1,2-Cycloaddition of Phosphinothioyl and Sulphonyl Isothiocyanates with Carbodi-imides

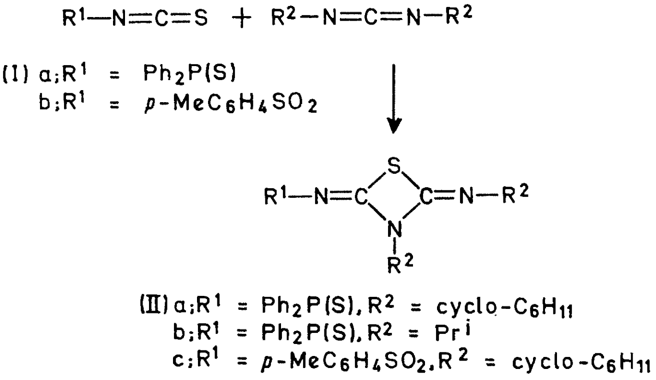
By Iwao Ojima and Naoki Inamoto*

(*Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo* 113, *Japan*)

Summary Diphenylphosphinothioyl and *p*-tolylsulphonyl isothiocyanates undergo 1,2-cycloaddition with carbodi-imides across the C=S bond to produce new 1,3-thiazetidine derivatives.

Since diphenylphosphinothioyl isothiocyanate (Ia) can be expected to undergo 1,2- or 1,4-cycloaddition to dienophiles, the reactions of this isothiocyanate with carbodi-imides were investigated.

When an equimolar mixture of the isothiocyanate (Ia) and dicyclohexyl carbodi-imide was heated at 90—95° for a few minutes, or heated in refluxing cyclohexane for 30 min, the 1 : 1 adduct (IIa) was obtained as colourless prisms in nearly quantitative yield: m.p. 120—122°, i.r. (Nujol) 1640 cm^{-1} ($\nu_{C=N}$), λ_{max} (cyclohexane) 223 (log ϵ 4·81) and 260sh (4·23) nm.



$R^1—N=C=S + R^2—N=C=N—R^2$

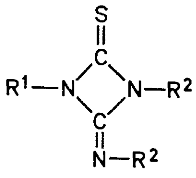
(I) a; R^1 = $Ph_2P(S)$
b; R^1 = $p\text{-}MeC_6H_4SO_2$

(II) a; R^1 = $Ph_2P(S)$, R^2 = cyclo-C_6H_{11}
b; R^1 = $Ph_2P(S)$, R^2 = Pr^i
c; R^1 = $p\text{-}MeC_6H_4SO_2$, R^2 = cyclo-C_6H_{11}

The above data confirm that the adduct (IIa) is a new 1,3-thiazetidine derivative. Since the strong absorption band at 223 nm is of too short a wavelength to be assigned to the π–π* transition of a C=S bond,[1] and an absorption band caused by n–π* transition could not be detected, also, the adduct did not catalyse the decomposition of sodium azide by iodine (Feigl test),[2] indicating the absence of a C=S group. The reaction of the isothiocyanate (Ia) with di-isopropyl carbodi-imide gave a similar 1 : 1 adduct (IIb).

Ulrich *et al.*[3] have reported that the 1,2-cycloaddition of a carbodi-imide and an isothiocyanate having an electron-withdrawing group always give a 1,3-diazetidine derivative (III). *p*-Tolylsulphonyl isothiocyanate (Ib) was allowed to react with dicyclohexyl carbodi-imide under conditions similar to those used by Ulrich *et al.*, and an 1 : 1 adduct (IIc), which gave a negative Feigl test, was obtained in nearly quantitative yield as colourless prisms: m.p. 144—146°, i.r. (Nujol) 1620 cm^{-1} ($\nu_{C=N}$), λ_{max} (cyclohexane) 229sh (log ϵ 4·43), 235sh (4·50), 248 (4·55), and 262sh nm (4·46).

Comparison of the C=N stretching vibrations (1620—1640 cm^{-1}) of these 1,3-thiazetidines (II) with those of the 1 : 1 adducts, (IIIa; 1655 and IIIb; 1600 cm^{-1}) also suggests that (IIIa) and (IIIb) are 1,3-thiazetidine derivatives.



(III) a; R^1 = $p\text{-}NO_2C_6H_4$, R^2 = cyclo-C_6H_{11}
b; R^1 = $p\text{-}MeC_6H_4SO_2$, R^2 = $o\text{-}MeC_6H_4$

These results show that the cycloaddition of the isothiocyanates having electron-withdrawing group, and carbodi-imides occurs across the C=S bond of the isothiocyanate to give 1,3-thiazetidine derivatives, and not across the C=N bond to give 1,3-diazetidine derivatives.

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[1] K. Hirayama, "Handbook of Ultraviolet and Visible Spectra of Organic Compounds," Plenum Press, New York, 1967, p. 87.

[2] F. Feigl, "Spot Tests in Organic Analysis," Fifth Eng. Ed., Elsevier Pub. Co., Amsterdam, 1956, pp. 228—233.

[3] H. Ulrich and A. A. R. Sayigh, *Angew. Chem. Internat. Edn.*, 1965, **4**, 520; H. Ulrich, "Cycloaddition Reactions of Heterocumulenes," Academic Press, New York, 1967, pp. 233—235.