was added and, after thorough mixing, the solution was poured into water. The two layers were separated. The benzene layer was dried over anhydrous magnesium sulfate and analyzed by gas-liquid partition chromatography.

The aqueous layer contained any halide ions formed, and these could be titrated potentiometrically with standard silver nitrate solution.

The procedure was modified according to the needs of the reaction. For acid-base titrations the whole of the contents of the reaction was titrated with standard acid, and the benzene was not added. For identification of benzenesulfinic acid ether was used instead of benzene, and the aqueous layer was diluted to a suitable concentration and examined in an ultraviolet spectrophotometer. The experimental procedure for the experiments in CH_3OD differed in that pentane was used instead of benzene. The pentane solution was passed through a short alumina column (*ca.* 2 cm), the pentane was cautiously evaporated under reduced pressure, and the infrared spectrum of the residue was examined.

The results of a number of experiments are summarized in Table I. No anisole was ever obtained as a product from **2a**.

Identification of Certain Products.—From a reaction of **2a** in the presence of phenol (Table I), the products were partitioned between benzene and water. The ultraviolet-visible spectrum of the aqueous layer showed an absorption maximum at 423 mμ, identical with that of an alkaline solution of 4-(*o*-chlorophenylazo)phenol.

From a reaction of 0.001 mole of **2a** with 25 ml of 0.05 *M* sodium methoxide, the product was poured into water, made slightly alkaline, and extracted with ether. The water layer was acidified and extracted thrice again with ether. The ultraviolet spectrum showed a band at 245–275 mμ with fine structure maxima at 259, 265, and 272 mμ. The spectrum was identical with that of an authentic sample of benzenesulfinic acid and different from that of an authentic sample of benzenesulfonic acid.

From the reaction of 0.001 mole of **2a** with 5 ml of 0.2 *M* sodium methoxide, the volatile products were distilled (heating with boiling-water bath) and collected. The presence of formaldehyde was estalished by a positive color test using a modified Schiff reagent.[16] The remainder of the distillate was dissolved in 20 ml of methanol, combined with a solution of methone (dimedone) in methanol, heated 30 min on the steam bath, and chilled overnight. White needles (28 mg) of the methone derivative of formaldehyde were obtained, mp 190.2° (lit.[16] 191.4°).

From reaction of 0.001 mole of **2a** with 0.001 mole of $NaOCH_3$ in 5 ml of CH_3OD, the chlorobenzene (isolated as described above) had an infrared spectrum resembling that of ordinary chlorobenzene and lacking bands characteristic of chlorobenzene-2-*d*. From the reaction of 0.002 mole of **2a** in 10 ml of 2 *M* $NaOCH_3$ in CH_3OD, the chlorobenzene obtained matched in infrared spectrum the best sample of chlorobenzene-2-*d* prepared by Zoltewicz and Bunnett.[12]

Action of Sodium Methoxide on Phosphonium Salt 4.—*o*-Chlorophenyltriphenylphosphonium iodide (**4**), mp 242° (lit.[14] 242–244°), was prepared by the method of Horner and Hoffmann.[14]

A mixture of **4** (0.5 mmole) and sodium methoxide (0.6 mmole) in 10 ml of methanol was boiled 5 min under reflux. The mixture was steam distilled, and the distillate was extracted with benzene. A known amount of bromobenzene was added to the extract which was then analyzed by gas–liquid partition chromatography. The yield of chlorobenzene was 93%. A similar experiment was performed but with methylene chloride as extraction solvent; chlorobenzene was again obtained, but there was no indication of benzene or anisole in the gas–liquid chromatogram.

To a solution of 0.004 mole of sodium methoxide in 5 ml of methanol-O-*d*, 834 mg (1.67×10^{-3} mole) of **4** was added. The resulting amber solution was heated 10 min at reflux. The product mixture was steam distilled, and the distillate was extracted with pentane. The pentane extract was dried over anhydrous magnesium sulfate, and the pentane was evaporated. The infrared spectrum of the residue was very similar to that of chlorobenzene-2-*d*[12] and different from that of ordinary chlorobenzene.

