1a was treated with amide base at −56 ± 2 °C in the probe of the spectrometer, and ^{1}H-

(5) It may be noted that Posner and Lentz[6] have reported that the apparent thermodynamic equilibrium between the enolates from 3-methyl-3-phenylcyclopentanone is altered in a regular manner as the base used is changed from LDEA to LDA to LTMP.

(6) G. H. Posner and C. M. Lentz, *J. Am. Chem. Soc.*, **101**, 934 (1979).

(7) L. T. Scott, K. J. Carlin, and T. H. Schultz, *Tetrahedron Lett.*, 4637 (1978).

(8) C. Kowalski, X. Creary, A. J. Rollin, and M. C. Burke, *J. Org. Chem.*, **43**, 2601 (1978).

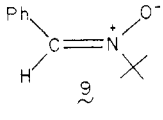
decoupled ^{13}C NMR spectra were recorded periodically. The signals from oxaziridine **1a** were lost quickly, but signals from imine **2** formed slowly, proving that an intermediate was formed in each case.

The reactions of 0.4 M **1a** with 1.7 M LDA studied by this method were the most informative (Figure 2 in the Supplementary Material). At −56 ± 2 °C the signals from **1a** were lost within 40 min; the first half-life appeared to occur at about 5 min. At the same time, signals from LDA diminished, and those from diisopropylamine increased. Small signals attributable to imine **2** were observed at 40 min, and other signals which were discernible could not be assigned to any structure. After the reaction mixture was warmed to 0 or 25 °C, the ^{13}C NMR spectrum recorded at −56 °C contained signals from imine **2**. By comparison of the integrated methine carbon signals from LDA and diisopropylamine at 40 min, approximately 2 equiv of LDA was consumed for each equivalent of **1a** which was reduced. Approximately 1 additional equiv of LDA was consumed when the reaction was warmed. Similar results were obtained at −35 ± 2 °C, at which temperature oxaziridine **1a** was consumed within 10 min. Signals from **2** were present after 15 min, but again, these continued to increase after all of the oxaziridine had been consumed. Comparison of the results of the ^{13}C NMR studies with those obtained when lower concentrations of reactants were used (Figure 1) indicates that in the case of the LDA reaction at the higher concentrations used in the NMR studies, a bimolecular (or higher order) reaction consuming **1a** was accelerated while the (presumably) unimolecular decomposition of intermediate to give **2** was not.

Both LDEA and LTMP react with **1a** faster than LDA does since when the oxaziridine was treated with these bases in ^{13}C NMR studies at −56 ± 2 °C, no signals from **1a** were discernible after 5 min. Again, imine **2** was not completely formed until the reaction solutions were warmed. Measurement of the amount of base consumed in each of these reactions was not possible. In the LDEA reaction the signals from LDEA became broadened and overlapped with those from diethylamine as soon as a portion of the LDEA was consumed, and in the LTMP reaction signals from impurities and solvents overlapped the base and amine signals.

Attempts to obtain indirect evidence for the production of hydroxylamine from the reaction of LTMP with **1a** were negative.[9]

Since **1a** is converted to *N*-*tert*-butylbenzaldimine *N*-oxide (**9**) by thermolysis,[1] we determined whether **9** could be an intermediate in the reactions of **1a** with amide base.

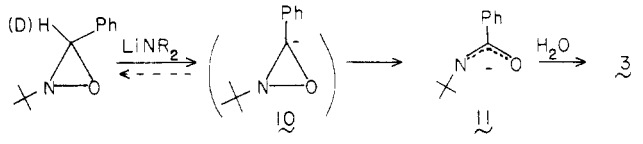


9

Nitrone **9** reacts with LDA to give a blue solution which contains a paramagnetic species. Subsequent quenching and workup of the reaction mixture showed that no **2** or **3** was formed but that a substantial amount of **9** was consumed to give unknown products.

Each of the pathways we have outlined for the production of imine **2** (Scheme I) involves formation of an intermediate which might be stable enough to accumulate during the reaction; however, pathways a and c require that the amide base be converted to hydroxylamine or imine, respectively. In the LDEA and LDA reactions, within the limits of detection in ^{13}C NMR spectroscopy, we only observed amide base and protonated amine from the reactions of **1a** with amide base, and our ESR studies indicated that hydroxylamine was not formed from the reaction of **1a** with LTMP.[9] Thus, we conclude that an electron-transfer pathway (b) is the most likely mechanism. Presumably THF is ultimately oxidized via hydrogen atom abstraction.[10] Such a process would consume 2 equiv of amide base per 1 equiv of oxaziridine. This electron-transfer pathway is consistent with the free-radical evidence in reactions of oxaziridines with strong organometals reported by Davis[4] and the amide base reductions reported by Scott.[7] In addition, with such a mechanism one can rationalize the facts that LTMP, which cannot reduce species via β-hydride transfer and should be the most hindered base for nucleophilic attack, gives the highest yield of reduced imine product and reacts with **1a** faster than LDA does.

