The Photochemistry of 4,4,5-Triphenyl-2-cyclohexen-1-one. Mechanistic and Exploratory Photochemistry. XXX[1]

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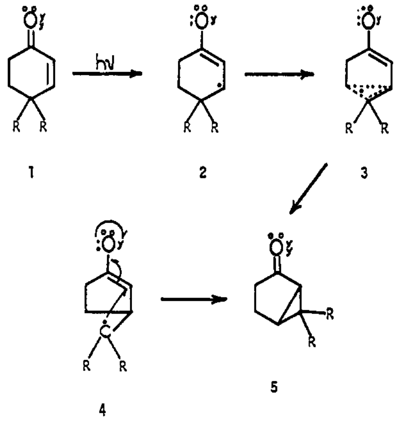
Abstract: The photochemistry of 4,4,5-triphenyl-2-cyclohexen-1-one was investigated for comparison with 4,4-diphenyl-2-cyclohexen-1-one, which undergoes phenyl migration, and with 4,5-diphenyl-2-cyclohexen-1-one, which rearranges by a type-A route. 4,4,5-Triphenyl-2-cyclohexen-1-one was found to follow the phenyl migration route. The reaction was very stereoselective with formation of the two 4,5,6-triphenylbicyclo[3.1.0]hexan-2-one stereoisomers having *trans*-phenyl groups on the cyclopropane ring. Also *cis*-3,4,5-triphenyl-2-cyclohexen-1-one and trace amounts of 2-(2,2-diphenylvinyl)-3-phenylcyclobutanone were formed. Evidence for a triplet route was provided by the "fingerprint method," utilizing acetophenone sensitization. Additionally, the photochemistry of the bicyclic ketones was studied. A stereoisomerization process was uncovered and evidence adduced for a mechanism in which bond 1,6 breaks and then recloses with different geometry. Also, a stereospecific isomerization of the bicyclic ketones to the 3,4,5-triphenyl-2-cyclohexen-1-ones was observed.

Two general types of rearrangements have been observed in the photolysis of 4-substituted 2-cyclohexenones. One is the type-A rearrangement[2] illustrated in Chart I. Examples have been provided by Gardner,[3] Chapman,[4] Jeger,[5] Zimmerman,[6,7] and their coworkers. The second type, outlined in Chart II, is the γ-β aryl migration which has been observed by Zimmerman and coworkers[8-10] and recently by Matsuura and Ogura[11] for Pummerer's ketone.

Chart I. The Type-A Rearrangement



The case of 4,5-diphenyl-2-cyclohexen-1-one studied by Zimmerman and Sam[7] (Chart III) was of special interest since, although either of the two pathways was an *a priori* possibility, isotopic tracer experiments

Chart II. The Aryl Migration Rearrangement

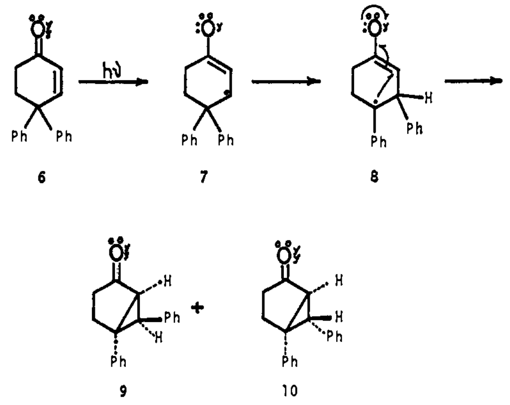
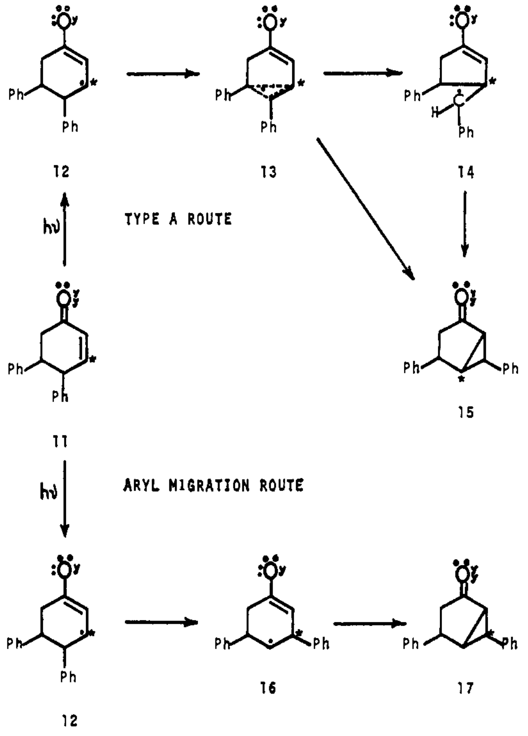


Chart III. Type-A and Aryl Migration Routes for 4,5-Diphenylcyclohexenone



* ^{14}C labeled at original C-3

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[1] Paper XXIX: H. E. Zimmerman, P. Hackett, D. F. Juers, and B. Schröder, *J. Amer. Chem. Soc.*, **89**, 5973 (1967).

