

## Metal Salt-catalysed Carbenoids. Part IX.<sup>1</sup> The Catalysts in Trialkyl Phosphite-Copper(I) Complex Catalysed Decomposition of Diazomalonic Esters in Cycloalkenes

By David S. Wulfman,\* Nguyen van Tinh, Robert S. McDaniel, and Billy W. Peace, Department of Chemistry, University of Missouri-Rolla, Rolla, Missouri 65401  
Charles W. Heitsch, Central Research Department, Monsanto Co., St. Louis, Missouri  
M. Tom Jones, jun., Department of Chemistry, University of Missouri-St. Louis, St. Louis, Missouri

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 have been prepared and examined but none proved as effective for decomposing compound (1) as bis(acetylacetonato)copper(II).

The utility of the chloro(trimethyl phosphite)copper(I) for decomposing compound (1) is a function of the means of preparation. The three general methods employed furnished samples having superposable i.r. spectra and superposable proton n.m.r. spectra but exhibited varying degrees of line broadening in the <sup>31</sup>P n.m.r.

The chiral mixed phosphite ligand bornane-2,3-diyl phenyl phosphite (3) derived from bornane-2,3-diol 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 phosphorus.

THE use of organophosphite ligands to solubilize copper(I) salts has received detailed examination by Moser<sup>3</sup> in the course of studying the homogeneous catalyzed decomposition of diazoacetic ester. More recently, work in this laboratory has been directed toward studies employing diazomalonates.<sup>4-6</sup> Other solubilizing agents have been employed with copper salts such as acetylacetonate,<sup>7</sup> and salicylaldehyde.<sup>8</sup> Generally, other groups do not permit appreciable quantities of the copper complex to enter solution unless highly polar solvents are employed such as acetonitrile.<sup>9</sup> Our finding that the optimum amount of catalyst for decomposing dimethyl diazomalonate is extremely small somewhat obviated the need for 'super' solubilizing agents.<sup>6</sup> The optimum amount of copper(II) fluoroborate or bis(acetylacetonato)copper(II) 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 no discontinuity in behaviour 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 behaviour with mixed mode systems (homogeneous/heterogeneous) paralleled in considerable detail that of homogeneous systems.

**Phosphite Ligands and Copper(I) Complexes.**—During the course of these studies, a number of phosphite-

copper(I) complexes of the type  $[\text{CuX}\{\text{P}(\text{OR})_3\}_n]$  (R = alkyl or aryl,  $n = 1, 2, \text{ or } 3$ ; and X = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, CN<sup>-</sup>, SCN<sup>-</sup>, and BF<sub>4</sub><sup>-</sup>) were prepared and their efficacy in carbenoid generation tested. Most often, these complexes were prepared by the method introduced by Arbuzov<sup>10,11</sup> and more recently used by Moser<sup>3</sup> and Nishizawa.<sup>12</sup> 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.<sup>13</sup> 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 dissolved readily in this solvent, but an insoluble material forms after a few minutes. Halogenated hydrocarbons are known to react with phosphites.<sup>14</sup> This reaction probably destroys the complexes, giving the free copper salt.

Nishizawa<sup>12</sup> reported his inability to prepare a halogenotris(phosphite)copper(I) complex but did not specify the exact phosphite used in this attempt; how-

<sup>1</sup> Part VIII, B. W. Peace and D. S. Wulfman, *Synthesis*, 1973, 137.

<sup>2</sup> Taken in part from the Ph.D. Dissertation of B. W. Peace, University of Missouri-Rolla, 1971.

<sup>3</sup> W. R. Moser, *J. Amer. Chem. Soc.*, 1969, **91**, 1135, 1141.

<sup>4</sup> D. S. Wulfman, F. C. Carman, B. G. McGiboney, E. K. Steffen, and B. W. Peace, *Preprints, Division of Petroleum Chemistry, American Chemical Society*, 1971, Vol. 16, Part B, No. 1.

<sup>5</sup> B. W. Peace and D. S. Wulfman, *Tetrahedron Letters*, 1971, 3799.

<sup>6</sup> B. W. Peace and D. S. Wulfman, *Chem. Comm.*, 1971, 1179.

<sup>7</sup> D. O. Cowan, M. M. Cooch, K. R. Kopecky, and G. S. Hammond, *J. Org. Chem.*, 1964, **29**, 1922.

<sup>8</sup> H. Nozaki, S. Moriuti, M. Yambe, and R. Noyori, *Tetrahedron Letters*, 1966, 59; H. Nozaki, H. Takaya, S. Moriuti and R. Noyori, *Tetrahedron*, 1968, **24**, 3655; *Tetrahedron Letters*, 1966, 5293.

<sup>9</sup> T. Shirafuji, Y. Yamamoto, H. Nozaki, *Tetrahedron*, 1972, **27**, 5353.

<sup>10</sup> A. Arbuzov, *Ber.*, 1905, **38**, 1171.

<sup>11</sup> A. Arbuzov, *J. Russ. Phys. Chem. Soc.*, 1906, **38**, 161, 193, 687.

<sup>12</sup> Y. Nishizawa, *Bull. Chem. Soc. Japan*, 1961, **34**, 1170.

<sup>13</sup> B. W. Peace, F. C. Carman, and D. S. Wulfman, *Synthesis*, 1971, 658.

<sup>14</sup> L. F. Fieser and M. Fieser, 'Reagents for Organic Synthesis,' Wiley, New York, 1968, p. 1247.

ever, most of his work centred on tri-isopropyl and triphenyl phosphite. The present work has shown that iodotris(trimethyl phosphite)copper(I) is easily prepared by the modified Arbuzov procedure. Nishizawa's results might be explained in terms of steric considerations. However, triphenyl phosphite 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 of reactants.<sup>10,11</sup> In solution the mono-complexes are primarily tetrameric and the bis-complexes are monomeric.<sup>12</sup>

In a few cases, phosphite-copper(I) complexes were prepared by the method of Beriger.<sup>15</sup> This involved addition of phosphorus 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 trialkyl phosphite-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 his co-workers<sup>16</sup> introduced a similar reductive procedure for the synthesis of trialkyl phosphite-copper(I) complexes.

