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METAL SALT CATALYZED CARBENOIDS—XV[1]

THE SYNTHETIC AND STRUCTURAL ASPECTS OF COPPER SALT CATALYZED ADDITIONS OF BIS-METHOXYCARBONYL CARBENE TO OLEFINS

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Abstract—Experimental and structural details are presented for the addition of *bis*-methoxycarbonyl carbene to a number of olefins employing homogeneous and heterogeneous catalyzed decompositions of dimethyl diazomalonate by copper and silver salts. The cyclopropanations are stereospecific and are accompanied by appreciable amounts of allylic C–H insertion products which could formally be derived from allylic radical or ionic intermediates. Cyclopropanation with *cis* 2-heptene proceeds 5·20 times as fast as with the *trans* isomer and cyclohexene reacts 4·90 times faster than 1-methyl cyclohexene when the catalyst is iodo(trimethyl phosphite)copper(I).

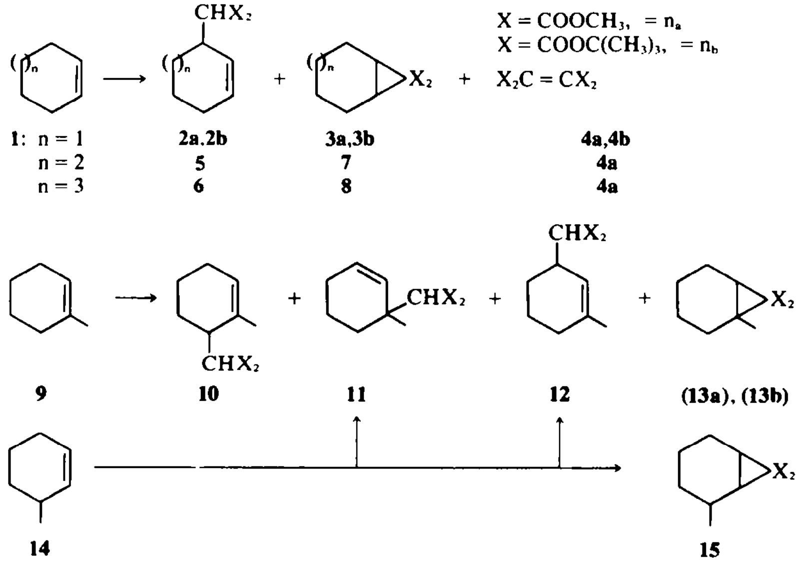
INTRODUCTION

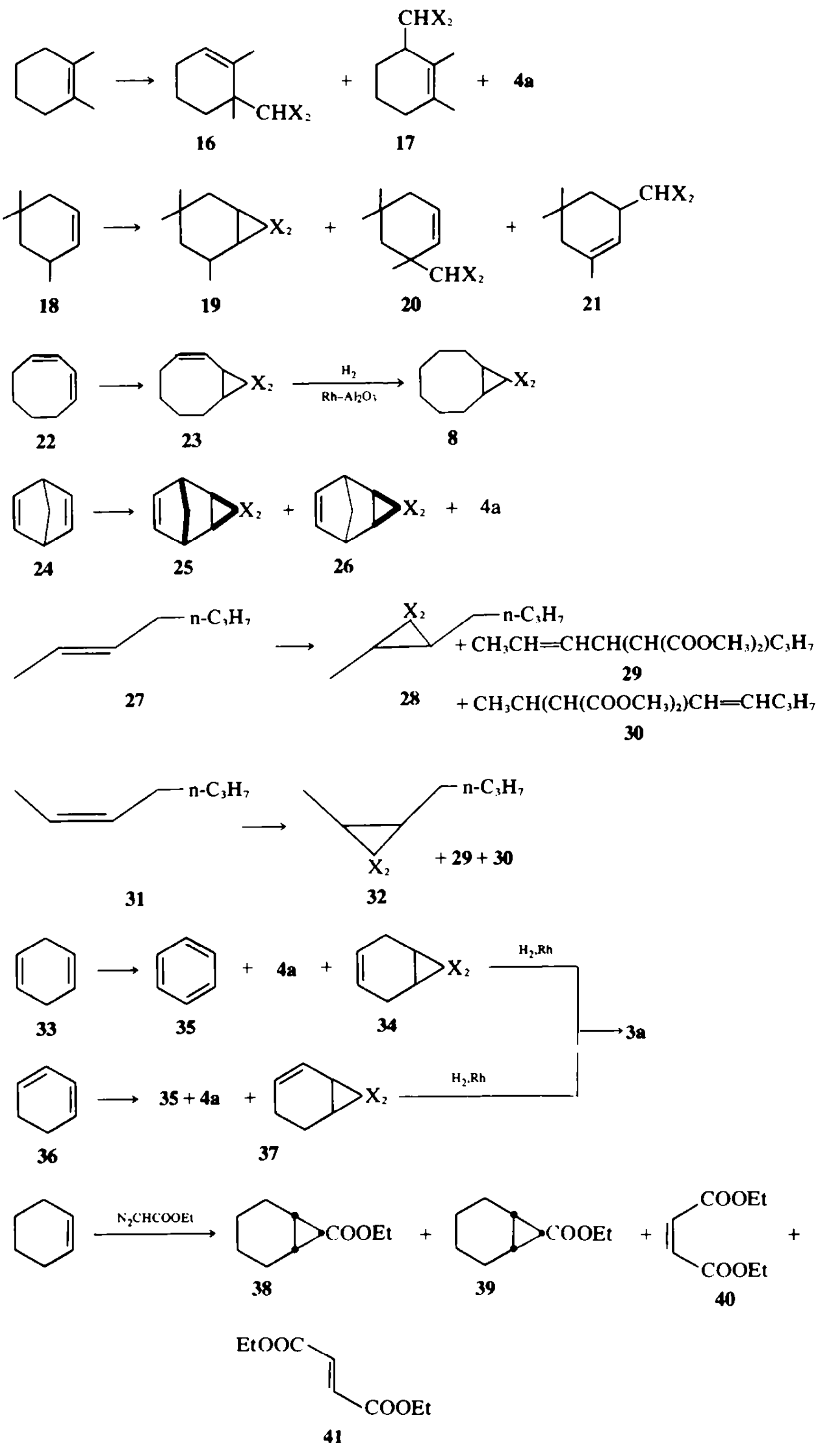
The photochemistry of dimethyl diazomalonate has been extensively treated by Jones[3] while only the basic results of the copper carbenoid chemistry has been reviewed.[4,5] The present paper is directed towards establishing the evidence upon which the structures of the many products previously reported[5,6] are based and to describe in detail the synthetic procedures involved in those cases which have not been reported or documented. The data which was garnered will be used in subsequent mechanistic treatments.

