Synthesis of 3-Substituted 5-Arylisoxazoles from α,β-Unsaturated Oximes

Angel Alberola*, J. Manuel Bañez, Luis Calvo,
M. Teresa Rodríguez Rodríguez and M. Carmen Sañudo

Departamento de Química Orgánica, Universidad de Valladolid,
47011 Valladolid, Spain

Received December 7, 1992

The synthesis of 3-substituted 5-arylisoxazoles from oximes of α,β-unsaturated ketones is studied. The formation of the isoxazole derivatives takes place by cyclization of oximes in the presence of iodine and potassium iodide. The presence of isoxazoline is detected. On the basis of the results a plausible mechanism is suggested.

J. Heterocyclic Chem., **30**, 467 (1993).

Studies of the reactivity of hydroxylamine with α,β-unsaturated ketones have shown that using an excess of sodium hydroxide [1] lead directly to isoxazolines and that the oximes of those ketones give the same sort of compounds by Beckmann reaction, in the presence of sulfuric acid [2].

An unequivocal method of synthesis of isoxazole derivatives, used in the preparation of substances related to natural products, is based on the oxidation of the oximes of α,β-unsaturated ketones [3]. This synthesis is of particular interest because of the ready availability of the starting material, but the mechanism of this reaction is not well understood.

In this paper, we report the synthesis of 3-substituted 5-arylisoxazoles according to the procedure of Büchi and Vederas [3] and we propose a plausible mechanism which allows us to explain the results.

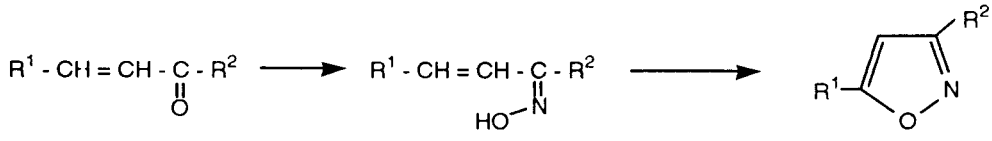
Results and Discussion.

The synthesis of 3-substituted 5-arylisoxazoles is shown in the Scheme I.

The ketones **2-7** and **9-10** were obtained by aldol condensation between an aromatic aldehyde (benzaldehyde and different *para*-substituted derivatives or furfural) and the corresponding ketone (acetone, butanone or acetophenone).

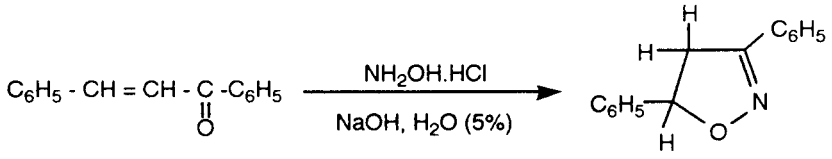
The synthesis of the oximes was carried out by three different methods each using a different base. The first method (method A) involved the reaction of the oxo compound with hydroxylamine hydrochloride in the presence of pyridine and absolute ethanol as solvent. In the second case (method B), the base used was aqueous potassium carbonate. The last method (method C) also in aqueous solution, used sodium hydroxide as base. The results are shown in Table 1. Method A is, in general, the one which led to better results, and, therefore, it was used more often than the others. In the synthesis of **18** by method C, the product resulting from the cyclization of the oxime **8**, 3,5-diphenyl-2-isoxazoline (**31**), is obtained in quite good yield (94%). The formation of this substance is a fact of great interest in relation to the problem of the isoxazole formation mechanism.

Scheme I



1	**11**	**21** : $R^1 = C_6H_5$, $R^2 = CH_3$
2	**12**	**22** : $R^1 = C_6H_5$, $R^2 = C_2H_5$
3	**13**	**23** : $R^1 = p\text{-}CH_3\,C_6H_4$, $R^2 = CH_3$
4	**14**	**24** : $R^1 = p\text{-}CH_3O\,C_6H_4$, $R^2 = CH_3$
5	**15**	**25** : $R^1 = p\text{-}(CH_3)_2N\,C_6H_4$, $R^2 = CH_3$
6	**16**	**26** : $R^1 = p\text{-}Cl\,C_6H_4$, $R^2 = CH_3$
7	**17**	**27** : $R^1 = p\text{-}NO_2\,C_6H_4$, $R^2 = CH_3$
8	**18**	**28** : $R^1 = R^2 = C_6H_5$
9	**19**	**29** : R^1 = 2-Furyl , $R^2 = CH_3$
10	**20**	**30** : R^1 = 2-Furyl , $R^2 = C_6H_5$

