the diethylbiphenyls was not attempted. However, the coupling products seem to have been prepared in very good yield based on vpc of the reaction mixture.

The preparation of 3,4′-diethylbiphenyl is described as a typical reaction. 3-Ethyliodobenzene (4.5 g, 0.019 mole) and 4-ethyliodobenzene (4.5 g, 0.019 mole) were added to a test tube (25 × 200 mm) maintained at *ca.* 200°. Activated copper (9.4 g) was added in portions over a 1-hr period. The reaction mixture was then heated for 4 hr (total, 5 hr) at about 250° and stirred occasionally with a thermometer. After cooling, the reaction mixture was extracted with boiling benzene (6 × 20 ml). Most of the benzene was then removed by distillation leaving a clear, yellow liquid. Vpc showed three major peaks, two of which were identified as the 3,3′ and 4,4′ isomers. The remaining peak was thus the 3,4′ isomer; hence it was trapped and analyzed. The infrared spectra (Table I) showed absorptions characteristic of both *meta* and *para* aromatic substitution.

Anal. Calcd for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.47; H, 8.67.

By analogous procedures the 2,4′ and the 2,3′ isomers were prepared and characterized.

Anal. Found for 2,3′-diethylbiphenyl: C, 91.53; H, 8.41. Found for 2,4′-diethylbiphenyl: C, 91.57; H, 8.48.

Infrared spectra were obtained on a Perkin-Elmer Model 237B spectrophotometer. A Beckman DB was employed in the ultraviolet analyses. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. A 12 ft × 0.25 in. silicone grease column was used for all of the gas chromatography investigations at the following conditions: column, 250°; injection port, 325°; detector, 345°; helium flow, 75 cc/min; pressure, 30 psi; bridge current, 125 ma.

Cycloaddition of Dimethylketene to Olefinic Substrates

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The recent report on the addition of ketenes to dienes and olefins prompts us to report our results from a similar study.[1] This paper describes the addition of dimethylketene to several olefinic substrates to produce good yields of the corresponding 1,2-cycloaddition products.

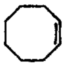
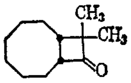
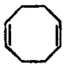
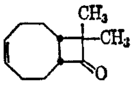
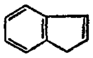
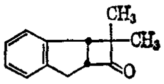
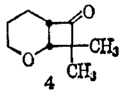
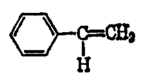
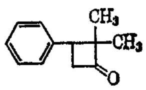
The reactions of ketene or disubstituted ketenes with sufficiently activated double bonds such as conjugated dienes,[1] vinyl ethers,[2] and enamines[3] proceed readily and generally in good yields. Simple olefinic substrates undergo a slower reaction with ketenes in which the dimerization of the ketene competes with the cycloaddition. Bestian and Günther[4] reported that the thermal decomposition of the acylal of dimethylketene in the presence of olefins at elevated temperatures leads to good yields of the 1,2-cycloadducts of dimethylketene with simple acyclic olefins and cyclohexene. Cyclic olefins such as cyclohexene, cyclooctene, and 1,5-cyclooctadiene have entered into cycloadditions with butylethylketene.[1]

Because of the accessibility of tetramethyl-1,3-cyclobutanedione (commercially inexpensive) and its known thermal decomposition into dimethylketene, it was chosen as the source material for this study of the addition of dimethylketene to several types of olefinic substrates. A modified ketene generator[5] was utilized to generate the dimethylketene from its dimer. The dimethylketene was carried by the nitrogen flow into the olefin which was heated in an oil bath. The mixture was then allowed to react overnight. The unreacted olefin was recovered by distillation and the adduct was either distilled or crystallized.

In this manner the reactions of dimethylketene with cyclooctene, 1,5-cyclooctadiene, styrene, indene, and dihydropyran were performed. In the latter three cases, the addition could yield different isomers depending on the direction of addition to the double bond. However, only one isomer was formed and the structural assignments of the products were ascertained by infrared, nmr, and deuterium exchange experiments. The results of this study are tabulated in Table I.

