# Halogenated Ketenes. 37. The Synthesis of Pyranones Utilizing the (4 + 2) Cycloaddition of Ketenes and Siloxy Dienes



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The reaction of diphenyl-, dichloro-, and chloroketenes with several siloxy dienes results in (4 + 2) and/or (2 + 2) cycloaddition products depending primarily on substitution in the diene. The (4 + 2) cycloaddition products are easily hydrolyzed to pyranones. These results are discussed in terms of a dipolar intermediate.

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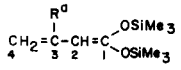
There are numerous reports in the literature on the cycloaddition of ketenes and conjugated dienes to yield (2 + 2) cycloaddition products (1). Since the synthetic methodologies for substituted vinylketene acetals have been published (2-5) the sythetic applicabilities of these dienes through Diels Alder-type cycloaddition reactions have recently enjoyed considerable attention (6,7). However, there are few reports in the literature dealing with (4 + 2) cycloaddition reactions of ketenes and dienes. Gouesnard reported the (4 + 2) cycloaddition of diphenylketene with alkoxy conjugated dienes and in an earlier report Martin, *et al.* reported the (4 + 2) cycloaddition of 2-methoxy-1,3-butadiene with both dimethyl- and diphenylketenes (8,9). This report describes a study of the reaction of ketenes with various alkoxy and trimethylsiloxy substituted conjugated dienes to yield (4 + 2) cycloaddition products which upon hydrolysis yield pyranones.

Table I

Bis-(trimethylsiloxy)-1,3-butadienes (Id, Ie)



| Compound | R | % Yield | Bp/mm | Molecular Formula | Analyses % Calcd./Found C | H |
|---|---|---|---|---|---|---|
| Id | $CH_3$ | 74 | 60-62/1 | $C_{11}H_{24}O_2Si_2$ | 54.10 | 9.84 |
| | | | | | 53.97 | 10.07 |
| Ie | H | 9 (a) | 42-44/0.05 | $C_{10}H_{22}O_2Si_2$ | 52.17 | 9.57 |
| | | | | | 52.30 | 9.40 |

(a) All efforts to improve the yield of this diene failed. *C*-Silylation competes favorably with *O*-silylation.

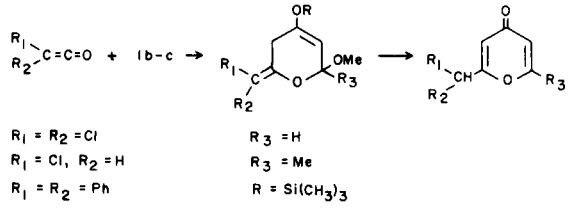
IR and $^1$H NMR Spectral Data

| Compound | IR, $cm^{-1}$ (Neat) | $^1$H NMR (deuteriochloroform) |
|---|---|---|
| Id | 1645, 1605, 920, 850 | 0.15, (s, 9 H), 0.20 (s, 9 H), 1.76 (s, 3 H), 4.05 (s, 1 H), 4.29 (s, 1 H), 4.50 (s, 1 H) |
| Ie | 1640, 1600, 920, 850 | 0.15, 0.17 (s, s, 18 H), 4.35 (m, 2 H), 4.65 (d, 1 H), 6.25 (m, 1 H) |

$^{13}$C NMR Spectral Data
(Deuteriochloroform - 76.9)

| Compound | C-1 | C-2 | C-3 | C-4 | C-a | Other atoms |
|---|---|---|---|---|---|---|
| Id | 151.4 | 87.1 | 140.4 | 107.1 | 23.2 | 0.3, −0.3 |
| Ie | 152.4 | 87.2 | 132.8 | 106.5 | − | 0.3 |

The ketenes employed in this study were dichloro-, chloro-, and diphenylketenes. The two chloroketenes are unstable and were generated *in situ* in the presence of the dienes from dichloroacetyl chloride and chloroacetyl chloride respectively using triethylamine. Diphenylketene is an isolable ketene and was prepared and freshly distilled prior to each cycloaddition reaction.

