The Reactions of 5-Aryl-2,3-dimethylisoxazolium Salts with Aromatic Aldehydes

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The reactions of the 3-methyl group in 5-aryl-2,3-dimethylisoxazolium tetrafluoroborates with aromatic aldehydes, in the presence of piperidine were studied. Isoxazolium salt reactivity is independent of the phenyl group substituent at C-5 on the isoxazolium salt ring. However, it does depend on the aldehyde structure.

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A characteristic feature of 3- and, especially, 5-methyl groups on isoxazole rings is the ability of these groups to undergo aldol type condensations and related reactions, but additional activation by electron-withdrawing 4-substituents was regarded as necessary [1,2]. By using strong bases, carbanionic intermediates may be generated from alkylisoxazoles without supplementary activation [2-4].

Where both 3- and 5-alkyl groups are present, that in the 5 position is more reactive [5].

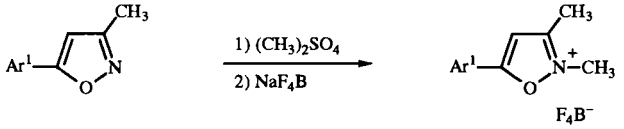
5-Alkylisoxazolium salts are deprotonated, under comparatively mild conditions, even more readily than the corresponding isoxazoles. In these compounds, however, deprotonation of 3-alkyl groups may compete, and the ratio of deprotonation in the 3- and 5-substituents is markedly influenced by the nature of the base [6].

In this paper, we report the reactivity of the 3-methyl group in 5-aryl-2,3-dimethylisoxazolium salts, in the presence of bases, with aromatic aldehydes, in order to establish the possible influence of the substituents in both the 5-aryl group of the isoxazolium salt and the aromatic aldehyde.

Results and Discussion.

Isoxazolium salts can be prepared by heating, in toluene, the isoxazole derivatives with dimethyl sulfate [7]. 5-Aryl-2,3-dimethylisoxazolium methasulfates were converted to the respective tetrafluoroborates. The results of these reactions are shown in Table 1.

Scheme I



1
2
3
4
5

6, Ar^1 = Ph
7, Ar^1 = *p*-CH_3Ph
8, Ar^1 = *p*-CH_3OPh
9, Ar^1 = *p*-ClPh
10, Ar^1 = *p*-NO_2Ph

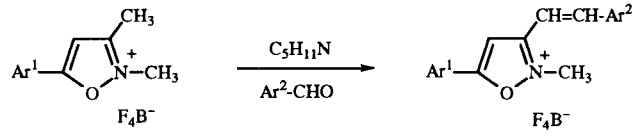
Table 1

Synthesis of 5-aryl-2,3-dimethylisoxazolium teTrafluoroborates

Isoxazole	Reaction Time	Product (%)
1	30	**6** (70)
2	36	**7** (70)
3	34	**8** (76)
4	37	**9** (67.5)
5	36	**10** (64)

The reactions of 2,3-dimethyl-5-arylisoxazolium tetrafluoroborate with benzaldehyde, in the presence of bases such as sodium hydride, sodium bicarbonate and pyridine under various conditions did not lead to satisfactory results. In contrast by using piperidine, benzyilidene derivatives were obtained (Scheme II).

Scheme II

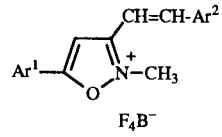


Different benzaldehyde derivatives, with electron-withdrawing and electron-donating substituents were used, in order to study the possible influence of these groups in the formation of arylidene derivatives.

The results of these reactions are summarized in Table 2.

On the basis of the results shown above, it was established that carbanionic intermediates at the C-3 methyl group can be generated from 5-aryl-2,3-dimethylisoxazolium tetrafluoroborates by using piperidine, but that if less active bases were used, these were not strong enough to move the acid-base equilibrium sufficiently towards the carbanion, and those with a high p*K*a led to ring opening.

