METHYLENECYCLOPROPANE IN THE [2+2+1] CYCLOADDITION REACTION WITH ACETYLENE DICOBALT HEXACARBONYL COMPLEXES

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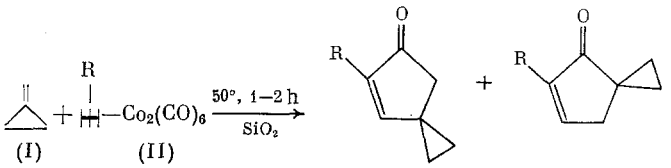
Methylenecyclopropane (I) undergoes cycloaddition with alkenes and heteroalkenes catalyzed by transition metal compounds through a formal [3+2] scheme with cleavage of the ring in (I) [1]. Under thermolysis conditions, (I) is also capable of undergoing [2+2] and [4+2] cycloaddition with ring retention [2].

No information is available on the participation of (I) in [2+2+1] cycloaddition with acetylene dicobalt hexacarbonyl complexes (II) (Khand–Pauson reaction [3]).



(I) (II) (III) (IV)

R	Yield of (III) + (IV)	(III)/(IV) ratio
H	46%	6 : 1
Me	58%	4,9 : 1
Ph	79%	4,4 : 1
	65%	5 : 1

We have discovered that (I) reacts readily with complexes (II) by [2+2+1] cycloaddition to form the corresponding cyclopentenone derivatives as a mixture of regioisomer (III) and (IV). However, under the standard conditions for the Khand–Pauson reaction in hexane solution at 20°C for 2-3 h [3], products (III) and (IV) are formed in ≤20% yields with complete conversion of the starting compounds. On the other hand, under our conditions for thermolysis on the surface of chromatographic adsorbents in the absence of a solvent [4], these reactions proceed smoothly with good yields of (III) and (IV).

The synthetic scope of the functional spiro[2.4]heptane derivatives obtained and the extension of this reaction to similar substrates are presently under study.

LITERATURE CITED

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