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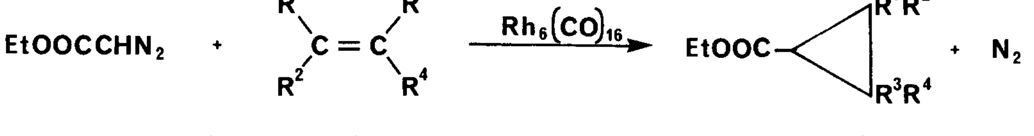
EXCEPTIONALLY EFFECTIVE CATALYSIS OF CYCLOPROPANATION REACTIONS BY THE HEXARHODIUM CARBONYL CLUSTER

Michael P. Doyle*, William H. Tamblyn, William E. Buhro, and Roberta L. Dorow
Department of Chemistry, Hope College, Holland, Michigan 49423

Hexadecacarbonylhexarhodium exhibits exceptional activity as a cyclopropanation catalyst in reactions between ethyl diazoacetate and alkenes that are remarkably free of competing processes.

Considered as reasonable models of metal surfaces,[1] metal cluster compounds have gained increased importance as catalysts for a broad selection of chemical transformations. Although they have not been previously employed for catalytic decomposition of diazo compounds, certain metal cluster compounds would appear to be eminently suitable as catalysts for transformations that potentially involve reactive metal carbenoid intermediates. Indeed, carbene derivatives of molecular clusters are implicated in catalytic carbon monoxide hydrogenation reactions,[2] and a μ_2-methylene osmium carbonyl cluster[3] as well as several dinuclear metal methylene complexes[4] have been characterized. We now wish to report the first use of a metal carbonyl cluster,* $Rh_6(CO)_{16}$, as an exceptionally effective catalyst for the cyclopropanation of olefins with ethyl diazoacetate (eq 1). In addition, we are now able to describe reaction conditions suitable to the production of cyclopropanes from olefins ranging from vinyl ethers to dienes and simple alkenes in uniformly high yield.



(1)

Table I describes the yields of cyclopropane products obtained when a representative series of alkenes was reacted with ethyl diazoacetate at 25°C in the presence of a catalytic amount of $Rh_6(CO)_{16}$, and compares these results with those from reactions performed under identical conditions in the presence of $PdCl_2 \cdot 2PhCN$ and $CuCl \cdot P(O\text{-}i\text{-}Pr)_3$. Similar comparisons were made with $Cu(acac)_2$ and $Pd(OAc)_2$, but the resulting cyclopropane yields were generally lower than with $CuCl \cdot P(O\text{-}i\text{-}Pr)_3$ or $PdCl_2 \cdot 2PhCN$, respectively. In a typical procedure,

Table I. Comparative Yields of Cyclopropane Derivatives from Transition Metal Catalyzed Reactions of Ethyl Diazoacetate with Representative Olefins[a]

Olefin	Time of EDA addition, hr	% Yield of cyclopropane[b]		
		$Rh_6(CO)_{16}$	$PdCl_2 \cdot 2PhCN$	$CuCl \cdot P(O\text{-}i\text{-}Pr)_3$
Ethyl vinyl ether	0.5	62	43	61
n-Butyl vinyl ether	0.5	69	34	51
2-Methoxypropene	0.5	72	66	67
Dihydropyran	0.5	82	41	18
3,4-Dihydro-2-ethoxy-2*H*-pyran	0.5	70	33	42
1-Methoxycyclohexene	0.5	59	39	54
Cyclohexene	6	88	31	28
Styrene	6	87	52	80
2,5-Dimethyl-2,4-hexadiene	6	87	20	55

[a] Ethyl diazoacetate (2.0 mmol) was added to the combination of olefin (20 mmol) and catalyst (0.01 mmol) at 25°C. [b] Products were identified by standard spectral analyses. Isolated yields are reported; sample purity was determined by GC analyses.