Scheme III



F_4B^-

11, Ar^1 = Ph, Ar^2 = *p*-$(CH_3)_2NPh$
12, Ar^1 = Ph, Ar^2 = *p*-CH_3OPh
13, Ar^1 = Ph, Ar^2 = *p*-CH_3Ph
14, Ar^1 = Ph, Ar^2 = Ph
15, Ar^1 = Ph, Ar^2 = *p*-ClPh
16, Ar^1 = Ph, Ar^2 = *p*-NO_2Ph
17, Ar^1 = *p*-CH_3Ph, Ar^2 = *p*-$(CH_3)_2NPh$
18, Ar^1 = *p*-CH_3Ph, Ar^2 = *p*-CH_3OPh
19, Ar^1 = *p*-CH_3Ph, Ar^2 = CH_3Ph
20, Ar^1 = *p*-CH_3Ph, Ar^2 = Ph
21, Ar^1 = *p*-CH_3Ph, Ar^2 = *p*-Cl
22, Ar^1 = *p*-CH_3Ph, Ar^2 = *p*-NO_2
23, Ar^1 = *p*-CH_3OPh, Ar^2 = *p*-$(CH_3)_2NPh$
24, Ar^1 = *p*-CH_3OPh, Ar^2 = *p*-CH_3OPh
25, Ar^1 = *p*-CH_3OPh, Ar^2 = *p*-CH_3Ph
26, Ar^1 = *p*-CH_3OPh, Ar^2 = Ph
27, Ar^1 = *p*-CH_3OPh, Ar^2 = *p*-Cl
28, Ar^1 = *p*-CH_3OPh, Ar^2 = *p*-NO_2
29, Ar^1 = *p*-ClPh, Ar^2 = *p*-$(CH_3)_2NPh$
30, Ar^1 = *p*-ClPh, Ar^2 = *p*-CH_3OPh
31, Ar^1 = *p*-ClPh, Ar^2 = *p*-CH_3Ph
32, Ar^1 = *p*-ClPh, Ar^2 = Ph
33, Ar^1 = *p*-ClPh, Ar^2 = *p*-ClPh
34, Ar^1 = *p*-ClPh, Ar^2 = *p*-NO_2Ph
35, Ar^1 = *p*-NO_2Ph, Ar^2 = *p*-$(CH_3)_2NPh$
36, Ar^1 = *p*-NO_2Ph, Ar^2 = *p*-CH_3OPh
37, Ar^1 = *p*-NO_2Ph, Ar^2 = *p*-CH_3Ph
38, Ar^1 = *p*-NO_2Ph, Ar^2 = Ph
39, Ar^1 = *p*-NO_2Ph, Ar^2 = *p*-ClPh

Table 2

Reactions of 5-Aryl-2,3-dimethylisoxazolium Tetrafluoroborates with Aromatic Aldehydes in the Presence of Piperidine

R-C_6H_4CHO	Arylidene derivatives (%)				
(R)	**6**	**7**	**8**	**9**	**10**
$(CH_3)_2N$	**11** (50)	**17** (57)	**23** (64)	**29** (47)	**35** (69)
CH_3O	**12** (56)	**18** (69)	**24** (52)	**30** (40)	**36** (64)
CH_3	**13** (49)	**19** (39)	**25** (58)	**31** (52)	**37** (63)
H	**14** (34)	**20** (32)	**26** (49)	**32** (40)	**38** (34)
Cl	**15** (40)	**21** (33)	**27** (42)	**33** (6)	**39** (45)
NO_2	**16** (24)	**22** (18)	**28** (31)	**34** (2)	

In all cases the carbanion concentration in equilibrium with the initial compound was not very high, and the presence of a very active electrophilic reagent such as an aromatic aldehyde was necessary, in order to obtain the arylidene derivative. In fact, the reactions of 5-aryl-2,3-dimethylisoxazolium salts with other electrophilic agents which are not aromatic aldehydes - benzyl chloride, diethyl oxalate or acetone - and under various experimental conditions, did not lead to satisfactory results. This could be due to the low reactivity as electrophiles of these compounds.

Isoxazolium salt acidity is independent of the nature of the C-5 phenyl group on the isoxazolium salt ring. However, the final yield of arylidene derivatives depended on the aldehyde structure. Electron-donating substituents in the aldehyde led to a higher conjugation with the cationic nitrogen, and therefore the equilibrium was more favourable to the formation of arylidene derivatives. Consequently, yields were higher for aldehydes containing this type of substituent.

