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METAL SALT CATALYZED CARBENOIDS
THE CATALYSTS IN TRIALKYL PHOSPHITE COPPER(I) COMPLEX CATALYZED DECOMPOSITION OF DIAZO COMPOUNDS

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METAL SALT CATALYZED CARBENOIDS THE CATALYSTS IN TRIALKYL PHOSPHITE COPPER(I) COMPLEX CATALYZED DECOMPOSITION OF DIAZO COMPOUNDS

D. S. Wulfman, C. W. Heitsch,[2] Tom Jones,[3] Nguyen van Thinh,
R. S. McDaniel, and B. W. Peace[4]

Department of Chemistry, University of Missouri-Rolla,
Rolla, Missouri 65401

ABSTRACT

Partial rate data, asymmetric induction studies, interrupted experiments and additives studies indicate that copper(I) salt-phosphite complexes are destroyed during the course of reactions with dimethyl diazomalonate (1) and ethyl diazoacetate (2). All evidence is consistent with the copper(I) being oxidized to copper(II) and copper(0) being oxidized by impurities in the olefin which most probably are hydroperoxides.

Several new copper(I) salt-phosphite complexes were prepared and examined but none proved as effective for decomposing (1) as copper(II) _bis_ acetylacetonate.

The utility of the copper(I) chloride-trimethyl phosphite complex for decomposing (1) is a function of the means of preparation. The three general methods employed furnished samples having superposable i.r. spectra and superposable proton nmr spectra but exhibited varying degrees of line broadening in the P^{31} nmr.

The chiral mixed phosphite ligand 2-phenoxy-5,10,10-trimethyl-1,3-dioxa-2 phosphatricyclo$[5,2,1^{5,8},0^{4,9}]$ decane (3) derived from 2,3 bornadiol failed to induce any asymmetric induction in the reaction between (2) and styrene when complexed with copper(I) iodide even though the ligand is chiral at four carbons and phosphorous.

ACKNOWLEDGEMENTS

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Special thanks goes to my wife Phi for her encouragement.

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INTRODUCTION AND DISCUSSION

The use of organo-phosphite ligands to solubilize copper(I) salts has received detailed examination by Moser[5] in the course of studying the homogeneous catalyzed decomposition of diazo acetic ester. More recently, work in this laboratory has been directed toward studies employing diazomalonates.[6,7,8] Other solubilizing agents have been employed with copper salts such as acetylacetone,[9] and salicaldimines.[10] Generally, other groups do not permit appreciable quantities of the copper complex to enter solution unless highly polar solvents are employed such as acetonitrile.[11] Our finding that the optimum amount of catalyst for decomposing dimethyl diazo-malonate is extremely small somewhat obviated the need for "super" solubilizing agents.[8] The optimum amount of copper(II) fluoborate or copper(II) *bis*-acetylacetonate is soluble in refluxing cyclohexene, 1-methylcyclohexene and benzene under the conditions we normally employ.

In the course of catalyst concentration dependence studies, we found regular trends in behavior continued after the heterogeneous mode was entered. This was highly suggestive of the real catalyst as versus the formal catalyst continuing to increase in concentration. The behavior with mixed mode systems (homogeneous/heterogeneous) paralleled in considerable detail that of homogeneous systems.

Phosphites Ligands and Copper(I) Complexes

During the course of these studies, a number of phosphite copper(I) complexes of the type $(RO)_3P_n \cdot CuX$ (R = alkyl or aryl, n = 1, 2, or 3; and X = Cl^-, Br^-, I^-, CN^-, SCN^-, and BF_4^-) were prepared and their efficacy in carbenoid generation tested. Most often, these complexes were prepared by the method introduced by Arbuzov[12,13] and more recently used by Moser[5] and Nishizawa.[14] In this procedure, the phosphite was mixed with the appropriate mole ratio of copper(I) salt in benzene, followed by evaporation to dryness and recrystallization of the complex from chloroform. A modification of this process, made during this work, greatly simplified the synthesis.[15] The addition of an alcohol to the concentrated benzene solution causes instant precipitation of the complex. Material obtained in this way is pure and need not be recrystallized. The alcohol to be used should correspond to the phosphite portion of the complex. Aliphatic alcohols should not be used with aryl phosphite complexes since rapid ester exchange occurred under these conditions. The use of chloroform as a recrystallization solvent should be avoided. The complexes dissolve readily in this solvent, but an insoluble material forms after a few minutes. Halogenated hydrocarbons are known to react with phosphites.[16] This reaction probably destroys the complexes, giving the free copper salt.

Nishizawa[14] reported his inability to prepare a *tris*(phosphite) copper(I) halide complex. He did not specify the exact phosphite used in this attempt, however, most of his work centered around tri-*iso*-propyl- and triphenylphosphite. The present work has shown that *tris*(trimethylphosphite) copper(I) iodide is easily prepared by the modified Arbuzov procedure. Nishizawa's results might be explained in terms of steric considerations. However, triphenylphosphite formed both mono and bis complexes with copper(I) chloride and bromide, while only the bis complex was obtained from the iodide salt irrespective of the mole ratio or reactants.[12,13]

Nishizawa[14] determined the degree of association of a number of his copper(I) halide-phosphite ester complexes. In those cases where 1:1 complexes existed, they were invariably in the form of aggregates having an average association ranging between 1.72 and 4.13. In benzene and cyclohexane the lowest values were 2.86 and 3.83. With bis complexes the range was 0.95 to 1.02 and these complexes were clearly monomeric.

In a few cases, phosphite copper(I) complexes were prepared by the method of Beriger.[17] This involved addition of phosphorous trihalide to mixtures of copper salt and alcohol in toluene and led to impure material. Beriger's method is a potentially attractive route to complexes derived from phosphites which are not readily available.

We found that trialkylphosphite copper(I) halide complexes can also be prepared by the action of a phosphite upon copper(II) salts. This procedure gives impure products and is inferior to our modification of the Arbuzov procedure. While this work was in progress, Carty and coworkers[18] introduced a similar reductive procedure for the synthesis of trialkylphosphite copper(I) complexes.

The properties of trimethylphosphite copper(I) chlorides obtained from the three different schemes discussed are of interest.

The infrared spectra of the complexes from all three preparations are identical through the range 4000-400 cm^{-1}, although the p^{31} nmr. patterns and their melting points are distinctly different. This appears to be a result of copper(II) impurities. The H' nmr spectra were identical.

Most of the trialkylphosphite copper(I) complexes used in our work were known compounds. However, almost all melting points reported in the older literature[12,13] for these complexes are incorrect, two by as much as 40°C. Some of these discrepencies were noted earlier by Nishizawa.[14] Table I compares the melting points found during the present study with those obtained by Arbuzov and Nishizawa. Low melting points appear to be due to impure copper salts since freshly prepared copper(I) chloride routinely gave the higher melting complexes.

Table 1

Possible Phosphorus Intermediates

The possible intermediacy of certain phosphorous compounds in the reactions of diazomalonates was studied. Compounds (1)[19] and (2)[20] are known to furnish products formally derivable from typical carbene reactions. The malonate analogues of (1) and (2) resulted in tar formation and no recognizable products when decomposed in cyclohexene.

