

Cyclization of Dicyanovinylidene with Two Diphenylacetylene Units to form a 6,6-Dicyanofulvene Derivative

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Summary Reaction of $(\text{NC})_2\text{C}=\text{C}(\text{Cl})\text{Mo}(\text{CO})_3\text{C}_6\text{H}_5$ with diphenylacetylene in boiling benzene results in the cyclization of dicyanovinylidene with two diphenylacetylene units to give green 6,6-dicyano-1,2,3,4-tetra-phenylfulvene.

DICYANOVINYLLIDENE (I) has been obtained as both a bridging^{1,2} and a terminal^{3,4,5} ligand in transition metal chemistry. This communication describes the first example of the use of dicyanovinylidene as a building block in organic synthesis.

Reaction of $(\text{NC})_2\text{C}=\text{C}(\text{Cl})\text{Mo}(\text{CO})_3\text{C}_6\text{H}_5$ (II) with diphenyl-

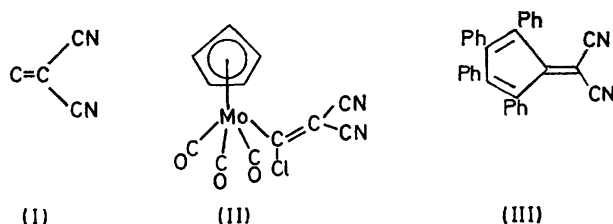
acetylene in a 1:2.8 mole ratio in boiling benzene for 2 h followed by chromatography on Florisil gave as the least strongly adsorbed fraction a weak yellow-green band. Elution of this band with dichloromethane followed by crystallization from mixtures of dichloromethane and

complexes of (III) from the brown metal-containing fractions remaining on the chromatography column after removal of (III) have been unsuccessful owing to our present inability to separate mixtures of closely related complexes.

The 6,6-dicyanofulvene derivative (III) may be regarded as the dicyanomethylene analogue of the well-known tetraphenylcyclopentadienone. Furthermore, the formation of (III) from the cyclization of dicyanovinylidene with two diphenylacetylene units is analogous to the formation of tetraphenylcyclopentadienone from two acetylene units and one carbon monoxide unit from a metal carbonyl.⁶ The use of the molybdenum complex $(\text{NC})_2\text{C}=\text{C}(\text{Cl})\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$ (II) as a source of dicyanovinylidene (I) in the synthesis of (III) probably involves a transfer of chlorine from carbon to the metal similar to the use of trihalogenoalkylmercurials such as PhHgCCl_3 as sources of dihalogenocarbenes.⁷ Further experience with $(\text{NC})_2\text{C}=\text{C}(\text{Cl})\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$ is necessary in order to determine whether this reagent can transfer dicyanovinylidene (I) only to a substrate such as diphenylacetylene which can bond concurrently to the molybdenum atom.

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hexane gave a 16% yield of green crystalline $\text{Ph}_4\text{C}_4\text{C}=\text{C}(\text{CN})_2$ (III) m.p. 216–217°; Similar reactions between $(\text{NC})_2\text{C}=\text{C}(\text{Cl})\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$ (II) and diphenylacetylene in other aprotic solvents (*e.g.* tetrahydrofuran or xylene) at temperatures in the range 65–135° gave similar yields (9 to 13%) of $\text{Ph}_4\text{C}_4\text{C}=\text{C}(\text{CN})_2$ (III). However, the yield of (III) could be markedly improved (up to 48%) upon oxidation of the crude reaction mixture with excess ethanolic ceric ammonium nitrate before isolating the product by chromatography. This last observation suggests the presence of metal complexes of (III) in the crude product from $(\text{NC})_2\text{C}=\text{C}(\text{Cl})\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$ and diphenylacetylene, but all attempts to isolate and characterize pure molybdenum

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