ONE-STEP SYNTHESIS OF DIAZIRINES FROM O-TOSYL KETOXIMES AND ALKOXYAMINES*

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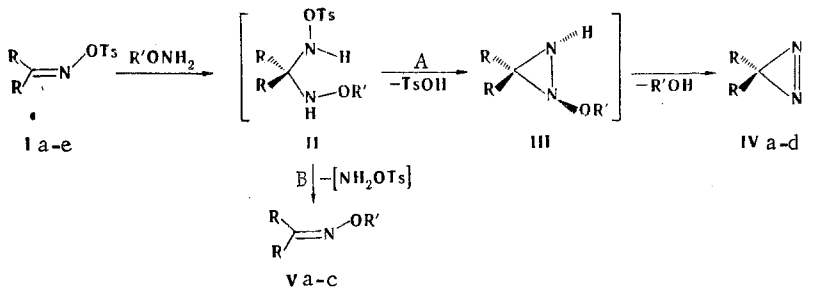
The reaction of O-tosyloximes of acetone, hexafluoroacetone, and mesoxalic acid esters with alkoxyamines leads to the corresponding diazirines, while the reaction of benzophenone O-tosyloxime with methoxyamine gives only benzophenone O-methyloxime. O-Esters of acetoxime were isolated along with 3,3-dimethyldiazirine also in the reaction of O-tosylacetoxime with alkoxyamines. Nucleophilic attack of alkoxyamines on O-tosyloximes of mesoxalates is realized at the carbon atom of not only the C=O bond but also at the carbon atom of the C=O bond, and the latter leads to fragmentation of the O-tosyloxime to give N-alkoxycarbamates, a cyanocarbonate ester, and p-toluenesulfonic acid. In the presence of triethylamine, which blocks the C=N bond, the reaction of the mesoxalate O-tosyloxime proceeds only via the fragmentation pathway. The mechanism of the formation of diazirines in the reaction of O-tosylketoximes with alkoxyamines is discussed.

O-Sulfonylketoximes react with primary amines to give 1-alkyldiaziridines [3, 4]. We have observed that the reaction of O-tosyloximes Ia-d with alkoxyamines does not result in the formation of 1-alkoxydiaziridines III but rather leads to diazirines IVa-d [2, 5]:



(1)

I, IV a R=Me; b R=CF_3; c R=CO_2Me; d R=CO_2Et; e R=Ph; V a R=R'=Me; b R=Me, R'=CH_2Ph; c R=Ph, R'=Me

Thus the one-step synthesis of diazirines is carried out without the use of such dangerously explosive reagents as dichloro- or difluoroamine (for example, see [6, 7]).

Reaction (1) is realized through intermediate gem-diamine II, the rate of formation and subsequent transformations of which are determined by the nature of substituents R and the basicity of the O-substituted hydroxylamine. In the presence of the electron-acceptor CF_3, CO_2Me, and CO_2Et groups, which increase the electrophilicity of the azomethine bond of O-tosyloximes Ib-d, reaction (1) takes place readily in the cold (from 0 to −10°C). O-Tosyloxime Ie, with the less electronegative substituent R = Ph, reacts with methoxyamine at 20°C, whereas Ia, with the electron-donor substituent R = Me, reacts only upon heating to 50-80°C with excess alkoxyamine (Table 1). The weakly basic O-mesitoyl- and O-mesitylenesulfonylhydroxylamine [8] do not react even with the most electrophilic O-tosyloxime Ic (in acetonitrile in the presence of potassium carbonate at 20°C for 48 h).

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TABLE 1. Reaction of O-Tosylketoximes with Alkoxyamines

O-Tosyl-ketoxime	Alkoxyamine	Reaction conditions		Yield, %			
		temp., °C	solvent	IV	V	R'OH	VI
Ia	$MeONH_2$	50—70	—	—	36*	62*	—
Ia	$PhCH_2ONH_2$	80	—	16	42*a, †	48*, ‡	—
Ib	$MeONH_2$	0	—	84	—	—	—
Ib	$PhCH_2ONH_2$	0	—	61	—	94	—
Ic	$MeONH_2$	from −5 to −10	MeCN	38[d]	—	—	43
Ic	$EtONH_2$	from −5 to −10	MeCN	81	—	—	14
Ic	$MeONH_2$, Et_3N	from −5 to −7	MeCN	—	—	—	88
Id	$EtONH_2$	from −5 to −7	MeCN	69	—	—	33 a
Ie	$MeONH_2$	20	MeCN	—	94	—	—

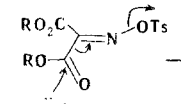
*Determined from the PMR spectra. †The yield after purification was 41%. [c]Characterized in the form of the p-nitrobenzoate. **Diazirine IVc was also obtained by oxidation of dimethyl diaziridine-3,3-dicarboxylate (VIII) with tert-butyl hypochlorite (see the experimental section).