TABLE I

DIMETHYLKETENE–OLEFIN ADDUCTS AND YIELDS

Olefin[a]	Product structure	% yield
	 **1**	77^b
	 **2**	55^b
	 ^{d} **3**	64^b
	 ^{e} **4**	42^c
	 **5**	20^c

[a] In all runs a 3–5 *M* excess of olefin to starting dimer was utilized. [b] Yield based on unrecovered olefin. [c] Yield based on dimer, assuming a quantitative conversion to monomer. [d] The formation of this adduct is reported in ref 1 in a 12% yield using hexane as the solvent. No structural evidence was presented. [e] Previously reported in ref 2a in a 73% yield using ether as the solvent. No structural evidence was presented.

The nmr spectra for **1** and **2** are listed in the Experimental Section. The structure of the indene–dimethylketene adduct was established as **3** by the nmr spectrum (solution in carbon tetrachloride) which showed a 1 H doublet of triplets at 4.0 ppm for the tertiary hydrogen adjacent to the carbonyl group,[1,6] a 3 H singlet at 0.7 and a 3 H singlet at 1.37 ppm for the dissimilar methyl groups, a 3 H multiplet pattern spread over 2.6–3.7 ppm for the benzylic hydrogens (this pattern showed two unsymmetrical doublets centered at 3.0 for 2 H and 3.6 ppm for 1 H along with

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[1] J. C. Martin, P. G. Gott, V. W. Goodlett, and R. H. Hasek, *J. Org. Chem.*, **30**, 4175 (1965).

[2] (a) R. H. Hasek, P. G. Gott, and J. C. Martin, *ibid.*, **29**, 1239 (1964), and references cited therein; (b) J. C. Martin, V. W. Goodlett, and R. D. Burpitt, *ibid.*, **30**, 4309 (1965); (c) R. Husigen, L. Feiler, and G. Binsch, *Angew. Chem. Intern. Ed. Engl.*, **3**, 753 (1964).

[3] G. Berchtold, G. R. Harvey, and G. E. Wilson, Jr., *J. Org. Chem.*, **30**, 2642 (1965), and references cited therein.

[4] H. Bestian and D. Günther, *Angew. Chem. Intern. Ed. Engl.*, **2**, 612 (1963).

[5] W. E. Hanford and J. C. Sauer, *Org. Reactions*, **3**, 136 (1946).

[6] E. J. Corey, R. B. Mitra, and H. Uda, *J. Am. Chem. Soc.*, **86**, 487 (1964).

smaller adjacent peaks), and a 4 H singlet with some adjacent smaller bands at 7.4 ppm for the aromatic protons. The nmr of **3** in pyridine shifted all peaks upfield, but the doublet of triplet was still present at 3.6 ppm and the 3 H multiplet was opened up into a more complex multiplet pattern spread over the region 1.8–3.0 ppm. The reaction of diphenylketene with indene has recently been reported[7] to yield the analogous diphenyl adduct (structure established by a chemical degradation of the adduct).

The structure of the dihydropyran–dimethylketene adduct was established as **4** by the nmr spectrum which showed a doublet for 1 H at 3.85 ppm ($J = 6$ cps). Treatment of the adduct with potassium carbonate in deuterium oxide resulted in the exchange of one hydrogen for deuterium, and the nmr (carbon tetrachloride solution) showed a 1 H singlet at 3.85 ppm. This proton at 3.85 ppm can then be assigned to the position adjacent to the oxygen atom and the carbon bearing the geminal dimethyl group. On deuteration the proton adjacent to the carbonyl group is exchanged and, because of the smaller coupling of deuterium to hydrogen, a singlet pattern appears. This result is only consistent with structure **4**.

The styrene adduct was established as structure **5** by the nmr pattern which was run in carbon tetrachloride solution. Two sharp methyl singlets (3 H each) appeared at 0.70 and 1.25 ppm, the peak (3 H) at 3.25 resembled an A_2B pattern with a strong slightly split peak in the center of two smaller peaks, and a multiplet (5 H) appeared at 7.15 ppm for the aromatic protons. No protons appeared in the region of 2 ppm where the β protons of cyclobutanone absorb.[8] Furthermore, treatment of the adduct with sodium deuteroxide in deuterium oxide exchanged two hydrogens with deuterium and the 3 H pattern at 3.25 ppm was changed into a broad 1 H singlet at 3.25 ppm.

