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Reaction of a Chromium Carbene Complex with 1-Azadienes and the Synthesis of Trisubstituted Pyrroles.

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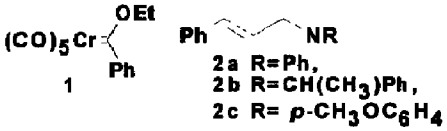
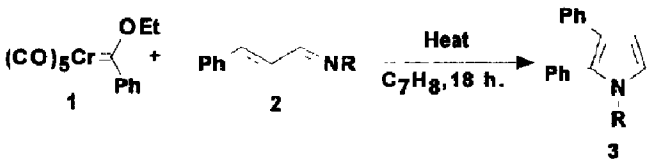
ABSTRACT:-Thermolysis of chromium carbene complexes with 1-azadienes leads to formation of trisubstituted pyrroles in good yield.

Over the last ten years the reactivity of chromium carbene complexes has been studied intensively and many synthetically important reactions have been discovered[1]. It has been shown that thermolysis of these complexes with alkenes[2], alkynes[3], and α,β-unsaturated esters[4] leads to formation of cyclopropanes[2,4] and substituted napthalenes[3]. Photolysis of the complexes in the presence of imines leads to the formation of β-lactams in high yield[5]. The thermal reaction of complex **1** with simple imines has been shown to lead to a multitude of products in very low yield and is therefore of limitted synthetic value[6].



By contrast the thermal reaction of these complexes with 1-azadienes however, appears to be a neglected area of chromium carbene chemistry. In this communcation we report the preliminary results obtained from our study of the thermolysis of chromium carbene complex **1** with 1-azadienes **2a**,b, and **c**. As far as we are aware this represents the first example of the thermal reaction between chromium carbene complex **1** and 1-azadienes. Complex **1** and 1-azadienes **2a**,**b** and **c** used for this work were synthesised in accordance with literature procedures[7,8].

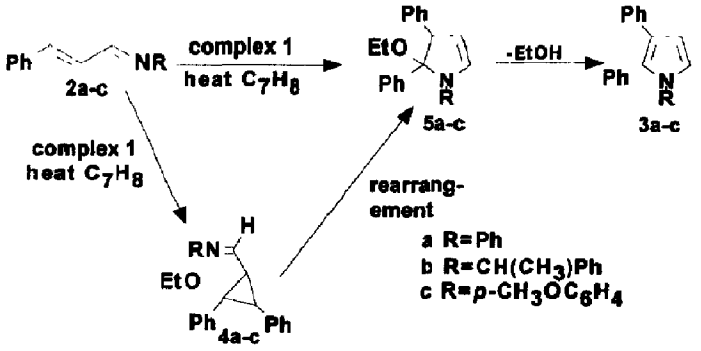
A solution of complex **1** and 1-azadiene **2a**,**b** or **c** in toluene was heated at reflux for 18 h under an atmosphere of nitrogen to give a dark mixture. Removal of the solvent followed by chromatography lead to isolation of the major reaction products which were indentified as pyrroles **3a**, **b** or **c** on the basis of their spectrocopic and analytical data[9,10].



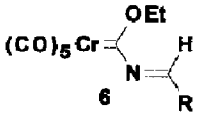
1-azadiene	R	Pyrrole	Yield(%)
2a	Ph	3a	50
2b	$CH(CH_3)Ph$	3b	54
2c	$p\text{-}CH_3OC_6H_4$	3c	60

Although the mechanism for this ultimate [1+4] hetroannulation reaction is uncertain it may proceed via the intermediacy of cyclopropanes **4** which under the reaction conditions rearrange to yield **5a**,**b** or **c**. Loss of ethanol from **5a**,**b** or **c** then yield pyrroles **3a**,**b** or **c**. Alternatively 1,4-addition of carbene derived from **1** across the 1-azadiene **2a**,**b**, or **c** will lead directly to **5a**,**b** or **c** and hence a pyrrole after loss of ethanol. Similar mechanisms have been previously

hypothesised to describe the formation of furans from chromium carbene complexes and α,β-unsaturated ketones[4]. In each cases only a single 1,2,3,-trisubstituted pyrrole was observed. The remaining materials in the product mixture were identified as the polymerisation of products of the 1-azadienes used in these reactions.



Pyrrole synthesis via chromium carbene complexes has previously been reported[11], it is of note however, that such procedure requires the formation of the more elaborate carbene complexes **6** which is heated with terminal or internal alkynes to give 2,4,5- or 2,3,5-trisubstituted and 1,2,3,4-tetra-substituted pyrroles respectively.



The procedure reported in this paper represents a new route for the synthesis of substitued pyrroles from simple and readily accessible precursors which is complementary to the procedure previously reported. The scope of this reaction for the synthesis tetra- and penta- substituted pyrroles from more highly substituted 1-azadienes is currently under investigation and will be the subject of a full paper.

We thank the University of Surrey for financial support.

References and Notes

1. Dötz, K. H; In "*Organometallics in Orgenic Synthesis: Aspects of a Modern Interdisciplinary Field*;" Dieck, H.T; and De Meijere, A; Eds.; Springer: Berlin, 1988; and Wulff, W. D; In "*Comprehensive Organic Synthesis*;" Flemming, I; and Trost, B. M; Eds.; Pergamon Press plc: New York, **1991**, 5. 1065
2. Brookhart, M; and Studabaker, W. B; *Chem. Rev.*, **1987**, 87, 411; Murray, C. K.; Wulf, W. D.; Yang, D. C.; *Pure and Appl. Chem.*, **1988**, 60, 137.
3. Dötz, K. H.; Mühlemeier, J.; Orama, O.; Schubert, J.; *J. Organomet. Chem.*, **1983**, 244, 187.
4. Wienand, A.; Reissig, H. U.; *Organometallics*, **1990**, 9, 3133.
5. Hegedus, L. S.; *Pure and Appl. Chem.*, **1990**, 62, 691.
6. Dragisich, V.; Murray, C.K.; Warner, B. P.; Wulff, W. D.;Rogers, R .D.; *Organometallics*, **1990**, 9, 3142.
7. Danks, T. N.; Thomas, S. E.; *J. Chem. Soc., Perkin Trans 1.*, **1990**, 761.
8. Fischer, E. O.; Maasböl, A.; *Angew. Chem., Int. Ed. Engl.*, **1964**, 3, 580.
9. In a typical experiment chromium carbene complex **2** (0.62 g, 1.90 mmol) and 1-azadiene **1b** (0.46 g, 1.96 mmol) were dissolved in toluene (20 ml) and the resulting solution was heated at reflux for 18 h under an atmosphere of nitrogen. The reaction mixture was allowed to cool to room temperature and was filtered through a plug of alumina to remove the chromium residues. The solvent was removed under reduced pressure to yield a dark oil. This oil was chromatographed on silica using diethyl ether/light petroleum (1:4) as the eluent to yield pyrrole **3b** as a yellow oil (0.33 g, 54 %).
10. All compounds gave satisfactory spectroscopic and elemental data.
11. Dragisich, V.; Murray, C. K.; Warner, B. P.; Wulff, W. D.; Rogers, R .D.; *J. Am. Chem. Soc.*, **1990**, 112, 1251.

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