Acta Chemica Scandinavica, 1995: 49: 778–780
Printed in Belgium – all rights reserved

ACTA
CHEMICA SCANDINAVICA
ISSN 0904–213X

Short Communication

New Disubstituted Carbanion Ylides from Pyridazine

Ionel Mangalagiu

University 'Al.I.Cuza' Iasi, Faculty of Chemistry, Organic Chemistry Department, B-dul Copou, Nr. 11, Iasi-6600, Romania

Mangalagiu, I., 1995. New Disubstituted Carbanion Ylides from Pyridazine. – Acta Chem. Scand. 49: 778–780 © Acta Chemica Scandinavica 1995.

In order to obtain new stable disubstituted ylides in the pyridazine series and to establish correlations between structure and reactivity, we have investigated the reactions between 3-(*p*-halogenophenyl)pyridazinium ylides and *p*-chlorophenyl isocyanate. The reaction pathway of cycloimonium ylides with aromatic isocyanates or isothiocyanates depends on the structure of the ylidic heterocycle.[1] The [3 + 2] dipolar cycloaddition with isocyanates gives azabicycles[2] whereas nucleophilic attack gives disubstituted ylides.[3,4]

Results and discussion

Previously we have devised a method for the preparation of 3-(*p*-halogenophenyl)pyridazinium ylides **9–14**.[5,6] The method was an adaption of the Kröhnke salt reaction.[7]

Monosubstituted pyridazinium ylides can be represented by a mesoionic structure (**a**) or by a 1,3-dipolar structure (**b**). The reaction between *p*-chlorophenyl isocyanate and the ylides **9–14**, theoretically, could proceed in two ways. 1. We can obtain disubstituted ylides **15–20** (with **A**-type structure), as a result of a nucleophilic attack of the ylidic carbon (**9–14a**) on *p*-chlorophenyl isocyanate. 2. We can obtain new azabicycles (with **B**-type structure), as a result of a [3 + 2] dipolar cycloaddition of the ylides **9–14b** to *p*-chlorophenyl isocyanate (Scheme 1).

Experimentally it was found that the product formed between 3-(*p*-halogenophenyl)pyridazinium ylides (**9–14**) (obtained *in situ* from the corresponding cycloimonium salts **3–8**) with *p*-chlorophenyl isocyanate gave the disubstituted ylides **15–20** (**A**). The structure of **A**-type products **15–20** was proved through elemental and spectral analyses.

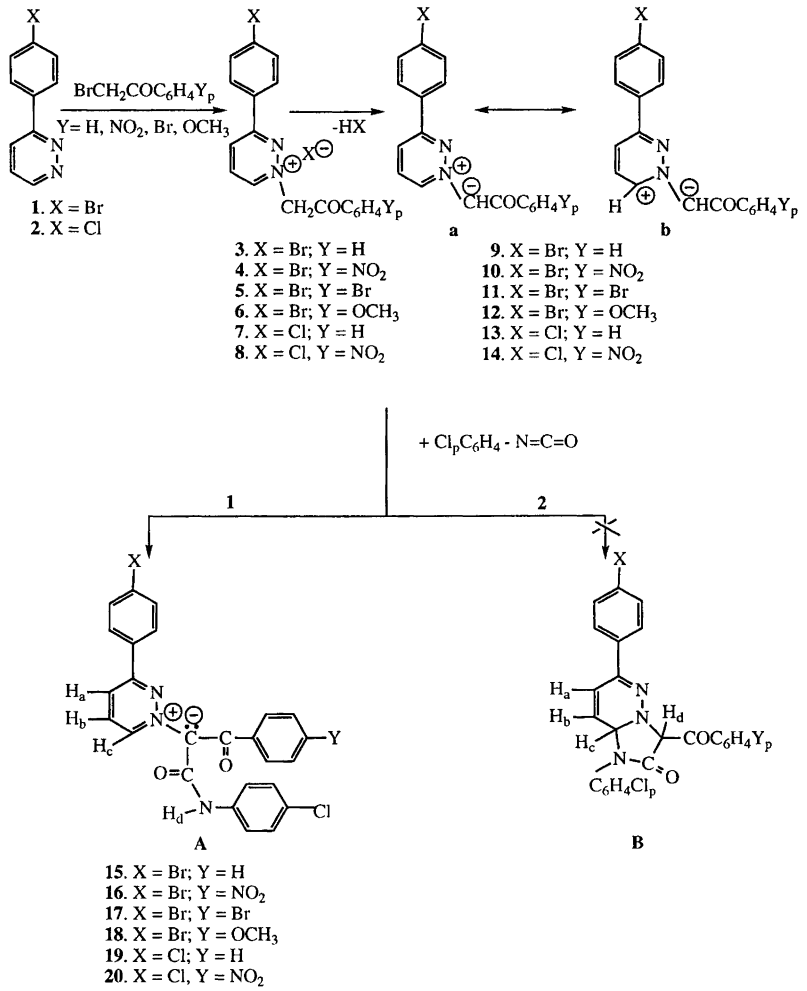
Obviously, the data furnished by the elemental analyses (C, H, N) are compatible with both types of structure, **A** or **B**, but, the data furnished by the IR and ^{1}H NMR spectra confirm the disubstituted carbanion ylides **15–20**, according to the type 1 reaction (Scheme 1). Thus, in the ^{1}H NMR spectra of the products **15–20**, H_d appears at 12.00 ppm for the ylide **18** and 12.40 ppm for the ylide **15**. These facts prove that H_d is an amidic proton (–NH–CO–). H_c is present as two doublets (because it has a vicinal coupling with H_b and a long-range coupling with H_a), at chemical shifts of 9.15 ppm from the ylide **18** and 9.65 ppm for the ylide **15**. The fact that these two protons, H_d and H_c, appear at such high chemical shifts, excludes the azabicyclic structure (**B**), where they should be at much lower chemical shifts. The chemical shifts of H_c and H_d are in accordance with the electronic effects of the substituents in the *para* position of the phenyl ring ($-C_6H_4-X_p$; X = Br, Cl) and of the benzoyl ring ($-CO-C_6H_4-Y_p$; Y = H, NO_2, Br, OCH_3). The remaining protons appear at chemical shifts and with coupling constants in accordance with the proposed structure.