Scheme II



8 **31**

Table 1

Synthesis of Oximes of α,β-Unsaturated Ketones

Ketone	Method	Time Reaction	Product (%)
1	B	6 h	**11** (93)
1	A	2 h	**11** (67)
2	A	3 h	**12** (60)
3	C	20 min	**13** (50)
4	A	2.30 h	**14** (50)
4	C	20 min	**14** (21)
5	C	20 min	**15** (40)
5	A	2 h	**15** (78)
6	A	2.30 h	**16** (49)
7	A	2 h	**17** (87)
8	C	2 h	**31** (94)
8	A	2.30 h	**18** (10)
9	B	6 h	**19** (95)
10	A	2 h	**20** (86)

The conversion of the oximes in the isoxazole derivatives was carried out by heating with iodine and potassium iodide, for eight hours, in a THF-water solution containing sodium bicarbonate; it was noticed that shorter reaction times led to substantially higher yields in the isoxazole synthesis. On the other hand, it was observed that the use of twice the amount of iodine and potassium iodide relating to that reported in the original procedure [3] gave higher yields. The results are summarized in Table 2.

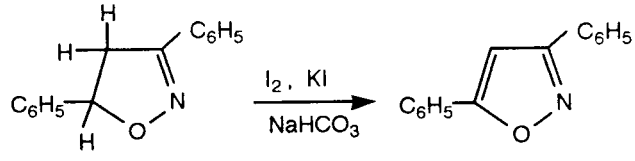
It should be pointed out that all attempts to synthesize 3-methyl-5-(4-dimethylaminophenyl)isoxazole (**25**), using different experimental conditions, were unsuccessful. On the other hand, in the preparation of **21** and **24**, if the oxime and the oxidizing agent were used in equimolar ratio, a mixture of the isoxazole (65%) and the untransformed starting material (35%) was obtained. 3,5-Diphenylisoxazole (**28**) was obtained in satisfactory yield by oxidation of the isoxazoline **31** with iodine and potassium iodide.

Table 2

Synthesis of 3-substituted 5-Arylisoxazoles

Oxime	Isoxazole (%)
11	**21** (98)
12	**22** (93)
13	**23** (89)
14	**24** (96)
16	**26** (92)
17	**27** (90)
31	**28** (65)
18	**28** (65)
19	**29** (76)
20	**30** (80)

Scheme III



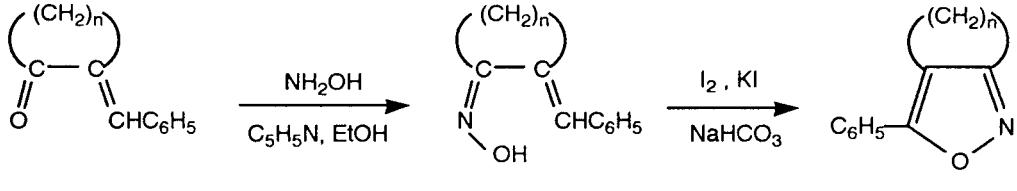
This study was extended to α,β-unsaturated cyclic ketones containing an exocyclic double bond. The ketones chosen were 2-benzylidenecyclopentanone (**32**), 2-benzylidenecyclohexanone (**33**) and 2-benzylidenecycloheptanone (**34**), and they were transformed to isoxazole derivatives following the Scheme IV. The results are shown in Table 3.

Table 3

Synthesis of Bicyclic 5-Arylisoxazoles

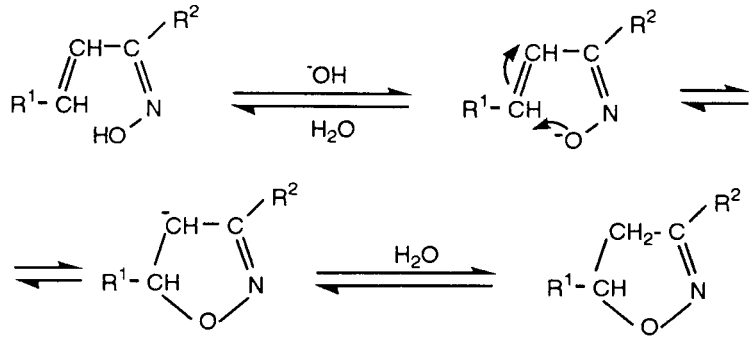
Keton	Oxime (%)	Isoxazole (%)
32	**35** (26)	**38** (72)
33	**36** (93)	**39** (85)
34	**37** (79)	**40** (91)

