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Preliminary communication

CORRELATION BETWEEN CATALYTIC CYCLOPROPANATION AND YLIDE GENERATION

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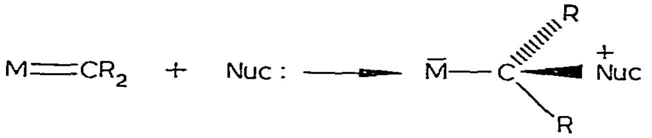
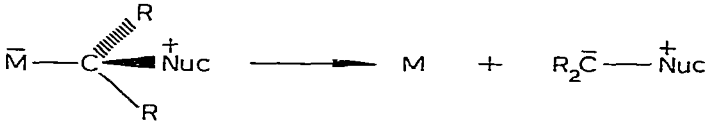
Summary

A linear correlation for catalytic effectiveness exists between cyclopropanation of n-butyl vinyl ether and ylide generation with allyl methyl sulfide in reactions with ethyl diazoacetate. Twenty-two representative transition metal compounds have been examined, and ruthenium is identified for the first time to exhibit catalytic potential comparable to copper and rhodium catalysts for carbene transformations.

Copper compounds have been previously employed for the catalytic production of sulfur ylides from diazo compounds [1], rhodium(II) acetate has been reported to catalyze the production of stable sulfur ylides derived from thiophenes [2], and we have recently communicated the remarkable facility of rhodium(II) acetate and hexadecacarbonylhexarhodium for catalytic ylide generation from a variety of allylic substrates under mild conditions [3]. Ylide generation is consistent with the formation of reactive electrophilic metal carbene intermediates [4,5] that characteristically undergo nucleophilic addition at the carbene carbon (eq. 1). Catalysis results from subsequent dissociation of the catalytically active metal species with formation of the product ylide (eq. 2). Since allyl ylides undergo the facile symmetry allowed [2,3]



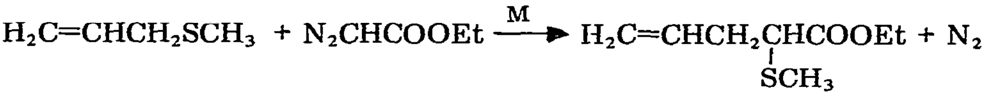
(1)



(2)

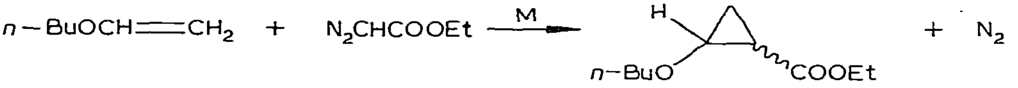
sigmatropic rearrangement [6,7], the use of allylic nucleophiles provides an efficient trap for the initially formed ylide products, and neither allylic sulfides nor tertiary amines undergo competing cyclopropanation in metal-catalyzed reactions.

Few transition metal compounds beyond those of copper have been described as catalytically active for carbenoid transformations [8] and, except for cyclopropanation reactions which are subject to diverse mechanistic interpretations [9], no convenient test of catalyst potential in carbenoid transformations has been developed. Since ylide generation is based upon nucleophilic addition to an electrophilic carbene, the formation of products from allylic ylide rearrangement in transition metal-catalyzed reactions should be an effective, although indirect, indicator of transient carbene complexes. We wish to report the use of allyl methyl sulfide as an efficient trap for electrophilic carbenes generated during reactions of ethyl diazoacetate with a broad selection of transition metal compounds (eq. 3) and to describe the striking correlation between ylide generation and cyclopropanation of n-butyl vinyl ether (eq. 4).



$$H_2C{=}CHCH_2SCH_3 + N_2CHCOOEt \xrightarrow{M} H_2C{=}CHCH_2\underset{\substack{|\\ SCH_3}}{C}HCOOEt + N_2 \qquad (3)$$

(I)



(4)

(II)

TABLE 1

COMPARATIVE PRODUCT YIELDS FOR CATALYTIC YLIDE TRANSFORMATION OF ALLYL METHYL SULFIDE (% I) AND CYCLOPROPANATION OF n-BUTYL VINYL ETHER (% II) WITH ETHYL DIAZOACETATE[a]

Entry	Catalyst	%I	%II	Entry	Catalyst	%I	%II
1	Cu bronze[b]	95	95	12	$Fe_2(CO)_9$	7	7
2	$CuCl \cdot P(O\text{-}i\text{-}Pr)_3$	95	71[c]	13	$Fe_3(CO)_{12}$	17	18
3	$Cu(acac)_2$	82	71	14	$Fe(acac)_3$	4	6
4	$Pd(PPh_3)_4$	40	31	15	$Ru_3(CO)_{12}$	96	65
5	$PdCl_2 \cdot 2PhCN$	50	34[c]	16	$Os_3(CO)_{12}$	4	13
6	$Co_2(CO)_8$	17	18	17	$Re_2(CO)_{10}$	14	18
7	$Co(OBz)_2$	4	4	18	$Cr(CO)_6$	2	2
8	$Rh_6(CO)_{16}$	96	86[c]	19	$Mo(CO)_6$	35	38
9	$[Rh(CO)_2Cl]_2$	96	58[c]	20	$Mo_2(OAc)_4$	3	15
10	$Rh_2(OAc)_4$	91	86[c]	21	$W(CO)_6$	1	12
11	$Fe(CO)_5$	2	16	22	Cp_2ZrCl_2	2	4