EXPERIMENTAL

Melting points are uncorrected. 5-Aryl-3-methylisoxazoles were prepared by established procedures [8]. The infrared spectra were determined using a Pye Unicam SP-1100 spectrophotometer. Nuclear magnetic resonance were determined at 60 MHz using a Varian T-60 A spectrometer using dimethyl sulfoxide-d_6 or trifluoroacetic acid solutions and TMS as the standard reference; chemical shifts were measured on the δ scale. Elemental analyses were determined using a Perkin-Elmer 240 B analiser. Solvents and reagents were purified by conventional methods.

1. Synthesis of 5-Aryl-2,3-dimethylisoxazolium Tetrafluoroborates.

A mixture of 5-aryl-3-methylisoxazoles (0.1 mole) and dimethyl sulfate (0.11 mole) in 100 ml of dry toluene was refluxed for the appropriate time (Table 1). Subsequently, the toluene layer was separated and the oily layer was washed several times with ether. The product was dissolved in water and a solution of sodium tetrafluoroborate was added to give the 5-aryl-2,3-dimethylisoxazolium tetrafluoroborate.

2,3-Dimethyl-5-phenylisoxazolium Tetrafluoroborate (**6**).

This compound was obtained as a white solid, mp 163-164° (from ethanol-water); ir (nujol): 1615 (isoxazole), 1060 (F_4B^-), 770, 690 cm^{-1}; ^{1}H-nmr (DMSO-d_6): 7.65 (m, 5H), 7.50 (s, 1H), 4.30 (s,

3H), 2.65 (s, 3H).

Anal. Calcd. for $C_{11}H_{12}NOBF_4$: C, 50.61; H, 4.60; N, 5.37. Found: C, 50.72; H, 4.56; N, 5.25.

2,3-Dimethyl-5-(*p*-methylphenyl)isoxazolium Tetrafluoroborate (**7**).

This compound was obtained as a yellow solid, mp 167-168° (from ethanol-water); ir (nujol): 1630 (isoxazole), 1050 (F_4B^-), 830 cm^{-1}; ^{1}H-nmr (DMSO-d_6): 7.90 (d, 2H), 7.60 (d, 2H), 7.45 (s, 1H), 4.45 (s, 3H), 2.85 (s, 3H), 2.60 (s, 3H).

Anal. Calcd. for $C_{12}H_{14}NOBF_4$: C, 52.40; H, 5.09; N, 5.09. Found: C, 52.28; H, 5.12; N, 4.98.

2,3-Dimethyl-5-(*p*-methoxyphenyl)isoxazolium Tetrafluoroborate (**8**).

This compound was obtained as a yellow solid, mp 168-169° (from ethanol-water); ir (nujol): 1625 (isoxazole), 1280, 1070 (F_4B^-), 840 cm^{-1}; ^{1}H-nmr (DMSO-d_6): 7.95 (d, 2H), 7.60 (s, 1H), 7.25 (d, 2H), 4.30 (s, 3H), 3.90 (s, 3H), 2.65 (s, 3H).

Anal. Calcd. for $C_{12}H_{14}NO_2BF_4$: C, 49.52; H, 4.81; N, 4.81. Found: C, 49.65; H, 4.83; N, 4.69.

5-(*p*-Chlorophenyl)-2,3-dimethylisoxazolium Tetrafluoroborate (**9**).

This compound was obtained as a white solid, mp 159-160° (from ethanol-water); ir (nujol): 1610 (isoxazole), 1050 (F_4B^-), 830 cm^{-1}; ^{1}H-nmr (carbon tetrachloride-DMSO-d_6): 7.95 (d, 2H), 7.65 (d, 2H), 7.65 (s, 1H), 4.30 (s, 3H), 2.65 (s, 3H).

Anal. Calcd. for $C_{11}H_{11}NOBClF_4$: C, 44.70; H, 3.73; N, 4.74. Found: C, 44.85; H, 3.70; N, 4.61.

2,3-Dimethyl-5-(*p*-nitrophenyl)isoxazolium Tetrafluoroborate (**10**).