Scheme IV



32 : n = 3 **35** : n = 3 **38** : n = 3
33 : n = 4 **36** : n = 4 **39** : n = 4
34 : n = 5 **37** : n = 5 **40** : n = 5

Scheme V

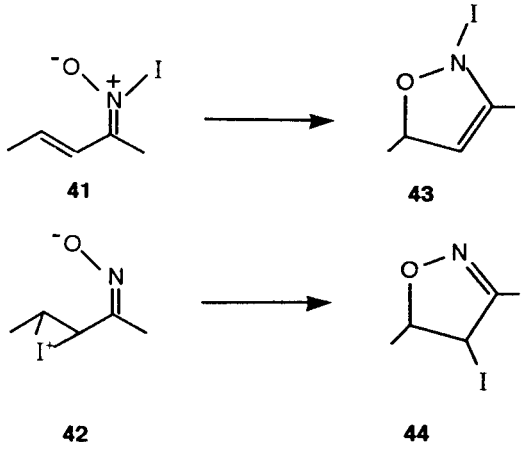


On the basis of the formation of the isoxazoline **31** and the results reported by Meisenheimer [4] it could be deduced that the oximes obtained from α,β-unsaturated ketones cyclized to isoxazolines probably according to Scheme IV, but that they cannot be transformed directly into the isoxazole derivatives without the presence of an oxidizing agent.

The same result is achieved if the unsaturated oxime has a good leaving group [5], which determines the formation of the isoxazole compound through an elimination process.

The formation of isoxazole derivatives by cyclization of unsaturated oximes in the presence of iodine and sodium bicarbonate, should go, according to Büchi and Vederas [3], through any of the two intermediates **41** and **42**, which lead to **43** and **44**, respectively, and subsequently to the aromatic heterocyclic system.

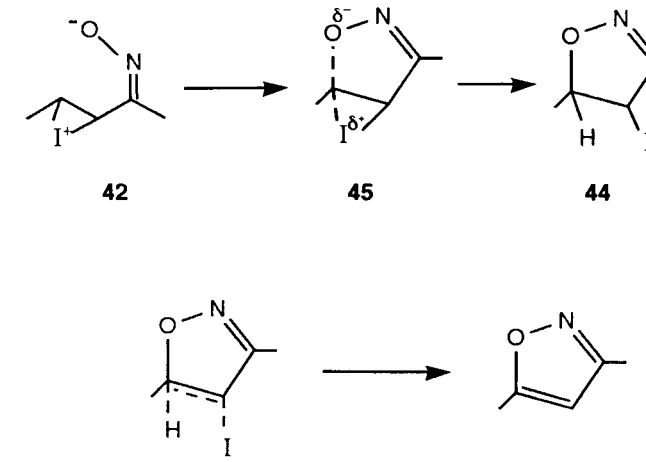
Scheme VI



Kaufmann *et al.* [6] isolated the intermediate referable to **44** and this showed that the conversion of unsaturated oximes to isoxazole derivatives goes *via* iodonium ion, that subsequently cyclizes to 4-iodo-2-isoxazoline (**44**) by internal nucleophilic substitution.

The results obtained in our study confirm this point of view, since the group bound to the carbon atom, on which the cyclization takes place, does not influence the yield of the process. This allows us to consider that the intermediate **41** in not very probable, since in this the unsaturated system is conjugated with the aromatic substituent on the β carbon atom and so the groups on the aromatic ring should have some sort of influence in the cyclization reaction. On the contrary, in a dipolar intermediate ion like **42**, the carbon atom in β of the oximate is positive enough to be attacked easily by the anionic oxygen. If this attack involves the cyclic transition state, **45**, the substituents should not have an appreciable influence.

