Rhodium(I) Induced Carbonylation of Azirines to Isocyanates

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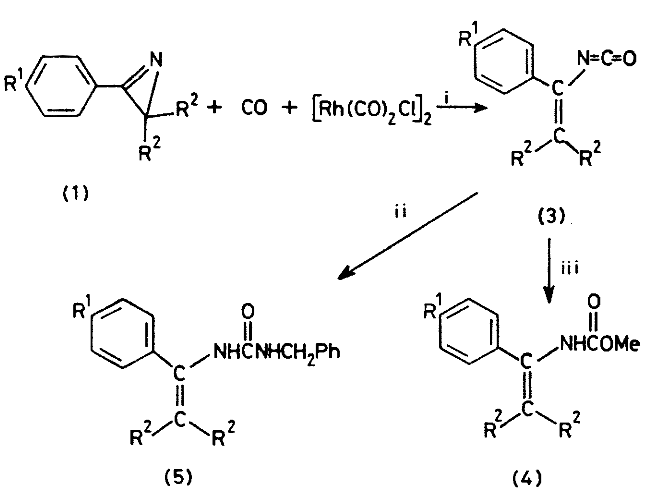
Summary 2-Arylazirines react with carbon monoxide and chlorodicarbonylrhodium(I) dimer, at room temperature or below, to give isocyanates (also ureas and carbamates by appropriate reaction) in good yields.

AZIRINES undergo a variety of interesting and useful ring-cleavage reactions in the presence of metal containing compounds.[1] In order to intercept the intermediates in these reactions, as well as to realize useful organic synthesis, we have investigated the carbonylation of azirines in the presence of metal complexes. This communication describes the carbonylation of azirines by rhodium(I) complexes.

Treatment of a 2-arylazirine (**1**, R = H, Br, Me, or OMe, R^2 = H; R^1 = H, R^2 = Me) with 0·5 mol equiv. of chlorodicarbonylrhodium(I) dimer (**2**) and carbon monoxide affords the highly reactive vinyl isocyanates (**3**) (Scheme 1).



Scheme 1. i, C_6H_6; ii, $PhCH_2NH_2$; iii, MeOH.

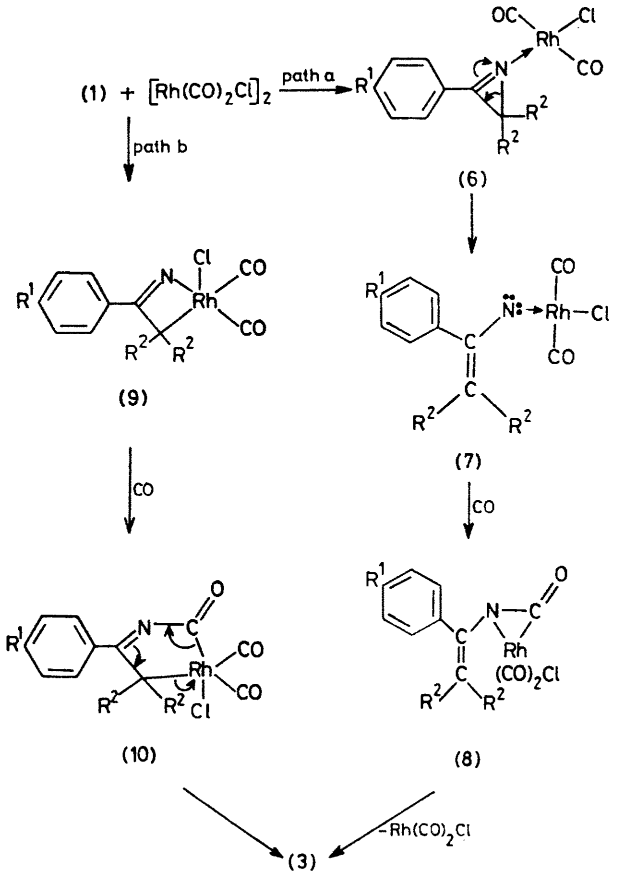
This reaction occurs under exceedingly mild conditions (room temperature or 5 °C, 1 atm of CO), and other rhodium(I) complexes could also be used [*e.g.*, $(Ph_3P)_2Rh(CO)Cl$]. No reaction occurred in the absence of the rhodium(I) complex. The vinyl isocyanates (**3**) were isolated and characterized as such or, more conveniently, as carbamates (**4**) or ureas (**5**) obtained by treatment with methanol and benzylamine, respectively. The yields for (**3**)—(**5**) are listed in the Table.