When *bis*-methoxycarbonyl carbenoids react with olefins, three basic processes are observed. These are, cyclopropanation, C–H insertion and carbene dimer formation [*tetrakis*-methoxycarbonylethylene]. Minor processes involving reduction to malonic ester and formation of 1,1,2,2 *tetrakis*-methoxycarbonyl ethane are frequently observed at levels less than one percent except in the cases of 1,4 and 1,3 cyclohexadiene where these become important processes along with aromatization and with the *bis*-pivaloyl methane derivitive of copper(II). In a previous paper we have discussed the synthesis, properties, employment and fate of a variety of homogeneous catalysts which have been employed in these studies.[6] The general results reported here are summarized in Scheme 1.

RESULTS AND DISCUSSION

Stereospecificity. One of the basic questions commonly investigated in the case of carbenes is the question of spin multiplicity. This problem is most frequently approached by assigning singlet character to sterospecific cyclopropa-





Scheme 1.

nation and triplet character to non-stereospecific cyclopropanation.[7] Some workers question the validity of such assignments[8] and they clearly are of questionable relevance with copper catalyzed and silver catalyzed processes for they are not chemically comparable to photochemical or thermal processes observed with dimethyl diazomalonate. The cyclopropanation processes are stereospecific (singloid)[9] while triploid C–H insertion processes are occurring (Table 2).

exo–endo; Syn:Anti *ratios*. While examining various catalysts, a brief examination of the effect of catalyst structure and concentration upon the stereochemistry of dimer formation and cyclopropanation was undertaken employing diazoacetic ester. There was reason to believe

Table 1(a). Effect of catalyst upon yield in the reaction of dimethyl diazomalonate with cyclohexenes

Catalyst	Olefin	Cyclohexene			1-Methylcyclohexene					1,2-Dimethylcyclohexene		
	Products	3a	2a	4a	13a	10	11	12	4a	17	16	4a
Cu*		38.0[‡]	1.71[‡]	8.05[‡]	22.9[‡]	1.23[‡]	4.13[‡]	18.5[‡]	5.64[‡]	27.5[‡]	7.88[‡]	16.6[‡]
CuCl*		42.8	2.18	8.38	19.1	1.45	3.67	17.5	4.83	27.5	7.44	22.4
$CuSO_4$*		45.3	2.08	9.07	24.8	2.49	6.07	24.0	7.36	16.0	5.55	21.9
$(CH_3O)_3P$-CuCl[@]		63.7	4.67	18.4	29.6	2.30	10.7	26.0	5.15	32.8	10.4	19.5
$(CH_3O)_3P$-CuI[@]		73.5	5.98	11.5								
$Cu(AcAc)_2$[@]		78.1	5.92	12.4								
$(CH_3O)_3PCuCN$		41.5	0.94	1.0								
$(CH_3O)_3P$-CuNCS		28.1	1.80	1.8								
$(CH_3O)_3P$-CuBr[@]		68.1	6.63	20.6								
$(CH_3O)_3P$-$CuBF_4$		59.2	7.99	10.0								
$[(CH_3O)_3P]_2CuI$[@]		65.1	6.52	22.4								
$[(CH_3O)_3P]_3CuI$[@]		63.0	6.56	27.0								
$(C_6H_5O)_3PCuBr$[@]		72.7	7.39	19.9								
$[(CH_3)_2CHO]_3PCuCl$[@]		66.0	5.39	27.4								
$AgBF_4$*		19.6	3.40	8.20								

* heterogeneous systems

[‡] percent yield based on VPC analysis and available dimethyl diazomalonate

[@] optimized yield for cyclopropane formation.

Table 1(b). Copper(II) catalyst versus products in the reaction of diazomalonate in cyclohexene

CATALYST LIGAND	Product yield and relative to norcarane (3a)		(2a)		(4a)		(42)	
Dipivaloylmethane	0.89	(1.00)	0.07	(0.09)	6.75	(7.52)	3.99	(4.43)
Acetylacetone	79.45	(1.00)	2.54	(0.03)	8.07	(0.10)	0.93	(0.01)
Acetylacetone-f_3	8.47	(1.00)	0.68	(0.08)	0.28	(0.03)	0.40	(0.05)
Acetylacetone-f_6	18.44	(1.00)	0.94	(0.05)	17.25	(0.94)	0.72	(0.04)
Thenoyltrifluoro-acetylmethane	21.42	(1.00)	1.36	(0.05)	2.01	(0.09)	0.59	(0.03)
Benzoylacetyl-methane	9.83	(1.00)	0.26	(0.03)	7.37	(0.75)	2.47	(0.25)
Acetate · (H_2O)	22.59	(1.00)	1.96	(0.09)	7.14	(0.32)	1.84	(0.08)
Octoate	34.475	(1.00)	1.57	(0.05)	4.20	(0.12)	3.50	(0.10)
Stearate	32.53	(1.00)	2.13	(0.07)	4.04	(0.12)	3.74	(0.11)
Ethyl Acetoacetate	27.67	(1.00)	1.70	(0.06)	8.75	(0.32)	2.24	(0.08)

Table 2. Products and yields from the reaction of dimethyl diazomalonate with 2-heptenes

$(CH_3O)_3P\cdot CuX$ (0.14 mmole)	Isomer	Temp °C	Cyclopropyl Cis(32)	Trans(28)	Insertion (29 + 30)	Dimer (4a)
X = I	Cis	98	95.6	Trace	0.52	3.85
I	Cis	85	92.1	Trace	3.30	4.64
Br	Cis	85	87.6	Trace	7.08	5.32
Cl	Cis	85	81.3	Trace	12.8	6.00
I	Trans	98	0.00	76.0	6.60	17.4
I	Trans	85	0.00	69.8	17.6	11.6
Br	Trans	85	0.00	72.5	18.4	9.20
Cl	Trans	85	0.00	41.7	35.2	23.1

Table 3. Product distribution in the reaction of cyclohexene with ethyl diazoacetate using $[(CH_3O)_3P]_n\cdot CuI$ as catalyst

Catalyst (mmole)	n	Norcarane (39)	(38)	(38/39)	Dimer 41	40	(40/41)
0.140	1	7.90	0.65	12.0	0.088	0.123	0.715
5.00	1	2.91	1.16	2.51	0.218	0.710	0.307
0.140	2	7.87	0.684	11.5	0.100	0.150	0.667
5.00	2	0.965	0.946	1.02	0.077	0.254	0.304
0.140	3	8.05	0.533	15.1	0.067	0.111	0.608
5.00	3	0.333	0.832	0.40	0.00	0.00	

that two or more paths lead to this type of product when dimethyl diazomalonate was employed. Reasoning that these might have different steric requirements, we undertook the study reported in Table 3 employing ethyl diazoacetate. If a single process lead to the products **38** and **39** and another to **40** and **41**, the ratios **38**/**39** and **40**/**41** should be independent of catalyst concentration. It is clear that this is not the case and that selectivity can be appreciably altered by ligand structure and concentration. For cyclopropanation the extremes range from 4·8 : 1 to 37·8 : 1 (anti/syn).