Scheme VII



EXPERIMENTAL

Melting points are uncorrected. α,β-Unsaturated ketones were prepared by established procedures [7-16]. The synthesis of 3-methyl-5-phenyl- [17], 3-ethyl-5-phenyl-, 3,5-diphenyl- and 3-methyl-5-(*p*-methoxyphenyl)isoxazole were described previously [18]. The infrared spectra were determined using a Pye Unicam SP-1100 spectrophotometer. Nuclear magnetic resonance spectra were determined at 60 MHz on a Varian T-60 A spectrometer using deuteriochloroform or carbon tetrachloride solutions and with TMS as the standard reference; chemical shifts were measured on the δ scale. Elemental analyses were determined

using a Perkin-Elmer 240 B analyser. Solvents and reagents were purified by conventional methods.

1. Synthesis of the Oximes of α,β-Unsaturated Ketones.

Method A.

To a mixture of the same number of grams of α,β-unsaturated ketone and hydroxylamine hydrochloride, five times (by volume) of absolute ethanol and pyridine were added. The stirred reaction mixture was refluxed for two hours. After that, the ethanol and the pyridine were evaporated *in vacuo*. The residue was washed with water and the oxime was obtained as a solid, that was purified by recrystallization.

Method B.

To a mixture of the ketone, an excess of hydroxylamine hydrochloride and the same number of moles of potassium carbonate, a mixture of water and ethanol was added until the solution became clear. The system was refluxed for six hours. The reaction mixture was cooled and poured into ice. The oxime was obtained as a solid that was purified by recrystallization.

Method C.

The mixture of ketone, an excess of hydroxylamine hydrochloride and a 5% solution of sodium hydroxide was stirred. After dissolving the solid, ethanol was added to get a clear solution. The system was refluxed and after cooling, was poured into cold water. A solid was obtained. The purification of the compound was carried out as previously.

4-Phenyl-3-buten-2-one Oxime (**11**).

This compound was obtained as a white solid, mp 115-116° (from ethanol); ir (nujol): 3270 (OH), 1630 (C=N), 750, 700 cm^{-1}; ^{1}H-nmr (deuteriochloroform): 9.20 (s, 1H), 7.45 (m, 5H), 6.95 (s, 2H), 2.20 (s, 3H).

Anal. Calcd. for $C_{10}H_{11}NO$: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.59; H, 6.84; N, 8.71.

1-Phenyl-1-penten-3-one Oxime (**12**).

This compound was obtained as a white solid, mp 91-92° (from ethanol); ir (nujol): 3290 (OH), 1640 (C=N), 750, 710 cm^{-1}; ^{1}H-nmr (deuteriochloroform): 10.35 (s, 1H), 7.40 (m, 5H), 6.90 (s, 2H), 2.50 (q, 2H), 1.20 (t, 3H).

Anal. Calcd. for $C_{11}H_{13}NO$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.48; H, 7.52; N, 7.93.

4-(*p*-Methylphenyl)-3-buten-2-one Oxime (**13**).

This compound was obtained as a white solid, mp 126-127° (from ethanol); ir (nujol): 3250 (OH), 1612 (C=N), 975, 812 cm^{-1}; ^{1}H-nmr (deuteriochloroform): 7.70 (m, 4H), 7.30 (s, 2H), 2.80 (s, 3H), 2.60 (s, 3H).

Anal. Calcd. for $C_{11}H_{13}NO$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.43; H, 7.50; N, 8.01.

4-(*p*-Methoxyphenyl)-3-buten-2-one Oxime (**14**).

This compound was obtained as a white solid, mp 122-123° (from ethanol); ir (nujol): 3240 (OH), 1620 (C=N), 830 cm^{-1}; ^{1}H-nmr (deuteriochloroform): 7.35 (d, 2H), 6.85 (d, 2H), 6.80 (s, 2H), 3.80 (s, 3H), 2.15 (s, 3H).

Anal. Calcd. for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.33. Found: C, 69.02; H, 6.89; N, 7.26.

4-(*p*-Dimethylaminophenyl)-3-buten-2-one Oxime (**15**).

This compound was obtained as a white solid, mp 168-169° (from ethanol-water); ir (nujol): 3240 (OH), 1620 (C=N), 960, 810 cm^{-1}; ^{1}H-nmr (carbon tetrachloride-DMSO-d_6): 10.70 (s, 1H), 7.40-6.50 (m, 4H), 6.65 (s, 2H), 2.91 (s, 6H), 1.95 (s, 3H).