$Ph_3P{=}CHCOOEt$

(1)

$Ph_3P{=}N{-}N{=}CPh_2$

(2)

TABLE 1

MELTING POINTS OF TRIALKYLPHOSPHITE COPPER(I) HALIDES

Complex	Arbuzov[12,13]	Nishizawa[14]	This work
$(CH_3O)_3P\cdot CuCl$	190-2		229-30
$(CH_3O)_3P\cdot CuBr$	180-2		226-28
$(CH_3O)_3P\cdot CuI$	175-7		193-5
$(iso\text{-}C_3H_7O)_3P\cdot CuCl$	112-14	117	117-118
$(iso\text{-}C_3H_7O)_3P\cdot CuI$	184-5	199-200	199.5-200

Copper Catalysis

The nature of the active catalyst species in copper and copper salt diazo decompositions has been the subject of much discussion.[21-26] Two groups have observed the reduction of copper(II) chloride to copper(I) chloride by diazomethane and suggested the lower oxidation state was the actual catalyst.[22,23] D'yakonov[24] observed the formation of metallic copper from copper(II) sulfate during the decomposition of ethyl diazoacetate. The results of this study, however, clearly indicated that copper(II) was either the actual catalyst or, at least, a far more active catalyst than either elemental copper or copper(I).[25]

A broad claim that the processes involve copper(I) catalysis has been advanced by Salomon and Kochi.[26] Careful analysis of their accompanying data fails to substantiate this claim and the kinetic evidence is equally consistent with a copper(I) catalyzed pyrazoline pathway.[†] Extensive studies recently pursued in our laboratories indicate that copper(I) catalysis under our conditions is a physical impossibility on the basis of stoichiometrics. This point will be treated fully in a separate paper.

The oxidation of copper(0)[28] and copper(I)[29] by organic free radicals is well known and invariably peroxide impurities are present in olefins unless very special precautions are employed. We have observed the oxidation of copper(I) iodide (both complexed and

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[†] Footnote

Footnote

†Although catalyzed cycloadditions of diazocompounds to olefins have not been previously reported, ample precedents exist in the Diels-Alder literature (A. S. Onishchenko, "Diene Synthesis", Academy of Sciences of the USSR, Israel Program for Scientific Translations, Jerusalem, 1964). Corey[27] has reported a catalyzed Diels-Alder employing copper(II) fluoborate (many commercial samples contain some copper(I) salt). Complexation will lower the electron density of the olefin and increase its dipolarophilic character without altering the basic orbital symmetry considerations. The subsequent Δ'-pyrazolines should readily lose N_2 under the reaction conditions and furnish cyclopropanes and C-H insertion products via a hydrogen abstraction process.

uncomplexed) by excess benzoyl peroxide. In the absence of an added radical source, peroxide impurities in the olefin served to oxidize the copper(I) complex. This was conclusively demonstrated by the failure of ultra pure olefins to react in a normal manner with diazomalonates and copper(I) complexes. (Tables 2 and 3)

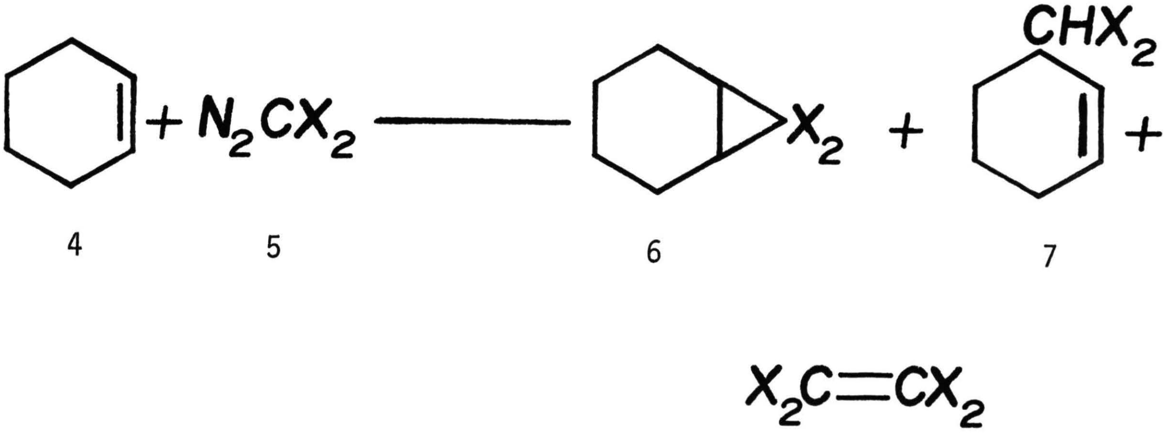
Tables 2 and 3

In the reaction of dimethyl diazomalonate with cyclohexene employing trimethylphosphite copper(I) halide catalyst, it was never possible to account for all the available diazo compound at the end of a reaction. Analysis of the reaction mixture after 10% of the diazomalonate had been added showed almost no recognizable products. After the first 10%, the reaction proceeded in an almost normal manner and after 30% reaction the product distribution was similar to those normally seen after allowing the reaction to go to completion. Thus, an initial prereaction can be postulated involving oxidation of copper(I) to the active species after which the reaction proceeds to the usual product distribution. (Table 4)

Table 4

The oxidation step was also indicated by the effects of several additives. The addition of trivalent phosphorus compounds reduced the efficacy of the copper phosphite catalyst but pentavalent phosphorus compounds had less effect. (Table 5) As trivalent phosphorus

Tables 5 and 6



4 5 6 7

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$X = COOMe$

TABLE 2a

PRODUCT DISTRIBUTION AND YIELDS IN THE REACTION OF CYCLOHEXENE AND DIMETHYL DIAZOMALONATE AS A FUNCTION OF CATALYST AND PEROXIDE CONTENT OF THE OLEFIN

	Percent Yield			
$(CH_3O)_3P\cdot CuZ$ 0.14 mmole	6	8	7	Ratios
Z = Br[a]	68.7	15.1	6.66	1.00:0.219:0.097
I[a]	74.3	12.9	7.43	1.00:0.174:0.100
Br[b]	22.0	1.88	2.08	1.00:0.085:0.095
I[b]	19.9	2.02	1.79	1.00:0.101:0.090
Br[c]	71.6	22.9	5.72	1.00:0.320:0.080
I[c]	78.8	15.0	5.92	1.00:0.191:0.075
No Catalyst[c,d]	9.45	1.82	0.00	1.00:0.192

[a] Commercial cyclohexene.

[b] Commercial cyclohexene filtered through alumina.

[c] Commercial cyclohexene filtered through alumina, then 0.07 mmole benzoyl peroxide added.

[d] 24 hr. at reflux.