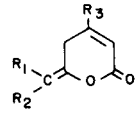


Dichloro-, chloro-, and diphenylketenes reacted smoothly with dienes Ib and Ic to yield the corresponding dihydropyrans which upon heating or methanolic hydrolysis yielded the substituted 4-pyranones in good overall yields as described in a preliminary communication (10).

Diphenylketene reacted with Ia in a similar manner except the (4 + 2) cycloaddition product upon hydrolysis yielded the dihydro-2-pyranone, IIa, which readily rearranged to the 2-pyranone, IIIa, upon treatment with triethylamine. Refluxing the dihydropyranone in benzene overnight did not result in conversion to the 2-pyranone; how-

Table II

Substituted-5,6-dihydro-2*H*-pyran-2-ones



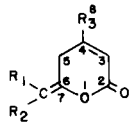
| Compound | $R_1$ | $R_2$ | $R_3$ | % Yield | Mp °C | Molecular Formula | Analyses % Calcd./Found C | H |
|---|---|---|---|---|---|---|---|---|
| IIa | Ph | Ph | OMe | 56 | 164-165 | $C_{19}H_{16}O_3$ | 78.08 | 5.48 |
| | | | | | | | 78.27 | 5.36 |
| IIb (a) | Cl | Cl | OMe | 30 | 129-130 | $C_7H_6Cl_2O_3$ | 40.38 | 2.88 |
| | | | | | | | 40.29 | 2.97 |
| IIc (a) | Cl | H | OMe | 23 | 47-57 | $C_7H_7ClO_3$ | 48.27 | 4.02 |
| | | | | | | | 47.87 | 4.10 |
| IId | Ph | Ph | Me | 68 | 123-124 | $C_{19}H_{16}O_2$ | 82.61 | 5.80 |
| | | | | | | | 82.85 | 5.74 |

(a) The yields reported are at 0°; at room temperature the yields are somewhat lower. The yield of acyclic product is 34% and 48% respectively in addition to IIb and IIc.

IR and $^1$H NMR Spectral Data

| Compound | IR, $cm^{-1}$ (film) C=C | C=O | $^1$H NMR (deuteriochloroform) |
|---|---|---|---|
| IIa | 1600, 1635 | 1710 | 3.20 (s, 2 H), 3.52 (s, 3 H), 5.03 (s, 1 H), 7.0 (10 H) |
| IIb | 1624, 1645 | 1730 | 3.4 (s, 2 H), 3.72 (s, 3 H), 5.1 (s, 1 H) |
| IIc | 1620, 1660 | 1720 | 3.15 (s, 2 H), 3.63 (s, 3 H), 5.02 (s, 1 H), 5.23 (s, 1 H) |
| IIc | 1620, 1660 | 1720 | 3.15 (s, 2 H), 3.63 (s, 3 H), 5.02 (s, 1 H), 5.23 (s, 1 H) |
| IId | 1635, 1640 | 1740 | 1.79 (s, 3 H), 3.08 (s, 2 H), 5.66 (s, 1 H), 7.0 and 71.08 (10 H) |

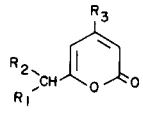
$^{13}$C NMR Spectral Data of Compounds IIa-d
(Deuteriochloroform, 77.00)



| Compound | C-2 | C-3 | C-4 | C-5 | C-6 | C-7 | C-8 | Other C-atoms |
|---|---|---|---|---|---|---|---|---|
| IIa | 171.3 | 88.9 | 139.7 | 30.6 | 163.4 | 124.7 | 56.0 | 129.9, 129.8, 128.4, 128.1, 127.7, 127.3, 126.8 |
| IIb | 169.9 | 88.8 | 140.7 | 29.3 | 161.0 | 107.3 | 56.5 | — |
| IIc | 170.5 | 88.9 | 143.8 | 30.3 | 161.9 | 99.2 | 56.4 | — |
| IId | 161.6 | 114.9 | 141.7 | 32.6 | 156.8 | 124.4 | 22.5 | 139.2, 137.8, 130.2, 130.0, 128.6, 127.9, 127.5, 127.0 |