1,4 *or* 1,2 *Addition.* With 1,3 dienes the possibility of 1,4 addition exists and this point was examined by employing 1,3 cyclohexadiene and 1,3 cyclooctadiene. Musso[10] had previously added *bis*-carboethoxycarbonyl carbenoids to cyclohexadiene and observed normal (1,2 addition). We obtained similar results with no 1,4 addition ($\leqslant 0{\cdot}1\%$) with either olefin.[11] Identification was established by reduction to the cyclopropane available from the related mono-olefin.

Competition studies, regioselectivities. The relative rates of addition of carbenes to olefinic substrates has received considerable attention and has been used in mechanistic arguments regarding copper carbenoids.[12-14] Thus, Kochi[14] found that the use of copper(I) trifluoromethanesulfonate and copper(I) fluoborate led to different selectivities, for the addition of CH_2 and $CHCO_2Et$ to olefins, than those observed with other copper catalysts. The difference was assigned to metalcarbenoid-olefin complexes with anions of extremely low nucleophilicity. This led to enhanced reactivity of the least substituted bond when highly ionized salts were employed in direct parallel with the known stability of copper(I) olefin complexes.[15] Our results with copper(I) iodide-trimethyl phosphite exhibited a similar preference with 1,2 dimethyl cyclohexene being unable to form any cyclopropane from *bis*(methoxycarbonyl) carbenoids and cyclohexene being 4·90 times more reactive than 1-methyl cyclohexene.[5,6,16] This preference can readily be ascribed as being a consequence of steric requirements of the much larger carbenoid.

The results with 1,4 dihydroindane are of interest from the standpoint of relative rates and because 1,4 dihydrobenzene furnishes low yields of cyclopropanes and often no C–H insertion products. With this compound, the yield of monoadduct was high and the ratio of 8,9 addition to 2,3 addition was 1:25. The experiment was performed at 140° as compared with 1,4 cyclohexadiene at ~83° and as previously noted, cyclopropanation becomes more important as the operating temperature is increased with all olefins. We interpret this temperature effect as indicating the processes are not of a free radical nature.

General olefin additions. Economic considerations prevented establishment of ideal conditions for adding the carbenoid to 1,4 dihydrobenzene and 1,2 dihydrobenzenes, however, with all other olefins a single standard set of conditions appeared to represent the optimum. The maximum yield possible ran approximately 90 percent based upon diazo compound with the remainder of the diazo compound being consumed by phosphite ligands[6] (similar or slightly higher yields were realized in a limited number of cases by employing the same amount of copper(II) acetylacetonate or copper(II) fluoborate as catalysts. The use of higher temperatures generally appeared to decrease the propensity for C–H insertion processes and operation at reflux proved desirable[17] (compare 1-methylcyclohexene at 83° and 110° Table 4 and note that relations between **10**, **11**, **12** also change).

This phenomenon was also suppressed by the use of hexafluorobenzene as co-solvent even though this necessitated operation at 83° or lower.[5]

Structures of insertion products. The structures of C–H insertion products were always related to the removal of the most weakly bound hydrogen (Scheme 1) but where two energetically equivalent position existed, insufficient information was gathered to establish firmly a trend relative to steric requirements. It would appear that the least hindered hydrogen is greatly prefered. The structures of the C–H insertion products were determined after isolation by preparative VPC, using NMR and IR spectroscopy, comparison with authentic samples, by inter-relation of two independent paths where applicable, degradation and using spot tests. The cyclopropanes from mono-olefins all gave negative permanganate and $Br_2(CCl_4)$ tests where C–H insertion products gave positive results. The two C–H insertion products from 3-methylcyclohexene and two of those from 1-methylcyclohexene were identical and clearly identifiable because the NMR of **12** exhibited a peak assignable to an allylic Me group and a single vinyl hydrogen whereas that of **11** had an unsplit Me group at a higher field and had two vinyl protons. The structure of **10** followed directly by a process of elimination whereas arguments from the IR and the NMR were equivocal. An interesting feature of all of the allylic CH insertion products was the presence of two strong IR bands for C=O at ~1725–1735 and ~1730–1750 cm^{-1}. The cyclopropanes only exhibited a single band ~1715–1720 cm^{-1}.

In the case of the C–H insertion products from the 2-heptenes, the assignments of gross structure are based upon the mass spectra. The two products would be expected to furnish a common ion of $M–CH(CO_2Me)_2$ but the olefins are 2 and 3 heptenes and as such would be expected to furnish different even mass fragments via McLafferty rearrangements with **30** losing ethylene (M-28) whereas **29** would lose propylene (M-42).[18]

The dimethyl 3-cyclohexenyl malonate was synthesized from the related bromo compound by the classical route.[19]

The identity of the products from aromatic substrates such as prehitene has proven difficult and the reactions were sufficiently complex themselves to warrant treatment as a separate paper in this series. The processes are far more complex than those reported by Julia, Ledon and Linstrumelle[4] for less highly substituted benzenes.

Cyclopropane structure assignments. The assignments of the structures to the cyclopropanes from *cis* and *trans* 2-heptene were made on the basis that each furnished a unique product different from that furnished by the other isomer. This fact strongly suggests that the products have the same configuration as starting materials. In that others have noted that copper catalyzed additions are stereospecific where the products are known,[20] it seems a safe assumption that the products do not result from processes proceeding with 100 percent inversion of configuration. No attempt has yet been made to establish the stereochemistry of the double bonds in the CH insertion products (**29** and **30**).

Table 4. Product yield (relative to cyclopropane)

CONDITION*	**13a**	**10**	**11**	**12**	**4a**	Total fraction C-H insertion
neat (9), 110°	23.21(1.00)	1.80(0.077)	8.38(0.361)	20.39(0.878)	3.69(0.159)	(1.316)
neat (9), 85°	18.04(1.00)	1.03(0.057)	5.16(0.286)	19.72(1.09)	8.56(0.474)	(1.433)
(9) in 90 mole % C_6F_6	24.62(1.00)	1.08(0.044)	1.62(0.066)	27.84(1.13)	7.99(0.324)	(1.240)

*catalyst concentration furnishing maximum yield of **13a** employed.

Table 5. Effect of additives upon yields and product distribution in the reaction of cyclohexene with dimethyl diazomalonate using $(CH_3O)_3P\cdot CuI$ as catalyst

Additive (30 mmole)	(3a)	(4a)	(2a)
None	63.92 (1.00)	13.25 (0.207)	4.69 (0.074)
CuCl	33.46 (1.00)	33.44 (1.00)	2.29 (0.071)
$(CH_3O)_3P$	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 (0.317)	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)
$CuCl_2$	55.00 (1.00)	17.96 (0.326)	5.34 (0.097)
$(CH_3O)_2HPO$	59.54 (1.00)	25.14 (0.422)	4.48 (0.077)

Solvent effects. Many olefins are not liquids and in some cases they are not sufficiently available to permit using them in excess as solvents. The use of co-solvents is therefore desirable. The solvents in Table 5 were examined and with the exceptions of benzene and hexafluorobenzene were found lacking. This may well be a consequence of ylid formation when solvents bearing hetero atoms with non-bonding electrons are employed[21] or abstraction of a radical from the solvent by the carbenoid. The use of benzene is possible because it is relatively inert to the carbenoid. The extrapolation to alkyl benzenes is dangerous because, as we have mentioned previously,[6] the benzenes having higher π or σ basicities are reactive substrates. In many cases they are most likely less reactive than simple olefins. The addition of small amounts of trimethyl phosphate as a co-solvent was found to be beneficial.[5]