The properties of chloro(trimethyl phosphite)copper(I) obtained from the three different schemes discussed are of interest. The i.r. spectra of the complexes from all three preparations are identical through the range 4000–400 cm<sup>-1</sup>, although the <sup>31</sup>P n.m.r. patterns and their m.p.s are distinctly different. This appears to be a result of copper(II) impurities. The <sup>1</sup>H n.m.r. spectra were identical.

Most of the trialkyl phosphite-copper(I) complexes used in our work were known compounds. However, almost all melting points reported in the older literature<sup>10,11</sup> for these complexes are incorrect, two by as much as 40 °C. Some of these discrepancies were noted earlier by Nishizawa<sup>12</sup> (see Experimental section). Low m.p.s appear to be due to impure copper salts since freshly prepared copper(I) chloride routinely gave the higher melting complexes.

*Partial Rates and Percent Yields.*—Data are reported as percent yield based upon diazo-compound and as relative rates with the cyclopropane product as the

\* Although catalysed cycloadditions of diazo-compounds 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 U.S.S.R., Israel Program for Scientific Translations, Jerusalem, 1964). Corey<sup>25</sup> has reported a catalysed Diels-Alder employing copper(II) fluoroborate (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<sup>1</sup>-pyrazolines should readily lose N<sub>2</sub> under the reaction conditions and furnish cyclopropanes and C-H insertion products *via* a hydrogen-abstraction process.

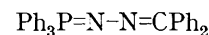
We have successfully decomposed the pyrazoline from dimethyl diazomalonate and dicyclopentadiene using copper fluoroborate as a catalyst to furnish the related cyclopropane in nearly quantitative yield.

internal standard. Both values are sensitive to the batch of reagents employed but with a given batch of olefin consistent trends occur in the partial rate data even when the yields appear to be dependent on no single factor. This is a consequence of the ability of the impurities in the olefin to alter the real catalyst concentration (*vide infra*) and the fact that yield is catalyst concentration dependent but partial rates are independent over a large range of catalyst concentrations.

*Possible Phosphorus Intermediates.*—The possible intermediacy of certain phosphorus compounds in the reactions of diazomalonates was studied. Compounds (1)<sup>17</sup> and (2)<sup>18</sup> 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.



(1)



(2)

*Copper Catalysis.*—The nature of the active catalyst species in copper and copper salt diazo decompositions has been the subject of much discussion.<sup>19–24</sup> Two groups have observed the reduction of copper(II) chloride to copper(I) chloride by diazomethane and suggested that the lower oxidation state was the actual catalyst.<sup>20,21</sup> D'yakonov<sup>22</sup> observed the formation of metallic copper from copper(II) sulphate 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).<sup>23</sup>

A broad claim that the processes involve copper(I) catalysis has been advanced by Salomon and Kochi.<sup>24</sup> Careful analysis of their accompanying data fails to substantiate this claim and the kinetic evidence is equally consistent with a copper(I)-catalysed 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)<sup>26</sup> and copper(I)<sup>27</sup> by

<sup>15</sup> E. Beriger, U.S.P. 2,931,826, April 5, 1960.

<sup>16</sup> W. A. Anderson, A. J. Carty, G. J. Polenik, and G. Schreiber, *Canad. J. Chem.*, 1971, **49**, 762.

<sup>17</sup> L. Horner and H. Oediper, *Chem. Ber.*, 1958, **91**, 434.

<sup>18</sup> D. R. Dalton and S. A. Liebman, *Tetrahedron*, 1969, **25**, 3321.

<sup>19</sup> D. S. Wulfman, B. W. Peace, and E. K. Steffen, *Chem. Comm.*, 1971, 1360.

<sup>20</sup> G. Wittig and K. Schwarzenbach, *Annalen*, 1961, **650**, 1.

<sup>21</sup> R. G. R. Bacon and H. A. O. Hill, *Quart. Rev.*, 1965, **19**, 95.

<sup>22</sup> M. I. Komendantov, I. A. D'yakonov, and T. S. Smirnova, *J. Org. Chem. U.S.S.R.*, 1966, **2**, 561. (*Chem. Abs.*, 1966, **65**, 7124).

<sup>23</sup> B. W. Peace and D. S. Wulfman, *Tetrahedron Letters*, 1972, 3903.

<sup>24</sup> R. G. Salomon and Jay K. Kochi, *J. Amer. Chem. Soc.*, 1973, **95**, 3300.

<sup>25</sup> E. J. Corey, V. Koellikev, and J. Neuffer, *J. Amer. Chem. Soc.*, 1971, **93**, 1491, 1493; M. I. Rybinskaya, and L. M. Korneva, *Russ. Chem. Rev.*, 1971, **40**, 247.

<sup>26</sup> G. A. Razunaer and V. N. Latyaena, *Zhur. obshechi Khim.*, 1958, **28**, 2233 (*Chem. Abs.*, 1958, **53**, 5186i).

<sup>27</sup> D. H. Heg, K. S. Y. Liang, and M. I. Perkins, *Tetrahedron Letters*, 1967, 1477.

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 uncomplexed) by an excess of 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 diazomalones and copper(I) complexes (Table 1).

TABLE 1

Product distribution and yields in the reaction of cyclohexene and dimethyl diazomalone as a function of catalyst and peroxide content of the olefin

[CuZ{P(OMe) <sub>3</sub> }] (0.14 mmole)	Percent yield			Ratios
	(6)	(8)	(7)	
Z = Br <sup>a</sup>	68.7	15.1	6.7	1.00 : 0.22 : 0.10
I <sup>a</sup>	74.3	12.9	7.4	1.00 : 0.17 : 0.10
Br <sup>b</sup>	22.0	1.9	2.1	1.00 : 0.085 : 0.095
I <sup>b</sup>	19.9	2.0	1.8	1.00 : 0.10 : 0.090
Br <sup>c</sup>	71.6	22.9	5.7	1.00 : 0.32 : 0.080
I <sup>c</sup>	78.8	15.0	5.9	1.00 : 0.19 : 0.075
No catalyst <sup>c,d</sup>	9.45	1.8	0.00	1.00 : 0.19

<sup>a</sup> Commercial cyclohexene. <sup>b</sup> Commercial cyclohexene filtered through alumina. <sup>c</sup> Commercial cyclohexene filtered through alumina, then 0.07 mmol benzoyl peroxide added. <sup>d</sup> 24 h at reflux.