Table III

Substituted 2-pyranones



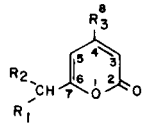
| Compound | $R_1$ | $R_2$ | $R_3$ | % Yield | Mp °C | Molecular Formula | Analyses % Calcd./Found C | H |
|---|---|---|---|---|---|---|---|---|
| IIIa | Ph | Ph | OMe | 95 | 129-130 | $C_{19}H_{16}O_3$ | 78.08 | 5.48 |
| | | | | | | | 77.98 | 5.55 |
| IIIb | Cl | Cl | OMe | 96 | 132-133 | $C_7H_6Cl_2O_3$ | 40.38 | 2.88 |
| | | | | | | | 40.30 | 2.96 |
| IIIc | Cl | H | OMe | 89 | 120-121 | $C_7H_7ClO_3$ | 48.27 | 4.02 |
| | | | | | | | 48.21 | 4.26 |
| IIId | Cl | H | OMe | 89 | 142-143 | $C_{19}H_{16}O_2$ | 82.61 | 5.80 |
| | | | | | | | 82.64 | 5.94 |
| IIIe | Cl | Cl | Me | 31 (a) | 122-123 | $C_7H_6Cl_2O_2$ | 43.54 | 3.11 |
| | | | | | | | 43.76 | 3.13 |

(a) In addition to this product a 55% yield of the (2 + 2) cycloadduct, Va, was formed.

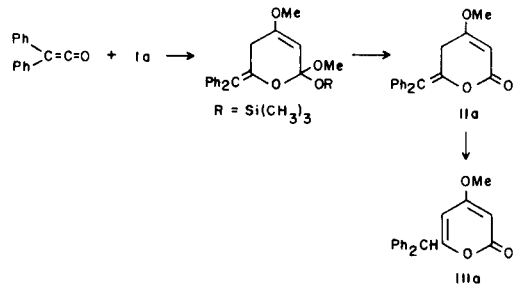
IR and $^1$H NMR Spectral Data

| Compound | IR, $cm^{-1}$ (film) C=C | C=O | $^1$H NMR (deuteriochloroform) |
|---|---|---|---|
| IIIa | 1600, 1640 | 1720 | 3.6 (s, 3 H), 5.0 (s, 1 H), 5.25 (d, 1 H), 5.45 (d, 1 H), 7.0 (m, 10 H) |
| IIIb | 1658 | 1719 | 3.69 (s, 3 H), 5.30 (d, 1 H), 6.01 (s, 1 H), 6.09 (d, 1 H) |
| IIIc | 1620, 1665 | 1730 | 3.67 (s, 3 H), 4.07 (s, 2 H), 5.26 (d, 1 H), 5.86 (d, 1 H) |
| IIId | 1600, 1640 | 1720 | 1.97 (s, 3 H), 4.98 (s, 1 H), 5.48 (s, 1 H), 5.70 (s, 1 H), 7.00 (m, 10 H) |
| IIIe | 1620, 1640 | 1720 | 2.15 (s, 3 H), 5.92 (s, 1 H), 6.13 (s, 1 H), 6.19 (s, 1 H) |

$^{13}$C NMR Spectral Data of Compounds IIIa-e
(Deuteriochloroform, 77.00)



| Compound | C-2 | C-3 | C-4 | C-5 | C-6 | C-7 | C-8 | Other C-atoms |
|---|---|---|---|---|---|---|---|---|
| IIIa | 170.8 | 87.9 | 164.2 | 102.5 | 166.0 | 55.3 | or 55.8 | 138.9, 128.9, 128.7, 127.3 |
| IIIb | 169.9 | 90.3 | 157.5 | 100.9 | 162.1 | 64.8 | 56.4 | — |
| IIIc | 170.5 | 89.4 | 158.7 | 101.9 | 163.4 | 40.9 | 56.1 | — |
| IIId | 165.0 | 108.0 | 155.7 | 111.2 | 162.5 | 55.4 | 21.4 | 139.2, 129.0, 128.6, 127.3 |
| IIIe | 160.2 | 106.2 | 155.2 | 114.5 | 156.4 | 65.2 | 21.5 | — |