In the IR spectra the CO amide bands are present at 1605 cm^{-1} (**16**) and 1660 cm^{-1} (**18**). The displacement of the CO amide bands to such low wavenumber, might be explained by the conjugation effect of the CO amidic group with the ylidic carbanion, and also through the electronic effects of the substituents in the *para* position of phenyl and benzoyl rings.

The ketone groups give bands at 1485 cm^{-1} (**16**) and 1510 cm^{-1} (**18**). The displacement of ketonic CO bands to such low wavenumber has also been observed by other researchers[8] in related cases. The positions of amide and ketone CO absorption bands are in accordance with the electronic effects of the substituents in the *para* position of phenyl (X) and benzoyl (Y) rings.

Conclusions

1. The reactions between 3-(*p*-halogenophenyl)pyridazinium ylides and heterocumulene yield disubstituted carbanion ylides. No cycloaddition reaction was observed. This means that the 3-(*p*-halogenophenyl)pyridazinium ylides have a strongly nucleophilic character with regard to the ylidic carbanion. 2. Six new disubstituted carbanion ylides have been obtained.



Scheme 1.

Experimental

The ^{1}H NMR spectra were recorded for samples in $CDCl_3$ at 80 MHz with a Bruker spectrometer. The IR spectra were recorded with a SPECORD-71 spectrometer for KBr discs.

*[3-(*p*-Halogenophenyl)pyridazin-1-ylium] (*p*-chlorophenylcarbamoyl)(*p*-R-benzoyl)methanides (***15–20***).* Cycloimmonium salt (1 mmol) was suspended in 20 ml benzene. The solution was heated and, when the benzene was boiling, 1 mmol triethylamine (dissolved in 3 ml benzene) was added. The triethylamine hydrobromide was filtered, and to the clear solution was added 1 mmol of *p*-chlorophenylisocyanate, dissolved in 20 ml benzene. The mixture was stirred at ambient temperature for 2 h. The formed product was isolated by filtration.

*[3-(*p*-Bromophenyl)pyridazin-1-ylium] (*p*-chlorophenylcarbamoyl)(benzoyl)methanide (***15***).* Orange–reddish crystals. Yield: 49%, m.p. 181–182°C. Anal. $C_{25}H_{17}BrClN_3O_2$: C, H, N; IR (KBr, cm^{-1}): 1628 (s), 1490 (s), 1580, 1550, 1470, 1440 (s–m), 3100–3000 (w). ^{1}H NMR ($CDCl_3$, ppm, TMS): δ: 12.40 (s, H_d), 9.70 (m, H_c), 8.55 (m, H_a, H_b), 7.00–7.80 (m, 13 H, aromatic).

