Homogeneous Copper(I) Catalysed Decomposition of Dimethyl Diazomalonate. The Role of the Counter Ion in Determining the Effective Spin Multiplicity

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Summary The reactions of olefin–dimethyl diazomalonate–trialkyl phosphite–copper(I) halide (catalyst) systems proceed *via* displacement of halide from the soluble catalyst, and this step appears to be rate determining; the leaving group ability of the anion influences the effective spin multiplicity distribution of the carbenoid species.

WE report a direct correlation between the effective spin multiplicity of a carbenoid reagent and the leaving group ability of the counter ion when the soluble catalyst systems, copper(I) salt–trialkyl phosphites,[1,2] are used to decompose dimethyl diazomalonate. We have also found that the addition of common anions drastically depresses the yields of all identifiable products.

We have observed the uncommon phenomenon of C–H insertion at the most substituted allylic position with concomitant rearrangements when copper catalysts were employed,[3] indicating that such systems proceed in part *via* triplet-like carbenoid species (Table 1).† The formation

TABLE 1

Effect of method of carbene generation on product distribution with 1-*methylcyclohexene as substrate*

	(III)		(IV)		(V)		(VI)		(VII)	
	Actual	Relative	Actual	Relative	Actual	Relative	Actual	Relative	Actual	Relative
Cu	22·9	1·00	1·23	0·054	18·5	0·810	4·13	0·180	5·64	0·122
CuCl	19·1	1·00	1·45	0·076	17·5	0·915	3·76	0·197	4·83	0·125
$CuSO_4$	24·8	1·00	2·49	0·100	24·0	0·965	6·07	0·244	7·36	0·146
$(MeO)_3P$–CuCl ..	29·6	1·00	2·30	0·077	26·0	0·878	10·7	0·360	5·15	0·086

† The data in Tables 1—3 were obtained as follows: a solution of 0·02 mol of dimethyl diazomalonate in 0·25 mol of olefin was added at the rate of 6 drops per min to 0·25 mol of olefin under reflux containing the catalyst. After 24 h at reflux, the excess of olefin was removed by distillation and the residue analysed by g.l.c. using diglyme as an internal standard.

TABLE 2

Effect of counter ion upon the product distribution with cyclohexene as substrate

0·14 mmol $(MeO)_3P$-CuZ	(I)		(VII)		(II)	
	Actual	Relative	Actual	Relative	Actual	Relative
Z = BF_4[a]	59·3	1·00	10·1	0·084	8·05	0·136
I	73·4	1·00	17·9	0·122	7·40	0·101
Br	68·5	1·00	21·1	0·152	6·75	0·097
Cl	63·7	1·00	18·4	0·144	4·67	0·074
SCN	28·2	1·00	18·3	0·032	1·81	0·064
CN	41·3	1·00	11·2	0·013	0·93	0·023

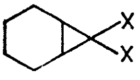
[a] Concentration less than 0·14 due to decomposition during transfer.

of allylic hydrogen insertion products together with rearrangement products clearly establishes the presence of either a radical or zwitterionic process. The variation with counter ion establishes a competition between the apparent triplet process and singlet process.

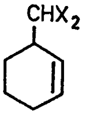
TABLE 3.

Effect of additives upon product distribution with cycolohexene as substrate

Catalyst	Additive	(I) Actual	(I) Relative	(VII) Actual	(VII) Relative	(II) Actual	(II) Relative
$(MeO)_3P$–CuI	None	73·40	1·00	17·90	0·122	8·05	0·136
$(MeO)_3P$–CuI	Me_4NI	3·40	1·00	0·00	—	7·23	0·120
$(MeO)_3P$–CuI	Me_4NBF_4	65·00	1·00	16·08	0·123	5·11	0·078



(I)



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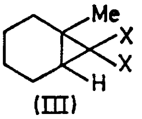

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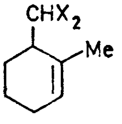

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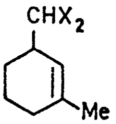
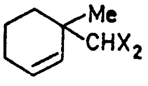


(V)



(VI)

$X_2C{=}CX_2$

(VII)

$X = CO_2Me$

A direct correlation exists between the extent of allylic C–H insertion and the leaving group ability of the counter ion (Table 2) as defined in nucleophilic substitution reactions at saturated carbon. It is of interest that the addition of one equivalent of tetramethylammonium iodide to the trimethyl phosphite–copper(I) iodide system almost completely suppressed the formation of norcarane and insertion products whereas tetramethylammonium fluoroborate had no appreciable effect. Similar effects were observable with the chloride. These data suggest that displacement of the counter ion by diazo-compound takes place in the rate-determining step or in a pre-equilibrium step. We would be hesitant to accept the presence of appreciable amounts of ionized material in the reaction mixture and would be looking for an alternate explanation except that the added salts were nearly completely soluble in the systems (Table 3).

None of these results requires invoking a complex involving olefin, catalyst, and diazo-compound or carbene as suggested by Moser.[2] Such complexes do seem likely on the basis of precedents. The relative reactivities of increasingly substituted olefins parallels the stability of copper(I) halide–substituted acrylic acid complexes.[4] In direct contrast with the photogenerated dimethoxycarbonyl-carbene,[5] the copper catalysed species exhibits a reduced reactivity towards increasingly substituted C–C double bonds. Thus the relative reactivities of the series, cyclohexene, 1-methylcyclohexene, and 1,2-dimethylcyclohexene are 5 : 1 : << 0·01. The olefins are clearly participating in the solubilization of the catalyst aggregates and are at least part of an outer co-ordination sphere. The results clearly reveal that the potential carbene is intimately associated with the catalyst and that the anion has a strong influence upon the spin multiplicity of the resulting carbenoid species.

The existing data can best be explained by a scheme involving attack of the diazo-compound upon the complex, displacement of the associated anion, loss of nitrogen from the resulting diazonium ion, displacement of the electronically deficient carbene by the anion, and subsequent addition to olefinic substrate. An alternate explanation may involve the degree of metal–metal orbital overlap in the catalyst aggregates[2] influencing the multiplicity.

We acknowledge partial support of this work by the National Science Foundation in the form of equipment grants and an Undergraduate Summer Research Fellowship to E.K.S.

(*Received, July 12th,* 1971; *Com.* 1200.)

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[2] W. R. Moser, *J. Amer. Chem. Soc.*, 1969, **91**, 1135, 1141.

[3] Musso (H. Musso and U. Beithan, *Ber.*, 1964, **97**, 2282) reported the isolation of up to 20% of the related benzenes from dihydrobenzenes as well as a comparable amount of malonic ester. Moser[2] reported no C–H insertion with diazoacetic ester.

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