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Photochemistry of Cyclopropene Derivatives. Synthesis and Photorearrangement of a 3-Acyl-Substituted Cyclopropene

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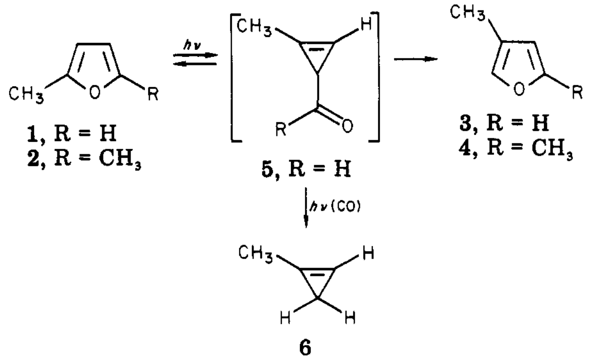
Two different approaches toward the synthesis of a 3-acyl-substituted 1,2,3-triphenylcyclopropene were investigated. The first involved treating triphenylcyclopropenyl perchlorate with the anion derived from 1,3-dithiane followed by hydrolysis of the resulting dithioacetal. Unfortunately, all attempts to obtain a carbonyl compound from the hydrolysis failed. The only product obtained corresponded to a 1,2-diphenyl-1,2-diacyl-substituted alkene. The second approach utilized for the synthesis involved treating 3-cyano-1,2,3-triphenylcyclopropene with methyllithium. The addition proceeded quite smoothly to give the desired 3-acetyl derivative in high yield. Irradiation of 1,2,3-triphenyl-3-acetylcyclopropene in benzene afforded a mixture of 2,3,4-triphenyl-2-cyclopentenone (60%), 2-methyl-3,4,5-triphenylfuran (27%), and 3-acetyl-1,2-diphenylindene (13%). The formation of the three products obtained can be rationalized in terms of a vinylcarbene intermediate. Several different pathways are available to this species, depending on the stereochemistry about the double bond and on the conformation the oxygen atom assumes in the cis intermediate. The formation of the 2-cyclopentenone derivative provides good support for the mechanism proposed some years ago to rationalize the photochemical rearrangement of 2,5-dimethylfuran.

Considerable interest has been focused in recent years on phototransposition reactions which have the net effect of interchanging atoms within a five-membered ring.[1,2] Examples have been reported for variously substituted heterocycles[3-8] and cyclopentadiene derivatives.[9-11] Bicyclo[2.1.0]pent-2-enes and 3-vinylcyclopropene analogues are the most commonly invoked intermediates responsible for these rearrangements; in some instances, such molecules have been detected and characterized.[12-16] A number of examples involving the photorearrangement of furans have been reported in the literature,[16-23] and some effort has been directed toward understanding the mechanism of this process. Investigations by Srinivason[18] and van Tamelen[16,17] have shown that the photorearrangement proceeds via a ring contraction–ring expansion route. For example, 2-methyl- (1) and 2,5-dimethylfuran (2) photoisomerize (Scheme I) to 3-methyl- (3) and 2,4-dimethylfuran (4). The reaction proceeds via an initial valence tautomerization of the furan to an acylcyclopropene followed by ring expansion.[16-18] Support for a ring-contracted species was obtained by the isolation of cyclopropene 6, which was suggested to be derived by loss of carbon monoxide from a transient cyclopropenecarboxyaldehyde.[18] In fact, when the 2- and 5-positions of the furan ring were substituted with alkyl groups, the ring-contracted product was sufficiently stable to be isolated. 3-Vinyl-substituted cyclopropenes are known to undergo photochemical reorganization to cyclopentadiene derivatives,[24-29] thereby providing a good analogy for the ring expansion of the acyl

Scheme I



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* John S. Simon Guggenheim Memorial Fellow, 1981–1982.

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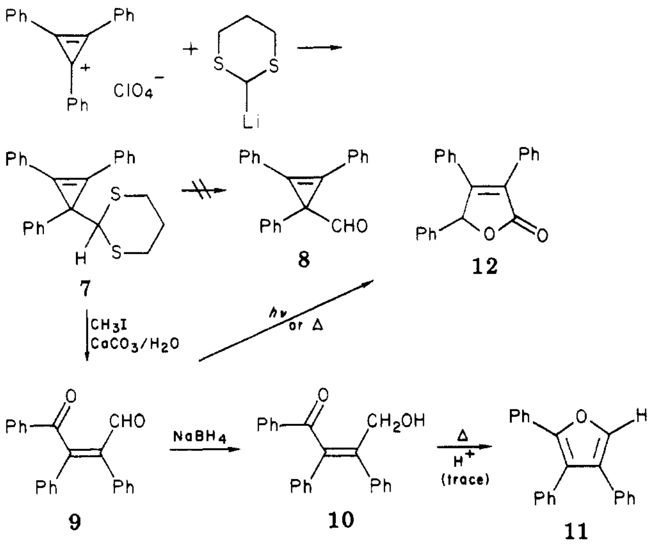
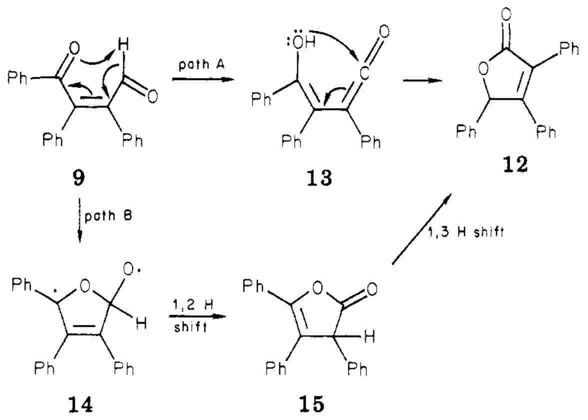
Scheme II

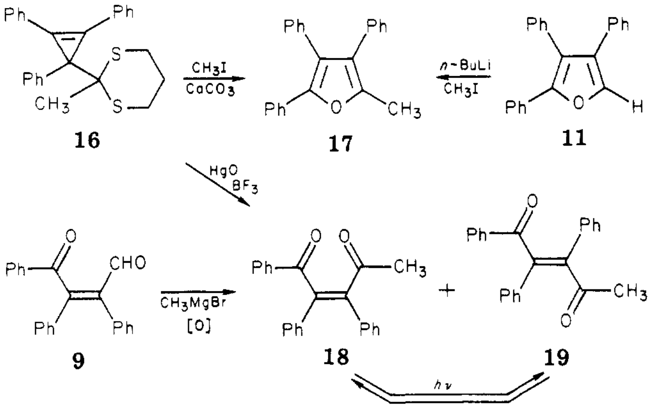


cyclopropene. Recent MO calculations predict that the photochemical opening of the cyclopropene ring should produce a vinylcarbene intermediate.[30] The vinylcarbene species can undergo reactions characteristic of a singlet or triplet methylene.[31] These include intramolecular hydrogen abstraction,[32,33] insertion into a C–H bond,[34] alkyl group migration,[35] and electrocyclization.[24-29] In view of our interest in the chemistry of cyclopropenes containing π-unsaturated groups,[36] we initiated a study exploring the photochemical rearrangement of 3-acylcyclopropenes to furan derivatives. We report here the results of this study which show that this system can react via several different pathways.

