

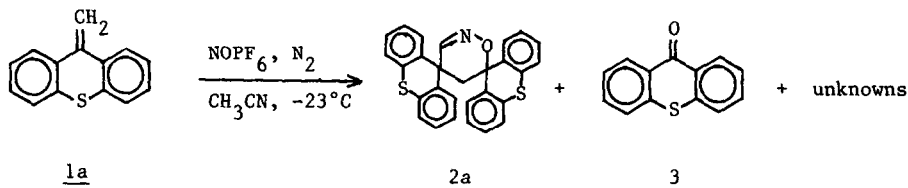
REACTIONS OF NITROSONIUM HEXAFLUOROPHOSPHATE WITH SOME OLEFINIC COMPOUNDS  
IN ACETONITRILE: ONE STEP SYNTHESIS OF 4H-5,6-DIHYDRO-1,2-OXAZINES

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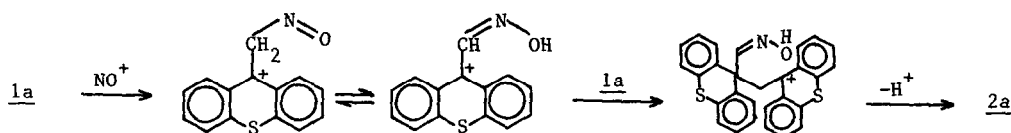
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Summary: Reactions of nitrosonium hexafluorophosphate or tetrafluoroborate with olefins having aryl groups at an olefinic carbon atom at low temperature in acetonitrile afforded 4H-5,6-dihydro-1,2-oxazines with two aryl groups at C-4 and C-6 in fair to good yields.

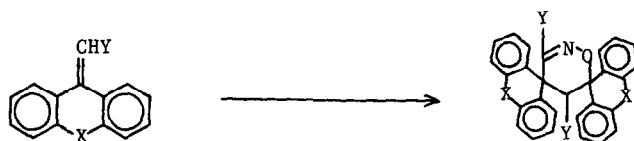
In the connection with the study on one-electron transfer from olefins using either nitrosonium hexafluorophosphate or tetrafluoroborate, known as good one-electron oxidant,<sup>1</sup> we have run the reaction of methylenethioxanthene(1a) with nitrosonium hexafluorophosphate in dried acetonitrile at  $-23^{\circ}\text{C}$  under nitrogen atmosphere.<sup>2</sup> From this reaction were obtained thioxanthene-9'-spiro-4-(4H-5,6-dihydro-1,2-oxazine)-6-spiro-9''-thioxanthene(2a) in 65% yield based on 1a, a traceable amount of thioxanthone(3), and small amounts of unknown mixture.



The formation of 2a can be rationalized by the addition of nitrosonium ion to the sterically less hindered olefinic carbon of 1a, followed by nucleophilic attack of another molecule of 1a, generating a new carbenium intermediate, which then undergoes cyclization to give 2a.



The following new 1,2-oxazines<sup>3</sup> were obtained using the foregoing method. Nitrosonium tetrafluoroborate was used for the preparations of 2e and 2g.



1b, X=S, Y=Me

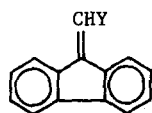
2b

1c, X=O, Y=H

2c

1d, X=O, Y=Me

2d

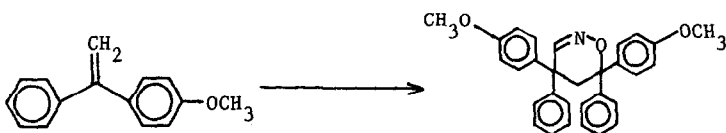


1e, Y=H

2e

1f, Y=Me

2f



1g

2g

The reaction of olefins having aryl groups at olefinic carbon atom with nitrosonium hexafluorophosphate or tetrafluoroborate gives 4H-5,6-dihydro-1,2-oxazines where acetonitrile works only as solvent. This result is in sharp contrast to the previously reported results<sup>4</sup> in which primary or secondary olefins such as propene, cis- or trans-2-butene, styrene, and cyclohexene reacted with nitrosonium tetrafluoroborate at  $-15^{\circ}$  to  $0^{\circ}\text{C}$  in acetonitrile to give 2-alkyl-N-hydroxyimidazolium tetrafluoroborate where acetonitrile acted as one of the reactants