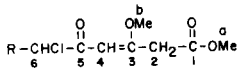


ever, a trace of triethylamine resulted in this rearrangement at room temperature.

Dichloroketene and chloroketene reacted with this diene to yield an acyclic product, IVa-b, as well as the dihydro-2-pyranone, IIb-c. The dihydro-2-pyranones were smoothly converted to the corresponding 2-pyranones by treatment with triethylamine to yield IIIb-c as indicated above. The use of a 10% excess of amine to generate the ketenes resulted in the isolation of the 2-pyranones from

Table IV

Methyl 6-Chloro-5-keto-3-methoxy-3-hexenoates



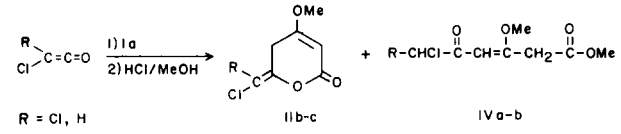
| Compound | R | % Yield | Molecular Formula | Analyses % Calcd./Found C | H |
|---|---|---|---|---|---|
| IVa | Cl | 34 | $C_8H_{10}Cl_2O_4$ | 39.83 | 4.15 |
| | | | | 39.48 | 4.32 |
| IVb | H | 48 | $C_8H_{11}ClO_4$ | 46.60 | 5.34 |
| | | | | 46.89 | 5.59 |

IR and $^1$H NMR Spectral Data

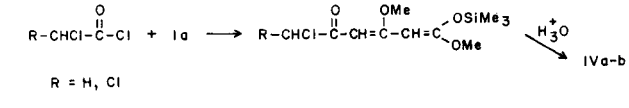
| | IR, $cm^{-1}$ (film) | $^1$H NMR (deuteriochloroform) |
|---|---|---|
| IVa | 1595, 1690, 1740 | 3.55 (s, 2 H), 3.65 (s, 3 H), 3.68 (s, 3 H), 5.63 (s, 1 H), 5.75 (s, 1 H) |
| IVb | 1590, 1680, 1735 | 3.58 (s, 2 H), 3.65 (s, 3 H), 3.66 (s, 3 H), 3.92 (s, 2 H), 5.68 (s, 1 H) |

$^{13}$C NMR Spectral Data
(Deuteriochloroform, 77.00)

| Compound | C-1 | C-2 | C-3 | C-4 | C-5 | C-6 | C-a | C-b |
|---|---|---|---|---|---|---|---|---|
| IVa | 185.4 | 39.0 | 168.2 | 94.0 | 172.7 | 70.7 | 56.4 | 51.8 |
| IVb | 189.8 | 38.5 | 168.4 | 96.6 | 169.6 | 48.6 | 55.8 | 51.4 |

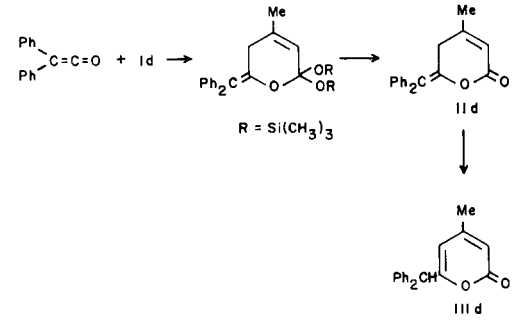


the reaction mixture. The acyclic product is the result of a reaction between the diene and the acid halide from which the chloroketenes were generated. This was demonstrated by the reaction of dichloroacetyl and chloroacetyl chlorides reacting with Ia to yield the acyclic product. A similar