Scheme III



Scheme IV



Results and Discussion

Earlier reports in the literature have shown that 3-substituted 1,2-diphenylcyclopropenes can be prepared by treating variously substituted cyclopropenyl cations with Grignard reagents.[37] In an attempt to prepare several 3-acyl-substituted cyclopropenes by an analogous route, we treated triphenylcyclopropenyl cation with the anion derived from 1,3-dithiane. We planned to hydrolyze the resulting cyclopropenyl-substituted dithiane to the desired carbonyl compound. This two-step sequence was particularly attractive since it appeared adaptable to the preparation of a number of acylcyclopropene derivatives which would be required for our photochemical studies. When dithiane 7 was allowed to react with methyl iodide in the presence of aqueous calcium carbonate, the expected aldehyde 8 was not obtained, but rather, a new compound, 9 (mp 160–161 °C), was isolated in 85% yield (Scheme II). On the basis of its molecular formula ($C_{22}H_{16}O_2$) and spectroscopic properties, this compound is considered to be 4-oxo-2,3,4-triphenyl-2-butenal. The assignment of structure 9 was confirmed in the following fashion. Re-

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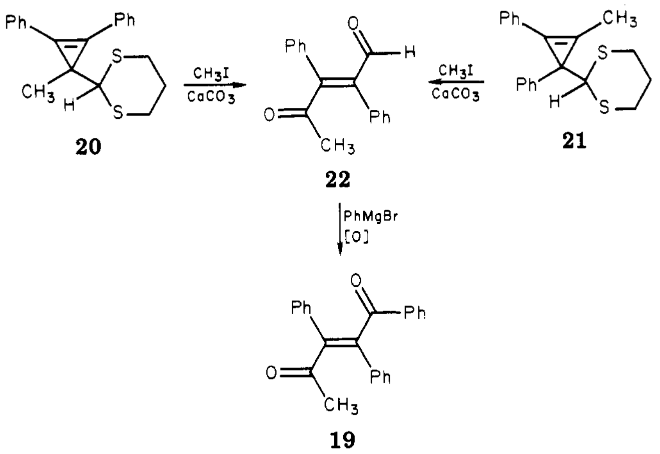
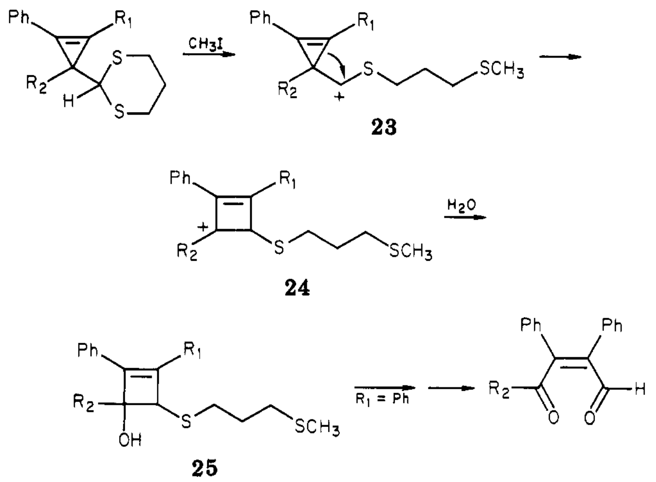
Scheme V



Scheme VI



duction of **9** with sodium borohydride followed by heating the resulting keto aldehyde **10** with a trace of acid gave 2,3,4-triphenylfuran (**11**) in high yield. The more stable *Z* stereochemistry is assigned to structure **9** in view of this result and the fact that keto aldehyde **9** was quantitatively converted to 3,4,5-triphenyl-2(5*H*)-furanone (**12**) on photolysis or thermolysis. The formation of furanone **12** is an interesting reaction which merits some comment. Two possible mechanisms can be considered. Path A (Scheme III) involves an initial [1,5] sigmatropic hydrogen shift to give a ketene intermediate **13** which subsequently cyclizes to the observed product. This reaction sequence is closely related to the mechanism suggested by Pirkle to account for the skeletal rearrangement of 2-pyrones.[38] An alternate path (B) which could also rationalize the rearrangement involves formation of diradical intermediate **14** which undergoes a 1,2 hydrogen shift followed by a subsequent tautomerization to the more stable ring system. The transformation of **9** to **14** is analogous to the ring–chain tautomerization exhibited by several 1,2-dicarbonyl substrates.[39,40] Numerous examples of the thermal transformations of *cis*-1,2-diacylalkenes to lactones have been reported in the literature, thereby providing a good analogy for path B.[41] At the current time the available data do not distinguish between the two mechanisms.

We have also studied the hydrolysis of the closely related 2-methyl-2-cyclopropenyl-substituted 1,3-dithiane **16**. When a sample of **16** was subjected to methyl iodide in the presence of aqueous calcium carbonate, the only product that could be isolated from the reaction mixture was 2-methyl-3,4,5-triphenylfuran (**17**) in 75% yield (Scheme IV). The structure of this material was established by an independent synthesis. Treatment of 2,3,4-triphenylfuran (**11**) with *n*-butyllithium followed by reaction with methyl iodide gave **17**. In a second approach to the hydrolysis of dithiane **16**, we treated this material with a mixture of mercuric oxide and boron trifluoride etherate according to the method of Vedejs and Fuchs.[42] In this case, a 2:1 mixture of (*Z*)-**18** and (*E*)-3,4,5-triphenyl-3-pentene-2,5-dione (**19**) was isolated in 72% overall yield. The isomeric olefins were readily interconverted on photolysis. The structure of **18** was established by comparison with an independently synthesized sample prepared from keto aldehyde **9**. Treatment of **9** with a single equivalent of methylmagnesium bromide followed by oxidation with pyridinium chlorochromate afforded **18** in high yield.

An attempt was also made to hydrolyze 2-(1-methyl-2,3-diphenylcyclopropen-1-yl)- (**20**) and 2-(1,3-diphenyl-2-methylcyclopropen-1-yl)-1,3-dithiane (**21**) with methyl iodide in the presence of calcium carbonate (Scheme V). Both of these compounds gave (*E*)-2,3-diphenyl-4-oxo-2-pentenal (**22**) as the exclusive product. The structure of **22** was established by its conversion to dione **19** by treatment with phenylmagnesium bromide followed by oxidation with pyridinium chlorochromate.

We now turn to a consideration of the origin of the products derived from the attempted hydrolysis of the cyclopropenyl-substituted dithianes. A number of explanations can account for the results. One possibility involves an initial hydrolysis of the dithioacetal ring followed by a subsequent oxidation. In fact (vide post), we have found that 3-acyl-substituted cyclopropenes are readily oxidized to 1,2-diacylalkenes on exposure to oxygen. A second mechanistic scenario is that these systems undergo cyclopropene ring expansion when subjected to the hydrolytic conditions. The hydrolysis of the dithioacetal ring is known to be relatively difficult, requiring heat and complexation of the sulfur by mercury[43] or, in other cases, silver-assisted oxidation with *N*-chlorosuccinimide or methyl iodide.[44] Attack of methyl iodide on one of the sulfur atoms of the dithioacetal ring followed by C–S bond cleavage would be expected to produce a cyclopropenylcarbinyl cation. Breslow and co-workers have previously shown that cyclopropenylcarbinyl carbonium ions readily undergo ring expansion to diphenylcyclobutenyl cations.[45] In our case, the resulting cation can be trapped with water to give a thio-substituted cyclobutenol, **25** (Scheme VI), which may undergo ring opening followed by a subsequent oxidation. The formation of **22** as the exclusive product from the attempted hydrolysis of cyclopropenes **20** and **21** is perfectly consistent with this explanation. In a third conceivable mechanism, the cyclopropenylcarbinyl cation undergoes ring opening to give an aryl-substituted vinyl carbonium ion which is ultimately trapped by water and oxidized to the final product. This mechanism, however, would not readily account for the exclusive formation of

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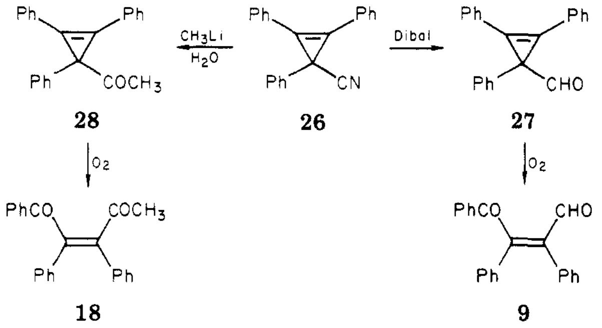
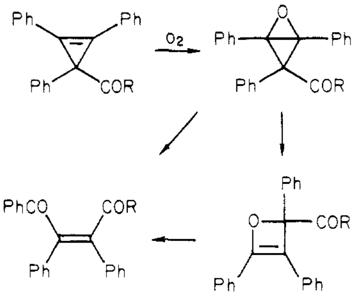
Scheme VII



Scheme VIII

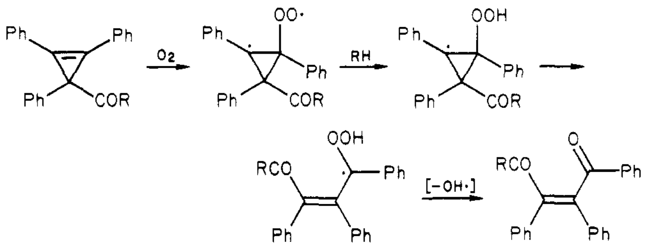


2,3-diphenyl-4-oxo-4-pentenal (**22**) from the hydrolysis of cyclopropenes **20** and **21**.