When acetylacetonatocopper(II) was employed as a catalyst, no peroxide effect was observed; this observation is consistent with copper(II) acting as the catalyst. When high purity copper powder was employed very similar results were obtained both with the metal present and with the metal removed prior to the addition of diazo-compound but subsequent to the refluxing for several hours with the olefin. This is suggestive of attack of the Cu<sup>0</sup> by olefin hydroperoxides and the resulting soluble copper-containing products acting as the sole catalyst (Table 2).

TABLE 2

'Copper(0) catalysed' and acetylacetonatocopper(II) catalysed reactions

Condition *	Percent yield		
	6	8	7
Thermal	12.7	Trace	0.0
Cu metal	38.0	8.1	1.7
Metal-free filtrate	36.0	7.2	2.8
Cu(acac) <sub>2</sub> peroxide-free	78.5	12.4	5.9
Cu(acac) <sub>2</sub> peroxide present (0.14 mmol (PhCOO) <sub>2</sub> )	78.1	12.4	5.8

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

In the reactions of dimethyl diazomalone with cyclohexene employing halogeno(trimethyl phosphite)copper(I) catalysts, 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 diazomalone had been added showed almost no recognizable products. After the first 10%, the reaction

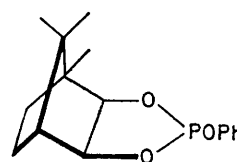
proceeded in an almost normal manner and after 30% reaction the product distribution was similar to those normally seen after allowing the reaction to go to completion (Table 3). Thus, an initial prereaction can

TABLE 3

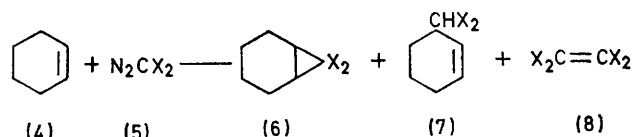
Effect of amount of available dimethyl diazomalone on its reaction with cyclohexene under optimum conditions using [CuI{P(OMe)<sub>3</sub>}]

Conditions	Percent yield (relative yield)		
	6	8	7
10% Usual reaction	0.15 (1.00)	0.00	0.270 (0.52)
Expected yields for 10% *	7.4 (1.00)	1.2 (0.16)	0.60 (0.08)
30% Usual reaction	12.1 (1.00)	2.1 (0.17)	1.4 (0.11)
Expected yields for 30% *	22.1 (1.00)	3.5 (0.16)	1.8 (0.08)
Expected yields for 20% *	14.7 (1.00)	2.3 (0.16)	1.2 (0.08)

\* Expected yields based on optimized yield using [CuI{P(OCH<sub>3</sub>)<sub>3</sub>}].



(3)



X = CO<sub>2</sub> Me

be postulated involving oxidation of copper(I) to the active species after which the reaction proceeds to the usual product distribution.

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 7, Experimental section). Since trivalent phosphorus compounds are known to react with peroxides,<sup>28</sup> 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 an excess of 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-halogen bond since a definite anion effect and a common ion effect were observed<sup>5</sup> (Tables 4a and 4b).

The trend in partial rate data as a function of the anionic ligand (Table 4a) follows the trend in softness of the anion. This is suggestive that the mechanism

<sup>28</sup> J. Boche and O. Runquist, *J. Org. Chem.*, 1968, **33**, 4285.

controlling partitioning of products between cyclopropanation and allylic C-H insertions involves appreciable charge separation. Therefore, we speculate that a

TABLE 4a

Effect of anion upon product distribution and yields in the reaction of cyclohexene with dimethyl diazomalonate

[CuX{P(OMe) <sub>3</sub> }] (0.14 mmol)	Percent yield (relative yield)		
	(6)	(8)	(7)
X = BF <sub>4</sub> *	59.6 (1.00)	7.3 (0.12)	8.1 (0.14)
I	74.2 (1.00)	12.9 (0.17)	7.4 (0.10)
Br	68.6 (1.00)	15.1 (0.22)	6.7 (0.097)
Cl	63.9 (1.00)	13.3 (0.21)	4.7 (0.064)
SCN	28.3 (1.00)	1.3 (0.046)	1.8 (0.064)
CN	41.5 (1.00)	0.8 (0.020)	0.9 (0.023)

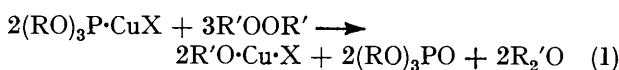
\* Concentration less than 0.14 mmol due to decomposition during transfer.

TABLE 4b

Effect of common ion on the reaction of cyclohexene with dimethyl diazomalonate

Catalyst (0.14 mmol)	Salt (0.14 mmol)	Percent yield (relative yield)		
		(6)	(8)	(7)
[CuI{P(OMe) <sub>3</sub> }]	None	74.2 (1.00)	12.9 (0.17)	7.4 (0.10)
[CuI{P(OMe) <sub>3</sub> }]	[(CH <sub>3</sub> ) <sub>4</sub> N]I	3.3 (1.00)	0.00	7.1 (2.12)
[CuI{P(OMe) <sub>3</sub> }]	[(CH <sub>3</sub> ) <sub>4</sub> N][BF <sub>4</sub> ]	63.7 (1.00)	11.4 (0.18)	5.00 (0.078)
[CuCl{P(OMe) <sub>3</sub> }]	None	63.9 (1.00)	13.3 (0.21)	4.7 (0.074)
[CuCl{P(OMe) <sub>3</sub> }]	[(CH <sub>3</sub> ) <sub>4</sub> N]Cl	8.6 (1.00)	1.6 (0.18)	0.00
[CuCl{P(OMe) <sub>3</sub> }]	[(CH <sub>3</sub> ) <sub>4</sub> N][BF <sub>4</sub> ]	49.3 (1.00)	5.3 (0.11)	4.1 (0.083)

copper(II)-alkoxyhalide is the active species [equation (1)]. Copper(II) may have been the active catalyst in almost all studies reported to date. Considering the very low 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. [It is widely believed that the copper(II) iodide does not exist; it is, however, a known compound.<sup>29</sup>]

Although copper alkoxides possessing a  $-\text{Cu}-\text{O}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{H}$  unit are not stable, examples exist where unsaturation in close proximity stabilizes copper derivatives by coordination with the  $\pi$  system.<sup>30-32</sup>

A troublesome aspect of our interpretation of Moser's results arises from the observation of optical inductions

\* We have been informed by Professor Landgrebe that the *cis*-isomer is of much lower specific rotation but that epimerization by base proceeds smoothly to furnish the optically active *trans*-isomer without any epimerization of the other asymmetric centre. He found that optical inductions were higher for the *cis*- than the *trans*-isomer which in turn suggests that if any of the *cis*-isomer were to be converted into *trans* during our studies the level of optical induction would be enhanced.

when tris(bornyl phosphite) 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 alternative will not be sensitive to this technique. Unfortunately Moser made no such determination.