This compound was obtained as a white solid, mp 145-146° (from ethanol-water); ir (nujol): 1635 (isoxazole), 1570 (NO_2), 1050 (F_4B^-), 830 cm^{-1}; ^{1}H-nmr (DMSO-d_6): 8.30 (d, 2H), 8.10 (d, 2H), 7.75 (s, 1H), 4.35 (s, 3H), 2.70 (s, 3H).

Anal. Calcd. for $C_{11}H_{11}N_2O_3BF_4$: C, 43.17; H, 3.60; N, 9.16. Found: C, 43.02; H, 3.64; N, 9.03.

2. General Procedure for the Reactions of Isoxazolium Salts with Aldehydes.

To a solution of the isoxazolium tetrafluoroborate and piperidine in absolute ethanol, a solution of the carbonyl compound was added. The molar ratio was 1:2 (isoxazolium salt:aldehyde). The system was refluxed for one hour. Subsequently, the reaction mixture was cooled and the solid precipitated from the solution was filtered.

3-(*p*-Dimethylaminostyryl)-2-methyl-5-phenylisoxazolium Tetrafluoroborate (**11**).

This compound was obtained as a red solid, mp 241-242° (from ethanol); ir (nujol): 1060 (F_4B^-), 810, 780, 700 cm^{-1}; ^{1}H-nmr (DMSO-d_6): 8.00-6.50 (m, 12H), 4.35 (s, 3H), 3.00 (s, 6H).

Anal. Calcd. for $C_{20}H_{21}N_2OBF_4$: C, 61.26; H, 5.36; N, 7.15. Found: C, 61.15; H, 5.32; N, 7.29.

3-(*p*-Methoxystyryl)-2-methyl-5-phenylisoxazolium Tetrafluoroborate (**12**).

This compound was obtained as a yellow solid, mp 280-281° (from ethanol); ir (nujol): 1050 (F_4B^-), 830, 780, 710 cm^{-1}; ^{1}H-nmr (DMSO-d_6): 8.10-6.85 (m, 12H), 4.40 (s, 3H), 3.85 (s, 3H).

Anal. Calcd. for $C_{19}H_{18}NO_2BF_4$: C, 60.19; H, 4.75; N, 3.70. Found: C, 60.31; H, 4.70; N, 3.52.

2-Methyl-3-(*p*-methylstyryl)-5-phenylisoxazolium Tetrafluoroborate (**13**).

This compound was obtained as a yellow solid, mp 291-292° (from ethanol); ir (nujol): 1060 (F_4B^-), 840, 779, 700 cm^{-1}; ^{1}H-nmr (DMSO-d_6): 8.10-7.00 (m, 12H), 4.35 (s, 3H), 2.30 (s, 3H).

Anal. Calcd. for $C_{19}H_{18}NOBF_4$: C, 62.84; H, 4.96; N, 3.86. Found: C, 62.91; H, 4.89; N, 3.98.

2-Methyl-5-phenyl-3-styrylisoxazolium Tetrafluoroborate (**14**).

This compound was obtained as a yellow solid, mp 268-269° (from ethanol); ir (nujol): 1060 (F_4B^-), 760, 700 cm^{-1}; ^{1}H-nmr (trifluoroacetic acid): 8.10-6.80 (m, 13), 4.25 (s, 3H).

Anal. Calcd. for $C_{18}H_{16}NOBF_4$: C, 61.92; H, 4.62; N, 4.01. Found: C, 61.81; H, 4.58; N, 4.15.

3-(*p*-Chlorostyryl)-2-methyl-5-phenylisoxazolium Tetrafluoroborate (**15**).

This compound was obtained as a yellow solid, mp 293-294° (from ethanol); ir (nujol): 1070 (F_4B^-), 830, 780, 700 cm^{-1}; ^{1}H-nmr (DMSO-d_6): 8.20-7.30 (m, 12H), 4.45 (s, 3H).

Anal. Calcd. for $C_{18}H_{15}NOBClF_4$: C, 56.35; H, 3.91; N, 3.65. Found: C, 56.42; H, 3.87; N, 3.52.

2-Methyl-3-(*p*-nitrostyryl)-5-phenylisoxazolium Tetrafluoroborate (**16**).

This compound was obtained as a brown solid, mp 224-225° (from ethanol); ir (nujol): 1060 (F_4B^-), 850, 750, 710 cm^{-1}; ^{1}H-nmr (trifluoroacetic acid): 8.50-7.00 (m, 12H), 4.45 (s, 3H).