Structures **3**–**5** were also predicted on the basis of the expected polarization of the reactant molecules.[1] Evidence is available with regard to the highly stereospecific nature of these cycloadditions in several cases.[2b,c]

The procedure described is a simple and convenient method for the preparation of *cis*-fused cyclobutanone rings.

Experimental Section

All nmr spectra were recorded with the Varian A-60 instrument using tetramethylsilane as an external standard for calibration.

General Procedure.—A modified ketene generator[6] was used to generate dimethylketene from tetramethyl-1,3-cyclobutanedione. In all runs 20 g of the dione was utilized. Over a period of 8 hr the dimethylketene was carried by the nitrogen stream into the olefinic substrate which was heated to 70–75° in a oil bath. The olefin was placed in what is normally the first Dry Ice–acetone trap. The second Dry Ice–acetone trap was used to collect any olefin and dimethylketene carried over from the reaction flask. The contents of the second trap were added to the first trap after the dimer was completely decomposed and the mixture was heated for about 12 hr at 75–80°. The product was isolated by distillation or crystallization.

10,10-Dimethyl-*cis*-bicyclo[6.2.0]decan-9-one (**1**).—Cyclooctene (44.8 g, 0.41 mole) was treated with dimethylketene and on vacuum distillation there was obtained 39.1 g of unreacted cyclooctene and 7.0 g (77% yield) of **1** boiling at 76–77° (0.3 mm). The infrared spectrum (neat) showed a strong carbonyl band (four-membered ring) at 5.64 μ. The nmr spectrum (neat) exhibited the following pattern: a sharp 3 H singlet at 0.90 (methyl group), a sharp 3 H singlet at 1.17 (methyl group), a broad multiplet pattern from 1.1 to 2.2 for approximately 13 H, and a 1 H doublet of triplets at 3.15 (proton adjacent to the carbonyl group) ppm.

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 80.19; H, 11.12.

10,10-Dimethyl-*cis*-bicyclo[6.2.0]dec-4-en-9-one (**2**).—With 1,5-cyclooctadiene (65.0 g, 0.60 mole) as the reactant, vacuum distillation of the mixture yielded 59.0 g of recovered 1,5-cyclooctadiene and 5.3 g (55% yield) of **2** was collected at 80–82° (0.5 mm). The infrared spectrum (neat) showed a strong carbonyl absorption at 5.66 μ. The nmr spectrum (neat) showed the following absorption pattern: sharp singlets at 0.80 and 1.0 (methyl groups), a broad multiplet centered at 1.9 and ranging from 1.3 to 2.5 (methylene groups and the tertiary hydrogen adjacent to the carbon bearing the geminal dimethyl group), a doublet of triplets at 3.30 (tertiary hydrogen adjacent to the carbonyl group), and a multiplet at 5.40 (olefinic protons) ppm. These peak areas were in the ratio of 6:9:1:2.

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.83; H, 10.25.

1,2,2a,7a-Tetrahydro-2,2-dimethyl-7H-*cis*-cyclobut[*a*]inden-1-one (**3**).—Indene (79 g, 0.68 mole) was treated with dimethylketene and on vacuum distillation 60 g of indene was recovered. The distillation residue solidified on cooling and was collected by filtration: 15.4 g, mp 61–62°, lit.[1] mp 60.5–62°. An additional 4.0 g of **3** was obtained by filtration of the mother liquor: mp 59–62°. The total weight of **3** was 19.4 g (64% yield). The analytical sample was prepared by sublimation.

Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.70; H, 7.47.

The infrared spectrum (potassium bromide) showed carbonyl absorption at 5.69 μ. The nmr spectrum was presented in the discussion.