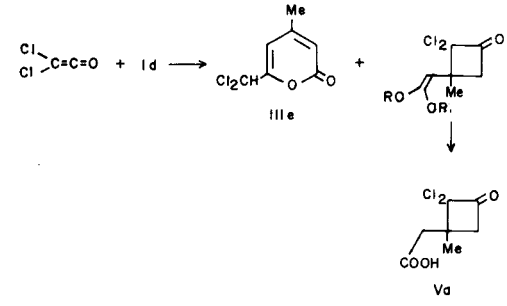


reaction of this type of diene with acetyl chloride has previously been reported (11).

3-Methyl-1,1-bis(trimethylsiloxy)-1,3-butadiene, Id, reacted with diphenylketene to yield the dihydropyran which upon hydrolysis yielded the dihydro-2-pyranone, IId, which also readily underwent rearrangement to the 2-pyranone, IIId, upon treatment with triethylamine.

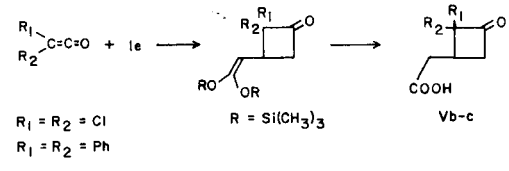


This diene reacted with dichloroketene to yield both a (4 + 2) and a (2 + 2) cycloaddition product. The use of an excess of triethylamine to generate dichloroketene resulted in isolation of a 31% yield of the 2-pyranone, IIIe (12).



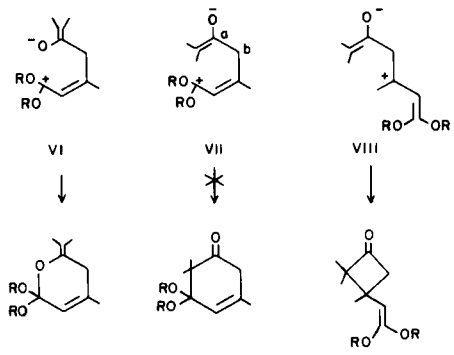
The cyclobutanone was obtained in 55% yield and was characterized after hydrolysis to the corresponding acid, Va.

The cycloaddition of 1,1-bis(trimethylsiloxy)-1,3-butadiene, Ie, with dichloro and diphenylketenes resulted in only the (2 + 2) cycloaddition products. The cyclobutanone from diphenylketene was hydrolyzed and characterized as the corresponding anilide. Considerable difficulty was encountered in the purification of the cyclobutanone and the derivatives derived from dichloroketene and Ie.



The most reasonable explanation accounting for the above described products involves the initial formation of a dipolar intermediate from the nucleophilic attack of the conjugated diene on the electrophilic sp-hybridized carbon atom of the ketene molecule. A consideration of the conformations of the dipolar intermediate which would lead to a (4 + 2) cycloadduct reveals that the steric interaction between the ketene substituents and the substituents in the 1-position of the diene in conformer VII prevents ring-closure to yield the cyclohexenone derivative, *i.e.*, the rotation around the Ca—Cb bond is much faster than the ring-closing step. The steric congestion in VI is

minimized and cyclization occurs readily to give the dihydropyran. Conformer VIII would be expected to be the




precursor to the (2 + 2) cycloaddition product, the cyclobutanone. Apparently, a substituent in the 3-position of the diene as well as the substituent on the ketene exerts a strong influence on the second ring closing step. Diphenylketene undergoes (4 + 2) cycloaddition with all four of the 3-substituted dienes studied but a (2 + 2) cycloaddition with the unsubstituted diene, Ie. Dichloroketene underwent a (4 + 2) and (2 + 2) cycloaddition with the 3-methyl derivative and only (2 + 2) cycloaddition when the 3-position was unsubstituted.