CONCLUSIONS

The copper salt catalyzed addition of *bis*(methoxy carbonyl)carbene to olefins is highly regioselective and is stereospecific for cyclopropanation. Insertion into carbon–hydrogen bonds is of increasing importance as the degree of substitution increases and as the reaction temperature is decreased. Bond insertion processes can be suppressed either by increasing the reaction temperature or by employing hexafluorobenzene as a diluent and solvent. Phosphite ligands have a deleterious effect even though they solubilize the catalyst.[6] The best catalyst for cyclopropanation is copper fluoborate operating in the homogeneous mode. The question of the valence state of the copper species remains unanswered although evidence indicating copper(II) catalysis can be adduced from the reported results.[6,22]

EXPERIMENTAL

B.pts and m.pts are corrected. Spectra were determined on a Varian A-56/60 NMR using TMS as an internal standard and a Perkin-Elmer 337 IR spectrophotometer using a polystyrene film as reference. Mass spectra were determined on a JEOL-D100 Double Focusing Mass Spectrometer. Gas chromatographic (VPC) analyses were performed using a Varian Aerograph model 90P and separations were carried out using a Varian Aerograph model A-700. All elemental analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan. The Term "solvent was removed" means by rotovaporation at water bath temperatures (75–90°C) unless otherwise stated.

The dimethyl malonate, malonic acid, cyclohexene, 1-methylcyclohexene, cycloheptene, 3-methylcyclohexene, 3,5,5-trimethylcyclohexene and 2-methyl-cyclohexanone employed were supplied by the Aldrich Chemical Co. *cis*- and *trans*-2-Heptene were supplied by the Chemical Samples Co. Cyclooctene and 1,3-cyclooctadiene were obtained from the Columbian Carbon Co. Trimethylphosphite was furnished by the Aldrich Chemical Co. All other phosphites were generously furnished as samples by the Mobile Chemical Co. Copper salts were supplied by the Research Organic/Inorganic Chemicals Corp.

Before their use, all olefins were distilled and stored under nitrogen or argon and over 4-A molecular sieves.

The rate of addition of diazo compound is important and was optimized. Hershberg type addition funnels with Ta, Pt or W wires were not suitable for use with diazoacetic esters for dimerization with accompanying pyrazoline formation (insoluble) occurred on the wire. A pressure equalizing pear-shaped reservoir was employed where the effluent passed lengthwise through the end of the stopcock plug after entering sidewise and turning approximately 110° to descend vertically into the outlet tube.

Preparation of starting materials

The preparation of p*-toluenesulfonyl azide.* *p*-Toluenesulfonyl azide was prepared by the method of Doering and DePuy.[23] When employing 0·892 mole *p*-toluenesulfonyl chloride we obtained 150 g of the azide (86%, reported 82%). The azide was washed 3 times with 100 ml water, once with 100 ml NaCl aq, dried over Na_2SO_4, then dried over $CaCl_2$ and stored over "Drierite". We have had no explosions with this compound and have stored samples at 25–30° for up to 2 yr.

The preparation of dimethyl diazomalonate. A soln of 132 g (0·67 mole) *p*-toluenesulfonyl azide, 71 g (0·70 mole) triethylamine (which had been stored over KOH pellets), and 93 g (0·70 mole) dimethyl malonate in 600 ml dry benzene was allowed to stand at room temp. overnight. The solid (*p*-toluenesulfonamide) was filtered off and washed with 100 ml cold benzene. The combined benzene solns were concentrated *in vacuo* (water) using a 60° water bath, and 200 ml hexane was added to precipitate the remaining *p*-toluenesulfonamide. After removal of the benzene-hexane solvent, the material was distilled to give 96·6 g (91%) of clear yellow oily dimethyl diazomalonate b.p. 42–44°/0·01 mm (lit. b.p. 63°/1 mm). NMR (CCl_4) showed the presence of 3–4% unreacted dimethyl malonate (the methyl ester hydrogen resonances of the diazo compound appear at γ6·20 and those of the unreacted malonate at γ6·34). The dimethyl malonate was removed by very slow distillation through a 6″ Vigareaux column. The unreacted dimethyl malonate distilled over at 32–34°/0·01 mm and the dimethyl diazomalonate at 40–41°/0·01 mm. In other runs it was found that the redistillation can be stopped after the dimethyl malonate is removed, as shown by the yellow color of the distillate. IR (neat) ν_{max} 2130 (s, C=N_2), 1740 and 1760 (s, C=N_2), 1695 (s, C=N), 1335 cm^{-1} (s, b). (Found: C, 37·87; H, 3·79; N, 17·64. Calc. $C_5H_6O_4N_2$: C, 37·96; H, 3·80; N, 17·72%).

The preparation of di-t-butyl malonate. Di-t-butyl malonate was prepared by the unpublished method of Korst.[24] A mixture of dry ethyl ether and 10 ml conc H_2SO_4 was placed in a 750 ml heavy wall ginger ale bottle, capped and placed in a freezer to cool. After cooling to −5°, the bottle was opened and 100 g (0·96 mole) malonic acid and 240 ml (3·0 mole) isobutylene (also at −5°) were added. The bottle was then recapped (pressure seal) and let stand in the hood with occasional shaking until the malonic acid dissolved (about 1 day). The bottle was again cooled to −5°, and the contents poured, with stirring, into a 3 l. beaker containing 150 g NaOH in 500 ml water and 500 g ice. The mixture was transferred to a separatory funnel, the aqueous layer was drawn off and extracted twice with ether. The ether extracts were combined with the organic layer, washed twice with 100 ml water, twice with 50 ml Na_2CO_3 aq, once with 100 ml NaCl aq and finally dried over Na_2CO_3. The ether was removed and crude ester distilled from alkali washed glassware to yield 117 g (57%) of colorless di-t-butyl malonate, b.p. 62–63°/1 mm (lit. b.p. 65–67°/1 mm). Korst[24] reported a 64% yield. IR(neat) had ν_{max} 2940 (s, C–H), 1740 (s, b, C=O), and 1143 cm^{-1} (s, b) among others. NMR (CCl_4) singlet γ8·55 (18H) and a singlet γ6·94 (2H).