Registry No.—**2a**, 13389-62-3; **2b**, 13389-63-4; (*o*-chlorophenyl)triphenylphosphonium iodide, 13389-64-5; sodium methoxide, 124-41-4; methanol, 67-56-1.

[16] J. F. Walker, "Formaldehyde," Reinhold Publishing Corp., New York, N. Y., 1953, p 367.

Further Studies on the Mechanism of Diphenylketene Cycloaddition[1]

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Diphenylketene undergoes 1,2 cycloaddition with cyclopentadiene, 1,3-butadiene, isoprene, and chloroprene to give substituted cyclobutanones. Cyclopentadiene is 240 times as reactive as 1,3-butadiene. In the cycloaddition of diphenylketene and isoprene, there is a predominance of the 1,2-cycloaddition product over the 3,4-cycloadduct. The cycloaddition of diphenylketene and chloroprene also produced both isomers, but the 3,4 cycloadduct predominated. These results are regarded as consistent with the near-concerted mechanism previously described.

Ketenes generally undergo 1,2-cycloaddition reactions with olefinic compounds to form substituted cyclobutanones.[2] While this characteristic reaction of ketenes has been known for many years, it has received relatively little attention from a mechanistic point of view. A very striking feature of this reaction is that only one of the two possible orientation isomers is produced with essentially all of the olefins and dienes that have been studied. However, this is the isomer that would be predicted on the basis of the diradical mechanism, dipolar mechanism, or a concerted process considering only bond polarizations. Another interesting feature of this cycloaddition reaction is that only 1,2 adducts are produced with dienes; no substituted cyclohexenones have been reported.[3]

Huisgen, Feiler, and Binsch have investigated the cycloaddition of diphenylketene and dimethylketene with both *cis*- and *trans*-propenyl propyl ether.[4] In both cases it was reported that the *cis* form reacted faster than the *trans* form. It was also reported that each of the two geometrically isomeric ethers had retained their original configurations in the cycloadduct. This stereoselective *cis* addition was interpreted as being strong evidence for a one-stage multicentered cycloaddition.

We have recently reported on the kinetics and mecha-

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[1] This work was supported by a Faculty Research Grant, North Texas State University, Denton, Texas.

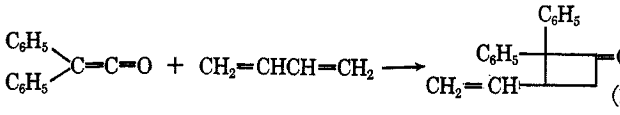
[2] R. N. Lacey, "The Chemistry of Alkenes," S. Patai, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 1197.

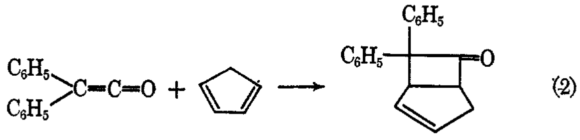
[3] J. C. Martin, P. G. Gott, V. W. Goodlett, and R. H. Hasek, *J. Org. Chem.*, **30**, 4175 (1965).

[4] R. Huisgen, L. Feiler, and G. Binsch, *Angew. Chem. Intern. Ed. Engl.*, **3**, 753 (1964).

nism of the cycloaddition of diphenylketene and dihydropyran.[5] It was reported that the reaction was mixed second order with $\Delta H^* = 9.0 \pm 0.1$ kcal/mole and $\Delta S^* = -43.5 \pm 2.2$ eu. The solvent effect for this reaction was found to be quite small. These results were interpreted to suggest a near-concerted mechanism with perhaps some charge separation in the transition state.