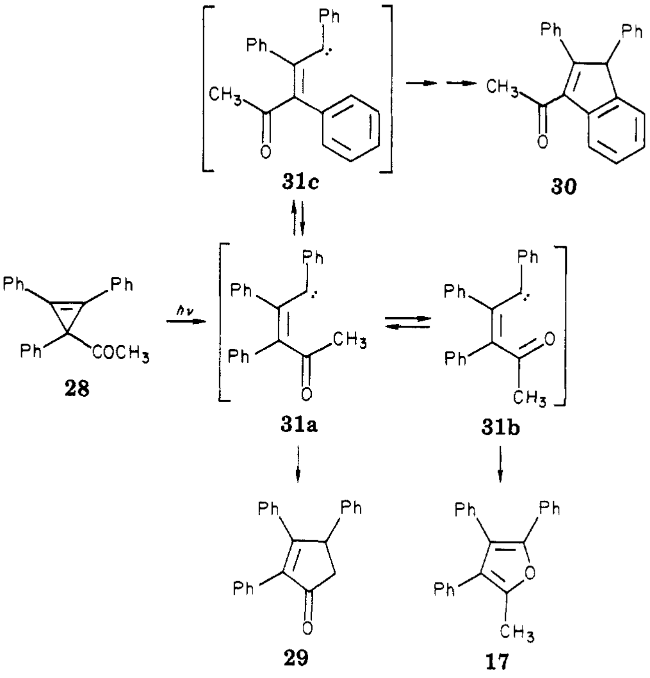
In view of our lack of success in preparing a representative 3-acylcyclopropene via the dithiane route, an alternative approach was used in an attempt to reach our ultimate goal. Addition of potassium cyanide to triphenylcyclopropenyl perchlorate afforded the 3-cyano-substituted cyclopropene **26** in excellent yield. The Dibal reduction of **26** proceeded cleanly to give 3-formyl substituted cyclopropene **27** (Scheme VII). This compound was very sensitive to air and, on exposure to ordinary atmospheric conditions, was rapidly oxidized to keto aldehyde **9**. The closely related 3-acetyl-substituted cyclopropene **28** could be prepared by treating **26** with methyllithium. The resulting ketone was slowly oxidized to dione **18** on being allowed to stand in solution in the presence of oxygen.

In line with earlier evidence for the intermediacy of vinylcarbenes in the photochemistry of cyclopropene derivatives,[31] it is tempting to suggest that the oxidation of **27** to **9** (and **28** to **18**) involves reaction of a transient vinylcarbene with molecular oxygen. This was shown not to be the case, however, since the irradiation of **27** or **28** in the presence of oxygen did not afford any detectable quantities of diones **9** or **18**. Two possible mechanistic schemes can be suggested to account for the observed oxidation. One path (Scheme VIII) involves the formation of a transient oxabicyclobutane intermediate which subsequently fragments to the observed products. Treatment of diaryl-substituted cyclopropenes with peracids is known to result in smooth oxidation of the three-membered ring to give α,β-unsaturated carbonyl products.[46-49] This reaction has been proposed to proceed via an oxabicyclobutane intermediate. Another possibility is that the transient oxabicyclobutane may rearrange first to an oxetene followed by a subsequent ring opening reaction. In such a case, the developing nonbonded interaction of the various substituents would control the stereochemistry of the ring-opening process. The presence of the oxygen atom destroys the disrotatory and conrotatory distinctions for fragmentations. An alternate path which could also rationalize the oxidation results is based on the assumption that oxygen reacts with the highly strained π-bond of the cyclopropene ring according to the sequence of reactions outlined in Scheme IX. This scheme requires that the peroxy radical abstract a hydrogen atom from some undefined hydrogen donor in order for the ketone to be formed. Further work is necessary before these various paths can be distinguished.

Scheme IX



Scheme X



The availability of 1,2,3-triphenyl-3-acetylcyclopropene (**28**) allowed us to evaluate its excited-state behavior. Irradiation of **28** in benzene led to a mixture of three compounds (Scheme X) which were identified as 2,3,4-triphenyl-2-cyclopentenone (**29**, 60%), 2-methyl-3,4,5-triphenylfuran (**17**, 27%), and 3-acetyl-1,2-diphenylindene (**30**, 13%). The structure of cyclopentenone **29** was readily established by examination of its characteristic spectral properties [NMR ($CDCl_3$, 90 MHz) δ 2.61 (dd, 1 H, J = 18.0, 3.0 Hz), 3.26 (dd, 1 H, J = 18.0, 8.0 Hz), 4.58 (dd, 1 H, J = 8.0, 3.0 Hz), 7.03–7.46 (m, 15 H)] and by comparison with an authentic sample.[50]

The formation of the three products obtained from the irradiation of **28** can be rationalized in terms of a vinyl-

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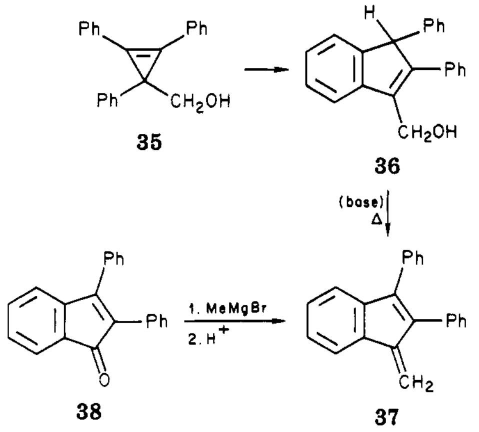
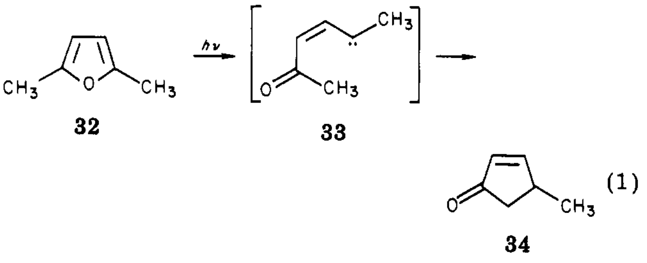
Scheme XI

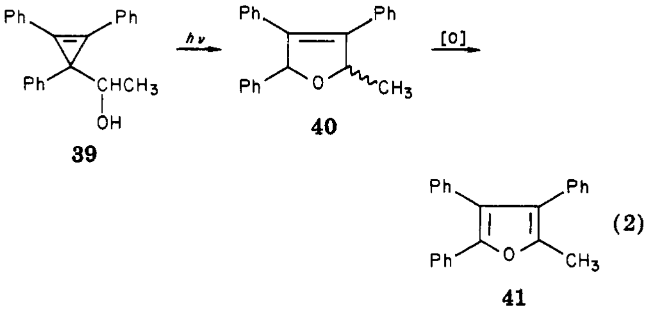


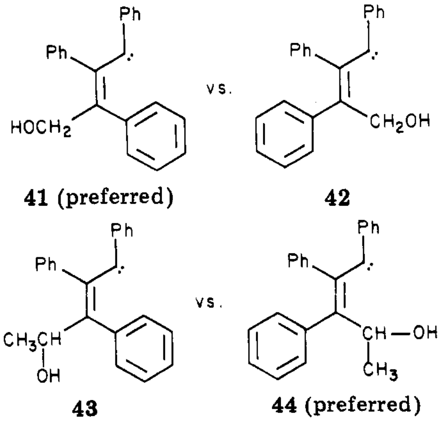
carbene intermediate. Several different pathways are available to this intermediate depending on the stereochemistry about the double bond and on the conformation the oxygen atom assumes in the cis intermediate. Vinylcarbene **31b** has the proper cisoid conformation of the oxygen atom and the carbene center to close to furan **17**. If the oxygen atom exists in a transoid relationship to the carbene center, closure to a furan is unlikely for steric reasons. Instead, insertion into the neighboring methyl group occurs to produce cyclopentenone **29**. This reaction provides additional support for the mechanism proposed some years ago by Srinivason and Boue to rationalize the formation of 4-methylcyclopent-2-enone (**34**) from the irradiation of 2,5-dimethylfuran (**32**,[51] eq 1). These authors suggested that vinylcarbene **33** functions as an intermediate in this novel rearrangement. Finally, the formation of indene **30** from the irradiation of **28** can be accounted for in terms of an electrocyclization reaction of the *trans*-vinylcarbene **31c** to an isoindene intermediate which subsequently undergoes a [1,5] sigmatropic shift to give the aromatic indene system.[27-29] To account for the ratio of indene to furan and cyclopentenone, we need to postulate a preference for formation of the cisoid vinylcarbene in the photochemical ring-opening reaction. This seems quite reasonable on the assumption that van der Waals repulsions is the controlling factor in the ring-opening reaction.