The preparation of di-t-butyl diazomalonate.[25] A soln of 54 g (0·25 mole) di-t-butyl malonate, 25 g (0·25 mole) triethylamine and

43 g (0·25 mole) *p*-toluenesulfonyl azide in 500 ml dry benzene was allowed to stand at room temp. for 4 weeks. The diazo compound was worked up as previously described for the dimethyl analogue to yield 60 g material boiling at 40–50°/0·01 mm. On slow redistillation, 25 ml unreacted ester was recovered (b.p. 34–36°/0·01 mm) and 28·5 g (47%) yellow di-t-butyl diazomalonate (b.p. 38–40°/0·01 mm) was collected. NMR (CCl$_4$) showed a sharp singlet at γ3·50 as the only peak. IR (neat) ν_{max} 2130 (s, C=N$_2$) 1725 and 1750 cm^{-1} (s, C=N). (Found: C, 54·66; H, 7·26; N, 11·48. Calc. for $C_{11}H_{18}O_4N_2$: C, 54·51; H, 7·45; N, 11·62%).

The preparation of 1,2-*dimethylcyclohexanol.* A Grignard reagent was prepared by adding a soln of 113·4 g (0·93 mole) MeI in 200 ml anhyd ether to 22·6 g (0·93 mole) dry shiny Mg turnings plus a crystal of I$_2$ in 200 ml anhyd ether at a rate just fast enough to maintain gentle refluxing. After addition of MeI was complete, the mixture was refluxed an additional 1 hr, then cooled in an ice bath. A soln of 100·0 g (0·89 mole) 2-methylcyclohexanone in 200 ml anhyd ether was then added over a period of 2 hr with stirring. When the addition was complete, the mixture was refluxed 1 hr. The mixture was poured into a beaker of ice and the complex destroyed with conc HCl and water. The organic layer was separated and the aqueous layer was extracted twice with 200 ml ether. The combined organic solns were washed with 100 ml water, 50 ml 5% Na$_2$S$_2$O$_3$, 50 ml 10% NaHCO$_3$, again with 50 ml water, and finally washed with 100 ml NaCl aq and dried over Na$_2$SO$_4$. Removal of the ether gave 120 g (94%) alcohol which was used without further purification. The IR spectrum showed only a trace of unreacted ketone.

The preparation of 1,2-*dimethylcyclohexene.* 1,2-Dimethylcyclohexene was prepared by the method of Hammond and Nevitt.[26] A crystal of I$_2$ was added to 100 g 1,2-dimethylcyclohexanol and the mixture distilled to give a mixture of olefins and water. The olefin layer was drawn off and the aqueous layer extracted twice with 50 ml petroleum ether (30–60°). The combined organics were washed once with 25 ml water, once with 50 ml sat NaCl aq, then dried over Na$_2$SO$_4$. After removal of solvent, the liquid was distilled through a 1·2 m spinning-band column. Fractions were collected at 124–125° (2-methylmethylenecyclohexane), 130–131·3° (2,3-dimethylcyclohexene), and at 135·9–136·5° (1,2-dimethylcyclohexene). A total of 75 g of desired olefin was collected. VPC showed +99% purity, NMR(CCl$_4$) broad peak τ8·09, sharp singlet τ8·42 (CH$_3$). Some of the ring protons lie under this last peak.

Reactions involving diazomalonic esters

Tetramethoxycarbonylethylene (**4a**). A soln of 0·5 g (2·20 mmole) trimethylphosphite copper(I) chloride in 50 ml benzene was heated at reflux while a soln of 15·8 g (0·1 mole) dimethyl diazomalonate in 50 ml benzene was added at the rate of 6 drops per min. N$_2$ evolution stopped within 4 hr after the addition of diazo compound was complete. The mixture was filtered, the benzene removed, and the solid taken up in hot MeOH. After three recrystallizations (MeOH), the white needles, m.p. 119–120° (lit. 119–120). IR (KBr) ν_{max} 2940, 2680 (w, C–H), 1725 (s, C=O) and 1645 cm^{-1} (w, C=C); NMR (CCl$_4$), sharp singlet τ6·13 only, yield 10·1 g (77%).

1,1,2,2-*Tetramethoxycarbonylethane.* A soln of 19·8 g (0·15 mole) dimethyl malonate and 32 mg (0·14 mmole) trimethylphosphite copper(I) chloride in 50 ml benzene was heated under reflux while a soln of 15·8 g (0·1 mole) dimethyl diazomalonate in 50 ml benzene was added at the rate of 6 drops per min. When N$_2$ evolution ceased (~6 hr), the mixture was filtered, the benzene removed, and the resulting oil taken up in MeOH. On cooling, a solid formed. After three recrystallizations (MeOH), 14 g (53%) of a white compound, m.p. 136–137° (lit. 135[27]) was obtained; IR (CHCl$_3$) ν_{max} 2960 (w, C–H) and 1725 cm^{-1} (s, C=O); NMR singlets τ6·22 (12H) and τ5·83 (2H).

Addition of dimethyl diazomalonate to cyclohexene. A 20 mg sample of trimethylphosphite copper(I) chloride (0·14 mmole) was dissolved in 25 ml cyclohexene and the soln heated under reflux. A soln of 3·16 g (0·02 mole) dimethyl diazomalonate in 25 ml of the same olefin was added at the rate of 6 drops per min from a constant rate dropping funnel. After an additional 12 hr under reflux, the excess olefin was removed. VPC ($5' \times \frac{1}{4}''$ 5% SE-30, 160°C; injector and detector temp, 210°; helium flow rate, 30 ml/min of the residue showed the presence of 4 compounds. Comparison of VPC retention times showed the major component to be **3a**. Two of the other compounds were identified by the same method, as **4a** and 1,1,2,2-tetramethoxycarbonylethane. The fourth component was identified as **2a** by independent synthesis and comparison of VPC retention times.

Synthesis of dimethyl (3-*cyclohexenyl*)*malonate* (**2a**). A soln of 16·1 g (0·1 mole) 3-bromocyclohexene, 13·2 g (0·1 mole) dimethyl malonate and 5·4 g (0·1 mole) NaOMe in 200 ml anhyd MeOH was heated at 60° for 12 hr. The solvent was removed to leave a mixture of salt (NaBr) and an oil. The oil was taken up in ether, the soln filtered and the ether removed. The slightly colored residue was distilled to give 22·0 g colorless oil coming over at 68–71°/0·01 mn. The NMR (CCl$_4$) showed a multiplet centered at τ4·34 (2H, vinyl), a sharp singlet τ6·30 (6H, COOMe), doublet τ6·77 (1H, malonyl), multiplet τ7·17 (1H, substituted allylic position), broad multiplet τ8·34 (6H, ring protons). IR (neat) showed two CO bands, 1725 and 1750 and ν_{max} 1645 cm^{-1} (w, C=C).

Addition of dimethyl diazomalonate to 1-*methylcyclohexene.* A soln of 32 mg (0·14 mmole) trimethylphosphite copper(I) chloride in 100 ml 1-methylcyclohexene was heated under reflux while a soln of 31·6 g (0·2 mole) dimethyl diazomalonate in 100 ml olefin was added at the rate of 6 drops per min using a constant rate dropping funnel. When the addition was complete, reflux was continued for 12 hr. After removal of the excess olefin, the residue was distilled at 70–90°/0·01 mm. On redistillation, 34·0 g of colorless oil was collected between 58–60°/0·01 mm. VPC showed 4 components and the NMR spectrum showed vinyllic character. (Found for the mixture: C, 63·63; H, 8·00. Calc. for $C_{12}H_{18}O_4$: C, 63·71; H, 8·01%).