Oxaziridine Isomerization Reaction. The product distribution displayed in Figure 1 suggests that no intermediate such as **10** accumulates in the conversion of **1a** to **11**. Other experiments lead us to conclude that intermediate **10** does not even have transitory existence. Treatment of **1a** with LDA at −78 °C for 15 min followed by treatment with deuterium oxide returned **1a** with no (<5%) deuterium at C-3 as determined by ^1H NMR spectroscopy. Similarly, treatment of **1a** with 0.10 M LDA in the presence of 0.10 M diisopropylamine-*N*-*d* for 1 h at −78 °C gave **1a** with no deuterium incorporation, and treatment of ring-deuterated **1b** with 0.10 M LDA and 0.10 M diisopropylamine at −78 °C for 1 h or at −49 °C for 1.5 h gave no protio **1a**. In the last experiment ca. 30% of **1b** had been consumed in the reactions leading to **2** and **3**. These results show that **10** is not formed reversibly from **1**.



When varying amounts of diisopropylamine were added to LDA solutions before addition of **1a** and percent yields of **2** and **3** were determined, we found little effect of amine concentration on the rates of the reactions. Thus the reaction of 0.013 M **1a** in a solution containing 0.10 M LDA and 0.10 M diisopropylamine was quenched after 97 min at −48 °C and found to contain **2** and **3** in 13.8 and 16.7% yields, respectively. An identical reaction with the exception that the diisopropylamine concentration was raised to 0.20 M gave **2** and **3** in 13.9 and 17.4% yields, respectively. The nearly equal amounts of **2** and **3** from these two reactions reinforce our conclusion that cyclic intermediate **10** is not formed reversibly from **1a**. In addition, this indicates that the intermediate formed in the reduction reaction is not protonated by amine before it decomposes to **2**.

Our final test for the existence of **10** was a measure of the kinetic isotope effect in the reaction leading ultimately

(9) The product mixture from the reaction of LTMP and **1a** was treated with oxygen, and the amount of 2,2,6,6-tetramethylpiperidine *N*-oxyl (**8**) formed was measured by quantitative ESR spectroscopy. The small amount of **8** detected was comparable to the amount formed in a blank experiment. A complete description of these results, the experimental details, and references are available as Supplementary Material.

(10) We are not aware of a study of the rate of reaction of diisopropylamino radical with THF; however, Roberts and Ingold[11] reported that only a low concentration of this radical was present upon photolysis of tetraisopropyltetrazene in THF, which indicates that the diisopropylamino radical reacts rapidly with THF.

(11) J. R. Roberts and K. U. Ingold, *J. Am. Chem. Soc.*, **95**, 3228 (1973).

to **3**. Due to the complex kinetic behavior suggested in Figure 1, we chose to measure the ratio of products **2** and **3** at the end of the reaction to determine the relative pseudo-first-order rate constants for each pathway. When protiooxaziridine **1a** was treated with excess LDA at 0 °C, the ratio of **2** to **3** obtained was 69:31. Under identical conditions, deuterated **1b** gave a **2** to **3** ratio of 80:20. This change in the product ratio gives a primary kinetic isotope effect, k_H/k_D, of 1.8 for the reaction leading to **3** if we assume that the rates of imine formation from **1a** and **1b** are equal.[12]

The small primary isotope effect[13] of 1.8 at 0 °C is consistent with a mechanism wherein the benzamide anion **11** is formed directly from **1** without intervention of intermediate **10**. This reaction would be highly exothermic since a strong base, LDA, reacts with the strained three-membered-ring heterocycle to give a much weaker base, an amide anion, in which strain energy has been relieved. Quantitative estimation of ΔH of the reaction is not possible since bond energies for the N–O single bond are not available.[14] However, a crude estimation of the free-energy change based on the estimated pK_a's of diisopropylamine (>34)[15] and benzamide (25),[17] the expected strain energy of ca. 35 kcal/mol for the heterocycle,[14] and an assumption that bond energy changes and entropy effects are negligible, would be $\Delta G > 50$ kcal/mol. The transition state in such an exothermic reaction would be reached early, and a small isotope effect would be predicted. Alternatively, we expect that formation of **10** from **1** in a rate-limiting step would be less exothermic, since the heterocyclic ring is not cleaved and **1** would be substantially less acidic than **3**. Accordingly, this reaction should have a large primary isotope effect.