Anal. Calcd. for $C_{18}H_{15}N_2O_3BF_4$: C, 54.85; H, 3.81; N, 7.11. Found: C, 54.71; H, 3.77; N, 7.23.

3-(*p*-Dimethylaminostyryl)-2-methyl-5-(*p*-methylphenyl)isoxazolium Tetrafluoroborate (**17**).

This compound was obtained as a red solid, mp 250-251° (from ethanol); ir (nujol): 1060 (F_4B^-), 950, 815 cm^{-1}; ^{1}H-nmr (DMSO-d_6): 8.00-6.60 (m, 11H), 4.30 (s, 3H), 3.05 (s, 6H), 2.40 (s, 3H).

Anal. Calcd. for $C_{21}H_{23}N_2OBF_4$: C, 62.09; H, 5.70; N, 6.89. Found: C, 61.91; H, 5.65; N, 6.78.

3-(*p*-Methoxystyryl)-2-methyl-5-(*p*-methylphenyl)isoxazolium Tetrafluoroborate (**18**).

This compound was obtained as an orange solid, mp 271-272° (from ethanol); ir (nujol): 1178 (Ph-O-C), 1040 (F_4B^-), 830 cm^{-1}; ^{1}H-nmr (DMSO-d_6): 8.10-6.90 (m, 11H), 4.40 (s, 3H), 3.80 (s, 3H), 2.45 (s, 3H).

Anal. Calcd. for $C_{20}H_{20}NO_2BF_4$: C, 61.09; H, 5.13; N, 3.56. Found: C, 61.18; H, 5.17; N, 3.49.

2-Methyl-5-(*p*-methylphenyl)-3-(*p*-methylstyryl)isoxazolium Tetrafluoroborate (**19**).

This compound was obtained as a yellow solid, mp 270-271° (from ethanol); ir (nujol): 1050 (F_4B^-), 950, 825 cm^{-1}; ^{1}H-nmr (DMSO-d_6): 8.30-7.20 (m, 12H), 4.40 (s, 3H), 2.39 (s, 3H), 2.41 (s, 3H).

Anal. Calcd. for $C_{20}H_{20}NOBF_4$: C, 63.68; H, 5.43; N, 3.71. Found: C, 63.71; H, 5.30; N, 3.54.

2-Methyl-5-(*p*-methylphenyl)-3-styrylisoxazolium Tetrafluoroborate (**20**).

This compound was obtained as a yellow solid, mp 267-268° (from ethanol); ir (nujol): 1060 (F_4B^-), 955, 820, 765, 690 cm^{-1}; ^{1}H-nmr (DMSO-d_6): 8.30-7.20 (m, 12H), 4.45 (s, 3H), 2.45 (s, 3H).

Anal. Calcd. for $C_{19}H_{18}NOBF_4$: C, 62.83; H, 4.99; N, 3.85. Found: C, 62.75; H, 4.95; N, 3.98.

3-(*p*-Chlorostyryl)-2-methyl-5-(*p*-methylphenyl)isoxazolium Tetrafluoroborate (**21**).

This compound was obtained as a yellow solid, mp 273-274° (from ethanol); ir (nujol): 1070 (F_4B^-), 950, 825 cm^{-1}; ^{1}H-nmr (DMSO-d_6): 8.00-7.00 (m, 11H), 4.40 (s, 3H), 2.45 (s, 3H).

Anal. Calcd. for $C_{19}H_{17}NOBClF_4$: C, 57.39; H, 4.30; N, 3.52. Found: C, 57.51; H, 4.25; N, 3.43.

2-Methyl-5-(*p*-methylphenyl)-3-(*p*-nitrostyryl)isoxazolium Tetrafluoroborate (**22**).

This compound was obtained as an orange solid, mp 259-260° (from ethanol); ir (nujol): 1530 and 1360 (NO_2), 1060 (F_4B^-), 995, 830 cm^{-1}, ^{1}H-nmr (DMSO-d_6): 8.20-7.20 (m, 11H), 4.45 (s, 3H), 2.45 (s, 3H).