All reactions were run as follows: A solution of 0.02 mole of dimethyl diazomalonate in 0.25 mole of cyclohexene was added at the rate of 6 drops per min to 0.25 mole of refluxing olefin containing the catalyst or catalyst plus peroxide. After 24 hours 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 2b

EFFECT OF BENZOYL PEROXIDE[a] ON THE REACTION OF DIMETHYL DIAZOMALONATE WITH CYCLOHEXENE AT VARIOUS CONCENTRATIONS OF $(CH_3O)_3P \cdot CuX$

Catalyst	Conc. (mmole)	Percent Yield[†] (Relative Yield)		
		6	8	7
X=I	0.0700	73.79(1.00)	12.39(0.168)	5.32(0.072)
I	0.1400	75.95(1.00)	15.98(0.210)	5.88(0.077)
I	0.2800	68.90(1.00)	27.01(0.392)	5.06(0.074)
Br	0.0700	71.73(1.00)	13.13(0.183)	5.49(0.077)
Br	0.1400	71.56(1.00)	23.91(0.334)	5.72(0.080)
Br	0.2800	70.96(1.00)	19.45(0.274)	5.86(0.081)
Cl	0.0700	79.36(1.00)	17.96(0.226)	6.01(0.076)
Cl	0.1400	78.51(1.00)	13.05(0.172)	6.24(0.079)
Cl	0.2800	50.52(1.00)	37.41(0.740)	3.36(0.067)

[†] Percent yield based on G.C. analysis against an internal standard.

[a] Olefins were filtered through alumina and benzoyl peroxide added to give a 1:1 mixture of benzoyl radicals and catalyst.

TABLE 2c

EFFECT OF PREOXIDIZED CATALYST UPON THE REACTION OF DIMETHYL DIAZOMALONATE WITH CYCLOHEXENE[a]

Catalyst	Method of Oxidation	Percent Yield[†] (Relative Yield)		
		6	8	7
$(CH_3O)_3P \cdot CuI$	A	76.36(1.00)	18.58(0.243)	6.00(0.079)
$(CH_3O)_3P \cdot CuI$	B	75.68(1.00)	13.00(0.173)	5.64(0.075)
$(CH_3O)_3P \cdot CuI$	B (Extracted)	69.67(1.00)	9.91(0.142)	4.72(0.068)
CuI	Benzoyl Peroxide	67.35(1.00)	4.04(0.059)	4.04(0.060)
CuI	Benzoyl Peroxide[c]	68.49(1.00)	9.36(0.137)	6.91(0.101)
$(CH_3O)_3P \cdot CuI$	B[b]	79.96(1.00)	10.73(0.134)	6.30(0.079)

[a] All samples of cyclohexene were treated with alumina immediately before use.

[b] Addition of dimethyl diazomalonate carried out in the presence of 0.1 g of p-dinitrobenzene.

[c] Oxidized product recrystallized from tetrahydrofuran.

[†] Percent yield based on G.C. analysis against an internal standard.

TABLE 3

"COPPER(O) CATALYZED" AND COPPER(II) ACETYL ACETONATE CATALYZED REACTIONS

Condition*	Percent Yield† (Relative Yield)		
	6	8	7
Thermal	12.7	Trace	0.00
Cu Metal	38.0	8.05	1.71
Metal free filtrate	36.0	7.20	2.78
$Cu(AcAc)_2$ Peroxide free	78.5	12.4	5.92
$Cu(AcAc)_2$ Peroxide present (0.14 mmole $(\phi COO)_2$)	78.1	12.4	5.81

*All reactions were initiated under nitrogen to prevent atmospheric oxidation.

†Percent yield based on G.C. analysis against an internal standard.

TABLE 4

EFFECT OF AMOUNT OF AVAILABLE DIMETHYL DIAZOMALONATE ON ITS REACTION WITH CYCLOHEXENE UNDER OPTIMUM CONDITIONS USING $(CH_3O)_3P{\cdot}CuI$

Conditions	Percent Yield[†] (Relative Yield)		
	6	8	7
10% Usual Reaction	0.15(1.00)	0.00	0.270(0.515)
Expected Yields for 10%[*]	7.35(1.00)	1.15(0.157)	0.598(0.081)
30% Usual Reaction	12.10(1.00)	2.10(0.174)	1.36 (0.113)
Expected Yields for 30%[*]	22.05(1.00)	3.45(0.157)	1.79 (0.081)
Expected Yields for 20%[*]	14.70(1.00)	2.30(0.157)	1.20 (0.081)

[*] Expected yields based on optimized yield using $(CH_3O)_3P{\cdot}CuI$.

[†] Percent yield based on G.C. analysis against an internal standard.

TABLE 5

EFFECT OF ADDITIVES UPON YIELDS AND PRODUCT DISTRIBUTION IN THE REACTION OF CYCLOHEXENE WITH DIMETHYL DIAZOMALONATE USING $(CH_3O)_3P \cdot CuCl$ (0.14 mmole) AS CATALYST

Additive (0.14 mmole)	Percent Yield[†] (Relative Yield)		
	6	8	7
None	63.92(1.00)	13.25(0.207)	4.69(0.074)
$(CH_3O)_3P$	46.07(1.00)	21.18(0.460)	3.75(0.082)
$(CH_3O)_3PO$	68.13(1.00)	16.23(0.238)	5.92(0.087)
$(CH_3O)_2CH_3PO$	60.58(1.00)	19.20(0.316)	5.08(0.084)
$[(CH_3)_2N]_3P$	49.94(1.00)	24.28(0.486)	4.61(0.092)
$[(CH_3)_2N]_3PO$	45.82(1.00)	17.34(0.378)	3.72(0.081)
$(CH_3O)_2HPO$	59.54(1.00)	25.14(0.422)	4.48(0.077)

[†] Percent yield based on G.C. analysis against an internal standard.

TABLE 6a

RELATIVE PRODUCT DISTRIBUTIONS IN THE REACTION OF CYCLOHEXENE WITH DIMETHYL DIAZOMALONATE (0.14 mmole) AS CATALYST*

Catalyst	Percent Yield† (Relative Yield)		
	6	8	7
$(CH_3O)_3P \cdot CuI$	74.23(1.00)	12.88(0.174)	8.09(0.136)
$[(CH_3O)_3P]_2 \cdot CuI$	65.96(1.00)	13.33(0.202)	6.60(0.100)
$[(CH_3O)_3P]_3 \cdot CuI$	63.64(1.00)	7.79(0.122)	6.60(0.103)
$[(CH_3O)_3P] \cdot CuCl$ (A)	64.07(1.00)	9.20(0.144)	4.70(0.070)
(A) + 30mg CuCl	33.54(1.00)	23.22(0.692)	2.37(0.071)
(A) + 30mg $CuCl_2$	55.13(1.00)	12.47(0.223)	5.36(0.097)

*Amounts determined relative to an internal standard added after reaction was complete.

†Percent yield based on G.C. analysis against an internal standard.

TABLE 6b

EFFECT OF ANION UPON PRODUCT DISTRIBUTION AND YIELDS IN THE REACTION OF CYCLOHEXENE WITH DIMETHYL DIAZOMALONATE

$(CH_3O)_3P \cdot CuX$ (0.14 mmole)	Percent Yield[†] (Relative Yield)		
	6	8	7
X = BF_4[*]	59.55(1.00)	7.25(0.122)	8.09(0.136)
I	74.23(1.00)	12.88(0.174)	7.42(0.101)
Br	68.64(1.00)	15.11(0.220)	6.68(0.097)
Cl	63.92(1.00)	13.25(0.207)	4.69(0.064)
SCN	28.31(1.00)	1.31(0.046)	1.82(0.064)
CN	41.53(1.00)	0.81(0.020)	0.94(0.023)

[*] Concentration less than 0.14 mmole due to decomposition during transfer.