Table. Products obtained from Rh^I induced carbonylation of 2-arylazines.[a]

(1) R^1	R^2	Products	Yield[b]/%	M.p. or b.p. (mmHg)/°C
H	H	(**3**)	74	57-60 (4)[c]
		(**4**)	71	
		(**5**)	64	124—125
H	Me	(**3**)	73	89—91 (5)[d]
		(**4**)	54	76—78
		(**5**)	48	150—152
Me	H	(**5**)	43	90—91
OMe	H	(**5**)	27	113—115
Br	H	(**3**)	81	147 (10)
		(**4**)	40	
		(**5**)	96	136—138

[a] Satisfactory analytical results (C, H, N) were obtained for all new compounds. [b] Product yields are based on reactant azirine. [c] Lit. b.p. 99 °C at 25 mmHg (J. Hoch, *Compt. rend.*, 1935, **201**, 733). [d] Lit. b.p. 96 °C at 8 mmHg [L. I. Samarai, O. V. Vishnevskii, and G. I. Derkach, *J. Org. Chem.* (*U.S.S.R.*), 1970, **6**, 469].

The i.r. spectra of the isocyanates (**3**) display intense absorptions at 2270—2281 cm^{-1} characteristic of the isocyanate function. Carbonyl stretching bands for (**4**) and (**5**) are observed at 1740—1745 and 1649—1658 cm^{-1}, respectively. The olefinic protons of (**3**)—(**5**) give signals in the n.m.r. spectra at δ 4·97—5·63. Molecular ion peaks are observed in the mass spectra of the isocyanates and the carbamates, but not the ureas which exhibit $[M - HNCO]^+$ peaks.



Scheme 2

Vinyl isocyanates may arise from azirines *via* complexed vinyl nitrenes (Scheme 2, path a). Vinyl nitrenes have been proposed as intermediates in a number of thermal reactions of azirines.[2] The nitrene complex (**7**) would be formed by carbon–nitrogen bond cleavage of the azirine ring, the cleavage being promoted by initial formation of an N-donor ligand complex (**6**). The formation of a nitrogen–rhodium bond in (**6**) would weaken the carbon–nitrogen single bond of the three-membered ring. Ligand migration (**7** → **8**), followed by decomplexation, would afford the isocyanate (**3**).

Aromatic isocyanates have been obtained by the carbonylation of aryl azides under very drastic conditions (160—180 °C, 200—300 atm pressure).[3] This carbonylation reaction was believed to proceed *via* a nitrene intermediate.

Metallocycles are also possible intermediates in these reactions (Scheme 2, path b). Oxidative addition of (**1**) to the rhodium(I) complex would give the rhodium(III) complex (**9**), which on ligand migration (**10**) and subsequent decomplexation would afford the isocyanates (**3**).

The following general procedure was used. A mixture of 2-arylazirine (**1**) (4—10 mmol) and chlorodicarbonylrhodium(I) dimer (**2**) [2—5 mmol, 2 : 1 ratio of (**1**) : (**2**)] in benzene (40—80 ml) was stirred for 4 h at room temperature, or at 5—7 °C, in 1 atm of carbon monoxide. The solution was carefully concentrated, hexane (60—80 ml) was added, and the resulting mixture was filtered. After removal of hexane, the isocyanate was obtained by distillation. Addition of an excess of methanol or benzylamine to the hexane solution of (**3**) afforded (**4**) or (**5**), respectively.

In conclusion, the carbonylation of azirines in the presence of rhodium(I) complexes represents a simple and convenient method for the synthesis of vinyl isocyanates under remarkably mild conditions.

We are grateful to the National Research Council of Canada for support. T.S. is a participant in the Japan–Canada exchange of scientists programme.

(*Received*, 16*th January* 1979; *Com.* 043.)

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