Relatively pure samples of each component were collected by preparative VPC (20' × 3/8" Carbowax 20M, 180°C).

Fraction A (**10**). This fraction reacted rapidly with Br$_2$ in CCl$_4$ and with KMnO$_4$. NMR (CCl$_4$) broad multiplet τ4·50 (1H, vinyl), sharp singlet τ6·32 (6H, COOMe), broad multiplet τ6·92 (1H, malonyl), broad ill-defined multiplet τ8·17 and overlapping another multiplet τ9·00 (10H total, ring and CH$_3$ protons). IR (neat) showed two CO bands, 1725 and 1730, and ν_{max} 1605 cm^{-1} (w, C=C). (Found: C, 63·42; H, 7·86%). The compound was assigned the structure **10**.

Fraction B (**13**). This component required several minutes to show any reaction with Br$_2$ and with permanganate. NMR (CCl$_4$) sharp singlet τ6·32 (6H, COOMe), and two broad overlapping multiplets between τ7·59–9·00 including a sharp singlet at τ8·77. The total area between τ7·59–9·00 was 12H. IR (neat) ν_{max} 1720 (C=O) and 3050 cm^{-1} (w, cyclopropyl C–H). (Found: C, 63·20; H, 7·90%). The compound was assigned structure **13**. Ozonolysis of the original mixture followed by oxidative workup furnished the same compound from the neutral fraction. (IR superposition, VPC retention times).

Fraction C (**11**). This material rapidly decolorised both Br$_2$ in CCl$_4$ and permanganate. NMR (CCl$_4$) singlet τ4·54 (2H, vinyl), singlet τ6·30 (6H, COOMe), singlet τ6·67 (1H, malonyl) and two broad overlapping multiplets between τ7·84 and τ8·91, including singlets at τ8·45, τ8·65 and τ8·80. The total area in the τ7·84–8·91 region was 9H. IR (neat) showed the split CO, 1725 and 1730 cm^{-1} and ν_{max} 1625 cm^{-1} (w, C=C). (Found: C, 61·73; H, 7·73%). The compound was assigned structure **11**.

Fraction D (**12**). This material decolorised both Br$_2$ and permanganate rapidly. NMR (CCl$_4$) broad multiplet τ4·79 (1H, vinyl), singlet τ6·32 (6H, COOMe), doublet τ6·92 (1H, malonyl, J = 8 cps), broad multiplet τ7·17 (1H, substituted allylic position), and a broad multiplet τ8·34 (9H, methyl and ring protons). IR (neat) showed CO bands at 1735 and 1750 and ν_{max} 1635 cm^{-1} (w, C=C). (Found: C, 63·67; H, 8·03%). The compound was assigned structure **12**.

Addition of dimethyl diazomalonate to 1,2-*dimethylcyclohexene.* A 16 mg (0·07 mmole) sample of trimethylphosphite copper(I) chloride was added to 50 ml 1,2-dimethylcyclohexene and the soln heated under reflux. A soln of 15·8 g (0·1 mole) dimethyl diazomalonate in 50 ml of the same olefin was added at the rate of 6 drops per min using a constant rate dropping funnel. At the end of the addition, reflux was continued for a total of 24 hr. The excess olefin was removed and the resulting oil distilled to give a colorless oil distilling at 70–80°/0·01 mm. VPC revealed the presence of two compounds and the NMR spectrum showed vinyl character. (Found (for the mixture): C, 65·02; H, 8·30. Calc. for $C_{13}H_{20}O_4$: C, 65·01; H, 8·34%).

Relatively pure samples of each component were obtained by preparative VPC (20′ × 3/8″ carbowax 20M, 180°C).

Fraction A (**16**). The material of shortest retention time rapidly discolored Br_2 in CCl_4 and aqueous permanganate. NMR (CCl_4) multiplet τ4·60 (1H, vinyl), doublet τ6·37 (6H, COOMe, J = 8 c/s), singlet τ6·50 (1H, malonyl), singlet τ9·17 (3H, methyl) and broad multiplet between τ7·67 and τ9·00 from which a singlet rises at τ8·44. The total area under the multiplet was 9H. IR (neat) showed two CO bands, 1730 and 1745 and ν_{max} 1630 cm^{-1} (w, C=C). (Found: C, 64·35; H, 8·14%). The material was assigned structure **16**.

Fraction B (**17**). The second fraction decolorized Br_2 and permanganate soln. NMR (CCl_4) doublet τ6·34 (6H, COOMe), singlet τ6·50 (1H, malonyl), broad multiplet between τ7·75 and τ9·00 (13H, methyl and ring protons) including a sharp singlet at τ8·40. IR (neat) showed a doublet in the carbonyl region, 1725 and 1745 and ν_{max} 1630 cm^{-1} (w, C=C). (Found: C, 64·11; H, 8·05%). This material was assigned the structure **17**.

Addition of dimethyl diazomalonate to cycloheptene. A soln of 45 mg (6·14 mmole) trimethylphosphite copper(I) iodide in 25 ml cycloheptene (which had been distilled from Na) was heated under reflux while a soln of 3·16 g (0·02 mole) of the diazo compound in 25 ml olefin was added at the rate of 6 drops per min from a constant rate dropping funnel. After 24 hr under reflux, the excess olefin was removed, the residue taken up in MeOH, and filtered. VPC showed the presence of only one compound in addition to starting olefin. The MeOH soln was cooled and the resulting solid recrystallized twice to give 3·62 g (80%) m.p. 61–62°; IR (neat) ν_{max} 1720 cm^{-1} (vs C=O); NMR (CCl_4) doublet τ6·29 (6H, COOMe, J = 8 c/s) and an unresolved multiplet between τ7·67 and τ9·00 (12H, ring protons). (Found: C, 63·09; H, 7.67. (A. Spang reported difficulty with this analysis due to sublimation.) Calc. for $C_{12}H_{18}O_4$: C, 63·70; H, 7·96%). The MS exhibited a strong parent ion, $m/e = 226$. The compound was assigned the structure **7**.

Addition of dimethyl diazomalonate to cyclooctene. The reaction was performed as described for cycloheptene, except on a 0·05 mole scale. VPC of the crude product showed only one new component. After removal of the excess olefin by distillation, the residue was taken up in MeOH and allowed to crystalize. Two recrystallizations from MeOH gave 11·6 g (78%) of white solid, m.p. 68–69°; IR ($CHCl_3$) ν_{max} 1715 cm^{-1} vs C=O; NMR (CCl_4) singlet τ6·29 (6H, COOMe) and unresolved absorption between τ7·67 and τ9·00 (14H, ring protons). (Found: C, 65·00; H, 8·37. Calc. for $C_{13}H_{20}O_4$: C, 65·00; H, 8·33%). The compound was assigned the structure **8**.