We chose to prepare compound (3) from the related diol and triphenyl phosphite and form the related copper(I) iodide complex. This ligand is chiral at four carbons and at phosphorus. 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 1% induction would be readily observable for the *trans*-1-ethoxycarbonyl-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 mmol/0.14 mmol of catalyst) (Table 5) give added credence to this interpretation.

*Olefin Interactions with Catalysts.*—In an effort to ascertain the nature of olefin catalyst interactions, saturated solutions of copper(II) perchlorate and copper(II) fluoroborate were prepared in cyclohexene, 1-methylcyclohexene, 1,2,3,4-tetramethylbenzene, hexafluorobenzene, cyclo-octa-1,5-diene and cyclododeca-1,6,9-triene and e.s.r. spectra were observed at 298 K and 78 K. No fine structure was observed and it was not possible to determine the extent of co-ordination 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 high and low concentrations 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

<sup>29</sup> G. A. Barclay, B. F. Hoskins, and C. H. L. Kennard, *J. Chem. Soc.*, 1963, 5691; G. T. Morgan and F. H. Burstall, *ibid.*, 1926, 2018; H. J. S. King, *ibid.*, 1930, 2307; R. G. Wilkins and A. R. Burkin, *J. Chem. Soc.*, 1950, 132; J. P. Smith and W. W. Wendlandt, *J. Inorg. Nuclear Chem.*, 1964, **28**, 1157; A. G. Massey, in 'Comprehensive Inorganic Chemistry,' ed. A. F. Trotman-Dickenson, Pergamon, Oxford, 1973, vol. 3, p. 41.

<sup>30</sup> J. F. Normant, *Synthesis*, 1972, 63.

<sup>31</sup> G. Van Koten, A. J. Levsink, and J. G. Noltes, *Chem. Comm.*, 1970, 1107.

<sup>32</sup> T. Tsuda, T. Hashimoto, Y. Saegusa, *J. Amer. Chem. Soc.*, 1972, **94**, 658.

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 9a—c (Experimental section) reflect differing amounts of copper(II) present as an impurity and as a function of the means of catalyst synthesis. It is clear from the data that the systems behave in a qualitatively similar manner.

**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 forms solubilizing ligands which are phosphorus free. The amount of catalyst actually required is small and the fluoroborate 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 back-bonding than related copper(I) species. It is perhaps significant that silver salts (which are better for back-bonding) facilitate the Wolff rearrangements of  $\alpha$ -diazo-ketones whereas copper salts generally give high yields of carbenoid derived products.<sup>33</sup> 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.<sup>19</sup>

## EXPERIMENTAL

**Preparation of Dimethyl Triethoxyphosphoranylidenehydrazonomalonate.**—This ester was prepared by the method of Poshkus and Herweh.<sup>34</sup> Triethyl phosphite (83.0 g, 0.5 mol) and dimethyl diazomalonnate (79.0 g, 0.6 mol) furnished a yellow oil (149 g) which was removed and washed with pentane ( $\times 5$ ). An attempt to distil 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 ester used without further purification. The n.m.r. spectrum ( $\text{CCl}_4$ ) showed a quintet centred at  $\tau$  5.75 (6H,  $\text{CH}_2$ ), a singlet at  $\tau$  6.22 (6H,  $\text{CO}_2\text{Me}$ ), a triplet centred at  $\tau$  8.62 (9H,

Me), and a small amount of impurity (mostly pentane). The compound was assigned the structure dimethyl triethoxyphosphoranylidenehydrazonomalonate.

**Preparation of Dimethoxycarbonylmethylenetriphenylphosphorane.**—Dimethoxycarbonylmethylenetriphenylphosphorane was prepared by a modified procedure based on the method of Horner and Oediger.<sup>35</sup> A solution of triphenylphosphine (131 g, 0.5 mol) in dry benzene (1400 ml) was cooled to 10 °C. With stirring, a solution of bromine (25.8 ml, 0.5 mol) in carbon tetrachloride (50 ml) was added during 2 h. When the addition was complete, a solution of triethylamine (121.4 g, 1.2 mol) and dimethyl malonate (66.0 g, 0.5 mol) in benzene (400 ml) was added all at once. The solution was refluxed for 10 min. The solid (triethylamine hydrobromide) was filtered off and the solvent was removed by distillation to leave a red oil which solidified upon addition of pentane. This was dissolved in cyclohexane and filtered, treated with activated charcoal, and allowed to crystallize. Two recrystallizations gave light yellow crystals (156 g, 80%), m.p. 142—143 °C. The i.r. spectrum (KBr) showed bands at 1195  $\text{cm}^{-1}$  (s, P=C) and 1640  $\text{cm}^{-1}$  (m, C=O). The spectrum was almost identical to that reported for diethoxycarbonylmethylenetriphenylphosphorane.<sup>19</sup> The n.m.r. spectrum ( $\text{CHCl}_3$ ) showed a doublet centred at  $\tau$  6.20 (6H, COOMe) and a multiplet centred at  $\tau$  2.50 (15H, aromatic).

**Decomposition of Dimethyl Triethoxyphosphoranylidenehydrazonomalonate.**—A sample (5.54 g, 0.02 mol) of the ester was decomposed in cyclohexene as previously described for dimethyl diazomalonnate. Chloro(trimethyl phosphite)copper(I) (0.14 mmol) was used as catalyst. During the addition, a dark insoluble oil formed. Both the oil and the cyclohexene layer were analysed 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 triethoxyphosphoranylidenehydrazonomalonate using both complexed and uncomplexed copper(I) chloride. G.c. analysis of the reaction mixture showed the absence of all the products typical of the carbene additions.

