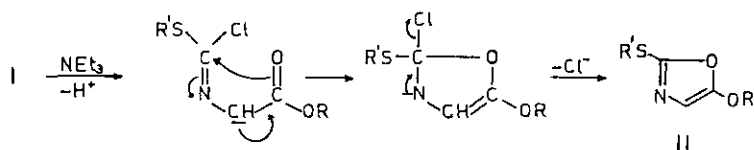


The first step consisted of the addition of arylsulfenyl chlorides to the carbenoid carbon of alkyl isocyanacetates: this reaction occurred very easily to give N-alkoxycarbonyl-S-arylisothiocarbamoyl chlorides Ia-f in quantitative yields. The second step consisted of the cyclization of Ia-f with NEt_3 ; this reaction also occurred very easily and oxazoles IIa-f were obtained in almost quantitative yields. It must be noted that isolation of isothiocarbamoyl chlorides I is unnecessary: the cyclization with NEt_3 can be performed on the crude reaction mixture with equally good results. Compounds Ia-c were isolated and characterized: these products are rather stable and can be stored for long periods without decomposition. In addition to the practical potentiality in the present synthesis, which readily provides 2-arylthio-5-alkoxyoxazoles in almost quantitative yields by an experimentally simple "one pot" procedure, this method has some interesting mechanistic features. A possible reaction pathway for the cyclization of isothiocarbamoyl chlorides I is reported in Scheme 2.

Scheme 2



The structure of compounds IIa-f was assigned on the basis of their ^1H -nmr and mass spectra. In the ^1H -nmr spectra of IIa-f a singlet signal at δ 6.10 - 6.38 was detected, due to the H-4 of the oxazole ring. In the mass spectra of IIa-f, besides the molecular ions, the fragment ion $[\text{CH}=\text{C}-\text{OR}]^+$ m/z 56 ($\text{R} = \text{Me}$) or m/z 70 ($\text{R} = \text{Et}$) was detected and this agrees with the formation of the oxazole ring. Furthermore the fragment ions $[\text{4-ClC}_6\text{H}_4\text{SCO}]^+$ m/z 171, $[\text{4-MeC}_6\text{H}_4\text{SCO}]^+$ m/z 151 and $[\text{PhSCO}]^+$ m/z 137 were detected in the mass spectra of IIId, IIe and IIIf, respectively.

EXPERIMENTAL

Melting points were obtained in open capillary tubes and are uncorrected. The ^1H -nmr spectra were recorded with a Perkin-Elmer R32 instrument for CDCl_3 solutions, chemical shifts are reported in ppm (δ) from TMS. The mass spectra were recorded with a Hewlett Packard 5790A GC MS instrument at 70 eV.

All of the compounds gave correct microanalyses.

2-Arylthio-5-alkoxyoxazoles (IIa-f)