Anal. Calcd. for $C_{12}H_{16}N_2O$: C, 70.56; H, 7.90; N, 13.71. Found: C, 70.49; H, 7.93; N, 13.65.

4-(*p*-Chlorophenyl)-3-buten-2-one Oxime (**16**).

This compound was obtained as a white solid, mp 120-121° (from ethanol-water); ir (nujol): 3270 (OH), 1630 (C=N), 820 cm^{-1}; ^{1}H-nmr (deuteriochloroform): 8.65 (s, 1H), 7.35 (s, 4H), 6.80 (s, 2H), 2.15 (s, 3H).

Anal. Calcd. for $C_{10}H_{10}NOCl$: C, 61.39; H, 5.15; N, 7.16. Found: C, 61.43; H, 5.08; N, 7.13.

4-(*p*-Nitrophenyl)-3-buten-2-one Oxime (**17**).

This compound was obtained as a white solid, mp 186-187° (from ethanol); ir (nujol): 3230 (OH), 1600 (C=N), 1525 and 1385 (NO_2), 970, 828 cm^{-1}; ^{1}H-nmr (DMSO-d_6): 8.05 (d, 2H), 7.47 (d, 2H), 6.90 (d, 1H), 6.70 (d, 1H), 2.00 (s, 3H).

Anal. Calcd. for $C_{10}H_{10}N_2O_3$: C, 58.25; H, 4.89; N, 13.58. Found: C, 58.28; H, 4.83; N, 13.63.

1,3-Diphenyl-2-propen-1-one Oxime (**18**).

This compound was obtained as a white solid, mp 198-199° (from ethanol); ir (nujol): 3220 (OH), 1610 (C=N), 760, 700 cm^{-1}; ^{1}H-nmr (deuteriochloroform): 11.55 (s, 1H), 7.75-7.10 (m, 12H).

Anal. Calcd. for $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.57; H, 5.82; N, 6.32.

4-(2'-Furyl)-3-buten-2-one Oxime (**19**).

This compound was obtained as a white solid, mp 60-61° (from ethanol); ir (nujol): 3260 (OH), 1640 (C=N) cm^{-1}; ^{1}H-nmr (deuteriochloroform): 7.35 (d, 1H), 6.80 (d, 1H), 6.70 (d, 1H), 6.60-6.30 (m, 2H), 2.05 (s, 3H).

Anal. Calcd. for $C_8H_9NO_2$: C, 63.56; H, 6.00; N, 9.27. Found: C, 63.60; H, 6.11; N, 9.21.

3-(2'-Furyl)-1-phenyl-2-propen-1-one Oxime (**20**).

This compound was obtained as a yellow liquid, bp 165° at 1 mm; ir (nujol): 3300 (OH), 1640 (C=N), 750, 710 cm^{-1}; ^{1}H-nmr (deuteriochloroform): 9.90 (s, 1H), 7.80-7.20 (m, 7H), 6.85 (d, 1H), 6.40 (d, 1H), 6.30 (d, 1H).

Anal. Calcd. for $C_{13}H_{11}NO_2$: C, 73.22; H, 5.20; N, 6.57. Found: C, 73.16; H, 5.23; N, 6.53.

2-Benzylidenecyclopentanone Oxime (**35**).

This compound was obtained as a yellow solid, mp 127-128° (from ethanol-water); ir (nujol): 3280 (OH), 1640 (C=N), 1610 (C=C), 850, 760, 700 cm^{-1}; ^{1}H-nmr (deuteriochloroform): 10.70 (s, 1H), 7.40 (s, 5H), 7.20 (s, 1H), 3.00-2.40 (m, 4H), 2.20-1.60 (m, 2H).

Anal. Calcd. for $C_{12}H_{13}NO$: C, 76.98; H, 7.00; N, 7.48. Found: C, 76.93; H, 6.94; N, 7.52.

2-Benzylidenecyclohexanone Oxime (**36**).

This compound was obtained as a white solid, mp 124-125° (from ethanol-water); ir (nujol): 3290 (OH), 1640 (C=N), 830, 770, 710 cm^{-1}; ^{1}H-nmr (deuteriochloroform): 7.70-7.20 (s, 6H), 6.90 (s, 1H), 2.80-2.40 (m, 4H), 2.00-1.40 (m, 4H).