Addition of dimethyl diazomalonate to 3-methylcyclohexene. The reaction was carried out as described for the addition to cycloheptene. VPC of the crude mixture showed a major component (85·5%), 6·42% dimer and 8·02% of material assumed to be insertion products. After removal of the excess olefin, the residual oil was distilled, the fraction between 72–75°/0·01 mm being collected. IR (neat) showed strong CO absorption at 1720 cm^{-1}, NMR (CCl_4) doublet, τ6·29 (6H, COOMe, J = 2 c/s) and unresolved absorption between τ7·67 and τ9·17 (12H, ring and Me protons) including a broad singlet at τ8·44. (Found: C, 63·80; H, 7·96. Calc. for $C_{12}H_{18}O_4$: C, 63·70; H, 7·96%). The compound was assigned the structure **15**. Two of the insertion products showed identical VPC retention times as two products from addition of the carbene to 1-methylcyclohexene and were assigned structures **11** and **12**.

Addition of dimethyl diazomalonate to 3,5,5-trimethylcyclohexene. The addition was carried out as previously described for cycloheptene. VPC of the crude product indicated a major component (91·70%), 8·30% of material assumed to be insertion products and the absence of any dimer. Distillation gave a water white liquid boiling at 83–89°/0·01 mm. NMR (CCl_4) showed sharp doublet τ6·29 (6H, COOMe, J = 2 c/s) and unresolved absorption between τ8·91 and τ9·91 (16H, ring and Me protons). IR (neat) showed CO absorption at 1720 cm^{-1}. (Found: C, 65·92; H, 8·59. Calc. for $C_{14}H_{22}O_4$: C, 65·87; H, 8·65%). The compound was assigned the structure **19**.

Addition of dimethyl diazomalonate to bicyclo[2.2.1] *hepta-2,5-diene.* The reaction was carried out in the usual manner. VPC of the crude mixture showed it to consist of 70% dimer and 15% each of the two other products, assumed to be the *endo* and *exo* cyclopropanes.[28]

Addition of dimethyl diazomalonate to 1,3-cyclooctadiene. The addition was carried out as described for cycloheptene. After removal of the excess diene by distillation, VPC of the crude mixture showed only one peak of high retention time. The residue was taken up in 20 ml MeOH and cooled. The crystals which formed were recrystallized 3 times from MeOH to give 10·8 g of white solid melting at 59–60°. NMR (CCl_4) singlet at τ4·37 (2H), doublet τ6·82 (6H, J = 3 c/s) and unresolved absorption between τ7·37 and τ9·10. (Found: C, 65·33; H, 7·61. Calc. for $C_{13}H_{18}O_4$: C, 65·60; H, 7·56%). The above data did not permit rigorous distinguishment between a 1,2- or 1,4-cyclo addition product.

Hydrogenation of adduct from 1,3-cyclooctadiene. A 5·0 g sample of the material obtained from addition of dimethyl diazomalonate to 1,3-cyclooctadiene, was taken up in 100 ml EtOH and hydrogenated at atmospheric pressure using a Joshel type hydrogenation apparatus employing 5% Rh on alumina (1·20 g) as catalyst. The hydrogenation stopped when one mole of H_2 had been consumed. The catalyst was removed, the soln concentrated to about 20 ml and the material allowed to crystallize. After recrystallization from EtOH, the hydrogenation product was shown to be identical to **8** obtained by addition of the carbene to cyclooctene by m.m.p., IR and NMR. On the basis of the above data, the carbene addition product was assigned the structure **23**.

Preparation of 1-methyl-7,7-dicarbomethoxynorcarane (**13**). A soln of 96 mg (0·42 mmole) trimethylphosphite copper(I) chloride in 300 ml 1-methylcyclohexene was heated under reflux in a 3-necked flask. With stirring, a soln of 158·2 g (1·0 mole) of dimethyl diazomalonate in 300 ml of the olefin was added at the rate of 6 drops per min from a constant rate dropping funnel. When the addition was complete, reflux was continued overnight. The excess olefin was removed and the resulting oil taken up in 600 ml EtOAc. The soln was cooled in a dry ice-acetone bath and excess O_3 (Welsbach generator) bubbled through. While still cold, 300 ml AcOH, 3 ml conc. HCl and 100 ml 30% H_2O_2 was added. This soln was allowed to warm, stand at room temp. for 24 hr, and was then poured into ice and neutralized with KOH aq. After removal of the organic layer, the aqueous layer was extracted 2 × 100 ml of ether. The combined organic layers were washed 2 × 50 ml water, 2 × $NaHCO_3$ (10%), again with water, and finally with 100 ml of sat NaCl aq. After drying (Na_2SO_4) and solvent removal, the oil was distilled to give a water clear liquid b.p. 48–115°/0·01 mm. On redistillation, b.p. 53–55°/0·01 mm it gave 100 g (43%) of the product. This material showed one peak on VPC. NMR (CCl_4) sharp singlet τ6·34 (6H, $COOCH_3$) and a singlet at τ8·80 (CH_3). The ring protons appeared as two overlapping multiplets between τ7·37 and τ9·14 (12H). IR (neat) ν_{max} 1725 (s, C=O) and 3050 cm^{-1} (w, cyclopropyl C–H). (Found: C, 63·57; H, 8·00. Calc. for $C_{12}H_{18}O_4$: C, 63·71; H, 8·01%).

Preparation of 7,7-di-t-butoxycarbonylnorcarane (**3b**). A soln of 16 g (0·07 mmole) trimethylphosphite copper(I) chloride in 50 ml cyclohexene was heated under reflux, and a soln of 24·2 g (0·1 mole) di-t-butyl diazomalonate in 50 ml cyclohexene was dropped in at the rate of 6 drops per min from a constant rate dropping funnel. After completion of the addition, reflux was continued overnight. After removal of the excess olefin, the oil was taken up in 20 ml EtOH and cooled. The crystals which formed were recrystallized three times from EtOH and dried to yield a white solid, m.p. 82·5–83°, 10·0 g (35%); NMR (CCl_4) doublet τ8·54. The ring protons appeared as two broad, overlapping peaks between τ7·54 and τ9·00; IR (KBr) ν_{max} 1710 (s, C=O) and 3050 cm^{-1} (w, cyclopropyl C–H). (Found: C, 68·82; H, 9·49. Calc. for $C_{17}H_{28}O_4$: C, 68·94; H, 9·45%).