[†] Percent yield based on G.C. analysis against an internal standard.

TABLE 6c

EFFECT OF COMMON ION ON THE REACTION OF CYCLOHEXENE WITH DIMETHYL DIAZOMALONATE

Catalyst	Salt	Percent Yield[†] (Relative Yield)		
		6	8	7
$(CH_3O)_3P\cdot CuI$	none	74.23(1.00)	12.88(0.174)	7.42(0.101)
$(CH_3O)_3P\cdot CuI$	$(CH_3)_4NI$	3.33(1.00)	0.00	7.08(2.12)
$(CH_3O)_3P\cdot CuI$	$(CH_3)_4NBF_4$	63.66(1.00)	11.36(0.178)	5.00(0.078)
$(CH_3O)_3P\cdot CuCl$	none	63.92(1.00)	13.25(0.207)	4.69(0.074)
$(CH_3O)_3P\cdot CuCl$	$(CH_3)_4NCl$	8.58(1.00)	1.57(0.183)	0.00
$(CH_3O)_3P\cdot CuCl$	$(CH_3)_4NBF_4$	49.33(1.00)	5.26(0.107)	4.08(0.083)

[†] Percent yield based on G.C. analysis against an internal standard.

compounds are known to react with peroxides,[30] this would reduce the peroxide available to oxidize copper(I) and give a poorer reaction. Alternatively this effect can be reasonably attributed to phosphorazene formation.

The oxidation of copper(I) iodide by excess benzoyl peroxide has been shown to liberate iodine. This was not the case with limited levels of peroxides or in the presence of phosphites until more than stoichiometric amounts of oxidant were added. The oxidized catalyst must have contained a copper to halogen bond since a definite anion effect and a common ion effect were observed.[7] Therefore, a copper(II)-alkoxyhalide would appear to be the active species (Eq. 1). Copper(II) might have been the active catalyst in almost all studies reported to date. Considering the very low

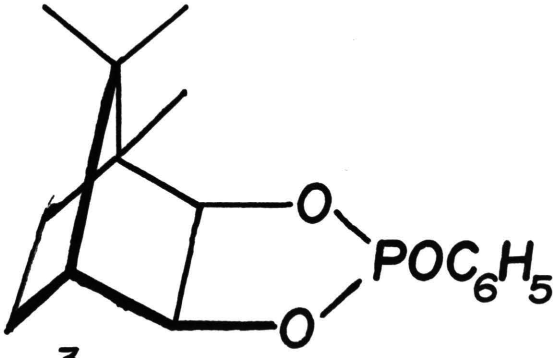
$$2(RO)_3P\text{-}CuX + 3R'OOR' \rightarrow 2R'O\text{-}Cu\text{-}X + 2(RO)_3PO + 2R'_2O \qquad (1)$$

catalyst concentration necessary for optimum results, most olefins probably contained sufficient peroxides to have generated the copper(II) species. In the case of complex ions and copper(I) salts, the presence of small amounts of copper(II) impurities would be expected except with copper iodide.

Although copper alkoxides with oxidizable hydrogens are not stable, examples exist where unsaturation in close proximity stabilizes copper-derivatives.[31-33]

A troublesome aspect of our interpretation of Moser's results arises from the observation of optical inductions when trisbornylphosphite is employed as a ligand. A very low but real level of optical induction was observed. The origin of this effect was ascribed to a chiral carbenoid. If the transition state is partially solvated by chiral molecules or the substrate is complexed to a chiral metal complex which catalyses pyrazoline formation, optical induction could also result. Successive dilution experiments might reveal the first of these alternatives but the chosen and last alternate will not be sensitive to this technique. Unfortunately Moser made no such determination.

We chose to prepare compound 3 from the related diol and triphenylphosphite and form the related copper(I) iodide complex. This ligand is chiral



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at four carbons and at phosphorous. When we decomposed diazoacetic ester in the presence of styrene using this complex at three different low concentrations, no optical induction was observed. In the system involved, as little as one percent induction would be readily observable for the trans 1-carboethoxy-2-phenylcyclopropane isolated by preparative gas chromatography. This product has a specific rotation in excess of 360°. We conclude that the complex was destroyed. From this we infer that Moser's results are a consequence of employing large quantities of chiral ligands which are oxidized to unspecified compounds some of which specifically solvate the carbene transfer process. Our observations on the effect of added trimethyl phosphate (0.14 mmole/0.14 mmole of catalyst) (Table 5) give added credence to this interpretation.

Moser[5] employed very pure olefins, but the actual catalyst used in his work was not established. Without mentioning optimum catalyst concentrations, Moser employed almost twenty times the optimum concentration of the copper(I) phosphite complexes employed in our studies. Copper(I) may have served as a less active catalyst. On the other hand, low concentrations of copper(II) could have been generated by traces of air present, diazo compound, by radicals from phosphorazene decompositions, or impure complexes (Moser did not furnish physical constants for his copper(I) phosphite complexes and we find that the melting points are depressed by copper(II) impurities but the melting point ranges remain narrow and this might lead one to assume higher homogeneity than justified).

Olefin Interactions With Catalysts

In an effort to ascertain the nature of olefin catalyst interactions, saturated solutions of anhydrous copper(II) perchlorate and copper(II) fluoborate were prepared in cyclohexene, 1-methyl cyclohexene, 1,2,3,4 tetramethyl benzene, hexafluorobenzene, cycloocta 1,5 diene and 1,6,9 cyclododecatriene and ESR spectra were observed at 298°K and 70°K. No fine structure was observed. It was not possible to determine the extent of coordination by analyses of hyperfine splitting.

The concentration of a given catalyst system influences the total yield of products and to some extent the relative amounts of the individual products. Although this effect is most evident at the high and low concentration and for cyclopropanation and C-H insertions, it is operative throughout the range for dimerizations. The observance of double maxima is a real phenomena and occurs with almost all catalysts and olefins examined. The underlying reason is not known. The difference in trends for dimerizations and for C-H insertions and cyclopropanation is a consequence of varying dependences upon catalyst for the two sets of processes with dimerization occurring with both a first and second order dependence.

The data in Tables 7a, 7b and 7c reflect differing amounts of copper(II) present as an impurity and as a function of the means of catalyst synthesis.