Anal. Calcd. for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.54; H, 7.55; N, 6.99.

2-Benzylidenecycloheptanone Oxime (**37**).

This compound was obtained as a white solid, mp 61-62° (from ethanol-water); ir (nujol): 3270 (OH), 1650 (C=N), 1610 (C=C), 830, 760, 700 cm^{-1}; ^{1}H-nmr (deuteriochloroform): 10.10 (s, 1H), 7.50 (s, 5H), 6.80 (s, 1H), 2.90-2.40 (m, 4H), 2.00-1.50 (m, 6H).

Anal. Calcd. for $C_{14}H_{17}NO$: C, 78.84; H, 7.09; N, 6.57. Found: C, 78.89; H, 7.03; N, 6.51.

3,5-Diphenyl-2-isoxazoline (**31**).

This compound was obtained as a white solid, mp 146-147° (from ethanol); ^{1}H-nmr (deuteriochloroform): 7.80-7.20 (m, 10H), 4.30 (t, 1H), 3.20 (q, 2H).

Anal. Calcd. for $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.75; H, 5.83; N, 6.25.

2. Synthesis of 3-Substituted 5-Arylisoxazoles.

To a solution of the oxime in THF, a sodium bicarbonate solution was added. The flask was protected from light and an aqueous solution of iodine and potassium iodide was added. The reaction mixture was stirred and refluxed for eight hours. After that, the system was diluted by a concentrated aqueous sodium bisulfate solution. The mixture was extracted with ether. After being dried, the organic layer was evaporated to give the crude products which were purified by recrystallization or by distillation.

3-Methyl-5-(*p*-methylphenyl)isoxazole (**23**).

This compound was obtained as a yellow solid, mp 83-84° (from ethanol); ir (nujol): 1630 (isoxazole), 835 cm^{-1}; ^{1}H-nmr (carbon tetrachloride): 7.55 (d, 2H), 7.15 (d, 2H), 6.20 (s, 1H), 2.35 (s, 3H), 2.25 (s, 3H).

Anal. Calcd. for $C_{11}H_{11}NO$: C, 76.30; H, 6.36; N, 8.09. Found: C, 76.42; H, 6.40; N, 7.92.

3-Methyl-5-(*p*-chlorophenyl)isoxazole (**26**).

This compound was obtained as a yellow solid, mp 93-94° (from ethanol); ir (nujol): 1630 (isoxazole), 840 cm^{-1}; ^{1}H-nmr (carbon tetrachloride): 7.65 (d, 2H), 7.40 (d, 2H), 6.10 (s, 1H), 2.35 (s, 3H).

Anal. Calcd. for $C_{10}H_8NOCl$: C, 62.02; H, 4.13; N, 7.24. Found: C, 62.15; H, 4.11; N, 7.30.

3-Methyl-5-(*p*-nitrophenyl)isoxazole (**27**).

This compound was obtained as a yellow solid, mp 173-174° (from ethanol); ir (nujol): 1615 (isoxazole), 1530 and 1365 (NO_2) cm^{-1}; ^{1}H-nmr (DMSO-d_6): 8.10 (d, 2H), 7.85 (d, 2H), 6.75 (s, 1H), 2.35 (s, 3H).

Anal. Calcd. for $C_{10}H_8N_2O_3$: C, 58.82; H, 3.92; N, 13.73. Found: C, 58.71; H, 3.95; N, 13.78.

3-Methyl-5-(2′-furyl)isoxazole (**29**).

This compound was obtained as a yellow liquid, bp 60° at 0.8 mm; ir (nujol): 1640 (isoxazole), 1540 (furan), 790 cm^{-1} (carbon tetrachloride): 7.60 (d, 1H), 6.90 (d, 1H), 6.60 (q, 1H), 6.30 (s, 1H), 2.30 (s, 3H); ms: m/z (relative intensity) 149 ($M^{+\cdot}$, 100), 117 (6), 106 (7), 95 (39), 82 (26), 66 (16).

Anal. Calcd. for $C_8H_7NO_2$: C, 64.43; H, 4.73; N, 9.39. Found: C, 64.50; H, 4.65; N, 9.47.

3-Phenyl-5-(2′-furyl)isoxazole (**30**).

