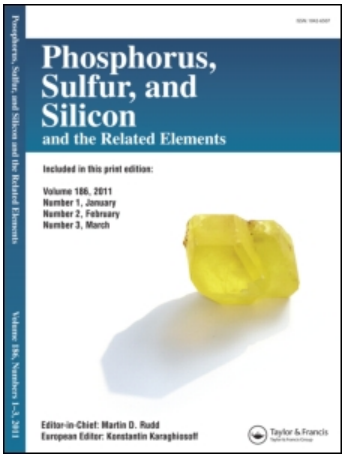

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OXIDATION OF BISIMINES TO BISOXAZIRIDINES USING BUFFERED OXONE

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N,N′-bisarylidenes are oxidized efficiently and rapidly to the stereoisomeric mixture of bisoxaziridines using buffered oxone.

Keywords: Bisimines; bisoxaziridines; buffered oxone; oxidation; three-membered heterocycles

Oxaziridines, heterocyclic compounds containing oxygen, nitrogen and carbon atoms in a three membered ring were first reported in the midfifties.[1] Oxaziridines have remarkably high configurational stability at nitrogen and can exist in isolable *cis* and *trans* isomers.[2,3] The imine-peroxyacid(*m*-CPBA) reaction generally provide a good rout to oxaziridines.[4–6] Recently, a rapid and efficient synthesis of oxaziridines and diarylnitrones using oxone is also reported.[7]

Because of intriguing stereochemical possibilities of bis-oxaziridines, a facile synthesis of this heterocyclic system could interesting from the synthetic as well as stereochemical point of view. In spite of these significance, few method have been reported for the synthesis of bisoxaziridines in the literature.[8,9] In this communication we wish to report an efficient and facile method for the synthesis of bis-oxaziridines using buffered oxone.

We are interested in the heterocyclic systems containing nitrogen.[10–13] As a part of a synthetic project, we were searching an efficient method for the synthesis of dinitrones. Since oxaziridines can be thermally isomerized to nitrones[14] we reasoned that bisoxaziridines should thermally isomerize to dinitrones.

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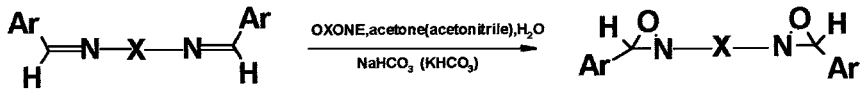
m-CPBA has been extensively used for the conversion of azomethines to oxaziridines.[9] Since this compound is not commercially available any more, we tried to use a more accessible and inexpensive reagent for oxidation of bisimines. Oxone in buffered aqueous acetone solution is reported to give dimethyldioxirane(DMD) that can be isolated by distillation.[7,15]

It is also reported that when acetonitrile is used as a solvent the active oxidizing agent is peroxyimidic acid [MeC(OOH)=NH]. Such a species formed from the reaction of acetonitrile and hydrogen peroxide has been demonstrated to be a useful reagent for the epoxidation of alkenes.[16] We investigated the reaction of bis-arylidenes with oxone and $KHCO_3$ in aqueous acetone or acetonitrile solution and found that the products are bisoxaziridines. Ethylenediamine-N,N′-bis(3-arylidenes) and 1,3-propanediamine-N,N′-bis(3-arylidenes) were oxidized to the corresponding 2,2′-(1,2-ethanediyl)bis(3-arylidene)oxaziridines and 2,2′-(1,3-propanediyl)bis(3-arylidene)oxaziridines (Scheme 1).