**Chloro(trimethyl phosphite)copper(I).**—**Method A.** The procedure given here is a modification of the method of Arbuzov.<sup>10,11</sup> A solution of trimethyl phosphite (12.4 g, 0.1 mol) (which had been dried over metallic sodium) in dry benzene (200 ml) was stirred while copper(I) chloride (9.9 g, 0.1 mol) was added. Initially, the salt was filtered off, the solvent was removed, and methanol (20 ml) was added. The white crystals which formed were filtered off and dried *in vacuo* (1 mmHg) at 50 °C for 3 h. The yield was 20.0 g (90%) of material, m.p. 192—193 °C (lit.,<sup>10,11</sup> 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 (Found: C, 16.15; H, 3.95; Cl, 15.9; Cu, 28.2; P, 14.05.†

\* At low catalyst concentrations the partial rates for dimer, allylic C—H insertion, and cyclopropanation remain relatively constant whereas at intermediate and high catalyst concentrations the dimer rapidly increases and successfully competes with the other processes. At no time is there any appreciable excess of diazo-compound present in the reaction (it is added dropwise) and the behaviour is only consistent with a differing dependence upon catalyst at low and high concentrations. Since there is a dependence at low catalyst concentration, the simplest explanation is that advanced above.

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

<sup>33</sup> L. L. Rodina and I. Korobitsyna, *Russ. Chem. Rev.*, 1967, **36**, 260.

<sup>34</sup> A. C. Poshkus and J. E. Herweh, *J. Org. Chem.*, 1962, **27**, 2700.

<sup>35</sup> L. Horner and H. Oediger, *Chem. Ber.*, 1958, **91**, 437.

Calc. for  $C_3H_9CuClO_3P$ : C, 16.14; H, 4.03; Cl, 15.92; Cu, 28.47; P, 13.90%.

**Method B.** This method was used by Beriger<sup>15</sup> in the preparation of trimethyl phosphite. A solution of dry methanol (4.80 g, 0.15 mol) in toluene (50 ml) was cooled to  $-10^\circ\text{C}$  and copper(I) chloride (4.95 g, 0.05 mol) was added. With stirring, phosphorus trichloride (6.53 g, 0.05 mol) was added at a rate sufficient to maintain the temperature between  $-5$  and  $-10^\circ\text{C}$ . The mixture was then warmed to room temperature (20 min), during which time hydrogen chloride gas was evolved. The white solid was filtered off, washed (cold pentane), dried *in vacuo* (1 mmHg,  $50^\circ\text{C}$  for 3 h). The melting point found was  $194$ – $196^\circ\text{C}$ . The i.r. spectrum ( $400$ – $4000\text{ cm}^{-1}$ ) was identical to that of the higher melting complex.

**Method C.** A solution of trimethyl phosphite (12.4 g, 0.1 mol) in dry benzene (100 ml) was stirred as copper(II) chloride (6.7 g, 0.05 mol) was added. After 30 min at reflux, the mixture was filtered and cooled. A total of 10.0 g (90%) of chloro(trimethyl phosphite)copper(I), m.p.  $194$ – $196^\circ\text{C}$ , was collected. This material was identical to that prepared by methods A and B as shown by comparison of their i.r. spectra ( $400$ – $4000\text{ cm}^{-1}$ ).

**Bromo(trimethyl phosphite)copper(I).**—Trimethyl phosphite (7.20 g, 0.05 mol) and anhydrous copper(I) bromide (7.17 g, 0.05 mol) in dry benzene after 30 min at reflux, gave after method A work-up, 11.7 g (88%) of complex, m.p.  $226$ – $228^\circ\text{C}$  (lit.,<sup>11</sup>  $180$ – $182^\circ\text{C}$ ) (Found: C, 13.15; H, 3.45; Br, 29.95; P, 11.6. Calc. for  $C_3H_9BrCuPO_3$ : C, 13.47; H, 3.36; Br, 29.88; P, 11.58%).

**Iodo(trimethyl phosphite)copper(I).**—A solution of trimethyl phosphite (7.20 g, 0.05 mol) in refluxing dry benzene and copper(I) iodide (9.55 g, 0.05 mol) gave after filtration and removal of uncomplexed salt an oil with some suspended solid after removal of solvent. Upon addition of methanol the oil solidified. The cooled solid was filtered, washed with cold methanol, dried *in vacuo* (1 mmHg) at  $50^\circ\text{C}$  for 3 h. The yield of material, m.p.  $193$ – $195^\circ\text{C}$  (lit.,<sup>10,11</sup> m.p.  $175$ – $177^\circ\text{C}$ ), was 14.1 g (84%).

**Cyano(trimethyl phosphite)copper(I).**—Dry trimethyl phosphite (7.20 g, 0.05 mol) in dry benzene was stirred as copper(I) cyanide (4.48 g, 0.05 mol) was added. The salt was completely dissolved after stirring at room temperature for 30 min. 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%).

**Thiocyanato(trimethyl phosphite)copper(I).**—The complex was prepared by method A described above for the copper(I) chloride complex. The yield of white solid, m.p.  $151$ – $153^\circ\text{C}$ , was 11.2 g (82%) (Found: C, 19.55; H, 3.85; P, 12.7; S, 13.05; N, 5.8. Calc. for  $C_4H_9CuNO_3PS$ : C, 19.55; H, 3.70; P, 12.63; S, 13.04; N, 5.70%).

**Fluoroborato(trimethyl phosphite)copper(I).**—In dry benzene (50 ml), trimethyl phosphite (1.24 g, 0.01 mol), and copper(I) fluoroborate-tris(toluene) (4.29 g, 0.01 mol) were mixed and stirred briefly at room temperature. The benzene was removed to give a slightly blue oil. Due to the instability of the fluoroborato-complex, no effort was made to crystallize or otherwise purify it.

**Iodobis(trimethyl phosphite)copper(I).**—Trimethyl phosphite (2.48 g, 0.02 mol) in dry benzene (20 ml) was stirred as copper(I) iodide (1.90 g, 0.01 mol) was added and re-

fluxed 30 min. The solution was filtered, the solution removed *in vacuo*, and methanol added. After cooling, crystals were collected and dried in the usual way to yield white crystals (4.00 g, 91%), m.p.  $69$ – $70^\circ\text{C}$  (lit.,<sup>10</sup> m.p.  $69$ – $70^\circ\text{C}$ ).

