Pyran-2-ylidene Carbene Complexes

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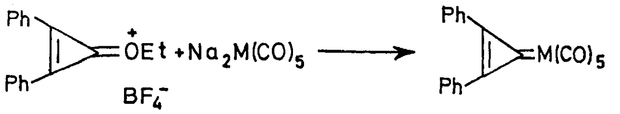
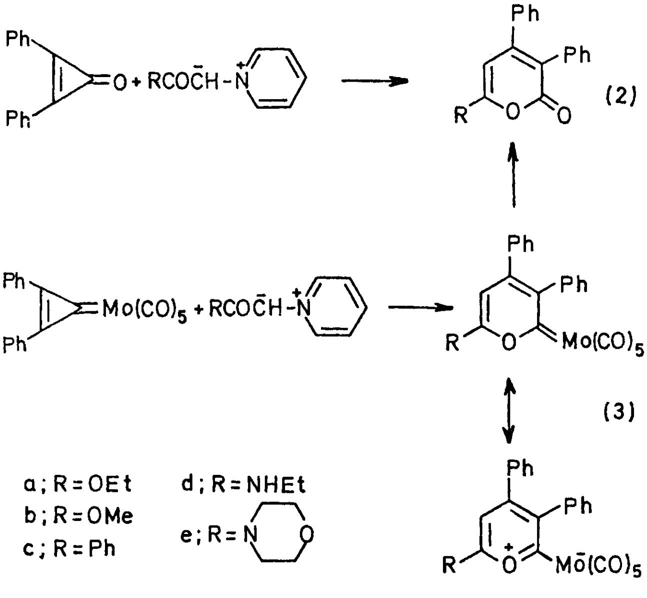
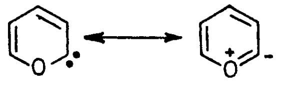
Summary Reaction of the cyclopropenylidene complexes (**1**) with pyridinium ylides gives stable pyran-2-ylidene complexes (**3**), a new type of carbene complex stabilised by 6π-electron delocalisation; some reactions of these complexes are described.

THE structural similarity between transition metal–carbene complexes and the corresponding carbonyl compounds makes a comparative study of their chemistry desirable, in order to assess the potential of the complexes as synthetic intermediates. Some such comparisons have been made between alkoxycarbene complexes and esters;[1] we have investigated the chemistry of the complexes (**1**), which are unusual in that they derive stabilisation from a delocalised 2π-electron system, rather than from a heteroatom substituent.



(1) a; M=Cr
b; M=Mo





(4)

Complex (**1a**) was first prepared by Öfele, from 3,3-dichloro-1,2-diphenylcyclopropene and sodium pentacarbonylchromate.[2] We find that this complex is also formed from 3-ethoxy-1,2-diphenylcyclopropenylium tetrafluoroborate, and that the carbene complex is more easily isolated from this reaction. The molybdenum complex (**1b**), yellow crystals, m.p. 180° (decomp.), is obtained in an analogous manner.

In contrast with diphenylcyclopropenone, the complexes (**1**) are resistant to ring opening by bases; *e.g.*, complex (**1b**) was recovered after being heated for 6 h with methanolic sodium methoxide. Photolysis of (**1b**), like that of diphenylcyclopropenone, gave diphenylacetylene (30%).

Reaction of diphenylcyclopropenone with pyridinium ylides or with phosphonium ylides gives 2-pyrones (**2**);[3] complex (**1b**) reacts analogously with pyridinium (but not phosphonium) ylides in ethanol at room temperature to give red, air-stable carbene complexes (**3a**—**c**) in good yields (55—80%). In agreement with the proposed structure (**3**), fully supported by analytical and spectroscopic data, oxidation of the complexes with lead tetra-acetate gave the corresponding 2-pyrones (**2**).

The 6-ethoxy-complex (**3a**) is subject to very ready nucleophilic displacement at the 6-position; it was converted into the 6-methoxy-derivative (**3b**) when set aside for 24 h in methanol containing a little triethylamine. The corresponding 6-ethoxy-2-pyrone (**2**; R = OEt) was stable under these conditions. Reaction of the complex (**3a**) with other nucleophiles also occurred readily; *e.g.*, phenyllithium, ethylamine, and morpholine gave complexes (**3c**—**e**) in good yields (60—70%).

The molybdenum complexes (**3**), and the analogous chromium complexes produced similarly from (**1a**), are derivatives of the novel carbene (4), for which high stability has been predicted by Gleiter and Hoffmann.[4] We believe that the conversion of (**1**) into (**3**) represents a new type of reaction in which a metal complex of one class of carbene (the 2π-cyclopropenylidenes) is converted into another (the 6π-pyranylidenes).

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