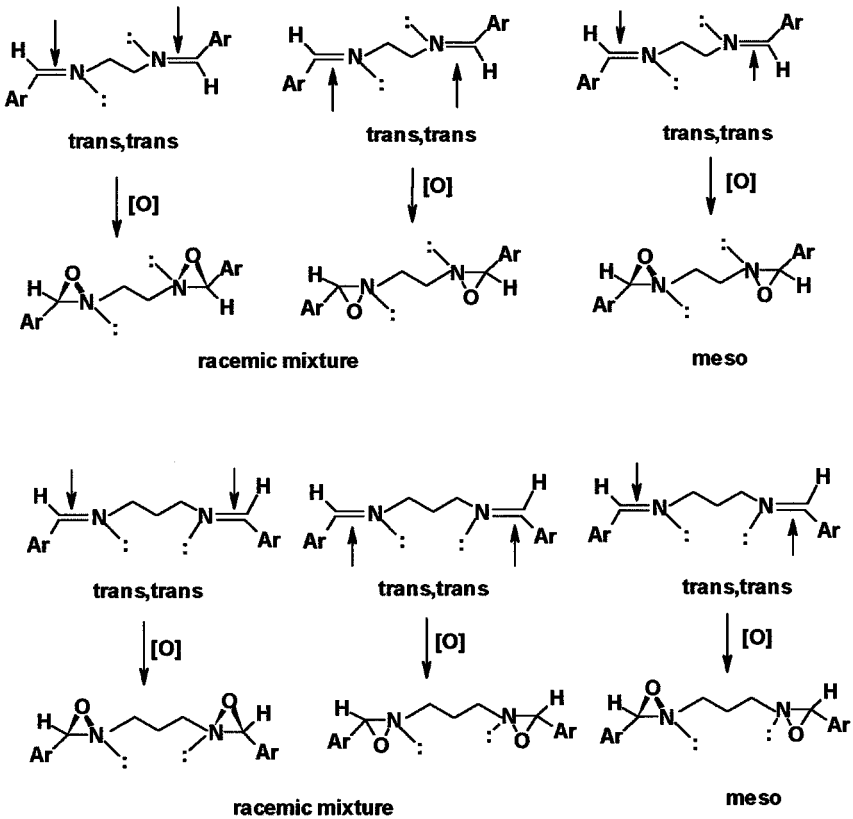
X=$(CH_2)_2$,$(CH_2)_3$

X	Ar	%Yields (acetone)	%Yields (acetonitrile)
$(CH_2)_2$	C_6H_5	96	98
$(CH_2)_2$	p-MeC_6H_4	97	96
$(CH_2)_2$	p-OMeC_6H_4	98	95
$(CH_2)_3$	C_6H_5	95	92
$(CH_2)_3$	p-MeC_6H_4	98	96
$(CH_2)_3$	p-OMeC_6H_4	97	98

SCHEME 1

It is noteworthy to mention that all the reactions should be conducted in an ice bath, since increase of the reaction temperature above 20°C, decreases the yields of the reaction drastically, probably due to hydrolysis of substrates to parent aldehydes and further oxidation. Utility of excess (three- and fourfold) oxone affected neither the reaction time nor the yields. The yields were also found to be essentially the same when either acetone or acetonitrile were used as solvent (Scheme 1). The conduction of those reactions in a solventless system using dry or wet-alumina/oxone (so called supported reagent) in the

presence of aprotic solvents such as hexane, dichloromethane, acetone or acetonitrile showed only recovered starting materials after 5 h reflux. It is noteworthy that the stable isomers of imines and bisimines are *trans* and *trans-trans* isomers respectively,[20] so the products are obtained by the oxidation of these isomers. The attacking process of the oxidant (dimethyldioxirane or peroxyimidic acid) to the *trans-trans* stereoisomers of bisimines caused the formation of the racemic and meso mixtures of bisoxaziridines (Scheme 2). In our experiments the ^{1}H NMR spectra of the obtained products from ethylenediamine-N,N′-bis(3-arylidenes) showed two signals for all protons and the ^{13}C NMR indicated that these compounds are a mixture of two isomers and the ratio of isomeric mixture is affected by substituents at the aromatic rings and methylene groups in the parent diamines (Scheme 2).