**Iodotris(trimethyl phosphite)copper(I).**—Trimethyl phosphite (3.72 g, 0.03 mol) and copper(I) iodide (1.90 g, 0.01 mol) 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 methanol (20 ml) but solidified when dried *in vacuo* (1 mmHg) at  $50^\circ\text{C}$  for 3 h. The yield was 4.72 g (84%) of material, m.p.  $118$ – $119.5^\circ\text{C}$  (Found: C, 19.05; H, 4.8; Cu, 11.45; I, 22.7; P, 16.4. Calc. for  $C_9H_{27}CuIO_9P_3$ : C, 19.2; H, 4.80; Cu, 11.3; I, 22.6; P, 16.5%).

**Bromo(triphenyl phosphite)copper(I).**—Triphenyl phosphite (3.10 g, 0.01 mol) in dry benzene (20 ml) was stirred as copper(I) bromide (1.44 g, 0.01 mol) was added. The mixture was stirred until all the salt dissolved. The benzene was removed and ether (15 ml) added. A seed crystal was obtained on a porous plate and added to the cooled ether solution. The crystals were collected and dried to give 3.20 g (91%), m.p.  $91$ – $92^\circ\text{C}$  (lit.,<sup>10,11</sup>  $90.5$ – $91.5^\circ\text{C}$ ).

**Iodo(triphenyl phosphite)copper(I).**—Triphenyl phosphite (6.20 g, 0.02 mol) and copper(I) iodide (3.82 g, 0.02 mol) in dry benzene (50 ml) were heated at reflux for 30 min. Filtration gave unchanged copper salt (1.91 g, 50%). The solvent was removed and the resulting oil taken up in ether (20 ml). Crystals were collected and dried to yield material (7.91 g, 98%), m.p.  $73$ – $75^\circ\text{C}$ . This is the m.p. reported<sup>10</sup> for the bis-complex. No further effort was made to prepare the mono-complex.

**Bromo(tricyclohexyl phosphite)copper(I).**—Freshly distilled cyclohexanol (15.0 g, 0.15 mol) in dry toluene (100 ml) was cooled to  $-10^\circ\text{C}$ , and copper(I) bromide (8.18 g, 0.05 mol) was added. With stirring phosphorus tribromide (13.6 g, 0.05 mol) was added at a rate such as to maintain the temperature below  $-5^\circ\text{C}$ . When the addition was complete, the mixture was allowed to warm to room temperature and then stirred for an additional 20 min. 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 1 h to remove pentane and hydrogen bromide. The solid was dried at  $35^\circ\text{C}$  at 1 mmHg. The complex did not melt but decomposed at  $60^\circ\text{C}$ . It also decomposed overnight at room temperature.

**Iodo(tri-isopropyl phosphite)copper(I).**—The reaction was carried out exactly as described for the trimethyl phosphite catalyst. After removal of the benzene, isopropanol (20 ml) was added and the mixture cooled. The white solid was filtered off and dried *in vacuo* (1 mmHg) at  $50^\circ\text{C}$  for 2 h. The yield of material, m.p.  $199.5$ – $200^\circ\text{C}$  (lit.,<sup>12</sup>  $199$ – $200^\circ\text{C}$ ), was 16.2 g (90%).

**Oxidation of Iodo(trimethyl phosphite)copper(I).**—**Method E.** Iodo(trimethyl phosphite)copper(I) (4.5 g, 0.014 mol) in benzene (25 ml) was warmed to  $50^\circ\text{C}$  and benzoyl peroxide (3.39 g, 0.014 mol) was added during 2 h in small portions. During the addition the solution became deep blue, but never completely homogeneous. The mixture was cooled and the solid filtered off and dried *in vacuo* at  $50^\circ\text{C}$  for 2 h. The blue solid melted at  $190$ – $205^\circ\text{C}$ .

**Method F.** Trimethyl phosphite (3.60 g, 0.025 mol) in dry benzene (50 ml) was treated with copper(I) iodide

(4.77 g, 0.025 mol) as described above. The hot solution of the complex was immediately treated with benzoyl peroxide (4.05 g, 0.025 mol) in small portions during 2 h. Late in the addition a solid formed. After all the peroxide had been added, the mixture was cooled and the blue solid filtered off. It melted at 243–249 °C. A part of the material was transferred to a Soxhlet extractor and extracted for 24 h 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 i.r. spectrum was similar but not identical to that of copper(II) benzoate (mull).

**Oxidation of Copper(I) Iodide.**—To copper(I) iodide (4.77 g, 0.025 mol), in dry benzene (50 ml) at 50 °C benzoyl peroxide (4.05 g, 0.025 mol) was added in small portions during 2 h. The solvent immediately assumed the characteristic colour of iodine. When the addition was complete, the solid that had formed was filtered off and washed free of iodine with benzene. The solid melted at 279–281 °C. Its i.r. 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 dioxan. After crystallization the material was a brilliant blue and melted at 285–286 °C. Analysis of this material indicated complexation of the salt with dioxan (Found: C, 54.9; H, 4.55. Calc. for  $C_{14}H_{10}O_4Cu \cdot C_4H_8O_2$ : C, 54.92; H, 4.57%).

**Camphorquinone (Bornane-2,3-dione).**—A solution of (+)-camphor (53.65 g, 0.352 mol), glacial acetic acid (53.6 ml), and freshly prepared and sublimed selenium dioxide (64.38 g, 0.815 mol) was heated at 140–150 °C for 5 h. The work-up was similar to that described previously by Evans, Ridgion, and Simonsen<sup>36</sup> and gave camphorquinone (58.27 g, 0.351 mol), m.p. 190–196 °C (lit.,<sup>37</sup> 190–195 °C).

**cis-Bornane-2,3-diol.** The camphorquinone from the previous experiment (58.27 g, 0.351 mol) was dissolved in isopropanol (800 ml) and sodium borohydride (13.25 g, 0.349 mol) was added and stirred for 48 h. Solvent was removed (ca. 80 °C) using a Buchi Rotovaporator, water (200 ml) was added, and the solution filtered. The solid so obtained was taken up in  $CH_2Cl_2$  (300 ml) and the filtrate was extracted with  $CH_2Cl_2$  ( $3 \times 300$  ml). The combined extracts were concentrated at 30 °C (rotovaporator). The residue was taken up in hot (1 : 1) benzene–light petroleum (b.p. 60–80 °C) and gave after recrystallization a white solid (25.2 g, 0.14 mol, 47.6%), m.p. 251–255 °C (lit.,<sup>38</sup> m.p. 253–255 °C for *cis*-diol). This was used without further purification.