General procedure- The calculated amount of the appropriate sulfenyl chloride in CH_2Cl_2 was slowly dropped into a solution of alkyl isocyanoacetate in CH_2Cl_2 , maintaining the temperature at -50°C . The resulting mixture was allowed to react at room temperature for 1 h³, then cooled at -20°C and treated with the calculated amount of NEt_3 . The resulting mixture was allowed to react at room temperature for 1 h and then evaporated to dryness. The residue was stirred with Et_2O and then filtered. Evaporation of the filtrate left IIa-f in almost quantitative yields. IIa: mp $90-91^\circ\text{C}$ from MeOH; $^1\text{H-nmr}$: 6.38(s,1H,H-4), 3.97(s,3H, CH_3); ms: $[\text{M}]^+$ m/z 286, $[\text{R}']^+$ m/z 156, $[\text{M-R}']^+$ m/z 130, $[\text{N-CH=C-OMe}]^+$ m/z 70, $[\text{CH=C-OMe}]^+$ m/z 56. IIb: mp $63-64^\circ\text{C}$ from MeOH; $^1\text{H-nmr}$: 6.37(s,1H,H-4), 4.32-4.08(q,2H, CH_2), 1.50-1.34(t,3H, CH_3); ms: $[\text{M}]^+$ m/z 300, $[\text{R}'\text{S}]^+$ m/z 188, $[\text{R}']^+$ m/z 156, $[\text{M-R}']^+$ m/z 144, $[\text{CH=C-OEt}]^+$ m/z 70. IIc: mp $66-67^\circ\text{C}$ from MeOH; $^1\text{H-nmr}$: 6.36(s,1H,H-4), 4.34-4.08(q,2H, CH_2), 1.52-1.36(t,3H, CH_3); ms: $[\text{M}]^+$ m/z 266, $[\text{R}'\text{S}]^+$ m/z 154, $[\text{R}']^+$ m/z 122, $[\text{CH=C-OEt}]^+$ m/z 70. IId: bp $140^\circ\text{C}/0.05\text{ mm Hg}$; $^1\text{H-nmr}$: 6.17(s,1H,H-4), 4.19-3.96(q,2H, CH_2), 1.44-1.28(t,3H, CH_3); ms: $[\text{M}]^+$ m/z 255, $[\text{R}'\text{SCO}]^+$ m/z 171, $[\text{R}'\text{S}]^+$ m/z 143, $[\text{R}']^+$ m/z 111, $[\text{CH=C-OEt}]^+$ m/z 70. IIe: bp $124^\circ\text{C}/0.05\text{ mm Hg}$; $^1\text{H-nmr}$: 6.10(s,1H,H-4), 4.14-3.90(q,2H, CH_2), 2.28(s,3H, CH_3 toluene), 1.40-1.24(t,3H, CH_3); ms: $[\text{M}]^+$ m/z 235, $[\text{R}'\text{SCO}]^+$ m/z 151, $[\text{R}'\text{S}]^+$ m/z 123, $[\text{R}']^+$ m/z 91, $[\text{CH=C-OEt}]^+$ m/z 70. II f: bp $122^\circ\text{C}/0.05\text{ mm Hg}$; $^1\text{H-nmr}$: 6.14(s,1H,H-4), 4.12-3.88(q,2H, CH_2), 1.37-1.21(t,3H, CH_3); ms: $[\text{M}]^+$ m/z 221, $[\text{R}'\text{SCO}]^+$ m/z 137, $[\text{R}'\text{S}]^+$ m/z 109, $[\text{R}']^+$ m/z 77, $[\text{CH=C-OEt}]^+$ m/z 70.

REFERENCES AND NOTES

- * Author to whom correspondence should be addressed.
1. See for example: U.Schöllkopf and R.Schröder, *Angew.Chem.*, 1971, 83, 358; D. Hoppe, *Angew.Chem.Int.Ed.*, 1974, 13, 789; U.Schöllkopf, *ibid.*, 1977, 16, 339; S.Maeda, M.Suzuki, T.Iwasaki, K.Matsumoto, and Y.Iwasawa, *Chem.Pharm.Bull.*, 1984, 32(7), 2536.
 2. I.J.Turchi, *Ind.Eng.Chem.Prod.Res.Dev.*, 1981, 20, 32; A.R.Katritzky and C.W. Rees, "Comprehensive Heterocyclic Chemistry", Vol.6, Part 4B, K.T.Potts, ed., Pergamon Press Ltd., Inc., Oxford, 1984, pp. 216-217.
 3. Evaporation of this solution left isothiocarbamoyl chlorides Ia-f. Ia: mp $56-57^\circ\text{C}$ from petroleum ether (bp $40-70^\circ\text{C}$); $^1\text{H-nmr}$: 4.32(s,2H, NCH_2), 3.72(s,3H, CH_3). Ib: mp $52-53^\circ\text{C}$ from petroleum ether (bp $40-70^\circ\text{C}$); $^1\text{H-nmr}$: 4.28(s,2H, NCH_2). Ic: undistillable oil; $^1\text{H-nmr}$: 4.26(s,2H, NCH_2).

Received, 24th March, 1986