Tables 7a, 7b and 7c

TABLE 7a

PRODUCT DISTRIBUTION AND YIELDS AS A FUNCTION OF $(CH_3O)_3P \cdot CuCl$ (METHOD A) CONCENTRATION IN THE REACTION OF DIMETHYL DIAZOMALONATE WITH CYCLOHEXENE

Catalyst (mmole)	Percent Yield[†] (Relative Yield)			Total Product (6 + 8 + 7)
	6	8	7	
0.0042	36.21(1.00)	2.40(0.066)	3.19(0.089)	41.80
0.0085	40.24(1.00)	6.13(0.152)	3.60(0.092)	49.97
0.0170	43.67(1.00)	7.56(0.173)	4.47(0.092)	55.70
0.0350	67.44(1.00)	4.65(0.068)	5.36(0.086)	77.45
0.0700	68.21(1.00)	8.42(0.123)	5.49(0.092)	82.12
0.1400	46.08(1.00)	6.95(0.151)	4.16(0.091)	57.19
0.2800	49.85(1.00)	9.10(0.183)	4.80(0.096)	63.75
0.5600	62.55(1.00)	15.87(0.254)	6.16(0.099)	84.58
1.120	22.14(1.00)	31.96(1.44)	2.50(0.110)	56.60
2.240	7.59(1.00)	40.88(5.39)	1.39(0.184)	49.86
4.480	3.84(1.00)	53.51(13.9)	3.82(0.980)	61.17

[†] Percent yield based on G.C. analysis against an internal standard.

TABLE 7b

PRODUCT DISTRIBUTION AND YIELDS AS A FUNCTION OF $(CH_3O)_3P\cdot CuCl$ (METHOD B) CONCENTRATION IN THE REACTION OF DIMETHYL DIAZOMALONATE WITH CYCLOHEXENE

Catalyst (mmole)	Percent Yield[†] (Relative Yield)			Total Product (6 + 8 + 7)
	6	8	7	
0.0042	8.11(1.00)	6.61(0.815)	0.00	14.72
0.0085	4.80(1.00)	7.51(1.56)	0.00	12.31
0.0170	40.67(1.00)	9.38(0.231)	3.19(0.078)	53.24
0.0350	43.76(1.00)	5.67(0.130)	3.14(0.072)	52.57
0.0700	35.18(1.00)	9.55(0.271)	2.68(0.076)	47.41
0.1400	63.92(1.00)	13.25(0.207)	4.69(0.074)	81.86
0.2800	61.77(1.00)	21.55(0.349)	5.32(0.086)	88.64
0.5600	33.81(1.00)	32.33(0.956)	2.33(0.069)	68.47
1.120	11.58(1.00)	19.07(1.65)	0.92(0.079)	31.57
2.240	7.38(1.00)	41.25(5.59)	5.30(0.718)	53.93
4.480	2.40(1.00)	33.20(13.8)	4.29(1.78)	39.89

[†] Percent yield based on G.C. analysis against an internal standard.

TABLE 7c

PRODUCT DISTRIBUTION AND YIELDS AS A FUNCTION OF $(CH_3O)_3P \cdot CuCl$ (METHOD C) CONCENTRATION IN THE REACTION OF DIMETHYL DIAZOMALONATE WITH CYCLOHEXENE

Catalyst (mmole)	Percent Yield[†] (Relative Yield)			Total Product (6 + 8 + 7)
	6	8	7	
0.0042	6.74(1.00)	7.96(1.18)	0.00	14.70
0.0085	31.83(1.00)	13.13(0.412)	5.53(0.174)	50.49
0.0170	36.89(1.00)	7.73(0.209)	3.13(0.085)	47.75
0.0350	58.00(1.00)	5.83(0.100)	3.05(0.052)	66.88
0.0700	60.49(1.00)	9.56(0.158)	4.34(0.072)	74.39
0.1400	51.91(1.00)	14.62(0.282)	3.74(0.072)	70.27
0.2800	42.21(1.00)	43.11(1.02)	2.83(0.068)	88.15
0.5600	16.30(1.00)	66.15(4.06)	1.42(0.087)	83.87
1.120	13.47(1.00)	64.41(4.78)	1.26(0.094)	79.14
2.240	10.98(1.00)	61.94(5.94)	1.34(0.122)	74.26
4.480	8.03(1.00)	35.80(4.46)	3.76(0.467)	47.62

[†] Percent yield based on G.C. analysis against an internal standard.

EXPERIMENTAL

Preparation of Dimethyl Mesoxalate Triethylphosphorazine

Dimethyl mesoxalate triethylphosphorazine was prepared by the method of Poshkus and Herweh.[34] A solution of 83.0 g (0.5 mole) of triethylphosphite in 200 ml of pentane was stirred at room temperature while 79.0 g (0.6 moles) of dimethyl diazomalonate in 200 ml of pentane was added over 2 hours. During the addition, the temperature rose to 34°C and a pentane in soluble oil formed. The yellow oil was removed and washed five times with pentane. An attempt to distill a portion of the material ended in its rapid decomposition at a pot temperature of 35-40°C. The pentane was removed under vacuum without heat and the phosphorazine used without further purification. The nmr spectrum (CCl_4) showed a pentuplet centered at τ 5.75 (6H, methylene), a singlet at τ 6.22 (6H, COOMe), a triplet centered at τ 8.62 (9H, Me), and a small amount of impurity (mostly pentane). The compound was assigned the structure dimethyl mesoxalate triethylphosphorazine.

Preparation of Dimethyoxycarbonylmethylenetriphenylphosphorane

Dimethyoxycarbonylmethylenetriphenylphosphorane was prepared by a modified procedure based on the method of Horner and Oediger.[35] A solution of 131 g (0.5 mole) of triphenylphosphine in 1400 ml of dry benzene was cooled to 10°C. With stirring, a solution of 25.8 ml (0.5 mole) of bromine in 50 ml of carbon tetrachloride was added over 2 hours. When the addition was complete, a solution of 121.4 g (1.2 moles) of triethylamine and 66.0 g (0.5 mole) of dimethyl malonate in 400 ml of benzene was added all at once. The solution was heated at reflux for 10 minutes then allowed to cool. The solid which formed (triethylamine hydrobromide) was removed by filtration and the solvent removed by distillation to leave a red oil. The oil solidified upon the addition of pentane. The solid was filtered, dissolved in cyclohexane, treated with activated characoal, then allowed to crystallize. After two recrystallizations, 156 g (80%) of light yellow crystals melting at 142-143°C were collected. The infrared spectrum (KBr) showed bands at 1195 cm^{-1} (s, P=C) and 1640 cm^{-1} (m, C=O). The spectrum was almost identical to that reported for diethyoxycarbonylmethylenetriphenylphosphorane.[21] The nmr spectrum ($COCl_3$) showed a doublet centered at τ 6.20 (6H, COOMe) and a multiplet centered at τ 2.50 (15H, aromatic).

Decomposition of Dimethyl Mesoxalate Triethylphosphorazine

A 5.54 g (0.02 mole) sample of dimethyl mesoxalate triethylphosphorazine was decomposed in cyclohexene as previously described for dimethyl diazomalonate. Trimethylphosphite copper(I) chloride (0.14 mmole) was used as catalyst. During the addition, a dark insoluble oil formed. Both the oil and the cyclohexene layer were analyzed by g.c. None of the normal carbene addition products were present in either phase of the reaction mixture.

The procedure was repeated using copper(I) chloride as catalyst. Again no recognizable products were formed.

Decomposition of Dimethoxycarbonylmethylenetriphenylphosphorane

The decomposition was carried out as described above for dimethyl mesoxalate triethylphosphorazine using both complexes and uncomplexed copper(I) chloride. G.c. analysis of the reaction mixture showed the absence of all the products typical of the carbene additions.