**Bornane-2,3-diyl Phenyl Phosphite (3) and Its Complex with Copper(I) Iodide.**—A solution of bornane-2,3-diol (25 g, 0.14 mol) in dry benzene (685 ml) was brought to reflux for 48 h after the addition of triphenyl phosphite (43.4 g, 0.14 mol). Copper(I) iodide (26.6 g, 0.14 mol) was added. After 2 h at reflux a slight amount (ca. 0.1 g) of copper salt which had not dissolved was removed by vacuum filtration with a drying tube between flask and aspirator. The solvent was removed on a rotovaporator at ca. 60 °C and gave a low-melting oily solid when cooled to ca. 25 °C.

<sup>36</sup> V. Dave and E. W. Warnhoff, 'Organic Reactions,' Wiley, New York, 1970, Vol. 18, p. 212.

<sup>37</sup> W. C. Evans, J. M. Ridgion, and J. L. Simonsen, *J. Chem. Soc.*, 1934, 137.

Repeated attempts to obtain good crystalline material failed and the oily material was used as isolated for subsequent studies.

**Reaction of Ethyl Diazoacetate (EDA) with Styrene.**—Three otherwise identical runs were performed employing 0.170, 0.685, and 2.66 mmol of the complex of copper(I) iodide with compound (3). A solution of 5 ml of styrene (4.5 g, 43.3 mmol), EDA (2.28 g, 19.8 mmol) in benzene (20 ml) was added at a rate of 1 drop/15 s to a solution

TABLE 5

Effect of benzoyl peroxide<sup>a</sup> on the reaction of dimethyl diazomalonate with cyclohexene at various concentrations of  $[CuX\{P(OMe)_3\}]$

Catalyst	Conc. (mmol)	Percent yield (relative yield)		
		(6)	(8)	(7)
X = I	0.07	73.8 (1.00)	12.4 (0.17)	5.3 (0.072)
I	0.14	76.0 (1.00)	16.0 (0.21)	5.9 (0.077)
I	0.28	68.9 (1.00)	27.0 (0.39)	5.1 (0.074)
Br	0.07	71.7 (1.00)	13.1 (0.18)	5.5 (0.077)
Br	0.14	71.6 (1.00)	23.9 (0.33)	5.7 (0.080)
Br	0.28	71.0 (1.00)	19.5 (0.27)	5.9 (0.081)
Cl	0.07	79.4 (1.00)	18.0 (0.23)	6.0 (0.076)
Cl	0.14	78.5 (1.00)	13.1 (0.17)	6.2 (0.079)
Cl	0.28	50.5 (1.00)	37.4 (0.74)	3.4 (0.067)

<sup>a</sup> Olefins were filtered through alumina and benzoyl peroxide added to furnish solutions containing 1 equivalent of catalyst per 0.5 mol equiv. of peroxide.

TABLE 6

Effect of preoxidized catalyst upon the reaction of dimethyl diazomalonate with cyclohexene<sup>a</sup>

Catalyst	Method of oxidation	Percent yield (relative yield)		
		(6)	(8)	(7)
$[CuI\{P(OMe)_3\}]$	E	76.4 (1.00)	18.6 (0.24)	6.00 (0.079)
$[CuI\{P(OMe)_3\}]$	F	75.7 (1.00)	13.0 (0.17)	5.6 (0.075)
$[CuI\{P(OMe)_3\}]$	F (Extracted)	69.7 (1.00)	9.9 (0.14)	4.7 (0.068)
CuI	Benzoyl peroxide	67.4 (1.00)	4.0 (0.06)	4.0 (0.060)
CuI	Benzoyl peroxide <sup>c</sup>	68.5 (1.00)	9.4 (0.14)	6.9 (0.10)
$[CuI\{P(OMe)_3\}]$	F <sup>b</sup>	80.0 (1.00)	10.7 (0.13)	6.3 (0.079)

<sup>a</sup> All samples of cyclohexene were treated with alumina immediately before use. <sup>b</sup> Addition of dimethyl diazomalonate carried out in the presence of 0.10 g of *p*-dinitrobenzene. <sup>c</sup> Oxidized product recrystallized from *p*-dioxan.

TABLE 7

Effect of additives upon yields and product distribution in the reaction of cyclohexene with dimethyl diazomalonate using  $[CuCl\{P(OMe)_3\}]$  (0.14 mmol) as catalyst

Additive (0.14 mmol)	Percent yield (relative yield)		
	(6)	(8)	(7)
None	63.9 (1.00)	13.3 (0.21)	4.7 (0.074)
(MeO) <sub>3</sub> P	46.1 (1.00)	21.2 (0.46)	3.8 (0.082)
(MeO) <sub>3</sub> PO	68.1 (1.00)	16.2 (0.24)	5.9 (0.087)
(MeO) <sub>2</sub> MePO	60.6 (1.00)	19.2 (0.32)	5.1 (0.084)
(Me <sub>2</sub> N) <sub>3</sub> P	49.9 (1.00)	24.3 (0.49)	4.6 (0.092)
(Me <sub>2</sub> N) <sub>2</sub> PO	45.8 (1.00)	17.3 (0.38)	3.7 (0.081)
(MeO) <sub>2</sub> HPO	59.5 (1.00)	25.1 (0.42)	4.5 (0.077)

of catalyst in refluxing benzene (25 ml) during 2 h. After addition, reflux was maintained for 12 h; then the benzene

<sup>38</sup> H. Rupe and W. Thomen, *Helv. Chim. Acta*, 1947, **30**, 933.

was removed at *ca.* 60 °C using a rotovaporator. The crude product mixture was separated on a 3/8 in, 15 ft, 30% SE30 on Chromosorb W gas chromatographic column in a Varian Autoprep with the oven temperature 160 °C; injector 255 °C; detector 255 °C. The ratios of *cis*-adduct

TABLE 8

Relative product distributions in the reaction of cyclohexene with dimethyl diazomalonate and (0.14 mmol) of catalyst