Anal. Calcd. for $C_{19}H_{17}N_2O_3BF_4$: C, 55.91; H, 4.19; N, 6.86. Found: C, 56.03; H, 4.24; N, 6.74.

3-(*p*-Dimethylaminostyryl)-5-(*p*-methoxyphenyl)-2-methylisoxazolium Tetrafluoroborate (**23**).

This compound was obtained as a red solid, mp 254-255° (from ethanol); ir (nujol): 1050 (F_4B^-), 825 cm^{-1}; ^{1}H-nmr (DMSO-d_6): 8.05-6.50 (m, 11H), 4.50 (s, 3H), 3.90 (s, 3H), 3.05 (s, 6H).

Anal. Calcd. for $C_{21}H_{23}N_2O_2BF_4$: C, 59.74; H, 5.49; N, 6.63. Found: C, 59.62; H, 5.46; N, 6.75.

5-(*p*-Methoxyphenyl)-3-(*p*-methoxystyryl)-2-methylisoxazolium Tetrafluoroborate (**24**).

This compound was obtained as a yellow solid, mp 257-258° (from ethanol); ir (nujol): 1050 (F_4B^-), 1280 (Ph-O-C), 840 cm^{-1}; ^{1}H-nmr (DMSO-d_6): 8.30-7.10 (m, 11H), 4.45 (s, 3H), 3.95 (s, 3H), 3.50 (s, 3H).

Anal. Calcd. for $C_{20}H_{20}NO_3BF_4$: C, 58.70; H, 4.92; N, 3.42. Found: C, 58.63; H, 4.88; N, 3.56.

5-(*p*-Methoxyphenyl)-2-methyl-3-(*p*-methylstyryl)isoxazolium Tetrafluoroborate (**25**).

This compound was obtained as a yellow solid, mp 280-281° (from ethanol); ir (nujol): 1280 (Ph-O-C), 1060 (F_4B^-) cm^{-1}; ^{1}H-nmr (DMSO-d_6): 8.25-7.20 (m, 11H), 4.45 (s, 3H), 3.90 (s, 3H), 2.40 (s, 3H).

Anal. Calcd. for $C_{20}H_{20}NO_2BF_4$: C, 61.09; H, 5.12; N, 3.56. Found: C, 60.96; H, 5.09; N, 3.42.

5-(*p*-Methoxyphenyl)-2-methyl-3-styrylisoxazolium Tetrafluoroborate (**26**).

This compound was obtained as a white solid, mp 250-251° (from ethanol); ir (nujol): 1280 (Ph-O-C), 1060 (F_4B^-), 820 cm^{-1}; ^{1}H-nmr (trifluoroacetic acid): 7.65-6.60 (m, 12H), 3.90 (s, 3H), 3.50 (s, 3H).

Anal. Calcd. for $C_{19}H_{18}NO_2BF_4$: C, 60.13; H, 4.78; N, 3.69. Found: C, 60.28; H, 4.75; N, 3.76.

3-(*p*-Chlorostyryl)-5-(*p*-methoxyphenyl)-2-methylisoxazolium Tetrafluoroborate (**27**).

This compound was obtained as a yellow solid, mp 293-294° (from ethanol); ir (nujol): 1280 (Ph-O-C), 1050 (F_4B^-), 830 cm^{-1}; ^{1}H-nmr (DMSO-d_6): 8.20-7.05 (m, 11H), 4.45 (s, 3H), 3.90 (s, 3H).

Anal. Calcd. for $C_{19}H_{17}NO_2BClF_4$: C, 55.17; H, 4.14; N, 3.38. Found: C, 55.23; H, 4.11; N, 3.50.

5-(*p*-Methoxyphenyl)-2-methyl-3-(*p*-nitrostyryl)isoxazolium Tetrafluoroborate (**28**).

This compound was obtained as a yellow solid, mp 252-253° (from ethanol); ir (nujol): 1535 and 1395 (NO_2), 1280 (Ph-O-C), 1050 (F_4B^-) cm^{-1}; ^{1}H-nmr (DMSO-d_6): 8.50-7.95 (m, 11H), 4.55 (s, 3H), 3.95 (s, 3H).

Anal. Calcd. for $C_{19}H_{17}N_2O_4BF_4$: C, 53.80; H, 4.04; N, 6.60. Found: 53.68; H, 4.01; N, 6.72.