There have been several reports to prepare 4H-5,6-dihydro-1,2-oxazines: Diels-Alder condensations of nitrosoalkenes and alkenes<sup>5</sup> are useful in the preparation of some 4H-5,6-dihydro-1,2-oxazines. However, preparation of nitrosoalkenes seems to limit the use of this method. Another widely used approach is the cyclization of oximes either under acidic<sup>6</sup> or basic<sup>7</sup> conditions. But  $\beta,\gamma$ -unsaturated ketones are required for the precursors of oximes in the case where acidic conditions are employed. On the contrary, 1-halo-4-nitrobutane is required to prepare oxime for the cyclization under basic conditions. In addition, there has been one report that cyclopropyl ketones and hydroxylamine hydrochloride were used to make 4H-5,6-dihydro-1,2-oxazines.<sup>8</sup>

Since each method has its own applicability to the particular structures, reactions of olefins with aryl groups at olefinic carbons with nitrosonium hexafluorophosphate or tetrafluoroborate in acetonitrile at low temperature are conceivable for a simple method for the preparation of 4H-5,6-dihydro-1,2-oxazines with two aryl groups at 4 and 6 positions. The scope of this reaction is under study.

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#### References and Notes

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- General procedure: To a solution of 1a (1.50 g, 7.13 mmol) in dried  $\text{CH}_3\text{CN}$  (40 mL) was added dropwise with stirring in a period of 20 min a solution of  $\text{NOPF}_6$  (0.80 g, 4.57 mmol) in dried  $\text{CH}_3\text{CN}$  (80 mL) at  $-23^\circ\text{C}$ . Color of the solution changed immediately deep blue. After an additional stirring for 30 min, the reaction mixture was allowed to leave at room temperature, by the time blue color turned to dark purple. The reaction mixture was quenched with water (20 mL) followed by neutralization with 10% aq. NaOH and extraction with  $\text{CH}_2\text{Cl}_2$ . After removal of the solvent, the residue was chromatographed on silica gel (70-230 mesh ASTM, Merck, 2 x 15 cm) column. Elution with benzene gave traceable amounts of 3 and an unknown mixture (232 mg) showing many spots on thin layer chromatogram. Elution with ethyl acetate gave 2a (2.08 g, 4.63 mmol, 65%); mp  $249-250^\circ\text{C}$  (n-hexane-benzene);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  2.80(s, 2H,  $\text{CH}_2$ ), 6.80-8.05(m, 16H, Aromatic), 8.20(s, 1H,  $\text{CH}=\text{N}$ ); IR(KBr) 3040, 2989, 1580, 1560(C=N), 1460, 1440, 1250, 1180, 750, and  $635\text{ cm}^{-1}$ ; Anal. Calcd. for  $\text{C}_{28}\text{H}_{19}\text{NOS}_2$ : C, 74.80; H, 4.26; N, 3.11. Found: C, 74.56; H, 3.76; N, 3.11.
- 2b: 30% yield; mp  $274-275^\circ\text{C}$  ( $\text{CHCl}_3$ -ethyl ether);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  0.41(d, 3H, Me,  $J=7.5\text{ Hz}$ ), 2.46(s, 3H,  $\text{MeC}=\text{NO}$ ), 2.7(q, 1H, C-CH-C,  $J=7.5\text{ Hz}$ ), 6.85-7.85(m, 16H, Aromatic); IR(KBr) 3050, 2980, 1590(C=N), 1470, 1440, 1380, 1260, 1170, 1050, 800, 770, 750, and  $720\text{ cm}^{-1}$ ; MS m/e 477( $\text{M}^+$ ).