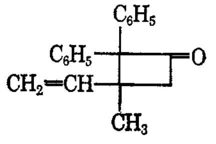
In the present paper we compare the rates of 1,2 cycloaddition of diphenylketene to cyclopentadiene and 1,3-butadiene whose reactivities toward maleic anhydride and 1,1-dichloro-2,2-difluoroethene have already been compared (eq 1 and 2).[6-8] The rates of

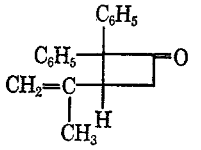

(1)


(2)

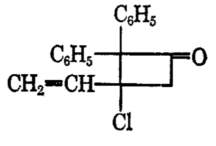
cycloaddition were followed by observing the rate of disappearance of diene by vpc.

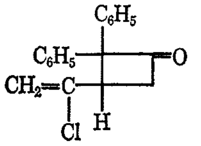
The cycloaddition of diphenylketene and isoprene (2-methyl-1,3-butadiene) can occur to form a 1,2-cycloaddition product or a 3,4-cycloaddition product.


1,2 cycloadduct


3,4 cycloadduct

Likewise, chloroprene (2-chloro-1,3-butadiene) can also form 1,2- and 3,4-cycloaddition products. These cycloadditions were effected in carbon tetrachloride at 40° and the isomer distributions were determined by pmr. All of the structures were determined by a combination of elemental analysis and infrared and pmr spectra.


1,2 cycloadduct


3,4 cycloadduct

Results and Discussion

The cycloaddition of diphenylketene and 1,3-butadiene yielded the 1,2-cycloaddition product, 2,2-diphenyl-3-vinylcyclobutanone. The cycloaddition with cyclopentadiene also produced a 1,2 cycloadduct, 7,7-diphenylbicyclo[3.0.2]hept-2-en-6-one. The rate data in Table I indicate that the cycloaddition with cyclopentadiene proceeds approximately 240 times faster than with 1,3-butadiene.

TABLE I

SECOND-ORDER RATE CONSTANTS FOR THE CYCLOADDITION OF DIPHENYLKETENE AT 30° IN TETRAHYDROFURAN

Diene	$k \times 10^6$, l./mole sec
1,3-Butadiene	1.17 ± 0.05
Cyclopentadiene	280.3 ± 1.00

Similar data have been reported for the Diels–Alder reaction between maleic anhydride and 1,3-butadiene and also for the reaction between maleic anhydride and cyclopentadiene.[6,7] These data show that the rate for Diels–Alder addition of maleic anhydride and cyclopentadiene proceeds approximately 1350 times faster than the reaction of maleic anhydride with 1,3-butadiene.

In a recent review, Huisgen has pointed out that a planar *cis* conformation of the diene system is an absolute prerequisite for the Diels–Alder addition.[9] Aston and co-workers have shown that 1,3-butadiene is a mixture of *cis* and *trans* conformers, with the latter predominating below 300°.[10] In the case of cyclopentadiene, however, the conjugated bonds are fixed in the *cis* position.

Consequently, the observed rate difference for the Diels–Alder reaction would be expected since cyclopentadiene exists in the preferred conformation while 1,3-butadiene exists primarily in the *trans* conformation and must undergo a change in conformation before reaction can occur.

Bartlett and co-workers have recently reported on a mechanistic investigation of the cycloaddition of 1,1-dichloro-2,2-difluoroethene with a variety of dienes.[8,11,12] It was established, quite convincingly, that this reaction was a 1,2 cycloaddition and that a diradical intermediate was formed as the first step in the cycloadditton. Cyclopentadiene was attacked only 70% as fast as 1,3-butadiene instead of being 1350 times as reactive as it is toward maleic anhydride in the Diels–Alder reaction. This indicates that the predominant *trans* conformation of 1,3-butadiene is preferred over the *cis* conformation exhibited by cyclopentadiene, the opposite of that required for the Diels–Alder reaction.