5-(*p*-Chlorophenyl)-3-(*p*-dimethylaminostyryl)-2-methylisoxazolium Tetrafluoroborate (**29**).

This compound was obtained as a red solid, mp 255-256° (from ethanol); ir (nujol): 1050 (F_4B^-), 800 cm^{-1}; ^{1}H-nmr (DMSO-d_6): 8.10-6.60 (m, 11H), 4.35 (s, 3H), 3.00 (s, 6H).

Anal. Calcd. for $C_{20}H_{20}N_2OBClF_4$: C, 56.29; H, 4.72; N, 6.56. Found: C, 56.15; H, 4.70; N, 6.71.

5-(*p*-Chlorophenyl)-3-(*p*-methoxystyryl)-2-methylisoxazolium Tetrafluoroborate (**30**).

This compound was obtained as a yellow solid, mp 290-291° (from ethanol); ir (nujol): 1070 (F_4B^-), 830 cm^{-1}; ^{1}H-nmr (DMSO-d_6): 7.30-6.90 (m, 11H), 4.40 (s, 3H), 3.85 (s, 3H).

Anal. Calcd. for $C_{19}H_{17}NO_2BClF_4$: C, 55.17; H, 4.14; N, 3.38. Found: C, 55.21; H, 4.16; N, 3.26.

5-(*p*-Chlorophenyl)-2-methyl-3-(*p*-methylstyryl)isoxazolium Tetrafluoroborate (**31**).

This compound was obtained as a yellow solid, mp 291-292° (from ethanol); ir (nujol): 1050 (F_4B^-), 815 cm^{-1}; ^{1}H-nmr (DMSO-d_6): 8.30-7.15 (m, 11H), 4.45 (s, 3H), 2.35 (s, 3H).

Anal. Calcd. for $C_{19}H_{17}NOBClF_4$: C, 57.39; H, 4.31; N, 3.52. Found: C, 57.46; H, 4.27; N, 3.61.

5-(*p*-Chlorophenyl)-2-methyl-3-styrylisoxazolium Tetrafluoroborate (**32**).

This compound was obtained as a yellow solid, mp 289-290° (from ethanol); ir (nujol): 1070 (F_4B^-), 820 cm^{-1}; ^{1}H-nmr (DMSO-d_6): 8.25-7.20 (m, 12H), 4.45 (s, 3H).

Anal. Calcd. for $C_{18}H_{15}NOBClF_4$: C, 56.30; H, 3.94; N, 3.65. Found: C, 56.44; H, 3.91; N, 3.52.

5-(*p*-Chlorophenyl)-3-(*p*-chlorostyryl)-2-methylisoxazolium Tetrafluoroborate (**33**).

This compound was obtained as a yellow solid, mp 275-276° (from ethanol); ir (nujol): 1080 (F_4B^-), 830 cm^{-1}; ^{1}H-nmr (DMSO-d_6): 8.30-7.30 (m, 11H), 4.40 (s, 3H).

Anal. Calcd. for $C_{18}H_{14}NOBCl_2F_4$: C, 51.71; H, 3.37; N, 3.35. Found: C, 51.83; H, 3.41; N, 3.28.

5-(*p*-Chlorophenyl)-2-methyl-3-(*p*-nitrostyryl)isoxazolium Tetrafluoroborate (**34**).

This compound was obtained as a white solid, mp 267-268° (from ethanol); ir (nujol): 1530 and 1360 (NO_2), 1070 (F_4B^-), 840 cm^{-1}; ^{1}H-nmr (trifluoroacetic acid): 8.40-7.40 (m, 11H), 4.40 (s, 3H).

Anal. Calcd. for $C_{18}H_{14}N_2O_3BClF_4$: C, 50.14; H, 3.29; N, 6.54. Found: C, 50.02; H, 3.32; N, 6.38.

3-(*p*-Dimethylaminostyryl)-2-methyl-5-(*p*-nitrophenyl)isoxazolium Tetrafluoroborate (**35**).

This compound was obtained as a brown solid, mp 239-240° (from ethanol); ir (nujol): 1530 and 1355 (NO_2), 1060 (F_4B^-), 950 cm^{-1}; ^{1}H-nmr (DMSO-d_6): 8.50-6.60 (m, 11H), 4.35 (s, 3H), 3.05 (s, 6H).