As a continuation of our investigations in this area, we became interested in determining whether diaryl-substituted vinylcarbenes would also undergo insertion into a neighboring alcohol functionality. In order to test for this possibility, we carried out a study dealing with the photochemistry of several hydroxy-substituted cyclopropenes. The first compound investigated was 1,2,3-triphenyl-3-(hydroxymethyl)cyclopropene (**35**). This material was prepared by the sodium borohydride reduction of 3-formylcyclopropene **27**. Irradiation of **35** in benzene afforded 3-(hydroxymethyl)-1,2-diphenylindene (**36**) as the exclusive product (Scheme XI). The structure of **36** was readily established from its characteristic spectral properties (see Experimental Section). Under slightly basic conditions, indene **36** was readily dehydrated to the methylene derivative **37**. The identity of **37** was established by comparison with an independently synthesized sample prepared from diphenylindenone **38**.

Attention was next turned to the photochemical behavior of 1-(1,2,3-triphenylcyclopropenyl)ethanol (**39**). Most interestingly, the photolysis of **39** in benzene afforded a 2:3 mixture of *cis*- and *trans*-1-methyl-2,3,4-triphenyl-1,4-dihydrofuran (**40**, eq 2). The mixture of isomers was readily oxidized to furan **17** on heating in the presence of palladium on carbon. No detectable quantities of an indene derivative were found in the crude photolysate. It would seem as though the initially generated vinylcarbene derived from the irradiation of **39** prefers to insert into the neighboring OH bond rather than to undergo electrocyclization to an indene derivative. The reason for this difference is probably steric in nature. In the case of cyclopropene **35**, there is a preference for formation of the least sterically congested vinylcarbene **41**. Steric interactions about the double bond will be minimized by having the two phenyl groups disposed in a trans relationship. The divalent carbon center finds itself in close proximity to the ortho position of the neighboring phenyl group, thereby allowing electrocyclic closure to occur. It is our belief that the difference in size of the 3-hydroxyalkyl substituent is the major factor responsible for the difference in photochemical behavior of cyclopropenes **35** and **39**. The vinylcarbene derived from **39** has the proper geometry required for insertion into the OH bond (i.e., **44**).





Examination of molecular models shows that the vinylcarbene with the phenyl and hydroxyethyl groups cis exhibits a slightly greater steric interaction than the isomer with the phenyl groups cis. The van der Waal repulsive forces between the two large groups is the decisive factor responsible for the formation of dihydrofuran **40**.

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[51] Boue, S.; Srinivason, R. *J. Am. Chem. Soc.* **1970**, *92*, 1824.

Experimental Section[52]

Preparation of 2-(1,2,3-Triphenyl-2-cyclopropen-1-yl)-1,3-dithiane (7). To a solution containing 1.47 g of 1,3-dithiane in 25 mL of tetrahydrofuran was added 7.5 mL of a 1.6 M *n*-butyllithium solution at −25 °C under a nitrogen atmosphere. After the mixture was stirred at −25 °C for 3 hr, the solution was added to a suspension containing 3.0 g of 1,2,3-triphenylcyclopropenyl perchlorate[53] in 100 mL of tetrahydrofuran at −78 °C. The mixture was stirred for 4 h at −78 °C and was then allowed to warm to room temperature. The excess anion was quenched with a saturated ammonium chloride solution, and the organic layer was taken up in ether. The ethereal layer was washed with water and dried over magnesium sulfate. The solvent was removed under reduced pressure and the resulting solid was recrystallized from ether to give 2.6 g (82%) of 2-(1,2,3-triphenyl-2-cyclopropen-1-yl)-1,3-dithiane (7): mp 209–210 °C; IR (KBr) 3.25, 3.30, 3.38, 3.45, 5.52, 6.23, 6.67, 7.10, 7.30, 7.70, 7.92, 8.13, 8.60, 9.10, 9.45, 9.90, 11.30, 12.10, 12.70, 13.50, 14.80 μm; UV (95% ethanol) 228 nm (ε 25 300), 314 (24 800), 330 (20 700); NMR ($CDCl_3$, 60 MHz) δ 1.77–2.18 (m, 2 H), 2.76–3.06 (m, 4 H), 5.30 (s, 1 H), 7.04–8.00 (m, 15 H); mass spectrum, *m/e* 386 (M^+), 267 (base).

Anal. Calcd for $C_{25}H_{22}S_2$: C, 77.68; H, 5.74. Found: C, 77.63; H, 5.78.

Hydrolysis of 2-(1,2,3-Triphenyl-2-cyclopropen-1-yl)-1,3-dithiane (7). To a solution containing 100 mg of dithiane 7 in 20 mL of acetone were added 40 mg of calcium carbonate, 1 mL of methyl iodide, and 1 mL of water. The reaction mixture was heated at 50 °C for 5 h. After the mixture cooled, the organic layer was taken up in ether, washed with water, and dried over magnesium sulfate. Removal of the solvent left a crude oil which was subjected to silica gel chromatography with a 10% ether–hexane mixture as the eluent. The first fraction contained 60 mg of recovered starting material. The second component isolated from the column contained 86 mg (85%) of a white solid (mp 160–161 °C) whose structure was assigned at 4-oxo-2,3,4-triphenyl-2-butenal (9) on the basis of its characteristic spectral properties: IR (KBr) 3.26, 3.50, 5.93, 5.97, 6.03, 6.25, 6.97, 9.30, 8.02, 8.32, 9.75, 9.83, 13.50, 13.81, 14.30 μm; UV (95% ethanol) 257 nm (ε 19 400); NMR ($CDCl_3$, 100 MHz) δ 10.16 (s, 1 H), 7.2–8.04 (m, 15 H); mass spectrum, *m/e* 312 (M^+, base), 284, 207, 178, 106.

Anal. Calcd for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16. Found: C, 84.37; H, 5.09.

A solution containing 30 mg of 9 in 30 mL of benzene was irradiated with a 450-W Hanovia lamp equipped with a Pyrex filter for 30 min. Removal of the solvent under reduced pressure left a solid which was purified by preparative thick-layer chromatography with a 10% ether–hexane mixture as the eluent. The major component isolated contained 24 mg (89%) of a crystalline solid (mp 125–126 °C) whose structure was shown to be 3,4,5-triphenyl-2(5*H*)-furanone (12) by comparison with an authentic sample (lit.[54] mp 125–126 °C): IR (KBr) 3.27, 3.29, 5.72, 6.10, 6.23, 6.78, 6.96, 7.24, 7.43, 7.80, 7.95, 8.50, 9.01, 9.30, 9.52, 10.02, 10.51, 12.04, 13.01, 13.62, 14.73 μm; NMR ($CDCl_3$, 90 MHz) δ 6.20 (s, 1 H), 6.9–7.5 (m, 15 H). Thermolysis of a 35-mg sample of 9 at 167 °C for 13 h with a benzene–pyridine mixture also produced a 70% yield of furanone 12.

Further support for the structure of 9 was obtained by reduction to the corresponding alcohol. To a solution containing 100 mg of 9 in 40 mL of methanol at 0 °C was added 25 mg of sodium borohydride. After being stirred for 2 h at 0 °C, the mixture was allowed to warm to room temperature. The organic layer was taken up in ether, washed with water, and dried over magnesium sulfate. Removal of the solvent under reduced pressure left a crystalline solid which was recrystallized from hexane–ether to give 75 mg (74%) of 4-oxo-2,3,4-triphenyl-2-buten-1-ol (10): white solid; mp 128–129 °C; IR (KBr) 2.92, 3.30, 3.52, 6.08, 6.25, 6.95, 7.25, 8.36, 9.52, 9.90, 11.60, 13.40, 14.60 μm; UV (95% ethanol) 250 nm (ε 16 000); NMR ($CDCl_3$, 60 MHz) δ 1.72 (br s, 1 H), 4.50 (s, 2 H), 6.96–7.93 (m, 15 H); mass spectrum, *m/e* 314 (M^+, base), 209, 178.

Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.05, H, 5.77. Found: C, 84.40; H, 6.11.

A solution containing 90 mg of 10 in 175 mL of benzene was irradiated with a 450-W Hanovia lamp equipped with a Pyrex filter sleeve for 30 min. Removal of the solvent under reduced pressure left a yellow solid which was subjected to preparative thick-layer chromatography with a 10% ether–hexane mixture as the eluent. The major component isolated from the thick-layer plate contained 49 mg (55%) of a crystalline solid (mp 115–116 °C) whose structure was assigned as 2,3,4-triphenylfuran (11) on the basis of its spectroscopic properties: IR (KBr) 3.28, 3.42, 5.69, 6.23, 6.76, 6.94, 7.30, 8.62, 11.20, 13.31, 13.60, 14.82 μm; UV (95% ethanol) 286 nm (ε 10 700), 226 (17 400); NMR ($CDCl_3$, 90 MHz) δ 7.65 (s, 1 H), 7.03–7.55 (m, 15 H); mass spectrum, *m/e* 296 (M^+, base), 267, 189, 165, 77.

Anal. Calcd for $C_{22}H_{16}O$: C, 89.16; H, 5.44. Found: C, 89.19; H, 5.48.

This same material could be prepared by heating 10 with a trace of *p*-toluenesulfonic acid in benzene at 80 °C for 18 h.

Preparation of 2-(1,2,3-Triphenyl-2-cyclopropen-1-yl)-2-methyl-1,3-dithiane (16). To a solution containing 360 mg of dithiane in 20 mL of tetrahydrofuran was added 2.6 mL of a 1.16 M *n*-butyllithium solution at −25 °C under a nitrogen atmosphere. After the mixture was stirred at −25 °C for 90 min, a solution containing 0.187 mL of methyl iodide in 5 mL of tetrahydrofuran was added at −5 °C. The mixture was stirred at 5 °C for 16 h, and then 2.6 mL of a 1.16 M solution of *n*-butyllithium was added to the mixture to re-form the tertiary carbanion. The mixture was stirred at −25 °C for 90 min and was then transferred to a suspension containing 734 mg of triphenylcyclopropenyl perchlorate in 20 mL of tetrahydrofuran at −78 °C. The solution was stirred at −78 °C for 4 h and was then allowed to warm to room temperature for 4 h. After the mixture was quenched with ammonium chloride, the organic layer was dried over magnesium sulfate and concentrated under reduced pressure to give 237 mg (30%) of a white solid (mp 199–200 °C) whose structure was assigned as 2-(1,2,3-triphenyl-2-cyclopropen-1-yl)-2-methyl-1,3-dithiane (16): IR (KBr) 5.54, 6.26, 6.72, 6.96, 13.45, 14.79 μg; UV (95% ethanol) 230 nm (ε 22 600), 312 (22 000), 330 (18 000); NMR ($CDCl_3$, 60 MHz) δ 1.94 (s, 3 H), 1.70–2.20 (m, 2 H), 2.60–3.13 (m, 4 H), 7.07–8.16 (m, 15 H); mass spectrum, *m/e* 400 (M^+), 267 (base).

Anal. Calcd for $C_{26}H_{24}S_2$: C, 77.98; H, 6.04. Found: C, 78.01; H, 6.08.

Hydrolysis of 2-(1,2,3-Triphenyl-2-cyclopropen-1-yl)-2-methyl-1,3-dithiane (16). Two methods were used in an attempt to hydrolyze dithiane 16 to the corresponding methyl ketone. The first method involved heating of a mixture of 150 mg of dithiane 16, 80 mg of calcium carbonate, and 2 mL of methyl iodide in 50 mL of acetone and 2 mL of water at 50 °C for 6 h. The solvent was removed under reduced pressure, and the residue was extracted with ether. The ethereal layer was washed with water and dried over magnesium sulfate. Removal of the solvent under reduced pressure left a yellow oil which was chromatographed on a silica gel column by using a 2% benzene–hexane mixture as the eluent. The major fraction contained 87 mg (75%) of a colorless solid (mp 146–147 °C) whose structure was assigned as 2-methyl-3,4,5-triphenylfuran (17) on the basis of its characteristic spectral properties: IR (KBr) 6.26, 6.70, 6.94, 7.22, 13.21, 14.45 μm; UV (95% ethanol) 297 nm (ε 15 400); NMR ($CDCl_3$, 90 MHz) δ 2.39 (s, 3 H), 6.92–7.46 (m, 15 H); mass spectrum, *m/e* 310 (M^+, base).

Anal. Calcd for $C_{23}H_{18}O$: C, 89.00; H, 5.85. Found: C, 88.97; H, 5.88.

The structure of this material was further verified by an independent synthesis which consisted of treating 2,3,4-triphenylfuran (11) with *n*-butyllithium followed by reaction with

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(52) All melting points and boiling points are uncorrected. Elemental analyses were performed by Atlantic Microlabs. The infrared absorption spectra were determined on a Perkin-Elmer Model 137 Infracord spectrophotometer. The ultraviolet absorption spectra were measured with a Cary Model 14 recording spectrophotometer using 1-cm matched cells. The proton magnetic resonance spectra were determined at 90 MHz by using a Varian EM-390 MHz spectrometer. Mass spectra were determined with a Perkin-Elmer RMU6 mass spectrometer at an ionizing voltage of 70 eV. All irradiations were carried out by using a 450-W Hanovia medium-pressure mercury arc lamp.

(53) Breslow, R.; Hover, H.; Chang, H. W. *J. Am. Chem. Soc.* **1962**, *84*, 3168.

(54) Rio, G.; Hardy, J. C. *Bull. Soc. Chim. Fr.* **1970**, 3578.

methyl iodide. To a solution containing 100 mg of 11 in 40 mL of ether was added 5 equiv of *n*-butyllithium in hexane at 0 °C. The mixture was allowed to warm to room temperature and was then heated at reflux for 4.5 h until the color had changed to a deep red. To this solution was added 5 equiv of methyl iodide. The mixture was heated at reflux for 1 h and the solution was quenched with a saturated ammonium chloride solution. The organic layer was taken up in ether, washed with water, and dried over magnesium sulfate. Removal of the solvent left 49 mg (48%) of 2-methyl-3,4,5-triphenylfuran (17) which was identical in every detail with the sample obtained from the hydrolysis of dithiane 16.

The second method used in an attempt to hydrolyze dithiane 16 to the corresponding methyl ketone involved reaction with mercuric oxide and boron trifluoride etherate. A mixture containing 200 mg of 16, 216 mg of red mercuric oxide, 142 mg of boron trifluoride etherate, and 8 mL of a 15% aqueous tetrahydrofuran solution was stirred at 25 °C for 10 min. At the end of this time, ether was added, and the precipitated salts were filtered. The ethereal layer was washed with a saturated sodium carbonate solution and dried over magnesium sulfate. Removal of the solvent left a crude oil which was subjected to preparative thick-layer chromatography with a 10% ether–hexane mixture as the eluent. The major component isolated from the column contained 80 mg (48%) of a clear oil whose structure was assigned as (*Z*)-3,4,5-triphenyl-3-pentene-2,5-dione (18): IR (neat) 5.88, 5.98, 6.25, 6.31, 6.68, 6.89 μm; UV (95% ethanol) 255 nm (ε 19000); NMR ($CDCl_3$, 90 MHz) δ 2.03 (s, 3 H), 7.06–7.59 (m, 13 H), 7.79–7.87 (m, 2 H).

Anal. Calcd for $C_{23}H_{18}O_2$: C, 84.64; H, 5.56. Found: C, 84.61; H, 5.48.

The structure of this material was verified by comparison with an independently synthesized sample. To a solution containing 260 mg of 4-oxo-2,3,4-triphenyl-2-butenal (9) in 100 mL of ether at 0 °C was added 0.87 mL of a methylmagnesium bromide solution. The mixture was stirred at 0 °C for 1 h and at room temperature for 2 h. After the mixture was quenched with ammonium chloride, the ethereal layer was dried over magnesium sulfate and concentrated under reduced pressure to give 250 mg (91%) of a crystalline solid (mp 157–158 °C) whose structure was assigned as 4-hydroxy-4-methyl-1,2,3-triphenylpenten-1-one on the basis of its spectral properties: IR (KBr) 2.88, 6.08, 6.14, 6.28, 6.35, 6.93, 7.25, 14.66 μm; UV (95% ethanol) 245 nm (ε 18900); NMR ($CDCl_3$, 90 MHz) δ 1.20 (d, 3 H, *J* = 6.0 Hz), 1.56 (s, 1 H), 4.92 (q, 1 H, *J* = 6.0 Hz), 7.07–7.82 (m, 5 H); mass spectrum, *m*/*e* 328 (M^+, base).