2c: 50% yield; mp  $244-244.5^\circ\text{C}$  (n-PrOH);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  3.13(s, 2H,  $\text{CH}_2$ ), 6.90-7.85(m, 17H, Aromatic and  $\text{CH}=\text{N}$ ); IR(KBr) 3030, 2950, 1660, 1570(C=N), 1450, 1320, 1245, 1200, 1090, 1040, 1000, 875, 750, and  $615\text{ cm}^{-1}$ .

2d: 42% yield; mp  $237-238^\circ\text{C}$  ( $\text{CH}_2\text{Cl}_2$ - $\text{MeCO}_2\text{Et}$ );  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  0.41(d, 3H, Me,  $J=7.3\text{ Hz}$ ), 2.56(s, 3H,  $\text{MeC}=\text{N}$ ), 2.73(q, 1H, C-CH-C,  $J=7.3\text{ Hz}$ ), 6.85-7.95(m, 16H, Aromatic); IR(KBr) 3040, 3010, 2970, 2960, 2930, 1595, 1570(C=N), 1475, 1445, 1375, 1300, 1280, 1260, 1240,

1100, 1030, 965, 895, 865, 850, 790, 750, 640, and 610  $\text{cm}^{-1}$ .

2e: 60% yield; mp(dec)  $263^\circ\text{C}$ ( $\text{CH}_2\text{Cl}_2$ -benzene);  $^1\text{H NMR}$ ( $\text{CDCl}_3$ )  $\delta$  3.30(s, 2H,  $\text{CH}_2$ ), 7.02-8.12 (m, 17H, Aromatic and  $\text{CH}=\text{N}$ ): IR(KBr) 3100, 2940, 1555( $\text{C}=\text{N}$ ), 1470, 1445, 1270, 1250, 1180, 800, 770, 755, 745, 725, 647, 540  $\text{cm}^{-1}$ ; MS m/e 385( $\text{M}^+$ ).

2f: 55% yield; mp(dec)  $286$ - $289^\circ\text{C}$ (n-PrOH);  $^1\text{H NMR}$ ( $\text{CDCl}_3$ )  $\delta$  1.31(d, 3H, Me,  $J=6.8$  Hz), 2.10 (d, A methyl group at C-3 couples with H at C-5, exhibiting a doublet at  $\delta$  2.10 ppm and a quartet( $J=2.9$  Hz) at  $\delta$  5.52 ppm and also H at C-5 couples with a methyl group at C-5( $J=6.8$  Hz), 3H,  $\text{MeC}=\text{N}$ ,  $J=2.9$  Hz), 5.52(m, C-CH-C), 6.30-7.80(m, 16H, Aromatic); IR(KBr) 3040, 3000, 2960, 1575( $\text{C}=\text{N}$ ), 1470, 1440, 1365, 1260, 1170, 810, and 735  $\text{cm}^{-1}$ ; Anal. Calcd. for  $\text{C}_{30}\text{H}_{23}\text{NO}$ : C, 87.14; H, 5.61; N, 3.39. Found: C, 86.79; H, 5.36; N, 3.07.

2g: 78% yield; mp  $63$ - $64^\circ\text{C}$ ( $\text{CCl}_4$ -n-hexane);  $^1\text{H NMR}$ ( $\text{CDCl}_3$ )  $\delta$  3.72(d, 2H,  $\text{CH}_2$ ), 3.77(s, 6H, 2MeO), 6.63-7.60(m, 18H, Aromatic), 7.70(s, 1H,  $\text{CH}=\text{N}$ ); IR(KBr) 3120, 2820, 1610( $\text{C}=\text{N}$ ), 1570, 1515, 1465, 1450, 1255, 1185, 1035, 835, 760, 703  $\text{cm}^{-1}$ .

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