This compound was obtained as a white solid, mp 77-78° (from ethanol-water); ir (nujol): 1640 (isoxazole), 1540 (furan), 770, 700 cm^{-1}; ^{1}H-nmr (carbon tetrachloride): 8.00-7.70 (m, 2H), 7.60-7.30 (m, 4H), 6.95 (d, 1H), 6.75 (s, 1H), 6.55 (q, 1H).

Anal. Calcd. for $C_{13}H_9NO_2$: C, 73.93; H, 4.26; N, 6.64. Found: C, 73.73; H, 4.22; N, 6.88.

5-Phenyl-3,4-trimethylenisoxazole (**38**).

This compound was obtained as a white solid, mp 104-105° (from ethanol-water); ir (nujol): 1650 (isoxazole), 770, 700 cm^{-1}; ^{1}H-nmr (carbon tetrachloride): 7.80-7.55 (m, 2H), 7.55-7.20 (m, 3H), 3.00-2.50 (m, 6H).

Anal. Calcd. for $C_{12}H_{11}NO$: C, 77.84; H, 5.95; N, 7.57. Found: C, 77.11; H, 5.93; N, 7.43.

5-Phenyl-3,4-tetramethylenisoxazole (**39**).

This compound was obtained as a white solid, mp 64-65° (from ethanol-water); ir (nujol): 1640 (isoxazole), 770, 710 cm^{-1}; ^{1}H-nmr (carbon tetrachloride): 7.80-7.60 (m, 2H), 7.60-7.20 (m, 3H), 3.00-2.40 (m, 4H), 2.00-1.50 (m, 4H).

Anal. Calcd. for $C_{13}H_{13}NO$: C, 78.39; H, 6.53; N, 7.04. Found: C, 78.30; H, 6.65; N, 7.05.

5-Phenyl-3,4-pentamethylenisoxazole (**40**).

This compound was obtained as a white solid, mp 75-76° (from ethanol-water); ir (nujol): 1650 (isoxazole), 750, 710 cm^{-1}; ^{1}H-nmr (carbon tetrachloride): 7.80-7.20 (m, 5H), 3.00-2.50 (m, 4H), 2.00-1.40 (m, 6H).

Anal. Calcd. for $C_{14}H_{15}NO$: C, 78.87; H, 7.04; N, 6.57. Found: C, 78.78; H, 7.12; N, 6.48.

REFERENCES AND NOTES

[1] K. V. Auwers and C. Brink, *J. Prakt. Chem.*, **137**, 102 (1933).

[2] A. H. Blatt and J. F. Stone, Jr., *J. Am. Chem. Soc.*, **53**, 1133, 4134 (1931).

[3] G. Büchi and J. C. Vederas, *J. Am. Chem. Soc.*, **94**, 9128 (1972).

[4] Meisenheimer, *Ber.*, **54**, 3206 (1921).

[5] C. Kashima, S. Shirai, N. Yoshiwara and Y. Omote, *J. Chem. Soc., Chem. Commun.*, 826 (1980).

[6] S. Kaufmann, L. Tökes, J. W. Murphy and P. Crabbe, *J. Org. Chem.*, **34**, 1618 (1969).

[7] H. Midorikawa, *Bull. Chem. Soc. Japan*, **27**, 131 (1954).

[8] J. Hanzlik and G. Bianchi, *Ber.*, **32**, 2282 (1899).

[9] R. E. Corbett and C. L. Davey, *J. Chem. Soc.*, 296 (1955).

[10] Beilstein, **14**, 72.

[11] Beilstein, **7**, 367.

[12] G. J. Leuck and L. Cejka, Organic Syntheses, Collective Volume **I**, John Wiley & Sons, New York, 1941, p 283.

[13] N. L. Drake and H. W. Gilbert, *J. Am. Chem. Soc.*, **52**, 4965 (1930).

[14] W. S. Emerson, G. H. Birum and R. I. Longley, *J. Am. Chem. Soc.*, **75**, 1312 (1953).

[15] J. D. Billimoria, *J. Chem. Soc.*, 1126 (1955).

[16] R. Baltzly, E. Lorz, P. Russel and F. Smith, *J. Am. Chem. Soc.*, **77**, 624 (1955).

[17] W. Lampe and J. Smolinska, *Rocz. Chem.*, **28**, 163 (1954).

[18] K. S. R. Krishna Mohan Rao and N. V. Subba Rao, *Indian J. Chem.*, **6**, 66 (1968).