8,8-Dimethyl-2-oxo-*cis*-bicyclo[4.2.0]octan-7-one (**4**).—Dihydropyran (63.5 g, 0.75 mole) was kept at 55–60° during the reaction and the mixture was allowed to stand overnight at room temperature. The excess olefin was removed under water aspirator pressure and the residual material distilled: 17.8 g (42% yield based on dimer), bp 57–63° (1.4 mm). The redistilled material boiled at 54–55° (1.2 mm), lit.[2a] bp 89–90° (11 mm). The infrared spectrum showed a strong carbonyl band at 5.67 μ. The nmr spectrum (neat) showed the following pattern: a 3 H singlet at 0.80 (methyl group), a 3 H singlet at 1.02 (methyl group), approximately a 4 H multiplet over 1.1–2.0 (ring methylenes not adjacent to the oxygen atom), a 3 H complex multiplet at 2.8–3.7 (methylene group adjacent to the oxygen atom and the proton adjacent to the carbonyl group), and a 1 H doublet at 3.80 ppm ($J = 6$ cps, tertiary hydrogen adjacent to the oxygen atom).

A mixture of 300 mg of **4**, 1 ml of deuterium oxide, and 50 mg of potassium carbonate was stirred under a nitrogen atmosphere for 5 hr at 45–50°. On cooling, the product was extracted into pentane; the pentane was dried over sodium sulfate and then removed by distillation. The nmr of the residue (carbon tetrachloride solution) had the following peaks: a 3 H singlet at 0.95 (methyl group), a 3 H singlet at 1.17 (methyl group), a 4 H broad multiplet pattern spread over 1.3–2.3 (ring methylenes not adjacent to the oxygen atom), a 2 H broad multiplet pattern over 2.8–3.8 (methylene group adjacent to the oxygen atom), and a 1 H singlet at 3.85 ppm (tertiary hydrogen adjacent to the oxygen atom and the carbon bearing the geminal dimethyl group).

2,2-Dimethyl-3-phenylcyclobutanone (**5**).—Styrene (71.0 g, 0.67 mole) was treated with dimethylketene and the mixture was then vacuum distilled. Styrene (30 g) was recovered and a considerable amount of unweighed polymer remained as a residue. The product **5** boiled at 70–90° (1 mm) and solidified on standing to yield 9 g (20% yield based on starting dimer) of a white crystalline solid, mp 36–37°. The boiling point of the compound was previously reported as 88° (1 mm). The infrared spectrum (potassium bromide) showed a strong carbonyl band at 5.65 μ. The nmr spectrum was presented in the discussion.

The adduct **5** was heated for 17 hr at 75–80° with deuterium oxide to which a small piece of sodium metal had been added. The mixture was cooled and the compound was extracted into carbon tetrachloride. The extract was dried over sodium sulfate and the solution was utilized for the nmr analysis. The spectrum showed the following pattern: a 3 H singlet at 0.70, a 3 H singlet

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[7] N. Campbell and H. G. Heller, *J. Chem. Soc.*, 5473 (1965).

[8] K. B. Wiberg and B. J. Nist, *J. Am. Chem. Soc.*, **83**, 1228 (1961).

at 1.25, a 1 H broad singlet at 3.25, and a 5 H multiplet at 7.15 ppm.

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Aluminum Chloride Catalyzed Diene Condensation. II.[1] Stronger Adherence to the Alder *endo* Rule

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It has been previously reported that aluminum chloride markedly catalyzes the Diels-Alder reactions of acrylates with dienes.[2] The effect of the methyl group in a diene molecule on the rate of the catalyzed and the uncatalyzed reaction was determined to provide an insight into the mechanism of the catalyzed reaction, and a heterolytic two-step mechanism was suggested in a recent article.[1]

Now we report on the stereochemical selectivity in the catalyzed condensation between cyclopentadiene and several dienophiles. Our original interest was to know to what extent the well-known Alder *endo* selectivity[3] would be preserved in this catalyzed modification of the Diels-Alder reaction, since if the reaction does not proceed by the four-center mechanism the stereochemical course of the reaction will not be controlled by the *principle of maximum accumulation of centers of unsaturation* and, therefore the Alder *endo* rule may not be observed in the catalyzed reaction.