Preparation of 1-*methyl*-7,7-*di*-*t*-*butoxycarbonylnorcarane* (**13b**). A soln of 64 mg (0·28 mmole) trimethylphosphite copper(I) chloride in 300 ml 1-methylcyclohexene was heated to reflux. With stirring, a soln of 121·0 g (0·5 mole) di-t-butyl diazomalonate in 300 ml of the same olefin was added at the rate of 6 drops per min using a constant rate dropping funnel. After the addition was complete, reflux was continued overnight. Upon removal of the excess olefin, the residue was taken up in 1200 ml MeOH and treated with excess O_3 while cooled in a dry ice–acetone bath. While still cold, 50 ml dimethyl sulfide[29] was added to the soln. Without removing from the cooling bath, the soln was allowed to warm to room temp. After 3 hr at room temp., the solvent was removed, the residue taken up in 500 ml 10% KOH, and 50 ml 40% H_2O_2 added.[30] This soln was allowed to stand at room temp. for 18 hr then extracted 3 times with ether. The ether soln was washed twice with water, once with sat NaCl aq, then dried over Na_2SO_4. After removal of the solvent, the oil was distilled, the main fraction coming over at 73–75°/0·01 mm. On standing at room temp., the colorless liquid partially solidified, 31 g (20%); NMR (CCl_4) sharp singlet at τ8·55 (COOtBu), singlet τ8·85 (CH_3). The ring protons appeared as two broad overlapping peaks between τ7·45 and τ8·90; IR (neat), ν_{max} 1710 (s, C=O) and 3050 cm^{-1} (w, cyclopropyl C–H). (Found: C, 69·24; H, 9·85; M.W., 319 (Rast) ~ MS had small P^+, $m/e = 310$. Calc. for $C_{18}H_{30}O_4$: C, 69·62; H, 9·67%).

Preparation of tetra-*t*-*butoxycarbonylethylene* (**4b**). A soln of 0·5 g trimethylphosphite copper(I) chloride in 50 ml benzene was heated under reflux while a soln of 24·2 g (0·1 mole) di-t-butyl diazomalonate in 50 ml benzene was added at the rate of 6 drops per min from a constant rate dropping funnel. Reflux was continued until N_2 evolution ceased (about 3 hr). After filtering, the solvent was removed and the residual oil taken up in 20 ml EtOH. On cooling, a solid was formed which was recrystallized 3 times from EtOH to give 6·5 g of white crystals melting at 169–170°; IR (KBr) ν_{max} 2980 (m) 2940 cm^{-1} (w, C–H), 1740, 1730 cm^{-1} (s, C=O), and 1640 cm^{-1} (w, C=C); NMR ($DCCl_3$) singlet τ8·47 as the only peak. (Found: C, 61·64; H, 8·53. M.W., (Chloroform) 428. Calc. for $C_{22}H_{36}O_8$: C, 61·68; H, 8·40%).

Addition of dimethyl diazomalonate to cis-2-*heptene*. The addition was carried out as previously described for cycloheptene using 96% pure *cis*-2-heptene. VPC on the crude mixture showed a major component, 95·6%, 3·36% carbene dimer and 0·52% each of two other compounds. The excess olefin was removed and the residue distilled, the fraction coming over at 60–63°/0·05 mm being collected. NMR (CCl_4) singlet τ6·30 (6H, COOMe) and an unresolved multiplet between τ8·05 and τ9·22 (14H). (Found: C, 63·13; H, 8·62. Calc. for $C_{12}H_{20}O_4$: C, 63·15; H, 8·77%). The compound was assigned the structure **32**.

Addition of dimethyl diazomalonate to trans-2-*heptene to form* **28**. The diazo compound was added to 99% pure *trans*-2-heptene in the manner previously described for cycloheptene. VPC on the crude mixture showed a major component (**28**), 76·0%, 17·4% carbene dimer and two unresolved components accounting for 6·60% of the mixture. These last two products disappeared from the VPC trace upon the addition of Br_2 to the mixture and are, therefore, insertion products and not the **31**. After removal of the excess olefin, the residue was distilled to give a colorless oil distilling over at 58–60°/0·05 mm. VPC on the distillate showed it to be pure and to be different from the adduct obtained from addition to the *cis* olefin (retention time, superposition of IR spectra). NMR (CCl_4) was similar to that of the *cis* adduct for the shape and positions of the individual peaks in the τ8·05–τ9·22 multiplet. (Found: C, 63·00; H, 8·71. Calc. for $C_{12}H_{20}O_4$: C, 63·15; H, 8·77%). The cyclopropanes derived from the 2-heptenes were assigned the same configuration as their starting olefins.

Catalysis studies

The effect of several catalysts on the addition of dimethyl diazomalonate to olefins (mainly cyclohexene and 1-methylcyclohexene) was studied with respect to the following variables: catalyst concentration, solvent, temp., additives and peroxide content of the olefin.

In all cases, the reactions were carried out as described below. All glassware was baked out overnight at 200°, and assembled while hot. Olefins were distilled and stored over 4-A molecular

The addition of dimethyl diazomalonate to an equimolar mixture of *cis*- and *trans*-2-heptene was carried out in the usual way using $(MeO)_3P$–CuI as catalyst. VPC of the reaction mixture showed 5·20 parts of the *cis*-cyclopropane to 1·00 part of the *trans* adduct.

Stereochemical studies

Reaction of ethyl diazoacetate with cyclohexene. Cyclohexene was treated with ethyl diazoacetate (0·02 mole) under conditions described earlier for dimethyl diazomalonate. The *mono*, *bis*, and *tris* trimethylphosphite complexes of copper(I) iodide were used as catalysts.[6,31] The resulting yields and product distributions are shown in Table 3 and are relative to an internal standard. The higher yields account for ~ 80% of the diazo compound. The units are arbitrary with internal standard = 10·00.

Stereospecificity study. Dimethyl diazomalonate was added to *cis*- and *trans*-2-heptene under a variety of conditions. In all cases, a small portion of the mixture was treated with Br_2–CCl_4 soln in order to distinguish insertion products from cyclopropyl products. The *cis* olefin was 96% pure and the *trans* isomer 99% pure (Table 2).

Table 6. Product distribution from the reaction of dimethyl diazomalonate with equimolar amounts of cyclohexene and 1-methylcyclohexene

Product	Relative Yield
3a	1.000
2a	0.000
13a	0.204
10	0.018
11	0.072
12	0.118

sieves unless otherwise stated. Dimethyl diazomalonate was distilled to 99·9% purity as shown by NMR.

General procedure. A 100 ml 3-necked, round-bottom flask was equiped with a magnetic stirrer, reflux condenser, $CaCl_2$ drying tube, and a constant rate dropping funnel. The catalyst was weighed in a glassine cup, carefully transferred to the flask and 25 ml of olefin added. The mixture was heated to the desired temp. with stirring. The diazo compound (0·02 mole) was dissolved in a second 25 ml portion olefin, and added to the heated catalyst soln at the rate of 6 drops per min (2·5 hr). Reaction was continued for a total of 24 hr. The mixture was filtered while hot and excess olefin (or solvent) removed by distillation. The residue was taken up in the minimum of chloroform, 1 ml triglyme was added (volumetric pipet) as an internal standard, and the mixture analyzed by VPC. Relative peak intensities were determined using a Beckman 10-in. ball and disc intergrating recorder. The numbers in all tables represent percent yields based on available diazo compound. The numbers in parenthesis are product distributions based on cyclopropane.

Competition studies. Equimolar amounts of cyclohexene and 1-methylcyclohexene were mixed and treated with dimethyl diazomalonate in the usual way using $(MeO)_3P$–CuI as catalyst. The resulting product distribution is shown in Table 6.

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