Anal. Calcd for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14. Found: C, 84.05; H, 6.19.

To 40 mg of the above alcohol in 1 mL of methylene chloride were added 45 mg of pyridinium chlorochromate and 5 mg of sodium acetate in 1 mL of methylene chloride. The mixture was stirred at 25 °C for 4 h, and then 5 mL of ether was added. The solution was filtered and concentrated under reduced pressure. The crude mixture was purified by thick-layer chromatography with a 5% ethyl acetate–hexane mixture as the eluent. The major fraction isolated from the column was identical with dione 18 obtained from the mercuric oxide hydrolysis of dithiane 16.

The minor component (20 mg, 24%) isolated from the dithiane hydrolysis was a clear oil whose structure was assigned as (*E*)-3,4,5-triphenyl-3-pentene-2,5-dione (19) on the basis of its spectral properties: IR (neat) 5.90, 5.99, 6.25, 6.32, 6.71, 6.91, 13.47, 14.49 μm; UV (95% ethanol) 250 nm (ε 15000); NMR ($CDCl_3$, 90 MHz) δ 2.07 (s, 3 H), 7.10–7.56 (m, 13 H), 7.89–8.03 (m, 2 H); mass spectrum, *m*/*e* 326 (M^+, base).

Anal. Calcd for $C_{23}H_{18}O_2$: C, 84.64; H, 5.56. Found: C, 84.61; H, 5.53.

Further support for this structure was obtained from the photolysis of the *Z* isomer 18. Irradiation of a 55 mg sample of 18 in 100 mL of benzene for 30 min with a 450-W Hanovia lamp equipped with a Pyrex filter gave a *Z*/*E* mixture of isomers. The *Z* isomer was separated from the *E* isomer by column chromatography and proved to be identical with the minor component isolated from the mercuric oxide dithiane hydrolysis.

Preparation of 2-(1-Methyl-2,3-diphenylcyclopropen-1-yl)-1,3-dithiane (20) and 2-(2-Methyl-1,3-diphenylcyclopropen-1-yl)-1,3-dithiane (21). A solution containing 15 mL of a 1.6 M *n*-butyllithium solution in hexane was added to a stirred solution containing 2.88 g of 1,3-dithiane in 40 mL of tetrahydrofuran at −25 °C. The reaction mixture was allowed to stir at −25 °C for 3 h and was then transferred to a stirred suspension containing 5.0 g of diphenylmethylcyclopropenyl perchlorate in 175 mL of tetrahydrofuran at −78 °C. The mixture was stirred at −78 °C for 4 h and was allowed to warm to room temperature over a 2.5-h period. The mixture was quenched with ammonium chloride, and the reaction mixture was concentrated under reduced pressure. The residue was taken up in ether, washed with water, and dried over magnesium sulfate. The solution was evaporated under reduced pressure to give 6.33 g of a dark brown oil. This oil was subjected to medium-pressure chromatography with a 1% ethyl acetate–hexane mixture as the eluent. The first component isolated from the column contained 2.0 g of a yellow solid which was recrystallized from ether to give 1.65 g (31%) of 2-(1-methyl-2,3-diphenylcyclopropen-1-yl)-1,3-dithiane (20): white crystalline solid; mp 119–120 °C; IR (KBr) 3.29, 3.32, 3.37, 5.58, 6.04, 6.32, 6.72, 6.96, 7.93, 8.61, 9.47, 11.20, 13.05, 14.90 μm; UV (95% ethanol) 228 nm (ε 25100), 314 (24600), 330 (21000); NMR ($CDCl_3$, 60 MHz) δ 1.60 (s, 3 H), 1.69–2.10 (m, 2 H), 2.60–2.92 (m, 4 H), 4.44 (s, 1 H), 7.05–7.78 (m, 10 H); mass spectrum, *m*/*e* 324 (M^+), 205 (base).

Anal. Calcd for $C_{20}H_{20}S_2$: C, 74.03; H, 6.21; S, 19.76. Found: C, 73.89; H, 6.29; S, 19.82.

The second component isolated from the column contained 2.12 g of a yellow solid which was recrystallized from ether to give 1.74 g (33%) of a crystalline solid (mp 90–91 °C) whose structure was assigned as 2-(2-methyl-1,3-diphenylcyclopropen-1-yl)-1,3-dithiane (21) on the basis of its spectral properties: IR (KBr) 3.26, 3.40, 5.45, 6.26, 6.37, 6.71, 7.02, 7.09, 7.24, 7.84, 8.06, 8.54, 11.04, 11.85, 12.76, 13.23, 14.10 μm; NMR ($CDCl_3$, 60 MHz) δ 1.73–2.17 (m, 2 H), 2.38 (s, 3 H), 2.70–3.02 (m, 4 H), 5.10 (s, 1 H), 6.97–7.73 (m, 10 H); mass spectrum, *m*/*e* 324 (M^+), 205 (base).

Anal. Calcd for $C_{20}H_{20}S_2$: C, 74.03; H, 6.21; S, 19.76. Found: C, 73.89; H, 6.26; S, 19.79.

Hydrolysis of 2-(1-Methyl-2,3-diphenylcyclopropen-1-yl)-1,3-dithiane (20) and 2-(2-Methyl-1,3-diphenylcyclopropen-1-yl)-1,3-dithiane (21). A mixture containing 400 mg of dithiane 20, 160 mg of calcium carbonate, 6 mL of methyl iodide, and 6 mL of water in 150 mL of acetone was heated at 50 °C for 6 h. The solvent was removed under pressure, and the residue was taken up in ether. The ethereal layer was washed with water and then dried over magnesium sulfate. Removal of the ether under reduced pressure left a dark oil which was chromatographed on a silica gel column with a 10% ether–hexane mixture as the eluent. The major component isolated from the column contained 89 mg (30%) of a pale yellow solid (mp 119–120 °C) whose structure was assigned as 2,3-diphenyl-4-oxo-2-pentenal (22) on the basis of its spectral properties: IR (KBr) 3.48, 5.91, 5.99, 6.71, 6.94, 7.22, 7.38, 8.02, 8.06, 8.58, 9.26, 13.16, 14.50 μm; NMR ($CDCl_3$, 90 MHz) δ 1.96 (s, 3 H), 7.26–7.45 (m, 10 H), 9.83 (s, 1 H); UV (95% ethanol) 257 nm (ε 19750); mass spectrum, *m*/*e* 260 (M^+), 232, 178, 155.

Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.43; H, 5.71.

The same aldehyde was also obtained when a sample of dithiane 21 was subjected to similar hydrolysis conditions. Further support for the structure of this material was obtained by its conversion to (*E*)-3,4,5-triphenyl-3-pentene-2,5-dione (19). To a solution containing 80 mg of aldehyde 22 in 50 mL of ether at 0 °C was added 0.2 mL of a phenylmagnesium bromide solution. After being stirred for 1 h at 0 °C, the solution was warmed to room temperature and stirred for an additional 2 h. The mixture was quenched with ammonium chloride, and the ethereal layer was dried over magnesium sulfate. The solvent was removed under reduced pressure to give a crude solid which was recrystallized from acetone–hexane to give 55 mg (52%) of a crystalline solid (mp 142–144 °C) whose structure is assigned as 4-hydroxy-4-phenyl-(*E*)-1,2,3-triphenylpenten-1-one on the basis of its spectral properties: IR (KBr) 2.93, 5.98, 6.72, 6.96, 7.27, 14.52 μm; UV (95% ethanol) 245 nm (ε 11000); NMR ($CDCl_3$, 90 MHz) δ 1.67 (s, 1 H), 1.79 (s, 3 H), 5.61 (s, 1 H), 7.0–8.02 (m, 15 H); mass spectrum, *m*/*e* 328 (M^+), 285, 105.

Anal. Calcd for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14. Found: C, 84.05; H, 6.15.