Anal. Calcd. for $C_{20}H_{20}N_3O_3BF_4$: C, 54.94; H, 4.61; N, 9.61. Found: C, 54.86; H, 4.63; N, 9.69.

3-(*p*-Methoxystyryl)-2-methyl-5-(*p*-nitrophenyl)isoxazolium Tetrafluoroborate (**36**).

This compound was obtained as an orange solid, mp 256-257° (from ethanol); ir (nujol): 1535 and 1350 (NO_2), 1180 (Ph-O-C), 1075 (F_4B^-), 955, 840 cm^{-1}; ^{1}H-nmr (DMSO-d_6): 8.50-6.90 (m, 11H), 4.40 (s, 3H), 3.85 (s, 3H).

Anal. Calcd. for $C_{19}H_{17}N_2O_4BF_4$: C, 53.80; H, 4.04; N, 6.60. Found: C, 53.68; H, 4.05; N, 6.68.

2-Methyl-3-(*p*-methylstyryl)-5-(*p*-nitrophenyl)isoxazolium Tetrafluoroborate (**37**).

This compound was obtained as an orange solid, mp 255-256° (from ethanol); ir (nujol): 1535 and 1360 (NO_2), 1070 (F_4B^-), 955 cm^{-1}; ^{1}H-nmr (DMSO-d_6): 8.45-7.10 (m, 11H), 4.45 (s, 3H), 2.40 (s, 3H).

Anal. Calcd. for $C_{19}H_{17}N_2O_3BF_4$: C, 55.91; H, 4.20; N, 6.86. Found: C, 56.02; H, 4.16; N, 6.80.

2-Methyl-5-(*p*-nitrophenyl)-3-styrylisoxazolium Tetrafluoroborate (**38**).

This compound was obtained as a yellow solid, mp 257-258° (from ethanol); ir (nujol): 1535 and 1355 (NO_2), 1060 (F_4B^-), 955, 760, 700 cm^{-1}; ^{1}H-nmr (DMSO-d_6): 8.60-6.80 (m, 12H), 4.45 (s, 3H).

Anal. Calcd. for $C_{18}H_{15}N_2O_3BF_4$: C, 54.85; H, 3.84; N, 7.11. Found: C, 54.73; H, 3.81; N, 7.25.

3-(*p*-Chlorostyryl)-2-methyl-5-(*p*-nitrophenyl)isoxazolium Tetrafluoroborate (**39**).

This compound was obtained as an orange solid, mp 240-241° (from ethanol); ir (nujol): 1540 and 1350 (NO_2), 1075 (F_4B^-), 955 cm^{-1}; ^{1}H-nmr (DMSO-d_6): 8.50-7.40 (m, 11H), 4.50 (s, 3H).

Anal. Calcd. for $C_{18}H_{14}N_2O_3BClF_4$: C, 50.44; H, 3.29; N, 6.54. Found: C, 50.36; H, 3.25; N, 6.67.

REFERENCES AND NOTES

[1] N. Kochetkov and D. Sokolov, *Adv. Heterocyclic Chem.*, **2**, 365 (1963).

[2] G. Renzi, V. Dal Piaz and S. Pinzauti, *Gazz. Chim. Ital.*, **99**, 753 (1969).

[3] J. Gainer, G. A. Howarth, W. Hoyle, S. M. Roberts and H. Suschitzky, *J. Chem. Soc., Perkin Trans. 1*, 994 (1976).

[4] R. G. Micetich, *Can. J. Chem.*, **48**, 2006 (1970).

[5] K. Bowden, G. Crank and W. J. Ross, *J. Chem. Soc. (C)*, 172 (1968).

[6] M. Ohashi, *Nippon Kagaku Zasshi*, **91**, 12 (1970).

[7] R. B. Woodward, R. A. Olofson, *Tetrahedron Suppl.*, **7**, 415 (1966).

[8] A. Alberola, J. M. Bañez, L. Calvo, M. T. Rodríguez Rodríguez, M. C. Sañudo, manuscript submitted for publication in *J. Heterocyclic Chem.*