In conclusion, lithium amide bases react with oxaziridine **1a** in two competing reactions. Reduction of the oxaziridine to an imine proceeds through a long-lived intermediate and appears to occur by an electron-transfer process which ultimately consumes 2 equiv of amide base. This pathway or a portion of it may be similar to one of the reactions of oxaziridines with Grignard and lithium reagents since Davis et al.[4] obtained evidence for free-radical participation in these reactions. Isomerization of oxaziridine **1a** occurs by simultaneous deprotonation and ring opening to give the corresponding amide anion **11** in a highly exothermic reaction.

Experimental Section

General Methods. All organometallic reactions were run under an inert atmosphere (nitrogen or argon), and all transfers were made by syringe. THF was distilled from benzophenone–sodium under nitrogen immediately before use. The amines, diethylamine, diisopropylamine, and 2,2,6,6-tetramethylpiperidine, were purchased (Aldrich) and distilled from calcium hydride under nitrogen. Temperatures were not corrected. ^{1}H NMR spectra of $CDCl_3$ solutions were recorded on a Varian T-60 or HA-100 spectrometer with internal Me_4Si. ESR spectra were recorded on a Varian E6S spectrometer. Gas chromatography (GC) was performed on a Varian 2400 chromatograph equipped with flame-ionization detectors on a 6 ft by $^1/_8$ in., 1.5% OV-101 on 100/120 Chromosorb G column.

***N-tert*-Butylbenzaldimine (2)** was prepared by the method of Pews[18] and Krimm.[19] The pale yellow oil was obtained in 72% yield: bp 100–110 °C (20 torr) [lit. bp 76 °C[18] (4 torr), 90–92 °C[19] (11 torr)]; ^{1}H NMR δ 8.3 (s, 1 H), 7.8 (m, 2 H), 7.4 (m, 3 H), 1.3 (s, 9 H).

2-*tert*-Butyl-3-phenyloxaziridine (1a) was prepared from **2** and *m*-chloroperoxybenzoic acid (Aldrich) in methylene chloride according to the method of Pews.[18] The clear, colorless oil was obtained in 62% yield: bp 54 °C (0.28 torr) (lit.[1] bp 61 °C (0.3 torr)); ^{1}H NMR δ 7.42 (m, 5 H), 4.72 (s, 1 H), 1.17 (s, 9 H).

2-*tert*-Butyl-3-deuterio-3-phenyloxaziridine (1b) was prepared via the deuterated analogue of imine **2** from benzaldehyde-*formyl-d*[20] by the above methods. The ^{1}H NMR spectra of the intermediate imine and compound **1b** contained no signals at δ 8.3 and 4.7, respectively.

***N-tert*-Butylbenzaldimine *N*-oxide (9)** was prepared from **1a** by the Emmons procedure[1] in 100% yield; mp 68–70 °C (lit.[1] mp 75–76 °C).

***N-tert*-Butylbenzamide (3)** was prepared from benzoyl chloride and excess *tert*-butylamine; mp 132–132.5 °C (lit.[21] mp 135.5 °C).

Diisopropylamine-*N-d*. A solution of 25 g (0.24 mol) of diisopropylamine in 50 mL of methylene chloride was shaken successively with three 10-mL portions of deuterium oxide (98% D). The organic phase was dried (Na_2SO_4) and distilled to give 15 g (60%) of diisopropylamine-*N-d*. A sample of the deuterioamine was dissolved in a solution of DCl in D_2O, and the ^{1}H NMR spectrum was recorded. A comparison of the corrected HOD signal integral with the amine methine signal integral showed that the amine contained less than 10% protium on nitrogen.

Attempted Incorporation of Deuterium into 1a. A. Ten milliliters of a 0.10 M solution of LDA in THF was cooled to −78 °C, and oxaziridine **1a** (50 μL, ca. 0.3 mmol) was added. After 15 min, the reaction mixture was quenched with deuterium oxide, diluted with ether, extracted with water and saturated aqueous sodium chloride solution, and dried (Na_2SO_4). Distillation of the solvent left **1a** with no (<5%) deuterium at C-3 (^{1}H NMR).

B. Oxaziridine **1a** (0.3 mmol) was treated with 10 mL of a THF solution which contained 1.0 mmol of LDA and 1.0 mmol of diisopropylamine-*N-d* at −78 °C for 1 h and then quenched with a 4% aqueous HCl solution. After workup as above, **1a** was obtained with no deuterium at C-3.

Attempted Incorporation of Protium into 1b. C. In a reaction similar to B above, **1b** was treated with LDA and diisopropylamine at −78 °C for 1 h to give after workup **1b** with no ^{1}H NMR signal at δ 4.7.