Trimethylphosphite Copper(I) Chloride

Method A. The procedure given here is a modification of the method of Arbuzov.[12,13] A solution of 12.4 g (0.1 mole) of trimethylphosphite (which had been dried over metallic sodium) in 200 ml of dry benzene was stirred while 9.9 g (0.1 mole) of copper(I) chloride was added. Initially, the salt was removed by filtration, the solvent was removed and 20 ml of methanol was added. The white crystals which formed were filtered and dried under vacuum (1 mm) at 50°C for 3 hours. The yield was 20.0 g (90%) of material melting at 192-193°C (Lit.[12,13] 190-192°C). In other runs using freshly prepared copper(I) chloride, the complex melted at 229-230°C. The higher melting complex was subjected to analysis. Analysis calculated for $C_3H_9O_3PCuCl$: C, 16.14; H, 4.03; Cl, 15.92; P, 13.90; Cu, 28.47. Found: C, 16.17; H, 3.95; Cl, 15.89; P, 14.04; Cu, 28.20.

Method B. This method was used by Beriger[17] in the preparation of trimethylphosphite. A solution of 4.80 g (0.15 mole) of dry methanol in 50 ml of toluene was cooled to -10°C and 4.95 g (0.05 mole) of copper(I) chloride was added. With stirring, 6.53 g (0.05 mole) of phosphorus trichloride was added at a rate sufficient to maintain the temperature between -5 and -10°C. After the addition, the mixture was warmed to room temperature (20 minutes), during which time hydrogen chloride gas was evolved. The white solid was filtered off, washed several times with cold pentane, then dried under vacuum (1 mm) at 50°C for 3 hours. The melting point of this complex was 194-196°C. The infrared spectrum (400-4000 cm^{-1}) was identical to that of the higher melting complex.

Method C. A solution of 12.4 g (0.1 mole) of trimethylphosphite in 100 ml of dry benzene was stirred as 6.7 g (0.05 mole) of copper(II) chloride was added. After 30 minutes at reflux, the mixture was filtered, cooled, and allowed to crystallize. A total of 10.0 g (90%) of trimethylphosphite copper(I) chloride melting at 194-196°C was collected. This material was identical to that prepared by methods A and B as shown by comparison of their infrared spectra (400-4000 cm^{-1}).

Trimethylphosphite Copper(I) Bromide

To a stirred solution of 7.20 g (0.05 mole) of trimethylphosphite in 50 ml of dry benzene was added 7.17 g (0.05 mole) of anhydrous copper(I) bromide. After 30 minutes at reflux, the mixture was filtered and the solvent removed. Methanol (20 ml) was added, and after cooling the crystals which formed were filtered and dried under vacuum (1 mm) at 50°C for 3 hours. A total of 11.7 g (88%) of complex melting at 226-228°C (lit.[13] 180-182°C) was collected. Analysis calculated for $(CH_3O)_3P\text{-}CuBr$: C, 13.47; H, 3.36; P, 11.58; Br, 29.88. Found: C, 13.16; H, 3.47; P, 11.61; Br, 29.94.

Trimethylphosphite Copper(I) Iodide

A solution of 7.20 g (0.05 mole) of trimethylphosphite in 50 ml of dry benzene was stirred as 9.55 g (0.05 mole) of copper(I) iodide was added. The mixture was heated for 30 minutes, then filtered hot to leave 0.1 g of uncomplexed salt. The benzene was removed to give an oil with some suspended solid in it. Upon addition of methanol, the oil solidified. After cooling, the solid was filtered off, washed several times with cold methanol, then dried under a 1 mm vacuum at 50°C for 3 hours. The yield of material melting at 193-195°C (lit.[12,13] 175-177°C) was 14.1 g (84%).

Trimethylphosphite Copper(I) Cyanide

A solution of 7.20 g (0.05 mole) of dry trimethylphosphite in 50 ml of dry benzene was stirred as 4.48 g (0.05 mole) of copper(I) cyanide was added. The salt was completely dissolved after stirring at room temperature for 30 minutes. The material obtained upon removal of the solvent failed to crystallize during the usual work up and could not be induced to do so. All solvent was removed by brief, room temperature vacuum distillation; the oily complex was used without further purification. The yield was 10.9 g (80%).

Trimethylphosphite Copper(I) Thiocyanate

The complex was prepared by Method A described above for the copper(I) chloride complex. The yield of white solid, m.p. 151-153°C, was 11.2 g (82%). Analysis calculated for $(CH_3O)_3P \cdot CuSCN$: C, 19.55; H, 3.70; P, 12.63; S, 13.04; N, 5.70. Found: C, 19.54; H, 3.87; P, 12.72; S, 13.04; N, 5.80.

Trimethylphosphite Copper(I) Fluoroborate

In 50 ml of dry benzene 1.24 g (0.01 mole) of trimethylphosphite and 4.29 g (0.01 mole) of copper(I) fluoroborate-tritoluene (generally supplied by an anonymous donor in the Central Research Laboratory, Monsanto Company) were mixed and stirred briefly at room temperature. The benzene was removed to give a slightly blue colored oil. Due to the instability of the fluoroborate salt, no effort was made to crystallize or otherwise purify the complex.

Bis-(Trimethylphosphite) Copper(I) Iodide

A solution of 2.48 g (0.02 mole) of trimethylphosphite in 20 ml of dry benzene was stirred as 1.90 g (0.01 mole) of copper(I) iodide was added. After 30 minutes at reflux, the solution was filtered, the solvent removed in vacuo, and methanol added. After cooling, the crystals which formed were collected and dried in the usual way. A total of 4.00 g (91%) of white crystals melting at 69-70°C (lit.[12] 69-70°C) was collected.

Tris-(Trimethylphosphite Copper(I) Iodide

A 3.72 g (0.03 mole) sample of trimethylphosphite and 1.90 g (0.01 mole) of copper(I) iodide were allowed to react as described above for the 2:1 complex. After removal of the benzene, an oil remained which did not solidify upon addition of 20 ml of methanol and dried under vacuum (1 mm) at 50°C for 3 hours. The yield was 4.72 g (84%) of material melting at 118-119.5°C. Analysis calculated for $[(CH_3O)_3P]_3 \cdot CuI$: C, 19.2; H, 4.80; I, 22.6; P, 16.5; Cu, 11.3. Found: C, 19.05; H, 4.80; I, 22.70; P, 16.40; Cu, 11.46.

Triphenylphosphite Copper(I) Bromide

A solution of 3.10 g (0.01 mole) of triphenylphosphite in 20 ml of dry benzene was stirred as 1.44 g (0.01 mole) of copper(I) bromide was added. The mixture was stirred until all the salt dissolved, (one hour). The benzene was removed and 15 ml of ether added (addition of methanol immediately gave the odor of trimethylphosphite) to dissolve the resulting oil. A seed crystal was obtained on a porous plate and added to the cooled ether solution. The crystals which formed were collected and dried to give 3.20 g (91%) of material melting at 91-92°C (lit.[12,13] 90.5-91.5°C).