The data presented here for the cycloaddition of diphenylketene with cyclopentadiene and 1,3-butadiene indicate a preferred conformation, namely the *cis* conformer, since cyclopentadiene reacted 240 times faster than 1,3-butadiene. However, an examination of molecular models reveals that cyclopentadiene is preferred on the basis of steric considerations. There appears to be a steric interaction between the vinyl group of 1,3-butadiene and a phenyl group of diphenylketene. There is much less of an interaction in the case of cyclopentadiene because the vinyl group is pinned back out of the way of the phenyl group. Even though it is tempting to relate or correlate this data to a particular mechanism, it seems that the difference in rates that we have observed is probably due largely to steric differences in the two systems.

The cycloaddition of diphenylketene and isoprene yields both the 1,2- and 3,4-cycloaddition products.

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[5] W. T. Brady and H. R. O'Neal, *J. Org. Chem.*, **32**, 612 (1967).

[6] D. Craig, J. J. Shipman, and R. B. Fowler, *J. Am. Chem. Soc.*, **83**, 2884 (1961).

[7] J. Sauer, *Angew. Chem.*, **74**, 252 (1962).

[8] P. D. Bartlett and L. K. Montgomery, *J. Am. Chem. Soc.*, **86**, 628 (1964).

[9] R. Huisgen, R. Grashey, and J. Sauer, "The Chemistry of Alkenes," S. Patai, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 912.

[10] J. G. Aston, G. Szasz, H. W. Woolley, and F. G. Brickwedde, *J. Chem. Phys.*, **14**, 67 (1946).

[11] P. D. Bartlett, L. K. Montgomery, and B. Seidel, *J. Am. Chem. Soc.*, **86**, 616 (1964).

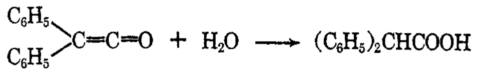
[12] L. K. Montgomery, K. Schueller, and P. D. Bartlett, *ibid.*, **86**, 622 (1964).

The pmr spectrum for the adduct shows two methyl singlets at τ 8.62 and 8.77 appropriate for methyl groups attached to vinylic and to saturated carbon atoms, respectively. The integrated ratio of these two signals was 1:1.5, the methyl substituent attached to saturated carbon giving the stronger signal. This, of course, indicates that the ratio of isomers is 1.5:1 in favor of the 1,2 cycloadduct.

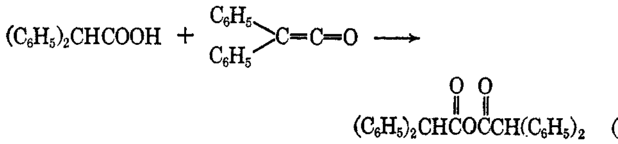
The diphenylketene chloroprene cycloaddition also produced a mixture of the 1,2- and 3,4-cycloaddition products. The pmr spectrum is consistent, with the major product being a mixture of the two isomers. The isomer distribution was determined by the relative areas of the methinyl and methylene signals.

A sample of this adduct was purified by several attempted recrystallizations from hexane and mixtures of hexane and benzene for elemental analysis and pmr so that assignments in the pmr spectrum could be made. Once the assignments for the methinyl (6.07) and methylene (6.75) protons were made, then the pmr spectrum from the reaction solution could be evaluated. The ratio of the areas of methylene to methinyl was 2.5:1, which indicated the isomer distribution was 4:1 in favor of the 3,4 cycloadduct.