D. At −49 °C, 26 mL of a THF solution which was 0.10 M in LDA and 0.10 M in diisopropylamine was added to 0.26 mmol of **1b**. After 1.5 h at −49 °C, a slight excess of water was added, and the THF solution was dried ($MgSO_4$). GC analysis indicated that ca. 30% of **1b** had been converted to **2** and **3**. Distillation of the solvent in vacuo and chromatography of the residue (alumina, methylene chloride elution) afforded **1b** which contained no detectable signal at δ 4.7 in the ^{1}H NMR spectrum.

Product Studies. A stock solution of each amide base was prepared by adding *n*-butyllithium in hexane to a solution of the amine in THF. Aliquots of the stock solution were diluted with THF to provide 2.0-mL base solutions which were 0.10, 0.20, and 0.40 M. A stock solution of 0.015 M oxiziridine **1a** containing an internal standard for GC of *n*-hexadecane was prepared. Then a 2.0-mL aliquot of the oxaziridine solution was added to each

(12) The rates of formation of imine from **1a** and **1b** may not be identical. If a secondary kinetic isotope effect exists, it should be inverse since the strained ring is probably broken in the rate-limiting step which would lead to a decrease in σ character in the C–H(D) bond. An inverse isotope effect in the reaction **1** → **2** requires that the primary kinetic isotope effect in the reaction **1** → **3** be *less* than 1.8. It may be possible that the entire isotope effect we observed could be attributed to such an inverse isotope effect in the reaction **1** → **2** where $k_H/k_D = 0.55$, but we believe this magnitude of effect is unrealistically great.[13]

(13) A. J. Kresge in "Isotope Effects on Enzyme-Catalyzed Reactions", W. W. Cleland, M. H. O'Leary, and D. B. Northrop, Eds., University Park Press, Baltimore, MD, 1977, p 37.

(14) S. W. Benson, "Thermochemical Kinetics", Wiley, New York, 1968.

(15) The two alkyl groups should raise the pK_a of diisopropylamine above that of cyclohexylamine which is in turn greater than that of triphenylmethane.[16]

(16) A. Streitwieser, Jr., C. J. Chang, W. B. Hollyhead, and J. R. Murdoch, *J. Am. Chem. Soc.*, **94**, 5288 (1972), and references therein.

(17) D. J. Cram, "Fundamentals of Carbanion Chemistry", Academic Press, New York, 1965.

(18) R. G. Pews, *J. Org. Chem.*, **32**, 1628 (1967).

(19) H. Krimm, *Chem. Ber.*, **91**, 1057 (1957).

(20) A. W. Burgstahler, D. E. Walker, Jr., J. R. Kuebrich, and R. L. Schowen, *J. Org. Chem.*, **37**, 1272 (1972).

(21) G. Schroeter, *Chem. Ber.*, **44**, 1201 (1911).

base solution at 0 °C, and the resulting mixture was maintained at 0 °C for 3 h before water (0.1 mL) was added. The liquid portion of each reaction mixture was combined with ether rinses of the reaction flask, and the resulting mixture was analyzed by GC. The average values of three or more GC area determinations were corrected with predetermined response factors to give yields of **2** and **3**. The results are given in Table I. In control experiments, mixtures of **2** and **3** were found to be unchanged after treatments similar to those described above.

Effect of Amine Concentration on Rates. A stock solution of 0.20 M LDA in THF was prepared, and 2-mL portions were placed in two tubes. Diisopropylamine was added to each tube to bring the concentration to 0.20 and 0.40 M, respectively. A THF stock solution containing 0.027 M oxaziridine **1a** and *n*-hexadecane was prepared, and 2 mL of this solution was added to each of the reaction tubes at −48 °C. The reactions were quenched with 0.05 mL of water after 97 min at −48 °C and analyzed by GC. After correction for formation of **2**, **3**, and **9** from pyrolysis of unreacted **1a**, the yields given in the text were found.

Product Yields as a Function of Time. An insulated bath equipped with an overhead stirrer was brought to −32 °C (bromobenzene/CO_2). Reaction tubes were charged with 2.0-mL aliquots of a THF stock solution which contained 0.20 M LDA and 0.20 M diisopropylamine. The tubes were equilibrated at −32 °C in the bath, and a 2.0-mL portion of a THF solution which contained 0.033 mmol of oxaziridine **1a** and *n*-hexadecane was added at −32 °C to each tube. At timed intervals the solutions were quenched with 0.10 mL of water. The solutions were transferred to vials and analyzed by GC. The yields of **2** and **3** shown in Figure 1 are corrected for pyrolysis of unreacted **1a** which produces small amounts of each product.