A 40-mg sample of the above alcohol, 45 mg of pyridinium chlorochromate, and 5 mg of sodium acetate in 2 mL of methylene chloride was stirred at 25 °C for 4 h. At the end of this time ether was added, and the mixture was filtered. The extracts were concentrated under reduced pressure to give a crude oil which was chromatographed on a thick-layer plate by using a 5% ethyl acetate–hexane mixture as the eluent. The major fraction isolated from the column (80%) was identical with an authentic sample of (*E*)-3,4,5-triphenyl-3-pentene-2,5-dione (**19**).

Preparation of 1,2,3-Triphenyl-3-formylcyclopropene (27). To a stirred suspension containing 2.20 g of triphenylcyclopropenyl perchlorate and 2.0 g of potassium cyanide in 50 mL of acetonitrile was added 50 mg of 18-crown-6. The mixture was allowed to stir at 0 °C for 2 h and then at room temperature for an additional 12 h. Removal of the solvent left a yellow oil which was taken up in ether and washed with water. The ethereal layer was dried over magnesium sulfate, and the resulting solid (1.2 g, 68%) was recrystallized from benzene–hexane to give 1,2,3-triphenyl-3-cyanocyclopropene (**26**) as a white solid, mp 143–144 °C (lit.[55] mp 144–145 °C).

To a solution containing 500 mg of 1,2,3-triphenyl-3-cyanocyclopropene (**26**) in 40 mL of benzene under a nitrogen atmosphere at 5 °C was added 1.35 mL of a 25% solution of Dibal in toluene. The reaction mixture was allowed to warm to room temperature over a 2-h period and was then quenched with a saturated ammonium chloride solution. The organic layer was taken up in ether, washed with water, and dried over magnesium sulfate. Removal of the solvent under reduced pressure left 340 mg (68%) of a yellow oil which was very labile and which readily decomposed on attempted purification. The structure of this labile compound was assigned as 1,2,3-triphenyl-3-formylcyclopropene (**27**) on the basis of its spectral properties: IR (neat) 3.25, 3.30, 3.40, 5.89, 6.18, 6.28, 6.70, 6.95, 9.30, 9.45, 9.80, 11.2, 13.5, 14.8 μm; NMR ($CDCl_3$, 90 MHz) δ 9.42 (s, 1 H), 6.83–7.80 (m, 15 H). When a 50-mg sample of this material was allowed to stand in solution (benzene) in the presence of oxygen, an 80% yield of 4-oxo-2,3,4-triphenyl-2-butenal (**9**) was obtained as the only identifiable product.

Preparation and Irradiation of 1,2,3-Triphenyl-3-acetylcyclopropene (28). To a stirred solution containing 586 mg of 1,2,3-triphenyl-3-cyanocyclopropene (**26**) in 50 mL of anhydrous ether at 0 °C was added 2.14 mL of a 1.4 M methyllithium solution. The reaction was allowed to stir at 0 °C for 3 h and was then quenched with a saturated ammonium chloride solution. The organic solvent was dried and concentrated under reduced pressure to give a white solid. This material was purified by silica gel column chromatography with a 5% acetone–hexane mixture as the eluent to give 170 mg (27%) of 1,2,3-triphenyl-3-acetylcyclopropene (**28**): mp 140–141 °C; IR (KBr) 5.94, 6.23, 6.70, 7.22 μm; UV (95% ethanol) 228 nm (ϵ 11 200), 285 (15 600), 297 (19 400), 327 (20 100), 337 (19 900); NMR ($CDCl_3$, 100 MHz) δ 2.02 (s, 3 H), 7.36–7.90 (m, 15 H); C^{13} NMR ($CDCl_3$) δ 2.62 (q), 44.3 (s), 113.4, 126.5, 128.0, 128.4, 128.7, 129.3, 129.8, 139.8 (s), 209 (s); mass spectrum, *m/e* 310 (M^+), 267 (base).

Anal. Calcd for $C_{23}H_{18}O$: C, 89.00; H, 5.85. Found: C, 88.98; H, 6.10.

When a sample of 3-acetylcyclopropene **28** was allowed to stand in a benzene solution in the presence of oxygen, (*Z*)-3,4,5-triphenyl-3-pentene-2,5-dione (**18**) was isolated as the major product in 78% yield.

A solution containing 175 mg of **28** in 150 mL of benzene was irradiated with a 450-W Hanovia lamp equipped with a Pyrex filter sleeve for 1 h. Removal of the solvent left a yellow oil. Analysis of the oil by NMR revealed the existence of three compounds in a ratio of 2:4:9. The crude oil was subjected to preparative thick-layer chromatography with a 5% acetone–hexane mixture as the eluent. The major component isolated from the thick-layer plate was shown to be 2,3,4-triphenyl-2-cyclopentenone [**29**: 60% yield; mp 138–139 °,c (lit.[50] mp 139.5–140.5 °C); NMR ($CDCl_3$, 90 MHz) δ 2.61 (dd, 1 H, J = 18.0, 3.0 Hz), 3.26 (dd, 1 H, J = 18.0, 8.0 Hz) 4.58 (dd, 1 H, J = 8.0, 3.0 Hz), 7.03–7.46 (m, 15 H)] by comparison with an authentic sample prepared according to the procedure of Yates and co-workers.[50] The second major component was identified as 2-methyl-3,4,5-triphenylfuran (**17**, 27%) by comparison with an authentic sample. The minor component present in the reaction mixture is assigned as 3-acetyl-1,2-diphenylindene (**30**) on the basis of its NMR spectrum which showed a methine proton at δ 5.03 (s, 1 H) and a methyl group at δ 2.50 (s, 3 H) as well as the aromatic protons (m, 14 H) at δ 7.10–8.0.

Preparation and Irradiation of 1,2,3-Triphenyl-3-(hydroxymethyl)cyclopropene (35). To a solution containing 204 mg of 1,2,3-triphenyl-3-formylcyclopropene (**27**) in 100 mL of methanol was added a 50 mg sample of sodium borohydride at 0 °C. The solution was stirred at room temperature for 2.5 h and was then extracted with ether. The ethereal layer was washed with water and dried over magnesium sulfate. Removal of the solvent under reduced pressure left a yellow oil which was subjected to silica gel chromatography with a 10% acetone–hexane mixture as the eluent. The major component isolated from the column contained 103 mg of a clear oil whose structure was assigned as 1,2,3-triphenyl-3-(hydroxymethyl)cyclopropene (**27**) on the basis of its spectral properties: IR (neat) 2.92, 3.26, 3.30, 3.36, 3.40, 3.47, 5.50, 6.28, 6.72, 6.92, 9.42, 9.80, 11.2, 13.5, 14.8 μm; UV (95% ethanol) 332 nm (ϵ 21 000), 315 (24 700), 228 (26 000); NMR ($CDCl_3$, 90 MHz) δ 1.53 (br s, 1 H), 4.47 (s, 2 H), 7.06–7.90 (m, 15 H); mass spectrum, *m/e* 298 (M^+), 267 (base), 77.

Anal. Calcd for $C_{22}H_{18}O$: C, 88.56; H, 6.08. Found: C, 88.42; H, 6.23.

A solution containing 120 mg of cyclopropene **35** in benzene was irradiated with a 450-W Hanovia lamp equipped with a Pyrex-glass filter under an argon atmosphere for 1.5 h. Removal of the solvent under reduced pressure left a yellow oil which was subjected to silica gel chromatography with a 10% acetone–hexane mixture as the eluent. The major component isolated from the column contained 75 mg of a clear oil whose structure was assigned as 3-(hydroxymethyl)-1,2-diphenylindene (**36**) on the basis of its spectral properties: IR (neat) 2.95, 3.25, 3.30, 3.42, 3.47, 6.28, 6.75, 6.88, 6.92, 9.15, 9.45, 9.80, 10.2, 11.2, 13.1, 13.6, 14.8 μm; NMR ($CDCl_3$, 90 MHz) δ 1.83 (br s, 1 H), 4.63–4.84 (m, 2 H), 4.97 (s, 1 H), 6.87–7.68 (m, 14 H). Indene **36** was quite reactive in the presence of acid and all attempts to obtain an analytical sample failed.