[a] Reactions were performed by addition of ethyl diazoacetate in anhydrous cyclohexane (2 *M*) through a Sage syringe pump (8 h) to a combination of the catalyst (0.5 mol%) and a 5-fold molar excess of either allyl methyl sulfide or n-butyl vinyl ether. Unless specified otherwise, reactions were run at 60°C for 8 h. Isolated product yields are reported, and results from duplicate reactions conform to a general precision of ±3% in reported yields. Except for reactions with Cu, Pd, Rh, and Ru catalysts, unreacted ethyl diazoacetate was recovered. [b] 11 mol%, based on ethyl diazoacetate. [c] Reactions were performed at 25°C; ethyl diazoacetate in anhydrous ethyl ether was employed.

Table 1 compares the yields of I and II formed in transition metal-catalyzed reactions of ethyl diazoacetate with allyl methyl sulfide and n-butyl vinyl ether, respectively. The catalysts, employed at 0.5 mol% based on ethyl diazoacetate, include typical representatives from each group of the transition series, and it is noteworthy that the initial oxidation state of the metal, its initial presence as a monomer or a cluster, and its attendant ligands exert little influence upon catalytic effectiveness. For example, copper and rhodium in any of their typical oxidation states, present as monomers, dimers, or clusters, and associated with a variety of ligands, are highly effective catalysts for both reactions. On the other hand, all of the iron compounds surveyed demonstrate uniformly low catalytic effectiveness. The results reported in Table 1 identify the ruthenium carbonyl cluster $Ru_3(CO)_{12}$ as a new catalyst for carbenoid transformations. Since the catalytic capabilities of ruthenium compounds for these processes have not been previously reported, they are currently being explored to determine their unique advantages. Two other ruthenium compounds,

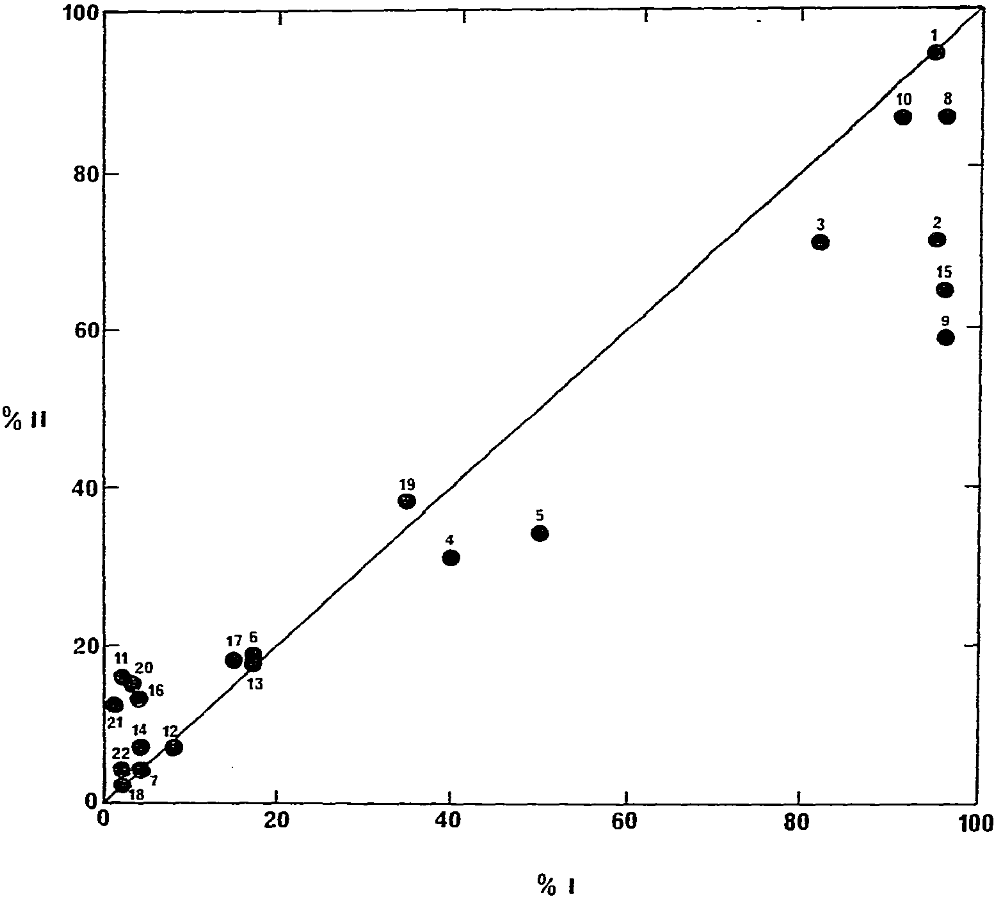


Fig. 1. Correlation between catalytic effectiveness in ylide generation (% I) and cyclopropanation (% II). The numbers displayed refer to catalytic entries in Table 1. The line drawn represents the ideal 1 : 1 linear correlation.