In the case of O-tosyloxime Ia we observed a competitive reaction involving fragmentation of gem-diamine II to O-alkylacetoximes Va, b (pathway B in scheme 1); the reaction of Ie with methoxyamine proceeds only via pathway B. The resulting O-tosylhydroxylamine is thermally unstable and under the reaction conditions undergoes decomposition via Eq. (2) (for example, see [9]):

$$3TsONH_2 \rightarrow TsO^-NH_4^+ + 2TsOH + N_2 \quad (2)$$

The corresponding O-alkyloximes were not detected in the products of the reaction of tosyloximes Ib-d with alkoxyamines. This is explained by the fact that the electronegative CF_3, CO_2Me, and CO_2Et substituents hinder the heterolysis of the C—N bond of gem-diamine II* because of its depolarization and the decrease in the basicity of the nitrogen atoms.

Nucleophilic attack of the alkoxyamine on O-tosyloximes, Ic, d as ambident electrophiles [3, 9] is realized at the carbon atom of not only the C=N bond but also at the carbon atom of the C=O bond. As a result, the reaction gives, in addition to diazirines IVc, d, N-alkoxycarbamic acid esters VIa-c (scheme 3), the yields of which depend substantially on the type of R' substituent: When methoxyamine is replaced by ethoxyamine, the yield of side product VI is reduced by a factor of more than three (Table 1).

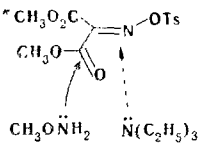


$$\longrightarrow RO_2C{-}NHOR' + [RO_2C{-}CN] + TsOH \quad (3)$$

VI a-c VII

VI a R=R'=CH_3; b R=CH_3, R'=C_2H_5; c R=R'=C_2H_5

When the reaction of tosyloxime Ic with methoxyamine is carried out in the presence of triethylamine, diazirine IVc is not formed at all, and the principal reaction product becomes urethane VIa. One might have assumed that triethylamine, as the most basic amine (pK_a 10.74 [12]), gives rise to fragmentation of tosyloxime Ic as in reaction (3) and that the resulting cyanocarbonate ester VII reacts with methoxyamine (pK_a 4.67 [13]) to give IVa. However, we demonstrated by a model experiment that the fragmentation of tosyloxime Ic under the influence of triethylamine in acetonitrile proceeds considerably more slowly (∿3 days at 20°C, as monitored from the PMR spectra of the reaction mixture) than the reaction under discussion (∿12 h at 0°C). Another explanation may be found by assuming the formation of a weak complex of the solvate type in which triethylamine as a p donor blocks the C=N bond of O-tosyloxime Ic, and attack by methoxyamine is realized only at the carbon atom of the C=O bond:



*Stable gem-diamines based on hexafluoroacetone [10] and mesoxalic ester [11] are known.

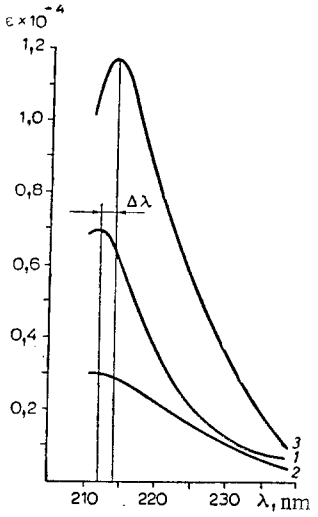


Fig. 1

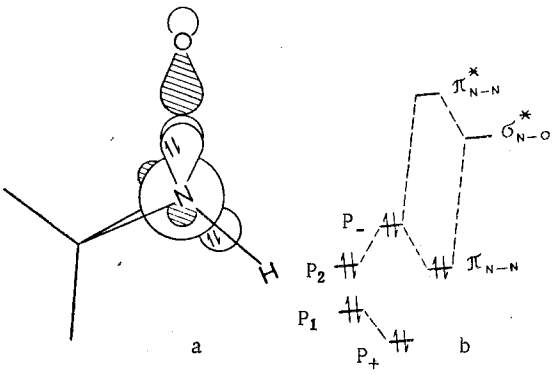


Fig. 2

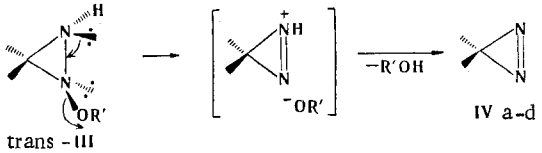
Fig. 1. UV spectra of dimethyl mesoxylate O-mesyloxime (I), triethylamine (2), and an equimolar mixture of them (3) in acetonitrile.