Catalyst	Percent yield (relative yield)		
	(6)	(8)	(7)
[CuI{P(OMe) <sub>3</sub> }]	74.2 (1.00)	12.9 (0.17)	8.1 (0.136)
[CuI{P(OMe) <sub>3</sub> }] <sub>2</sub>	66.0 (1.00)	13.3 (0.20)	6.6 (0.100)
[CuI{P(OMe) <sub>3</sub> }] <sub>3</sub>	63.6 (1.00)	7.8 (0.12)	6.6 (0.103)
[CuCl{P(OMe) <sub>3</sub> }] (G)	64.1 (1.00)	9.2 (0.14)	4.7 (0.070)
(G) + 30 mg CuCl	33.5 (1.00)	23.2 (0.69)	2.4 (0.071)
(G) + 30 mg CuCl <sub>2</sub>	55.1 (1.00)	12.5 (0.22)	5.4 (0.097)

TABLE 9a

Product distribution and yields as a function of [CuCl{P(OMe)<sub>3</sub>}] (Method A) concentration in the reaction of dimethyl diazomalonate with cyclohexene

Catalyst (mmol)	Percent yield (relative yield)			Total product [(6) + (8) + (7)]
	(6)	(8)	(7)	
0.0042	36.2 (1.00)	2.4 (0.066)	3.19 (0.089)	41.8
0.0085	40.2 (1.00)	6.1 (0.15)	3.60 (0.092)	50.0
0.0170	43.7 (1.00)	7.6 (0.17)	4.47 (0.092)	55.7
0.0350	67.4 (1.00)	4.7 (0.068)	5.36 (0.086)	77.5
0.0700	68.2 (1.00)	8.4 (0.12)	5.49 (0.092)	82.1
0.1400	46.1 (1.00)	7.0 (0.15)	4.16 (0.091)	57.2
0.2800	49.9 (1.00)	9.1 (0.18)	4.80 (0.096)	63.8
0.5600	62.6 (1.00)	15.9 (0.25)	6.16 (0.099)	84.6
1.120	22.1 (1.00)	32.0 (1.4)	2.50 (0.11)	56.6
2.240	7.6 (1.00)	40.9 (5.4)	1.39 (0.18)	49.9
4.480	3.8 (1.00)	53.5 (14.0)	3.82 (0.980)	61.2

to *trans*-adduct were 3.08, 3.61, and 4.48. The rotations were examined on a Kern polarimeter at concentrations of 0.8114M, 1.2914M, and 0.8700M in CHCl<sub>3</sub> at 25 °C. Zero

\* A referee has expressed concern over the reproducibility of results. When a single batch of olefin is employed over a period of less than one week, stored under argon after opening, and similar precautions are applied to catalysts and diazo-ester, absolute yield values from the g.c. integrations are better than ±0.4% (absolute) and relative yields are at least ±1% of the reported value. Without such precautions the yields are no better than ±4%. All the tabulated data were compiled under the most stringent conditions.

rotations were observed in each case. Reported <sup>3,8,9</sup> [α]<sub>D</sub><sup>20</sup>, ±410° for the *trans*-isomer.

*Comparisons of the Effects Resulting from Presence or Absence of Peroxides and General Conditions for Reactions with Dimethyl Diazomalonate.*—All reactions were run as follows. A solution of dimethyl diazomalonate (0.02 mol) in cyclohexene (0.25 mol) was added at the rate of 6 drops per min to refluxing olefin (0.25 mol) containing the catalyst or catalyst plus peroxide. After 24 h at reflux, the excess of olefin was removed by distillation, and the residue was analysed by g.l.c. using diglyme as an internal standard added after completion of the reaction.\*

TABLE 9b

Product distribution and yields as a function of [CuCl{P(OMe)<sub>3</sub>}] (Method B) concentration in the reaction of dimethyl diazomalonate with cyclohexene

Catalyst (mmol)	Percent yield (relative yield)			Total product [(6) + (8) + (7)]
	(6)	(8)	(7)	
0.0042	8.1 (1.00)	6.6 (0.82)	0.00	14.7
0.0085	4.8 (1.00)	7.5 (1.6)	0.00	12.3
0.0170	40.7 (1.00)	9.4 (0.23)	3.2 (0.078)	53.2
0.0350	43.8 (1.00)	5.7 (0.13)	3.1 (0.072)	52.6
0.0700	35.2 (1.00)	9.6 (0.27)	2.7 (0.076)	47.4
0.1400	63.9 (1.00)	13.3 (0.21)	4.7 (0.074)	81.9
0.2800	61.8 (1.00)	21.6 (0.35)	5.3 (0.086)	88.6
0.5600	33.8 (1.00)	32.3 (0.96)	2.3 (0.069)	68.5
1.120	11.6 (1.00)	19.1 (1.65)	0.9 (0.079)	31.6
2.240	7.4 (1.00)	41.3 (5.59)	5.3 (0.72)	53.9
4.480	2.4 (1.00)	33.2 (13.8)	4.3 (1.78)	39.9

TABLE 9c

Product distribution and yields as a function of [CuCl{P(OMe)<sub>3</sub>}] (Method C) concentration in the reaction of dimethyl diazomalonate with cyclohexene

Catalyst (mmol)	Percent yield (relative yield)			Total product [(6) + (8) + (7)]
	(6)	(8)	(7)	
0.0042	6.7 (1.00)	7.96 (1.18)	0.00	14.7
0.0085	31.8 (1.00)	13.13 (0.41)	5.53 (0.17)	50.5
0.0170	36.9 (1.00)	7.73 (0.21)	3.13 (0.085)	47.8
0.0350	58.0 (1.00)	5.83 (0.10)	3.05 (0.052)	66.9
0.0700	60.5 (1.00)	9.56 (0.16)	4.34 (0.072)	74.4
0.1400	51.9 (1.00)	14.62 (0.28)	3.74 (0.072)	70.3
0.2800	42.2 (1.00)	43.11 (1.02)	2.83 (0.068)	88.2
0.5600	16.3 (1.00)	66.15 (4.06)	1.42 (0.087)	83.9
1.120	13.5 (1.00)	64.41 (4.78)	1.26 (0.094)	79.1
2.240	11.0 (1.00)	61.94 (5.94)	1.34 (0.12)	74.3
4.480	8.0 (1.00)	35.80 (4.46)	3.76 (0.47)	47.6

[4/954 Received, 16th May, 1974]