The *endo vs. exo* adduct ratios for both the catalyzed and uncatalyzed reactions of cyclopentadiene with methyl acrylate, methyl methacrylate, methyl *trans*-crotonate, dimethyl maleate, and diethyl maleate in benzene at 30° were determined by gas-liquid partition chromatography (glpc) and are listed in Table I. Peak areas were used as the direct measure of the isomeric ratio and the values are probably correct to within a few per cent.[4]

The proportion of the *endo* adduct is enhanced by the catalysis by aluminum chloride in all the reactions now studied. Interestingly even with methyl methacrylate, which preferentially yields the *exo*-methoxycarbonyl adduct in the uncatalyzed reaction,[5] the *endo* adduct is the preferred product in the catalyzed reaction. Consequently we conclude that the catalyzed reaction invariably adheres to the Alder *endo* rule to a greater degree than does the uncatalyzed reaction, which is contrary to what we originally imagined.

TABLE I

endo–exo RATIO OF THE PRODUCTS FROM THE REACTIONS OF CYCLOPENTADIENE WITH VARIOUS DIENOPHILES[a]

Dienophile	Solvent[b]	Catalyst[c]	Reaction time, hr	Ratio[d,e] *endo*	*exo*
Methyl acrylate	A	U	7.5	80	20
	A	U	...	(83.1	16.9)[f]
	B	U	7.5	78	22
	B	C	0.5	95	5
	B	C	1.0	94	6
Methyl methacrylate	A	U	7.5	34	66
	A	U	...	(33.0	67.0)[f]
	B	U	7.5	31	69
	B	C	0.5	60	40
	B	C	1.0	60	40
Methyl *trans*-crotonate	E	U	24.	64	36
	E	U	...	(62.3	37.7)[f]
	B	U	24.	54	46
	B	C	0.5	94	6
	B	C	1.0	93	7
Dimethyl maleate	D	U[g]	4.0	72	28
	D	U[g]	...	(75	25)[h]
	B	U	5.0	73	27
	B	C	1.0	94	6
	B	C	2.0	94	6
Diethyl maleate	B	U	14.	73	27
	B	C	1.0	96	4
	B	C	2.0	95	5

[a] Reactions at 30° unless otherwise indicated. [b] A, acetonitrile; B, benzene; E, ethanol; D, dioxane. [c] U, uncatalyzed; C, aluminum chloride catalyzed. [d] From glpc peak area assuming equal thermal conductivity of the stereoisomers. [e] The results by previous workers are quoted in parentheses. [f] See ref 5. [g] At 70°. [h] See ref 9.

It is of further interest that the configuration of dienophile substituents is retained in the adduct of the catalyzed reaction too. Thus, the content of 5-norbornene-*trans*-2,3-dicarboxylates in the products from dimethyl and diethyl maleate reactions with cyclopentadiene was less than 0.3% (by glpc) in both the catalyzed and uncatalyzed reactions (even this slight contamination of the *trans* isomer might have been derived from the fumarate impurity in the maleate used).

Our present findings indicate that the catalyzed reaction may not necessarily be regarded as a heterolytic two-step reaction such that the two bond-forming steps take place in sequence. We rather prefer to regard the reaction as having a great deal in common with the uncatalyzed reaction.

To account for the higher *endo* selectivity three considerations come to mind: (1) steric hindrance in the transition states, (2) the enhanced degree of π interaction between the unsaturated centers of the addends, and (3) the polarity effect.

The steric hindrance between the methylene group of cyclopentadiene and the dienophile substituents in the transition state to the *exo* adduct has been invoked to interpret the variation of the *endo vs. exo* adduct ratio from reactions of cyclopentadiene with various dienophiles.[6] Such a steric hindrance may be larger when the dienophile substituent is complexed with aluminum chloride, making the catalyzed reaction more strongly *endo* selective than the uncatalyzed reaction. However, we do not give importance to this effect because the same increased stereospecificity is observed

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[1] Paper I: T. Inukai and T. Kojima, *J. Org. Chem.*, **31**, 1121 (1966).

[2] T. Inukai and M. Kasai, *ibid.*, **30**, 3567 (1965). See also references cited therein.

[3] M. C. Kloetzel, *Org. Reactions*, **4**, 1 (1948).

[4] See ref 5 for support of this assumption.

[5] J. A. Berson, Z. Hamlet, and W. A. Mueller, *J. Am. Chem. Soc.*, **84**, 297 (1962).

[6] J. G. Martin and R. K. Hill, *Chem. Rev.*, **61**, 537 (1961), section V.