Triphenylphosphite Copper(I) Iodide

A mixture of 6.20 g (0.02 mole) of triphenylphosphite and 3.82 g (0.02 mole) of copper(I) iodide in 50 ml of dry benzene was heated at reflux for 30 minutes. The mixture was filtered to give 1.91 g (50%) of unreacted copper salt. The solvent was removed and the resulting oil taken up in 20 ml of ether. The crystals which formed were collected and dried to yield 7.91 g (98%) of material melting at 73-75°C. This is the melting point reported[12] for the bis-complex. No further effort was made to prepare the mono complex.

Tricyclohexylphosphite Copper(I) Bromide

A solution of 15.0 g (0.15 mole) of freshly distilled cyclohexanol in 100 ml of dry toluene was cooled to -10 C, and 8.18 g (0.05 mole) of copper(I) bromide was added. With stirring, 13.6 g (0.05 mole) of phosphorous tribromide was added at a rate designed to maintain the temperature below -5°C. When the addition was complete, the mixture was allowed to warm to room temperature and stirred an additional 20 minutes. Cold pentane was added to decrease the solubility; the solid was filtered off and washed several times with pentane. A dam was placed on the filter and the material evacuated for one hour to remove pentane and hydrogen bromide. The solid was then dried in a 35°C vacuum oven at 1 mm. The complex did not melt but decomposed at 60°C. It also decomposed upon standing at room temperature overnight.

Triisopropylphosphite Copper(I) Iodide

The reaction was carried out exactly as described for the trimethylphosphite catalyst. After removal of the benzene, 20 ml of isopropanol was added and the mixture cooled. The white solid was filtered off and dried under vacuum (1 mm) at 50°C for 2 hours. The yield of material melting at 199.5-200°C (lit.[14] 199-200°C) was 16.2 g (90%).

Oxidation of Trimethylphosphite Copper(I) Iodide

Method A. A mixture of 4.5 g (0.014 mole) of trimethylphosphite copper(I) iodide in 25 ml of benzene was warmed to 50°C and 3.39 g (0.014 mole) of benzoyl peroxide was added over a 2 hour period in small portions. During the addition the solution became a deep blue color, but never completely homogeneous. The mixture was cooled and the solid filtered off and dried under vacuum at 50°C for 2 hours. The blue solid melted at 190-205°C.

Method B. A solution of 3.60 g (0.025 mole) of trimethylphosphite in 50 ml of dry benzene was treated with 4.77 g (0.025 mole) of copper(I) iodide as described earlier. The hot solution of the complex was immediately treated with 4.05 g (0.025 mole) of benzoyl peroxide in small portions over a period of 2 hours. Late in the addition a solid formed. After all of the peroxide had been added, the mixture was cooled and the blue solid filtered off. The solid melted at 243-249°C. A part of the material was transferred to a Soxhlet extractor and extracted for 24 hours with hexane. After drying, the sample melted at 258-262°C. Elemental analysis of the extracted solid showed the absence of phosphorus and iodine. The infrared spectrum was similar but not identical to that of copper(II) benzoate (mull).

Oxidation of Copper(I) Iodide

A 4.77 g (0.025 mole) sample of copper(I) iodide was placed in 50 ml of dry benzene at 50°C and 4.05 g (0.025 mole) of benzoyl peroxide added in small portions over a 2 hour period. The solvent immediately assumed the characteristic color of iodine. When the addition was complete, the solid that had formed was filtered off and washed free of iodine with cool benzene. The solid melted at 279-281°C. Its infrared spectrum (KBr) was very similar to that of copper(II) benzoate. The reported melting point of copper(II) benzoate is 280-282°C.

The solid was insoluble in most organic solvents, but a small amount was dissolved in refluxing tetrahydrofuran. After crystallization the material was brilliant blue in color and melted at 285-286°C. Analysis of this material indicated complexation of the salt with tetrahydrofuran. Analysis calculated for $C_{14}H_{10}O_4Cu \cdot C_4H_8O_2$: C, 54.92; H, 4.57. Found: C, 54.89; H, 4.57.[†]

[†] All microanalyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan.

Camphorquinone (2,3 Bornadione)

A solution of 53.65 g (0.352 mole) of d-camphor, 53.6 ml of glacial acetic acid and 64.38 g (0.815 mole) of freshly prepared and sublimed selenium dioxide was heated at 140-150°C for 5 hr. The workup was similar to that described previously by Evans, Ridgion and Simonsen[37] and furnished 58.27 g (0.351 mole) of camphorquinone, m.p. = 190-196°C (lit.[37] 190-195°C).

Cis Borna 2,3 diol

The camphorquinone from the previous experiment (58.27 g, 0.315 mole) was dissolved in 800 ml of isopropanol and 13.25 g (0.349 mole) of sodium borohydride was added. The resulting mixture was stirred for 48 hr with a magnetic stirrer. The solvent was removed at ~ 80° using a Buchi Rotovaporator, 200 ml of water was added and the mixture was filtered. The solid was taken up in 300 ml of CH_2Cl_2 and the aqueous layer was extracted with CH_2Cl_2 (3 x 300 ml). The combined extracts (~ 1200 ml) was concentrated at 30° on the rotovaporator. The residue was taken up in hot benzene-petroleum ether (60-80°C) (50/50) and furnished with a single recrystallization 25.2 g (0.14 mole, 47.6 percent) of a white solid, m.p. 251-255°C (lit.[38] m.p. 253-255°C for cis diol, trans diols both melt 230-231°C). This was used without further purification.

Phenyl-2,3-bornadiophosphite (3) and Its Complex with Copper(I) Iodide

A solution of 25 g of 2,3 bornadiol (0.14 mole) in dry benzene (685 ml) was brought to reflux for 48 hr after the addition of 43.4 g (0.14 mole) of triphenylphosphite. Then 26.6 g of copper(I) iodide (0.14 mole) was added and after 2 hr at reflux the slight amount (~ 0.1 g) of copper salt not dissolved was removed by vacuum filtration through a medium glass fritted funnel with the aid of an aspirator having a drying tube between flask and aspirator. The solvent was removed on a rotovaporator at ~ 60° and furnished a low melting oily solid when cooled to ~ 25°. Repeated attempts to obtain good crystalline material failed and the oily material was used as isolated for subsequent studies.

Reaction of Ethyldiazoacetate (EDA) with Styrene

Three otherwise identical runs were performed employing 0.170, 0.685 and 2.66 mmole of the complex of copper(I) iodide with (3). A solution of 5 ml (4.5 g, 43.3 mmole) of styrene, 2.28 g EDA (19.8 mmole) in 20 ml of benzene was added at a rate of 1 drop/15 sec. to a solution of catalyst in 25 ml of refluxing benzene over a period of 2 hr. After addition was complete reflux was maintained for 12 hr, then the benzene removed at ~ 60° using a rotovaporator. The crude product mixture was separated on a 3/8 inch, 15 ft., 30 percent SE30 on chromsorb W gas chromatographic column in a Varian Autoprep with the oven temperature 160°; injector, 255°; detector 255°. The ratios of cis adduct to trans adduct were 3.08, 3.61 and 4.48. The rotations were examined on a Kern polarimeter at concentrations of 0.8114 M, 1.2914 M and 0.8700 M in $CHCl_3$ at 25°. Zero rotations were observed in each case. Reported[5,10,11] $[\alpha]_D^{20}$, ± 410°C.