SCHEME 2

For example 2,2′-(1,2-ethanediyl)bis(3-phenyl)oxaziridine shows a 75:25 and 2,2′-(1,2-ethanediyl)bis[3-(4-methylphenyl)]oxaziridine

shows a 50:50 mixture of two isomers but in the case of 1,3-propanediamine-N,N′-bis(3-arylidenes) only one isomer is obtained. Steric interactions of aromatic segments and limitation in free rotation of carbon-nitrogen sigma bonds can be attributed to this phenomenon. For 1,3-propanediamine-N,N′-bis(3-arylidenes) which have three methylene groups between two nitrogen atoms, only one isomer is obtained in the oxidation process due to free rotation of carbon-nitrogen sigma bonds without any steric hinderances in the aromatic segments (Scheme 2).

In conclusion, we report here a rapid, inexpensive and new method for the synthesis of 2,2′-(1,2-ethanediyl)- and 2,2′-(1,3-propanediyl)bis(3-arylidene)oxaziridines under mild conditions; yields are high, reaction times are short, and working up is very simple.

EXPERIMENTAL

^{1}H NMR and ^{13}C NMR spectra were obtained using Bruker instrument at 500 and 125 MHz with $CDCl_3$ as solvent. Mass spectra were recorded using a Shimadzu QP1100EX instrument. Elemental analysis were performed on a Heraeus CHNO Rapid Analyzer instrument. Melting points were measured on a Stuart Scientific aparatus and are not corrected. Bisaldimines were prepared by the literature methods.[7,17–19] Ethylenediamine, 1,3-propanediamine, oxone, $KHCO_3$, benzaldehydes and solvents were obtained from Merck and were used without further purification.

General Procedure

To a 1-lit flask equipped with a magnetic stirrer was added the appropriate bisaldimines (5 mmol) in acetone or acetonitrile (31 ml) and $KHCO_3$ (3.5 mol equiv. based on oxone) in distilled water (62 ml) at 0°C. Oxone (10 mmol) was dissolved in distilled water (62 ml) and was poured onto the vigorously stirred mixture. The reaction mixture was stirred for 8 min (acetone reaction), 20 min (acetonitrile reaction), cooled to −5°C, and filtered. The filtered solid was washed with distilled water (2 × 50 ml), cooled petroleum ether (60–80) (2 × 25 ml), and crystalized from appropriate solvents and identified.

2,2′-(1,2-Ethanediyl)bis(3-phenyl)oxaziridine

Colorless crystals, recrystalized from EtOAc, mp 99–102°C, ^{1}H NMR ($CDCl_3$) (Major, 75%) δ 3.16–3.20 (m, 2H), 3.43–3.50 (m, 2H), 4.66 (s, 2H, oxaziridine H), 7.36–7.47 (m, 10H); (Minor, 25%) δ 3.07–3.09

(m, 2H), 3.45–3.60 (m, 2H), 4.67 (s, 2H, oxaziridine H), 7.36–7.47 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 59.66, 59.95, 80.54, 81.25, 127.70, 127.68, 128.48, 128.53, 130.13, 130.18, 134.38, 134.46; MS m/z 268.

2,2′-(1,2-Ethanediyl)bis[3-(4-methylphenyl)]oxaziridine

Colorless crystals, recrystalized from CH_3OH, mp 111–114°C, ^{1}H NMR ($CDCl_3$) (isomer 1, 50%) δ 2.38 (s, 6H), 3.05–3.07 (m, 2H), 3.41–3.43 (m, 2H), 4.64 (s, 2H, oxaziridine H), 7.16–7.18 (d, 4H, j = 8.5 Hz), 7.28–7.30 (d, 4H, j = 8.5 Hz) (isomer 2, 50%) δ 2.37 (s, 6H), 3.15–3.18 (m, 2H), 3.34–3.38 (m, 2H), 4.63 (s, 2H, oxaziridine H), 7.21–7.23 (d, 4H, j = 8.5 Hz), 7.35–7.37 (d, 4H, j = 8.5 Hz) ^{13}C NMR ($CDCl_3$) δ 21.44, 21.48, 59.68, 59.95, 80.58, 81.29, 127.65, 127.70, 129.16, 129.23, 131.47, 131.56, 140.12, 140.19, MS m/z 296.