A solution containing 60 mg of indene **36** in 10 mg of tetrahydrofuran was added to a suspension containing 25 mg of sodium hydride in 5 mL of tetrahydrofuran. The reaction mixture was stirred for 3 h and the excess sodium hydride was quenched by water. The organic layer was extracted with ether, washed with water, and dried over magnesium sulfate. Removal of the solvent under reduced pressure left a yellow oil which was chromatographed on a silica gel column with hexane as the eluent. The major component isolated from the column contained 25 mg of a yellow oil whose structure was assigned as 1-methylene-2,3-diphenylindene (**37**) on the basis of its characteristic data: IR (neat) 3.27, 3.30, 3.39, 3.42, 3.50, 6.28, 6.80, 6.92, 7.00, 7.40, 7.80, 9.40, 9.80, 11.2, 13.2, 13.5, 14.7 μm; NMR ($CDCl_3$, 90 MHz) δ 5.71 (br s, 1 H), 6.23 (br s, 1 H), 6.70–7.81 (m, 14 H); mass spectrum, *m/e* 280 (M^+), 279 (base), 178, 77.

Anal. Calcd for $C_{22}H_{16}$: C, 94.25; H, 5.75. Found: C, 94.18; H, 5.70.

The structure of this compound was further verified by comparison with an independently synthesized sample. To a solution containing 500 mg of 1,2-diphenylindenone (**38**) was added 1.5 mL of a 2.3 M solution of methylmagnesium bromide in ether. The reaction mixture was stirred for 4 h, and the excess Grignard reagent was quenched with a saturated ammonium chloride solution. The organic extracts were dried and concentrated under reduced pressure. The resulting oil was treated with 15 mL of a 48% hydrobromic acid solution. The reaction mixture was then stirred for 2 h at room temperature. The organic layer was taken up in ether, washed several times with water, and dried over magnesium sulfate. Removal of the solvent under reduced pressure left a yellow oil which was chromatographed on a silica gel column with hexane as the eluent. The major component isolated from the column contained 242 mg of yellow oil which was identical in every respect with the sample of 1-methylene-2,3-diphenylindene (**37**) isolated from the base-induced rear-

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(55) Breslow, R.; Yuan, C. *J. Am. Chem. Soc.* **1958**, *80*, 5991.

rangement of (hydroxymethyl)indene **36**.

Preparation and Irradiation of 1-(1,2,3-Triphenylcyclopropen-1-yl)ethanol (39). To a solution containing 140 mg of 1,2,3-triphenyl-3-acetylcyclopropene (**28**) in 4 mL of methanol was added 125 mg of sodium borohydride. The solution was stirred at room temperature for 15 min, and then the solvent was removed under reduced pressure. The residue was taken up in ether, and the ethereal solution was washed with water and dried over magnesium sulfate. Removal of the solvent under reduced pressure left an oil which was subjected to preparative thick-layer chromatography with a 5% acetone–hexane mixture as the eluent. The major fraction contained 132 mg of a colorless oil whose structure was assigned as 1-(1,2,3-triphenylcyclopropen-1-yl)ethanol (**39**) on the basis of its spectral properties: IR (neat) 2.87, 5.48, 6.25, 6.69, 6.93, 9.36, 13.44, 14.70 μm; UV (95% ethanol) 228 nm (ϵ 5900), 316 (5400), 332 1300); NMR ($CDCl_3$, 90 MHz) δ 1.32 (d, 3 H, J = 7.0 Hz), 1.76 (s, 1 H), 5.15 (q, 1 H, J = 7.0 Hz), 7.09–7.96 (m, 15 H); mass spectrum, m/e 312 (M^+), 267 (base).

Anal. Calcd for $C_{23}H_{20}O$: C, 88.42; H, 6.45. Found: C, 88.39; H, 6.41.

A solution containing 180 mg of **39** in 150 mL of benzene was irradiated with a 450-W Hanovia lamp equipped with a Pyrex filter sleeve for 1 h. Removal of the solvent under reduced pressure left a yellow oil which was shown by NMR spectroscopy to consist of a 3:2 mixture of *trans*- and *cis*-1-methyl-2,3,4-triphenyl-1,4-dihydrofuran (**40**): NMR ($CDCl_3$, 90 MHz) major isomer δ 1.51 (d, 3 H, J = 7.5 Hz), 4.76 (s, 1 H), 5.09 (q, 1 H, J = 7.5 Hz); minor isomer δ 1.73 (d, 3 H, J = 7.5 Hz), 4.90 (s, 1 H), 5.17 (q, 1 H, J = 7.5 Hz). The isomeric mixture of cis and trans isomers was oxidized to 2-methyl-3,4,5-triphenylfuran (**17**) by heating a mixture containing the isomeric dihydrofurans with 5% palladium on carbon in refluxing xylene for 24 h. Removal of the solvent followed by column chromatography afforded 2-methyl-3,4,5-triphenylfuran (**17**) as the exclusive product.

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Registry No. **7**, 79918-99-3; **9**, 79919-00-9; **10**, 79919-01-0; **11**, 79919-02-1; **12**, 7404-46-8; **16**, 79919-03-2; **17**, 69490-59-1; **18**, 79919-04-3; (E)-**19**, 79919-05-4; **20**, 79919-06-5; **21**, 79919-07-6; **22**, 79919-08-7; **26**, 79919-09-8; **27**, 79919-10-1; **28**, 79919-11-2; **29**, 4970-80-3; **30**, 64749-01-5; **35**, 79919-12-3; **36**, 79919-13-4; **37**, 79919-14-5; **38**, 1801-42-9; **39**, 79919-15-6; *cis*-**40**, 79919-16-7; *trans*-**40**, 79919-17-8; 1,3-dithiane, 505-23-7; 1,2,3-triphenylcyclopropenyl perchlorate, 51778-20-2; 4-hydroxy-4-methyl-1,2,3-triphenylpenten-1-one, 79919-18-9; diphenylmethylcyclopropenyl perchlorate, 72612-89-6; 4-hydroxy-4-phenyl-(*E*)-1,2,3-triphenylpenten-1-one, 79919-19-0.

Structural Analysis of 5,6-Dideoxy-5-*C*-[(*R* and *S*)-phenylphosphinyl]-L-*ido*-hexopyranoses by 400-MHz Proton Nuclear Magnetic Resonance

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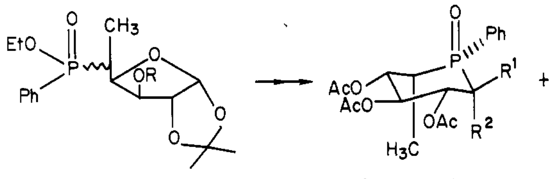
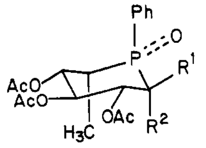
The 400-MHz ^1H NMR spectral analysis was performed on the five title compounds prepared from (5*RS*)-5,6-dideoxy-5-*C*-[(*RS*)-ethoxyphenylphosphinyl]-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranoses upon reduction with sodium dihydrobis(2-methoxyethoxy)aluminate, followed by the action of mineral acid and acetic anhydride. The results showed that the five products all had L-ido configuration with the pyranoid ring in the $^4C_1$(L) conformation; four of them were diastereomeric isomers at C-1 and the ring phosphorus atom, and the fifth was a further reduced 1-deoxy compound.

We reported in a previous paper[2] the preparation of five kinds of 5,6-dideoxy-5-*C*-(phenylphosphinyl)hexopyranoses from (5*RS*)-5,6-dideoxy-5-*C*-[(*RS*)-ethoxyphenylphosphinyl]-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranoses (**1** and **2**) in three steps. Of these, the two readily crystallized compounds with melting points of 199 and 215 °C were found by X-ray crystallographic analysis to possess the structures of 1,2,3,4-tetra-*O*-acetyl-5,6-dideoxy-5-*C*-[(*S*)-phenylphosphinyl]-L-*ido*-hexopyranoses **3** and **4**, respectively. However the structures of the other three products could not be established because their ^1H NMR spectra were not sufficiently resolved at 100 MHz. Thus we have taken the NMR spectra of all these products at 400 MHz, and we now describe the rest of the structures together with some interesting features of the first, detailed spectral data of these sugars having phosphorus in the hemiacetal ring.



1, R = H
2, R = THP

3, R^1 = H; R^2 = OAc
4, R^1 = OAc; R^2 = H
5, R^1 = R^2 = H



6, R^1 = H; R^2 = OAc
7, R^1 = OAc; R^2 = H

Results and Discussion

The proton absorptions of the structurally established products **3** and **4** were clearly separated from each other

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[1] (a) Okayama University. (b) The University of Alberta.

[2] Inokawa, S.; Yamamoto, K.; Kawamoto, H.; Yamamoto, H.; Lugar, P. *Carbohydr. Res.*, manuscript submitted for publication.

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