*[3-(*p*-Bromophenyl)pyridazin-1-ylium] (*p*-chlorophenylcarbamoyl)(*p*-nitrobenzoyl)methanide (***16***).* Cherry-red crystals. Yield: 58%, m.p. 187–188°C. Anal. $C_{25}H_{16}BrClN_4O_4$: C, H, N. IR (KBr, cm^{-1}): 1605 (s), 1510 (s); 1570, 1475, 1430 (s–m), 1530, 1335 (s), 3100–3000 (w). ^{1}H NMR ($CDCl_3$, ppm, TMS): δ: 12.15 (s, H_d), 9.60 (dd, H_c, $J_{cb} = 7.00$ Hz, $J_{ca} = 3.00$ Hz), 8.40–8.60 (m, H_a, H_b), 7.05–8.20 (m, 12 H, aromatic).

*[3-(*p*-Bromophenyl)pyridazin-1-ylium] (*p*-chlorophenylcarbamoyl)(*p*-bromobenzoyl)methanide (***17***).* Brown product. Yield: 54%, m.p. 142–144°C. Anal. $C_{25}H_{16}Br_2ClN_3O_2$: C, H, N. IR (KBr, cm^{-1}): 1628 (s), 1490 (s), 1580, 1550, 1440 (s–m), 3100–3000 (w). ^{1}H NMR ($CDCl_3$, ppm, TMS): δ: 12.10 (s, H_d), 9.30 (m, H_c), 8.65–8.85 (m, H_a, H_b), 7.00–8.50 (m, 12 H, aromatic).

[3-(p-Bromophenyl)pyridazin-1-ylium] (p-chlorophenylcarbamoyl)(p-methoxybenzoyl)methanide (**18**). Brown product. Yield: 48%, m.p. 140–142°C. Anal. $C_{26}H_{19}BrClN_3O_3$: C, H, N. IR (KBr, cm^{-1}): 1660 (s), 1485 (s); 1590, 1560, 1480, 1450 (s–m); 1260, 1170 (m), 3100–3000 (w). ^1H NMR ($CDCl_3$, ppm, TMS): δ 12.00 (s, H_d), 9.15 (m, H_c), 8.60–8.80 (m, H_a, H_b), 6.70–8.40 (m, 12 H, aromatic), 3.40 (s, OCH_3).

[3-(p-Chlorophenyl)pyridazin-1-ylium] (p-chlorophenylcarbamoyl)(benzoyl)methanide (**19**). Orange crystals. Yield: 54%, m.p. 178–179°C. Anal. $C_{25}H_{17}Cl_2N_3O_2$: C, H, N. IR (KBr, cm^{-1}): 1630 (s), 1492 (s), 1575, 1550, 1470, 1435 (s–m), 3100–3000 (w). ^1H NMR ($CDCl_3$, ppm, TMS): δ 12.40 (s, H_d), 9.65 (dd, H_c, $J_{cb} = 6.00$ Hz, $J_{ca} = 3.00$ Hz), 8.35–8.50 (m, H_a, H_b), 7.00–7.75 (m, 13 H, aromatic).

[3-(p-Chlorophenyl)pyridazin-1-ylium] (p-chlorophenylcarbamoyl)(p-nitrobenzoyl)methanide (**20**). Brick-coloured crystals. Yield: 59%, m.p. 181–182°C. Anal. $C_{25}H_{16}Cl_2N_4O_4$: C, H, N. IR (KBr, cm^{-1}): 1610 (s), 1510 (s), 1565, 1470, 1430 (s–m), 1520, 1330 (s), 3100–3000 (w). ^1H NMR ($CDCl_3$, ppm, TMS): δ 12.05 (s, H_d), 9.45 (dd, H_c, $J_{cb} = 7.00$ Hz, $J_{ca} = 3.00$ Hz), 8.40–8.60 (m, H_a, H_b), 7.00–7.80 (m, 12 H, aromatic).

References

1. Houben–Weyl: *Organische Stickstoff – Verbindungen mit einer C,N-Doppelbindungen*, Thieme, Stuttgart; New York, 1991, pp. 100–250.
2. Petrovanu, M., Sauciuc, A. and Zugravescu, I. *Rev. Roum. Chim. 14* (1969) 1153.
3. Caprosu, M., Druta, I. and Petrovanu, M. *Bull. IPI., XXIII s II* (1979) 71.
4. Petrovanu, M., Luchian, C., Surpateanu, G., Barboi, G. and Constantinescu, M. *Tetrahedron 39* (1983) 2417.
5. Mangalagiu, I., Caprosu, M., Druta, I. and Petrovanu, M. *Ann. Sci. Univ. Iassi 1, s1c* (1992) 52.
6. Mangalagiu, I., Druta, I., Caprosu, M. and Petrovanu, M. *Ann. Sci. Univ. Iassi 2, s2c* (1993) 72.
7. Kröhnke, F. *Chem. Ber. 68* (1935) 1177.
8. Henrich, C. A., Ritchie, R. and Taylor, W. C. *Aust. J. Chem. 20* (1967) 2467.

Received February 23, 1995.