Fig. 2. Geometry of the interacting p and σ^*_{N-O} orbitals (a) and schematic spacing of their energy levels (b) in trans-1-alkoxydiaziridine.

The 2-nm red shift (Δλ) of the absorption band at 212 nm (ε 7000) in the UV spectrum of dimethyl mesoxalate O-mesyloxime† in acetonitrile when an equimolar amount of triethylamine is added (Fig. 1) constitutes evidence in favor of the assumption of the formation of a solvate.

It must be noted that under the conditions of reaction (1) O-tosyloximes Ia, e absolutely do not undergo the Beckmann rearrangement, which is characteristic for O-sulfonylketoximes that do not contain electronegative substituents, particularly O-sulfoxyloximes of benzophenone [14]. As in the case of alkylamines [4], the addition of an alkoxyamine to the C=N bond is evidently realized more readily than ionization of the Ia, e molecules at the N–O bond.

Intramolecular S_N2 substitution in gem-diamine II leads to 1-alkoxydiaziridine III (pathway A, Scheme 1), which is converted to diazirines IVa-d by elimination of alcohol R'OH. The reason for the instability of diaziridine III evidently consists in the facile splitting out of $R'O^-$ as a result of the reaction of the antibonding orbital of the N–O bond (σ^*_{N-O}) with the nonbonding orbital of the unshared electron pair (UEP) of the adjacent nitrogen atom (p):



(4)

This reaction is particularly effective in the case of eclipsing of the p and σ^*_{N-O} orbitals (Fig. 2) if 1-alkoxydiaziridine III is produced, like 1-alkyldiaziridines [15, 16], in the form of the thermodynamically favorable 1,2-trans-invertomer.

It may be assumed that the sterically similar overlapping of the p and σ^*_{C-O} orbitals in 2-alkoxyaziridines [17, 18] also should lower their stability. However, such compounds cannot be isolated [17, 19], and elimination of alcohol from, for example, 2-isopropoxy-2-phenyl-3,3-dimethylaziridine is realized only upon heating in toluene [19]. The different stabilities of these N- and C-alkoxy derivatives are evidently due to not only the differ-

†The short-wave part of the UV spectrum of O-tosyloxime Ic in acetonitrile is overlapped by the absorption of the aryl chromophore of the TsO group [λ_{max} 230 nm (ε 13,000)].

ence in the energies of the σ^*_{N-O} and σ^*_{C-O} orbitals but also to the increase in the energy of the upper occupied p orbital of 1-alkoxydiaziridine because of the splitting of the nonbonding levels (Fig. 2b) that is characteristic for diaziridines and hydrazines [20].

A radical pathway for the elimination of R'OH from diaziridines III is unlikely, since N-alkoxyamines are not at all inclined to undergo homolysis of the N–O bond. For example, the closest analogs of III, viz., 1-alkoxyaziridines, are thermally stable [21]. An alternative mechanism of synchronous elimination can be excluded proceeding from the following reasoning. First, this sort of decomposition is possible only in the case of the thermodynamically unfavorable 1,2-cis-invertomer of diaziridine III. Second, the transition state, which includes four delocalized electrons, is antiaromatic [22], so that according to the Woodward–Hoffmann rule, this $[2_S + 2_S]$ process is prohibited with respect to symmetry [23] and consequently should have a higher energy barrier than the corresponding stepwise process (Scheme 4).

EXPERIMENTAL

The NMR spectra were obtained with Tesla BS-487C (^{1}H, 80 MHz, and hexamethyldisiloxane as the internal standard) and Jeol HNM-C-60 (^{19}F, 56 and 45 MHz, and CF_3CO_2H as the external standard) spectrometers. The IR and UV spectra were recorded with a UR-10 spectrometer and a Specord UV-vis spectrophotometer, respectively.

The alkoxyamines were synthesized by the method in [24]; O-tosyloximes Ia-d were also obtained by known methods [3, 14, 25, 26], respectively. The synthesis of diaziridine-3,3-dicarboxylic acid ester VIII and dimethyl mesoxylate oxime was described in [3].