Kinetic Isotope Effect. A THF stock solution containing 0.20 M LDA and 0.20 M diisopropylamine was prepared, and two 2.0-mL aliquots were equilibrated at 0 °C. To these solutions were added, respectively, 2.0 mL of a 0.015 M solution of **1a** with *n*-hexadecane and 2.0 mL of a 0.015 M solution of **1b** with *n*-hexadecane. After 3 h at 0 °C, the reactions were quenched with 0.05 mL of water and analyzed as described above. The reaction of **1a** gave **2** and **3** in a 69:31 ratio while the reaction of **1b** gave **2** and **3** in a 80:20 ratio.

Reaction of Nitrone 9 with LDA. A THF solution containing 0.010 M nitrone **9**, 0.21 M LDA, 0.41 M diisopropylamine, and *n*-hexadecane was equilibrated at 0 °C for 6.5 h during which time the solution became dark blue. The ESR spectrum of this solution contained a triplet with a_N = 12.5 G. The solution was quenched with water, and the resulting mixture was analyzed by GC. By comparison to the internal standard, 15% of nitrone **9** remained, and no **2** or **3** was present.

^{13}C NMR Studies. ^{1}H-decoupled ^{13}C NMR spectra were recorded on a JEOL PFT-100 instrument. Temperatures were measured with an iron–constantan thermocouple placed in an NMR tube in the instrument probe. Chemical shifts are reported relative to that of the β-carbon of THF which we define as δ 25. The experiments were performed in duplicate with an internal benzene-d_6 lock in one case and external chloroform-*d* lock in the other. The internal lock gave a better signal to noise ratio, but the benzene signals obscured the other aromatic signals. The ^{13}C NMR signals of interest at −56 °C are as follows: oxaziridine **1a**, δ 136 (aromatic C-1), 72 (ring C), 57 (quaternary C); imine **2**, δ 154 (imine C), 137 (aromatic C-1), 56 (quaternary C); LDA δ 51 (methine); diisopropylamine, δ 44 (methine).

The preparation of clean base solutions has been described.[22] Stock solutions of LDEA and LDA (ca. 2 M) were prepared and added to NMR tubes, and the tubes were cooled to −78 °C. For LTMP, 1 M solutions of base in THF/hexane were used. Oxaziridine **1a** was then added as a THF solution such that the final base concentration was ca. 1.7 M and the **1a** concentration was ca. 0.4 M (for LTMP 0.8 and 0.2 M, respectively). Benzene-d_6 (200 μL) was added when required. The tubes were placed in the NMR probe at the desired temperature and ^{1}H-decoupled FT NMR spectra were recorded periodically. A small tip angle of ca. 20° was used. The methine signals of LDA and diisopropylamine were integrated for comparison; we assumed comparable relaxation times and nuclear Overhauser effects for these signals. Qualitatively, the methyl signals of LDA and diisopropylamine were present in the same ratio as the methine signals although accurate integrations of these signals were not possible due to their proximity to the large THF β-carbon signal.

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Registry No. 1a, 3585-81-7; **1b**, 72918-19-5; **2**, 6852-58-0; **2**, deuterated analogue, 55103-96-3; **3**, 5894-65-5; **8**, 2564-83-2; **9**, 3376-24-7; benzoyl chloride, 98-88-4; *tert*-butylamine, 75-64-9; diisopropylamine-*N*-*d*, 25837-82-5; diisopropylamine, 108-18-9; 2,2,6,6-tetramethylpiperidine, 768-66-1.

Supplementary Material Available: Figure 2, showing ^{13}C NMR spectra of **1a**, **2**, and the reaction of **1a** with LDA at −56 °C at various times, and the material discussed in footnote 9 (3 pages). Ordering information is given on any current masthead page.

(22) M. A. Hoobler, D. E. Bergbreiter, and M. Newcomb, *J. Am. Chem. Soc.*, **100**, 8182 (1978).

Condensation of *p*-Benzoquinone with 4-Cyano- and 4-Nitroanilines. An Extension of the Nenitzescu Reaction

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A new synthesis of the 6-hydroxycarbazole ring involving the condensation of *p*-benzoquinone with various electron-withdrawing activated anilines has been presented. This procedure, an extension of the Nenitzescu reaction, gave multiple products identified on the basis of physical and spectral data. The corresponding mechanisms are described.

Among the intercalating antitumor ellipticines, 9-hydroxyellipticine (**1**) has been shown to be the most potent.[2,3] Several synthetic routes for its preparation have been described, but these require harsh experimental

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