ethyl diazoacetate was added to a 10-fold molar excess of the alkene over the specified time period and nitrogen evolution, usually complete within one hr following the time of addition, was used to monitor the progress of ethyl diazoacetate decomposition. The vinyl ethers were generally more reactive than 2,5-dimethyl-2,4-hexadiene which, in turn, was more reactive than cyclohexene. Product mixtures from the reactions employing $Rh_6(CO)_{16}$ were exceptionally simple, giving no evidence of allylic C-H insertion products that are commonly observed when copper catalysts are employed[5,6] but containing variable, although minor, amounts of diethyl maleate and fumarate. Product yields were reproducible when the same reaction conditions were employed and were not influenced by the use of a solvent, typically toluene, in the hexarhodium carbonyl cluster catalyzed reactions. Hexadecacarbonylhexarhodium is stable in air, and reactions performed under air provided only slightly lower yields of cyclopropane products (< 5%) than those performed under argon. No evidence of vinyl polymerization, even with the normally sensitive vinyl ethers, was observed.

Hexadecacarbonylhexarhodium was recovered quantitatively when cyclopropanation reactions were performed under an atmosphere of carbon monoxide. No significant differences in cyclopropane yields were observed when reactions between ethyl diazoacetate and butyl vinyl ether were performed under these conditions, relative to reactions performed under nitrogen. The ease of recovery of $Rh_6(CO)_{16}$, which is conveniently centrifuged from the reaction medium following addition of hexane, provides a useful economy for these transformations. Furthermore, when ethyl diazoacetate was subsequently added to the supernatant reaction solution from a reaction previously performed under carbon monoxide, and prior to hexane addition, cyclopropanation occurred over the same time period, and identical yields of cyclopropane products were obtained.

When neat ethyl diazoacetate was added over 6 hr to a 7-fold molar excess of 2,5-dimethyl-2,4-hexadiene at 60°C, ethyl chrysanthemate was produced in greater than 90% isolated yield, even when the ethyl diazoacetate/$Rh_6(CO)_{16}$ molar ratio was as high as 2000. Although these results do not define the upper limit of catalyst effectiveness, they do imply exceptional productivity for hexadecacarbonylhexarhodium as a cyclopropanation catalyst.[7] Under similar conditions, but with only equivalent amounts of the olefin and ethyl diazoacetate, ethyl chrysanthemate was formed in 50% yield, and only diethyl maleate and fumarate were observed as significant by-products. Even though we have not optimized reaction conditions that would allow synthetic uses of this process when the olefin is the limiting reagent, the potential for such uses is evident.

Although competing reactions have been identified in prior studies of the catalytic cyclopropanation of olefins,[5,9-11] effective control of these processes has been elusive, and reported yields of cyclopropane products have been variable. In the $Rh_6(CO)_{16}$ catalyzed processes we have generally observed that diethyl maleate and diethyl fumarate are the only significant by-products of cyclopropane formation and that the combined yields of these and the cyclopropane products approach quantitative accountability of the ethyl diazoacetate. If ethyl diazoacetate competes with the olefin for the reactive intermediate, presumably a metal carbene, then simply decreasing the available concentration of ethyl diazoacetate in the reaction medium should favor cyclopropane production. As described by the results in Table II, slow addition of ethyl diazoacetate medium provides a substantial increase in the yield of cyclopropane pro-

Table II. Effect of the Rate of Ethyl Diazoacetate Addition on the Yield of Cyclopropane Products in $Rh_6(CO)_{16}$ Catalyzed Reactions[a]

Olefin	Temp. C°	$\frac{[\text{Olefin}]}{[\text{EDA}]}$	Cyclopropane yield, % Immediate EDA add'n	Cyclopropane yield, % 6 hr EDA add'n
n-Butyl vinyl ether	25	10.0	62	87
Styrene	25	10.0	69	86
2,5-Dimethyl-2,4-hexadiene	60	7.0	48	91

[a] Reactions were performed as described in Table I.

ducts over that obtained when the diazo compound is added in one portion. A corresponding decrease in the yields of diethyl maleate and diethyl fumarate accompanies the increased yield of cyclopropane products and suggests that, optimally, quantitative yields of cyclopropane products can be obtained in $Rh_6(CO)_{16}$ catalyzed reactions in the limit as the concentration of ethyl diazoacetate approaches zero. Although not specified as significant in prior reports of cyclopropanation reactions that have employed copper,[9-11] palladium(II),[12] and rhodium(II) catalysts,[13] the effect of the rate of addition of the diazo compound on the yield of cyclopropane products should be an integral feature of catalyst evaluation.

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