In conclusion the specified ketenes and alkoxy or siloxy conjugated dienes readily undergo (4 + 2) cycloaddition reactions to yield dihydropyrans which are easily hydrolyzed to 4-pyranones or 2-pyranones depending on substitution in the diene. Substitution in the 3-position of the diene plays a significant role in the ring-closing step of the diolar intermediate and determines whether (4 + 2) or (2 + 2) cycloaddition occurs. The described (4 + 2) cycloaddition reactions of ketenes and dienes represents a new and versatile synthetic route to 4-pyranones and 2-pyranones (13).

## EXPRIMENTAL

Proton nmr and $^{13}C$ nmr spectra were recorded on a Perkin-Elmer R-24-B and a Jeol FX-90Q FT respectively employing deuteriochloroform as the solvent with tetramethylsilane as the internal standard. The infrared spectra were obtained on a Beckmann 1330 spectrophotometer.

All solvents and triethylamine were dried and purified by distillation from sodium-potassium alloy prior to use. Chloroacetyl and dichloroacetyl chlorides were distilled just prior to use for best results. Diphenylketene was prepared from diphenylacetyl chloride and freshly distilled prior to each cycloaddition.

Trimethylsilyl 3,3-dimethylacrylate (14).

A 39.1 g (0.24 mole) portion of hexamethyldisilazane was added to a stirred solution of 24.3 g (0.24 mole) of 3,3-dimethylacrylic acid in 50 ml of dry THF and 13 ml of pyridine at 0° under a nitrogen atmosphere. This was followed by the dropwise addition of 12.8 g (0.12 mole) of chlorotrimethylsilane, and stirring was continued at room temperature for another 17 hours. The reaction mixture was then filtered through Celite, concentrated on a rotatory evaporator and vacuum distilled at 38-39° (2 mm) to give 30 g (71%) of the ester; ir (neat): 1690, 1645, 850 $cm^{-1}$; $^1H$ nmr: $\delta$ 0.22 (s, 9H), 1.74 (s, 3H), 2.00 (s, 3H), 5.39 (s, 1H).

Trimethylsilyl Crotonate (14).

A 39.1 g (0.24 mole) portion of hexamethyldisilazane was added to a stirred solution of 20.7 g (0.24 mole) of crotonic acid in 50 ml of dry THF and 13 ml of pyridine at 0° under a nitrogen atmosphere. This was followed by the dropwise addition of 12.8 g (0.12 mole) of chlorotrimethylsilane and stirring was continued at room temperature for another 17 hours. The reaction mixture was then filtered through Celite, concentrated on a rotatory evaporator, and distilled at 42-44° (9 mm) to yield 30 g (80%) of the ester; ir (neat): 1700, 1650, 850 $cm^{-1}$; $^1H$ nmr: $\delta$ 0.2 (s, 9H), 1.67 and 1.78 (2 d, 3H), 5.3 and 5.54 (2 d, 1H), 6.2-6.82 (m, 1H).

1,1-Bis(trimethylsiloxy)-3-methylbutadiene (Id).

To a solution of LDA (0.172 mole) (15) cooled in a dry ice-acetone bath, was added 29.5 g (0.172 mole) of trimethylsilyl 3,3-dimethylacrylate over a 10-minute period. The solution was stirred for about 30 minutes and then quenched with 55 ml (0.43 mole) of chlorotrimethylsilane which was added fairly rapidly over a 10-minute period. The mixture was allowed to warm to room temperature, and stirred for an additional 2 hours. The solution was then filtered through Celite and concentrated on a rotatory evaporator and distilled.

1,1-Bis(trimethylsiloxy)butadiene (Ie).

To a solution of LDA (0.1 mole), cooled in a dry ice-acetone bath, was added 15.8 g (0.1 mole) of trimethylsilyl crotonate over a 5-minute period. The solution was stirred for about 30 minutes, and then quenched with 32 ml (0.25 mole) of chlorotrimethylsilane which was added fairly rapidly over a 5-minute period. The mixture was allowed to warm to room temperature, and stirred for an additional 2 hours. The solution was then filtered through Celite, and concentrated on a rotatory evaporator and distilled.