A small amount of diphenylacetic anhydride was isolated from the reaction mixture. The formation of this material can readily be explained on the basis of a small amount of water causing the hydrolysis of some diphenylketene, producing diphenylacetic acid which reacts with more ketene to produce the anhydride according to eq 3 and 4.[13]

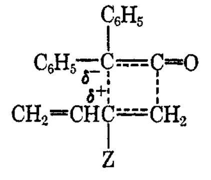


$$\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\!\!>\!C{=}C{=}O + H_2O \longrightarrow (C_6H_5)_2CHCOOH \qquad (3)$$

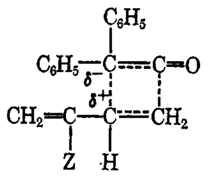


$$(C_6H_5)_2CHCOOH + \begin{matrix}C_6H_5\\C_6H_5\end{matrix}\!\!>\!C{=}C{=}O \longrightarrow (C_6H_5)_2CH\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}CH(C_6H_5)_2 \qquad (4)$$

These isomer distribution studies described above would seem to be very compatible with the previously reported work in that a near-concerted mechanism is able to account for the isomer distributions.[5] If indeed this cycloaddition proceeds by a near-concerted process as suggested, the transition states for cycloaddition with isoprene and chloroprene could be represented as I and II, respectively. In the case of isoprene, the methyl group contributes to the stability of the transition state by being substituted on the carbon atom bearing some carbonium ion character (I). In the other (II), the methyl group is attached to the vinyl system and makes no such contribution. The predominance of 1,2 over 3,4 addition to isoprene is thus expected by a near-concerted process with some charge separation in the transition state.



I



II

Z = Cl or CH_3

With respect to orientation in diphenylketene addition to chloroprene, the results are again well rationalized by a near-concerted process. The 1,2 adduct (I) has the chlorine atom attached to the carbon atom bearing the carbonium ion character and would be expected to destabilize this transition state. On the other hand, the 3,4 adduct (II) has the chlorine atom attached to the vinyl system and considerably less destabilization is expected. The predominance of the 3,4 adduct concurs some dipolar character in the transition state.

Bartlett and co-workers have reported on product distribution studies for 1,2 cycloaddition of 1,1-dichloro-2,2-difluoroethene with isoprene and chloroprene. In both cases, the 1,2 cycloadduct predominated over the 3,4 cycloadduct in a 6:1 ratio. Bartlett suggested that the similarity in orienting effect of chlorine and methyl substituents excludes an intermediate with any important amount of dipolar character but is very consistent with a two-step mechanism *via* a diradical intermediate.[11] The fact that the 1,2 cycloadduct in the chloroprene cycloaddition did not predominate strongly suggests that this cycloaddition is not a two-step process *via* a diradical intermediate.

It seems pertinent to emphasize at this time some previously reported data.[5] We have found that the cycloaddition of diphenylketene and dihydropyran in several different solvents of varying polarity shows only a very small solvent effect. This is interpreted to suggest that this cycloaddition does not proceed *via* a dipolar or zwitterionic intermediate.

Experimental Section

Diphenylketene was prepared by the dehydrochlorination of diphenylacetyl chloride with triethylamine in benzene.[14] The ketene was vacuum distilled prior to each run. Cyclopentadiene was obtained by the destructive distillation of commercially available dicyclopentadiene. The cyclopentadiene was redistilled prior to each run. Dihydropyran and isoprene were commercially available and were freshly distilled before use. Special purity 1,3-butadiene was obtained from Phillips Petroleum Co. and used without further purification. Chloroprene was commercially available as a 50% xylene solution and was distilled (bp 35–40° at 200 mm) before each run. All solvents employed in this study were refluxed over lithium aluminum hydride and distilled under a nitrogen atmosphere through a 30-plate Oldershaw column.

The rates of cycloaddition were followed by observing the rate of disappearance of the dienes by vpc employing *n*-heptane or *n*-nonane as an internal standard. An Aerograph AP-40 operating with a thermal conductivity detector was used with a 10 ft × 0.25 in. column packed with 15% Ucon and 2% Oronite on 30–60 mesh white Chromosorb. A constant-temperature water bath was employed and was heated with an immersion heating element coupled to a Fisher proportional temperature controller which afforded a temperature control of ±0.02°. Least-square rate constants were calculated on an IBM 1620 computer. Pmr determinations were obtained on a Varian A-60 instrument.