Benzophenone O-Tosyloxime (Ie). A solution of 1.91 g (0.034 mole) of KOH in 30 ml of water was added dropwise with stirring and cooling (5-10°C) to a solution of 7.89 g (0.04 mole) of benzophenone oxime in 35 ml of acetone, after which a solution of 5.72 g (0.03 mole) of p-toluenesulfonyl chloride in 45 ml of acetone was added, and stirring was continued at 10-15°C for 1 h. The reaction mixture was then diluted with cold water (45 ml), and the precipitate was removed by filtration, washed with 50% aqueous acetone and water, and dissolved in 50 ml of methylene chloride. The resulting solution was washed with a cold 10% aqueous solution of KOH and water and dried with calcium chloride. The solvent was removed *in vacuo* to give 8.34 g (83%) of Ie with mp 89-92°C. PMR spectrum (in $CDCl_3$): 2.32 (Me, s), 7.27 (Ph, H_A, m), and 7.83 ppm (H_B, d, J = 8 Hz). Found: C 68.5; H 5.0; N 4.1%. $C_{20}H_{17}NO_3S$. Calculated: C 68.4; H 4.9; N 4.0%.

Reaction of O-Tosyloxime Ia with Methoxyamine. A mixture of 4.55 g (0.02 mole) of Ia and 2.35 g (0.05 mole) of methoxyamine was maintained at 50°C for 5 h, after which it was cooled to 20°C, and the low-boiling reaction products were removed *in vacuo* (20 nm) into a trap (at −78°C) to give 1.02 g of a colorless liquid containing 0.40 g (60%) of methanol and 0.62 g (36%) of O-methylacetoxime Va; the molar ratio was 1:0.56 (according to the PMR spectrum of a solution in CCl_4). O-Ester Va was identified from the PMR spectrum [in CCl_4: 1.72 and 1.75 (Me_2C) and 3.67 ppm (MeO)] by the addition of a solution of the mixture of an authentic sample of Va with bp 72-74°C [27].

Reaction of O-Tosyloxime Ia with Benzyloxyamine. A mixture of 4.55 g (0.02 mole) of Ia and 5.17 g (0.042 mole) of benzyloxyamine was heated to 80°C *in vacuo* (100 mm) in a flask connected to a trap cooled to −78°C, during which spontaneous warming of the mixture to 130°C was observed. The mixture was then cooled, and the reaction products were extracted with absolute ether. The ether was removed *in vacuo*, and the residue was found to contain 2.75 g of a yellow oil containing 1.05 g (48%) of benzyl alcohol and 1.70 g (46%) of Vb; the molar ratio was 1:0.95 (according to the PMR spectra in C_6H_6). From the trap we isolated 0.23 g (16%) of diazirine Ia with bp 20°C (759 mm) [28]. PMR spectrum (in CCl_4): 0.99 ppm.

The mixture of benzyl alcohol and O-ester Vb was dissolved along with 1.50 g (0.015 mole) of triethylamine in 20 ml of absolute benzene, a solution of 2.78 g (0.015 mole) of p-nitrobenzoyl chloride in 20 ml of absolute benzene was added dropwise with stirring and cooling (from −3 to +5°C) to this solution, and the resulting mixture was maintained at 20°C for 10 h. The precipitate was removed by filtration and washed with benzene. The filtrate was evaporated *in vacuo*, and the residue was recrystallized from absolute ethanol to give 2.20 g (88%) of benzyl p-nitrobenzoate with mp 82-84°C (mp 83-84.5°C [29]). PMR spectrum (CCl_4): 5.32 (CH_2), 7.26 (Ph), and 8.11 ppm (C_6H_4). The mother liquor was evaporated

in vacuo, and the residue was distilled to give 1.50 g (41%) of O-ester Vb with bp 80-81°C (3 mm) (bp 190°C [30]). PMR spectrum (CCl_4): 1.73 (Me_2C), 4.84 (CH_2), and 7.13 ppm (Ph).

Reaction of O-Tosyloxime Ib with Alkoxyamines. A 6.70-g (0.02 mole) sample of Ib was placed in an ampul and cooled to −78°C, 0.05 mole of the alkoxyamine was added, and the ampul was sealed and maintained at 0°C for 10 h. It was then cooled to −78°C and opened, and the reaction product was recondensed *in vacuo* (100 mm) at 20°C. It was then purified by passing it through concentrated H_2SO_4 to give diazirine IVb with bp −14°C (760 mm) (Table 1) (bp −14 to −12°C [31]). ^{19}F NMR spectrum (CCl_4): −10.7 ppm. Mass spectrum, m/e (relative intensity, %): 178 (M^+, 6), 159 (2), 150 (1), 131 (55), 100 (100), 69 (72), 43 (7), 31 (12), 28 (48) (compare with [32]). In the case of benzyloxamine the reaction products were extracted from the residue in the ampul with absolute ether after recondensation of diazirine IVb. After removal of the ether, the residue was distilled *in vacuo* to give 2.03 g (Table 1) of benzyl alcohol with bp 93-96°C (20 mm) and n_D^{20} 1.5395.