Typical Procedure for Dichloroketene and Chloroketene Cycloadditions with the Dienes.

A solution of 0.0275 mole of freshly distilled dichloroacetyl chloride or chloroacetyl chloride in 50 ml of dry ether was added over a 1 hour period to a stirred solution of 0.025 mole of diene and 0.025 mole of triethylamine in 250 ml of dry ether at 22-25° under a nitrogen atmosphere. The resulting mixture was stirred for an additional 30-minute period after the addition was complete. The amine salt was removed by filtration and the filtrate concentrated on a rotatory evaporator. Hydrolysis was accomplished by dissolving the residue in 5-6 ml of dry methanol and adding 3-4 drops of concentrated hydrochloric acid. This solution was stirred for 2 hours and the methanol removed under vacuum. The cycloadduct was purified by column chromatography on Sargent Welch silica gel 60, 70-230 mesh using ether/petroleum ether (1:9) as eluent.

Typical Procedure for the Cycloaddition of Diphenylketene with the Dienes.

To a stirred solution of 0.25 mole of the diene in 15-20 ml of dry ether was added 0.025 mole of diphenylketene under a nitrogen atmosphere at 22-25°. The reaction was monitored by ir, and when the ketene band at 2100 $cm^{-1}$ had disappeared (usually about 15-20 minutes after the addition), the ether was evaporated under reduced pessure and the residue hydrolyzed with 5-6 ml of methanolic hydrogen chloride. The residue was purified by column chromatography as described above.

2-(2,2-Dichloro-1-methyl-3-oxocyclobutyl)acetic Acid (Va).

This compound was derived from dichloroketene and Id and obtained as outlined in the general procedure to yield 2.9 g (55%), mp 99.5-100°; ir (film): 1710, 1805 $cm^{-1}$; $^1H$ nmr: $\delta$ 1.49 (s, 3H), 2.83 (s, 2H), 2.89 (d, 1H), 3.42 (d, 1H), 10.70 (s, 1H); $^{13}C$ nmr (deuteriochloroform, 77.0 ppm): 1-176.7, 2-54.4, 1'-43.1, 2'-92.1, 3'-192.3, 4'-41.0, 5'-23.1.

*Anal.* Calcd. for $C_7H_8Cl_2O_3$: C, 40.00; H, 3.81. Found: C, 39.81; H, 3.99.

2-(2,2-Diphenyl-3-oxocyclobutyl)acetanilide.

The acid resulting from the chromatographed and hydrolyzed cycloadduct from 0.7 g (0.003 mole) of Ie and 0.6 g (0.003 mole) of diphenyl-

ketene, was treated with thionyl chloride in refluxing benzene for 6 hours. The benzene and excess thionyl chloride were removed under vacuum and the residue was dissolved in benzene (10 ml) and 1 ml of aniline was added dropwise at room temperature. The reaction was stirred for another 5 hours and then concentrated under vacuum. The oily residue was crystallized from hot benzene and hexane to yield 0.2 g (19% based on diene or ketene) with mp 155-156°; ir (film): 3200-3500, 1765, 1650 $cm^{-1}$; $^1H$ nmr: $\delta$ 2.32 (d, 2H), 2.80-3.60 (m, 3H), 3.9 (quintet, 1H), 5.06 (s, 1H), 7.13 (m, 15H); $^{13}C$ nmr (deuteriochloroform, 77.0 ppm): 1-169.4, 2-49.7, 1'-31.5, 2'-78.1, 3'-208.8, 4'-40.4, other atoms - 140.2, 139.0, 137.5, 128.9, 128.5, 127.9, 127.4, 127.1, 124.6, 124.3, 120.0.

*Anal.* Calcd. for $C_{24}H_{21}NO_2$: C, 81.13; H, 5.92; N, 3.94. Found: C, 81.09; H, 5.95; N, 4.11.

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