CONCLUSIONS

We are forced to conclude that the phosphorus ligands consume diazo compound which does not result in carbenoid products. The role of the phosphites is one of solubilization until such time as the diazo compound converts the phosphites into new solubilizing agents or form solubilizing ligands which are phosphorous free. The amount of catalyst actually required is small and the fluoborate and perchlorate are sufficiently soluble in olefins to reach the optimum level. The degree of aggregation of the real (vs. the formal) catalyst is unknown and this information is not readily accessible. The apparent role of copper is that of a Lewis Acid. There would appear to be no _a priori_ reasons for limiting the active copper species to copper(II) even though our studies with diazomalonic esters lead to that conclusion. The key features of copper(II) are stronger acid strength but weaker backbonding than related copper(I) species. It is perhaps significant that silver salts (which are better for backbonding) facilitate the Wolff rearrangements of α diazoketones whereas copper salts generally give high yields of carbenoid derived products.[39] The apparent contradiction in our studies is that copper(II) chloride by itself, or as an impurity, is a poorer catalyst than copper(I) chloride based systems. This is clearly a common ion effect where chloride ion suppresses the catalyzed processes. The mechanistic rationale has been treated previously and will be treated fully in a subsequent paper.[21]

References

1. For Paper VIII, see B. W. Peace and D. S. Wulfman, *Synthesis*, 137 (1973).

2. Central Research Department, Monsanto Co., St. Louis, Missouri.

3. Department of Chemistry, University of Missouri-St. Louis, St. Louis, Missouri.

4. a) Taken in part from the PhD Dissertation of B. W. Peace, University of Missouri-Rolla, 1971.
   b) National Science Foundation, Summer Research Fellow, 1970.

5. W. R. Moser, *J. Amer. Chem. Soc.*, **91**, 1135, 1141 (1969).

6. D. S. Wulfman, F. C. Carman, B. G. McGiboney, E. K. Steffen and B. W. Peace, *Preprints*, *Division of Petroleum Chemistry*, *American Chemical Society*, Vol. 16, Part B, No. 1, 1971.

7. B. W. Peace and D. S. Wulfman, *Tetrahedron Letters*, 1971, 3799.

8. B. W. Peace and D. S. Wulfman, *J. Chem. Soc. (D)*, 1971, 1179.

9. D. D. Cowan, M. M. Cooch, K. R. Kopecky and G. S. Hammond, *J. Org. Chem.*, **29**, 1922 (1964).

10. H. Nozaki, S. Moriuti, M. Yambe and R. Noyori, *Tetrahedron Letters*, 59 (1966); H. Nozaki, H. Takaya, S. Moriuti and R. Noyori, *Tetrahedron*, **24**, 3655 (1968); *Tetrahedron Letters*, 5293 (1966).

11. T. Shirafuji, Y. Yamamoto, H. Nozaki, *Tetrahedron*, **27**, 5353 (1972).

12. A. Arbuzov, *Ber.*, **38**, 1171 (1905).

13. A. Arbuzov, *J. Russ. Phys. Chem. Soc.*, **38**, 161, 193, 687 (1906).

14. Y. Nishizawa, *Bull. Chem. Soc. Japan*, **34**, 1170 (1961).

15. B. W. Peace, F. C. Carman and D. S. Wulfman, *Synthesis*, 658 (1971).

16. L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N.Y., 1968, p. 1247.

17. E. Beriger, U.S. Patent 2,931,826, April 5, 1960.

18. W. A. Anderson, A. J. Carty, G. J. Polenik and G. Schreiber, *Canadian J. Chem.*, **49**, 762 (1971).

19. L. Horner and H. Oediper, *Chem. Ber.*, **91**, 434 (1958).

20. D. R. Dalton and S. A. Liebman, *Tetrahedron*, **25**, 3321 (1969).

21. D. S. Wulfman, B. W. Peace and E. K. Steffen, *J. Chem. Soc. (D)*, 1360 (1971).

22. G. Wittig and K. Schwarzenbach, *Ann.*, **650**, 1 (1961).

23. R. G. R. Bacon and H. A. O. Hill, *Quart. Rev.*, **19**, 95 (1965).

24. M. I. Komendantov, I. A. D'yakonov and T. S. Smirnova, *J. Org. Chem. USSR* (Engl. Transl.), **2**, 561 (1966). *C. A.*, **65**, 7124 (1966).

25. B. W. Peace and D. S. Wulfman, *Tetrahedron Letters*, 1972, 3903.

26. R. G. Salomon and Jay K. Kochi, *J. Amer. Chem. Soc.*, **95**, 3300 (1973).

27. E. J. Carey, V. Koellikev and J. Neuffer, *J. Amer. Chem. Soc.*, **93**, 1491, 1493 (1971); M. I. Rybinskaya and L. M. Korneva, *Russ. Chem. Rev.* *(Engl. Transl.)*, **40**, 247 (1971).

28. G. A. Razunaer and V. N. Latyaena, *Zhur. Obshkhei Khirm*, **28**, 2233 (1958). *C. A.*, **53**, 5186i (1958).

29. D. H. Heg, K. S. Y. Liang and M. I. Perkins, *Tetrahedron Lett.*, 1477 (1967).

30. J. Boche and O. Runquist, *J. Org. Chem.*, **33**, 4285 (1968).

31. J. F. Normant, *Synthesis*, 63 (1972).

32. G. Van Koten, A. J. Levsink and J. G. Noltes, *Chem. Commun.*, 1107 (1970).

33. T. Tsuda, T. Hashimoto, T. Saegusa, *J. Amer. Chem. Soc.*, **94**, 658 (1972).

34. A. C. Poshkus and J. E. Herweh, *J. Org. Chem.*, **27**, 2700 (1962).

35. L. Horner and H. Oediger, *Chem. Ber.*, **91**, 437 (1958).

36. V. Dave and E. W. Warnhoff, "Organic Reactions," Vol. 18, Wiley, New York, N.Y., 1970, p. 212.

37. W. C. Evans, J. M. Ridigion and J. L. Simonsen, *J. Chem. Soc.*, 137 (1934).

38. H. Rupe and W. Thomen, Helv. Chim. Acta, **30**, 933 (1947).

39. L. L. Rodina and I. Korobitsyna, Russ. Chem. Rev. (Engl. Transl.), **36**, 260 (1967).

VITA

On April 16, 1948 Nguyen van Thinh was born in Phu Tho, Viet Nam. He attended the Nguyen Tri Phuong elementary school in Saigon for his primary education and graduated from the Chu van An high school, Saigon, South Viet Nam in June 1967. From September 1967 to November 1970 he was enrolled at the University of Saigon as a college student, where he received his dual B.Sc. Degree in Chemistry and Physical Sciences in 1970.

He resumed his studies in the Fall semester of 1971 at the University of Missouri-Rolla as a candidate for the Degree of Master of Science in Chemistry.

He married Miss Ho Thi Phi, daughter of Mr. and Mrs. Ho-Nghia on January 2, 1973.