Reaction of O-Tosyloximes Ic, d with Alkoxyamines. A 0.06-mole sample of the alkoxyamine was added dropwise with stirring and cooling from −5 to −10°C to a solution of 7.88 g (0.025 mole) of Ic, d in 30 ml of absolute acetonitrile, after which stirring was continued at 0°C for 4 h, and the mixture was allowed to stand overnight at the same temperature. The precipitate was removed by filtration, the filtrate was evaporated *in vacuo*, and the reaction products were extracted from the residue with absolute ether. The ether was removed, and the residue was recrystallized from absolute methanol (at from −30 to −20°C) and sublimed at 20°C (1 mm) to give diazirine IVc with mp 50-51°C (dec.) (Table 1). IR spectrum (KBr): 1730 and 1750 cm^{-1} (C=O). UV spectrum (in MeOH): λ_{max} 289 nm (log ε 1.66). PMR spectrum (in C_6D_6): 3.21 ppm (MeO). Found: C 38.2; H 3.7; N 18.0%. $C_5H_6N_2O_4$. Calculated: C 38.0; H 3.8; N 17.7%.

After freezing out from methanol, diazirine IVd was subjected to molecular distillation at 20°C (1 mm) onto a cold surface (−78°C) to give a product with n_D^{20} 1.4248 (Table 1). IR spectrum (thin layer): 1740 and 1760 cm^{-1} (C=O). UV spectrum (in MeOH): λ_{max} 289 nm (log ε 1.89). PMR spectrum (in C_6D_6): 0.78 (Me, t, J = 7.0 Hz) and 3.75 ppm (CH_2, q). Found: C 45.3; H 5.5; N 15.1%. $C_7H_{10}N_2O_4$. Calculated: C 45.2; H 5.4; N 15.0%.

The mother liquor after recrystallization of diazirine IVc, d was evaporated *in vacuo*, and the residue was distilled to give the corresponding N-alkoxycarbamic acid esters (Table 1). Compound VIa had bp 79-80°C (10 mm) and n_D^{20} 1.4221. PMR spectrum (in C_6H_6): 3.24 (MeO_2C, s) and 3.29 ppm (MeON, s). Found: C 34.2; H 6.9; N 13.4%. $C_3H_7NO_2$. Calculated: C 34.3; H 6.7; N 13.3%. Compound VIb had bp 55-58°C (2 mm) and n_D^{20} 1.4520 [bp 56-57°C (2 mm) and n_D^{25} 1.4246]. PMR spectrum (in C_6H_6): 0.90 (Me, t, J = 6.8 Hz), 3.30 (MeON, s), and 3.63 ppm (CH_2O, q).

Reaction of O-Tosyloxime Ic with Methoxyamine in the Presence of Triethylamine. The preceding method gave 5.1 g of N-methoxyurethane VI (Table 1), which was identical to an authentic sample, from 15.75 g (0.05 mole) of Ic, 2.59 g (0.055 mole) of methoxyamine, and 6.07 g (0.06 mole) of triethylamine.

Reaction of O-Tosyloxime Ie with Methoxyamine. A solution of 5.27 g (0.015 mole) of Ie and 2.35 g (0.05 mole) of methoxyamine in 30 ml of absolute acetonitrile was maintained at 20°C for 17 h, after which the precipitate was removed by filtration, and the filtrate was evaporated *in vacuo*. The reaction product was extracted from the residue with absolute ether. The ether was removed, and the residue was recrystallized from alcohol to give 2.99 g of O-ether Vc with mp 58.5-60°C (mp 60-61°C [34]). PMR spectrum (in CCl_4): 3.83 (MeO, s) and 6.90 ppm (Ph_2C, m).

Oxidation of Dimethyl Diaziridine-3,3-Dicarboxylate (VIII). A solution of 1.08 g (10 mmole) of tert-butyl hypochlorite in 7 ml of the same solvent was added dropwise with stirring and cooling from −20 to −30°C to a solution of 0.80 g (5 mmole) of ester VIII in 10 ml of absolute ether or methylene chloride, after which the mixture was stirred at 0°C for 30 min. The solvent was evaporated *in vacuo*, and the residue was sublimed at 20°C (1 mm) to give 0.78 g (99%) of diazirine IVc with mp 50-51°C (dec.), which was identical to a genuine sample.

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