TABLE 2

ELECTROPHILIC SELECTIVITIES OF TRANSITION METAL CATALYSTS TOWARDS YLIDE GENERATION AND CYCLOPROPANATION[a]

Entry	Catalyst	k_3/k_4 [b]
1	Cu bronze	10.6
2	$CuCl \cdot P(O\text{-}i\text{-}Pr)_3$	11 [c]
5	$PdCl_2 \cdot 2PhCN$	18
10	$Rh_2(OAc)_4$	10.7
15	$Ru_3(CO)_{12}$	93
19	$Mo(CO)_6$	23

[a] Reactions were performed at 60°C as described in Table 1, generally using 1—2 mol% of the catalyst.
[b] Calculated from the relationship $(k_3/k_4) = ([BVE]/[AMS])$ (%I/%II) where BVE is n-butyl vinyl ether and AMS is allyl methyl sulfide. The molar ratio [AMS]/[BVE] ranged from 0.057 to 0.23, and the minimum amount of AMS was maintained in excess of the total molar amount of ethyl diazoacetate.
[c] Variation in this value was observed with increasing [AMS]/[BVE]. The ratio reported was determined as the limiting value as [AMS] → 0.

$[Ru(CO)_3Cl_2]_2$ and $(Ph_3P)_2RuCl_3(NO)$, exhibit exceptional reactivity for ylide generation (98% yield of I), but both catalysts polymerize butyl vinyl ether.

A plot of the data from Table 1, given in Fig. 1, clearly infers a linear correlation between catalytic effectiveness in ylide generation and cyclopropanation. Transition metal compounds that are efficient catalysts for cyclopropanation also display at least an equivalent effectiveness for ylide generation. Individual deviations from an exact linear correlation are evident but can be regarded as consequences of the relative sensitivities of the two substrates or their attendant products towards specific catalysts. This direct correlation is indicative of identical reaction intermediates for cyclopropanation and ylide generation and suggests that the allyl ylide rearrangement process can be employed to detect the formation of transient electrophilic metallocarbenes.

Competitive metal-catalyzed reactions of ethyl diazoacetate with n-butyl vinyl ether and allyl methyl sulfide, which were performed with transition metal catalysts selected from Table 1 and employed a minimum of three molar ratios of reactant ether to sulfide, substantiate that cyclopropanation and ylide generation occur through identical reaction intermediates. Plots of %I/%II verses the molar ratio of reactant sulfide to ether were both linear and intersected at the origin. In addition, the ratio of rate constants for ylide formation relative to cyclopropanation (k_3/k_4), obtained from these plots and reported in Table 2, describe a spectrum of electrophilic selectivities for these transition metal catalysts. Copper and rhodium catalysts exhibit similar relatively low selectivities whereas $Ru_3(CO)_{12}$, which deviates substantially from a linear correlation in Fig. 1, is exceptionally selective for ylide generation. The implication of these results are currently under investigation.

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References

1 W. Ando, Acc. Chem. Res., 10 (1977) 179.

2 R.J. Gillespie, J. Murray-Rust, P. Murray-Rust, and A.E.A. Porter, J. Chem. Soc. Chem. Commun., (1978) 83.

3 M.P. Doyle and W.H. Tamblyn, Abstracts of Papers, 181st National Amer. Chem. Soc. Meeting, Atlanta, Georgia, March 29—April 3, 1981, ORGN-148.

4 (a) C.P. Casey, T.J. Burkhardt, C.A. Bunnell, and J.C. Calabrese, J. Amer. Chem. Soc., 99 (1977) 2127; (b) C.P. Casey, S.W. Polichnowski, A.J. Shusterman, and C.R. Jones, Ibid., 101 (1979) 7282.

5 J.P. Fackler, Jr., and C. Paparizos, J. Amer. Chem. Soc., 99 (1977) 2363.

6 R.W. Hoffmann, Angew. Chem. Int. Ed. Engl., 18 (1979) 563.

7 R.W. Jemison, T. Laird, W.D. Ollis, and I.O. Sutherland, J. Chem. Soc., Perkin I, (1980) 1436, 1450.

8 (a) M.P. Doyle, W.H. Tamblyn, W.E. Buhro, and R.L. Dorow, Tetrahedron Lett., 22 (1981) 1783; (b) A.J. Anciaux, A.J. Hubert, A.F. Noels, N. Petiniot, and Ph. Teyssie, J. Org. Chem., 45 (1980) 695; (c) H.J. Callot and C. Piechocki, Tetrahedron Lett., 21 (1980) 3489; (d) A. Nakamura, A. Konishi, Y. Tatsuno, and S. Otsuka, J. Amer. Chem. Soc., 100 (1978) 3443, 3449.

9 D.S. Wulfman, G. Linstrumelle, and C.F. Cooper, in S. Patai (Ed.), The Chemistry of Diazonium and Diazo Groups, John Wiley & Sons, New York, 1978.