2,2′-(1,2-Ethanediyl)bis[3-(4-methoxyphenyl)]oxaziridine

Colorless crystals, recrystalized from CH_3OH, mp 132–134°C, ^{1}H NMR ($CDCl_3$) (isomer 1, 50%) δ 3.04–3.05 (m, 2H), 3.34–3.39 (m, 2H), 3.80 (s, 6H), 4.59 (s, 2H, oxaziridine H), 6.85–6.87 (d, 4H, j = 8.5 Hz), 6.90–6.92 (d, 4H, j = 8.5 Hz); (isomer 2, 50%) δ 3.12–3.16 (m, 2H), 3.31–3.34 (m, 2H), 3.81 (s, 6H), 4.58 (s, 2H, oxaziridine H), 7.28–7.30 (d, 4H, j = 8.5 Hz), 7.36–7.38 (d, 4H, j = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 55.30, 55.36, 59.60, 59.88, 80.43, 80.16, 113.80, 113.83, 126.42, 126.50, 129.06, 129.08, 161.09, 161.14; MS m/z 328.

2,2′-(1,3-Propanediyl)bis(3-phenyl)oxaziridine

Colorless crystals, recrystalized from ethylacetate, mp 40–43°C, ^{1}H NMR ($CDCl_3$): δ 2.14–2.18 (m, 2H), 2.61–2.70 (m, 2H), 3.20–3.31 (m, 2H), 4.50 (s, 2H, oxaziridine H), 7.30–7.4 (m, 10H); ^{13}C NMR ($CDCl_3$): δ 26.81, 59.50, 80.54, 127.70, 128.48, 130.13, 134.3; MS m/z 282; CHN: calcd for $C_{17}H_{18}N_2O_2$: C 73.34, H 6.38, N 9.92; found: C 73.50, H 6.42, N 9.90.

2,2′-(1,3-Propanediyl)bis[3-(4-methylphenyl)]oxaziridine

Colorless crystals, recrystalized from methanol, mp 67–70°C, ^{1}H NMR ($CDCl_3$): δ 2.15–2.19 (m, 2H), 2.30 (s, 6H), 2.74–2.79 (m, 2H), 3.34–3.39 (m, 2H), 4.53 (s, 2H, oxaziridine H), 7.18–7.20 (d, 4H, j = 8.5 Hz), 7.29–7.31 (d, 4H, j = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 21.40, 26.80, 59.59, 80.56, 127.54, 129.23, 131.70, 140.15; MS m/z 310; CHN: calcd for $C_{19}H_{22}N_2O_2$: C 73.55, H 7.10, N 9.03; found: C 73.51, H 7.12, N 9.10.

2,2′-(1,3-Propanediyl)bis[3-(4-methoxyphenyl)]-oxaziridine

Colorless crystals, recrystalized from methanol, mp 107–110°C, ^{1}H NMR ($CDCl_3$): δ 2.14–2.18 (m, 2H), 2.72–2.77 (m, 2H), 3.32–3.37 (m, 2H), 3.81 (s, 6H), 4.51 (s, 2H, oxaziridine H), 6.88–6.95 (d, 4H, j = 8.5 Hz), 7.32–7.48 (d, 4H, j = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 26.85, 55.36, 59.55, 80.41, 113.98, 126.71, 129.00, 161.11; MS m/z 342; CHN: calcd for $C_{19}H_{22}N_2O_4$: C66.67, H 6.43, N 8.19; found: C 66.70, H 6.40, N 8.21.

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