Diphenylketene and Cyclopentadiene Cycloaddition.—To a 30-ml reaction bottle containing 0.779 g (0.0119 mole) of cyclopentadiene was added 21 ml of THF and 2 ml of *n*-nonane as an internal reference. The solution was placed in the temperature bath at 30° and allowed to equilibrate. A 1.136-g (0.00585 mole) portion of diphenylketene was then added by means of hypodermic syringe. The rate of cycloaddition was followed by observing the rate of disappearance of diene by vpc.

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[13] It is interesting to note that about 2 mg of water would result in the formation of about 50 mg of diphenylacetic anhydride.

[14] H. Staudinger, *Ber.*, **44**, 1619 (1911).

At the conclusion of the reaction, the solution was washed with dilute sodium carbonate solution, water, and dried over anhydrous magnesium sulfate. After filtration, the solution was evaporated with stirring under a nitrogen atmosphere. There was obtained 6.1 g (91%) of 7,7-diphenylbicyclo[3.0.2]hept-2-en-6-one, mp 87.5–89° (lit.[15] mp 88–89°).

Diphenylketene and 1,3-Butadiene Cycloaddition.—A solution of 150 ml of THF and 25 ml of *n*-heptane was saturated with 1,3-butadiene. This resulted in a 2.02 *M* solution of diene in THF. A 21-ml portion of this solution was placed into a reaction bottle and 4.36 g (0.022 mole) of diphenylketene was added. This resulted in a reaction solution which was 1.74 *M* in diene and 0.899 *M* in diphenylketene. The rate of cycloaddition at 30° was followed by observing the rate of disappearance of 1,3-butadiene by vpc.[16]

At the conclusion of the cycloaddition, the solution was washed with a dilute sodium hydroxide solution, water, and dried over anhydrous magnesium sulfate. After filtration, the solution was evaporated with stirring under a nitrogen atmosphere. The resultant oil was recrystallized from heptane. There was obtained 3.0 g (55%) of 2,2-diphenyl-3-vinylcyclobutanone as a white solid which melted at 52–55°. Infrared analysis showed a cyclobutanone–carbonyl absorption at 1780 cm^{-1} and a carbon–carbon unsaturation at 1595 cm^{-1}. A pmr spectrum revealed a multiplet centered at τ 2.8 (aromatic protons), a multiplet at 4.8 (vinyl protons), a multiplet centered at 6.3 (methinyl proton), and a multiplet centered at 7.0 attributed to the nonequivalent methylene protons. The protons were in a ratio of 10:3:1:2.

Anal. Calcd for $C_{18}H_{16}O$: C, 87.10; H, 6.45. Found: C, 87.1; H, 6.29.

Diphenylketene and Isoprene Cycloaddition.—To a solution containing 3.4 g (0.050 mole) of isoprene in 16 ml of carbon tetrachloride was added 4.0 g (0.020 mole) of diphenylketene. This solution was maintained at 40° for 10–12 days.[17] The reaction solution was then washed with dilute sodium hydroxide solution, water, and dried over anhydrous magnesium sulfate. After filtration, a portion of the filtrate was taken for a pmr determination. The remainder of the filtrate was evaporated under a nitrogen atmosphere yielding an oil. There was obtained 3.8 g (70%) of mixed isomers which could not be recrystallized.

Infrared analysis of the oil showed an absorption at 1780 cm^{-1} (cyclobutanone–carbonyl) and one at 1595 cm^{-1} (carbon–carbon unsaturation). A pmr spectrum of the carbon tetrachloride filtrate containing the mixed isomers showed a multiplet at τ 2.8 (aromatic protons), multiplets at 3.9 and 4.9 (vinyl protons), a multiplet at 6.05 (methinyl proton), a multiplet centered at 6.95 (methylene protons), and singlets at 8.62 and 8.77 (methyl protons attached to vinylic and to saturated carbon atoms, respectively). The methyl signals were in the ratio of 4:6 with the methyl substituent attached to saturated carbon giving the stronger signal. This gives an isomer distribution of 1.5:1 of 1,2 adduct over 3,4 adduct.

Anal. Calcd for $C_{19}H_{18}O$: C, 87.02; H, 6.87. Found: C, 86.90; H, 6.60.

Diphenylketene and Chloroprene Cycloaddition.—A solution containing 3.8 g (0.043 mole) of freshly distilled chloroprene in 17 ml of carbon tetrachloride was treated with 4.0 g (0.020 mole) of diphenylketene. The resultant solution was maintained at 40° for 2 weeks.[18] The reaction solution was then washed with dilute sodium carbonate solution, water, and dried over anhydrous magnesium sulfate. After filtration, an aliquot of the filtrate was removed for a pmr determination. Evaporation of the remaining filtrate yielded 5 g of an oil. Numerous efforts to crystallize the cycloadduct were unsuccessful but the original oil was separated into three components as a result of these attempted recrystallizations from hexane and hexane–benzene mixtures.

One component was shown to be the dimer of chloroprene by comparison of the pmr spectrum to the spectrum of chloroprene dimer. A second component was shown to be diphenylacetic anhydride. Pmr spectrum showed a multiplet at τ 2.85 (aromatic protons) and a singlet at 5.1 (methinyl proton). These signals were in the ratio of 10:1, respectively. The melting point of this crystalline material was 97–98° (lit.[19] mp 98°). The third component was shown to be the mixed isomers of the cycloaddition of diphenylketene and chloroprene. Infrared analysis showed the cyclobutanone carbonyl absorption at 1790 cm^{-1} and also the double bond stretching occurring at 1600 cm^{-1}. The pmr spectrum in carbon tetrachloride showed a multiplet at τ 2.82 (aromatic protons), a multiplet centered at 5.2 (vinyl protons), a multiplet centered at 6.0 (methinyl proton), and a multiplet centered at 6.75 (methylene protons). The area ratios were 16:3:1:2.5.

Anal. Calcd for $C_{18}H_{15}ClO$: C, 76.46; H, 5.31. Found: C, 75.8; H, 5.17.

The pmr spectrum of the reaction solution as described above had a ratio of methylene protons to the methinyl proton of 2.5:1. This means the isomer distribution is 4:1 in favor of the 3,4-cycloaddition product.

Registry No.—Diphenylketene, 525-06-4; 7,7-diphenylbicyclo[3.0.2]hept-2-en-6-one, 5452-28-8; 2,2-diphenyl-3-vinylcyclobutanone, 13368-81-5; 1,2 adduct of diphenylketene with isoprene, 13368-82-6; 3,4 adduct of diphenylketene with isoprene, 13368-83-7; 1,2 adduct of diphenylketene with chloroprene, 13368-84-8; 3,4 adduct of diphenylketene with chloroprene, 13368-85-9.

Acknowledgment.—The authors wish to express their gratitude to Dr. William H. Glaze for discussing the pmr spectra.

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[15] L. I. Smith, C. L. Agre, R. M. Leekley, and W. W. Prichard, *J. Am. Chem. Soc.*, **61**, 7 (1939).

[16] A control run was made to determine the degree of dimerization of 1,3-butadiene under these conditions. Dimerization occurred to approximately 15% during the course of the reaction. A plot of per cent dimerization against time gave a linear relationship over the period of time for which the rate of reaction was followed. This plot was utilized to obtain correction factors for determining the diene concentration at each sampling point in the reaction.

[17] The amount of dimerization of isoprene was found to be negligible under these reaction conditions.

[18] Chloroprene dimerized to the extent of about 20% as was shown by pmr.

[19] C. D. Hurd, R. Christ, and C. L. Thomas, *J. Am. Chem. Soc.*, **55**, 2589 (1933).