[2] H. E. Zimmerman, *Science*, **153**, 837 (1966).

[3] W. W. Kwie, B. A. Shoulders, and P. D. Gardner, *J. Amer. Chem. Soc.*, **84**, 2268 (1962).

[4] O. L. Chapman, T. A. Rettig, A. I. Dutton, and P. Fitton, *Tetrahedron Letters*, 2049 (1963).

[5] B. Nann, D. Gravel, R. Schorta, H. Wehrli, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **46**, 2473 (1963).

[6] (a) H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. W. Staley, and M. Semmelhack, *J. Amer. Chem. Soc.*, **88**, 1965 (1966); (b) *ibid.*, **88**, 159 (1966).

[7] H. E. Zimmerman and D. J. Sam, *ibid.*, **88**, 4905 (1966).

[8] H. E. Zimmerman and J. W. Wilson, *ibid.*, **86**, 4036 (1964).

[9] H. E. Zimmerman, R. C. Hahn, H. Morrison, and M. C. Wani, *ibid.*, **87**, 1138 (1965).

[10] H. E. Zimmerman, R. D. Rieke, and J. R. Scheffer, *ibid.*, **89**, 2033 (1967).

[11] T. Matsuura and K. Ogura, *ibid.*, **88**, 2602 (1966).

showed the type-A process to predominate very heavily. There are at least three possible reasons why 4,5-diphenyl-2-cyclohexen-1-one selects the type-A pathway rather than phenyl migration in contrast to the preference for phenyl migration in the closely related 4,4-diphenyl-2-cyclohexen-1-one system.[8] First, inspection of Chart III reveals that the phenyl migration route leads, after phenyl migration, to a species **16** in which the odd electron is localized[12] on C-4. However, in the case of 4,4-diphenyl-2-cyclohexen-1-one (**6**) the corresponding species **8** has the electron at C-4 delocalized[12] by the phenyl group not migrating. A second reason could be the greater relief of phenyl–phenyl van der Waals repulsion expected in the migration of a phenyl group in 4,4-diphenyl-2-cyclohexen-1-one than in 4,5-diphenyl-2-cyclohexen-1-one; this assumes more repulsion between geminal phenyl groups than between vicinal ones. The third consideration is phenyl delocalization at the odd-electron center at C-5 of species **13**. To the extent that odd-electron stabilization at C-5 is especially important, the C-5 phenyl group would facilitate the type-A rearrangement of 4,5-diphenyl-2-cyclohexen-1-one (**11**) relative to 4,4-diphenyl-2-cyclohexen-1-one (**6**). The corresponding species **3** (R = Ph) which would be formed in a type-A rearrangement of the 4,4 isomer would have no similar stabilization at C-5.[14]

The present research began with 4,4,5-triphenyl-2-cyclohexen-1-one (**18**) in an attempt to gain insight into the reasons for the markedly different behavior of the 4,4- and 4,5-diphenyl-2-cyclohexen-1-ones. It will be noted by reference to Table I that 4,4,5-triphenyl-2-cyclohexen-1-one has all of the favorable features found in the type-A rearrangement of **11** and in the aryl migration in **6**. Thus, this molecule **18** has the phenyl group at C-5, potentially capable of facilitating the type-A process (Chart IV), and the phenyl group at C-4, possibly helpful in phenyl migration. Accordingly, its mode of reaction should demonstrate the extent to which the absence of type-A rearrangement in 4,4-diphenyl-2-cyclohexen-1-one derived from lack of C-5 stabilization and the extent to which the absence of phenyl migration in 4,5-diphenyl-2-cyclohexen-1-one arose from lack of C-4 delocalization. Hence, if the aryl migration route were found to be preferred for 4,4,5-triphenyl-2-cyclohexen-1-one (**18**), then it could be concluded that 4,5-diphenyl-2-cyclohexen-1-one (**11**) did not undergo this aryl migration because of lack of C-4 stabilization. On the other hand, if **18** were found to prefer the type-A rearrangement, it could be concluded that 4,4-diphenyl-2-cyclohexen-1-one (**6**) failed to undergo the same process because of lack of C-5 stabilization. This approach thus assesses the relative importance of stabilization at C-4 compared to C-5.

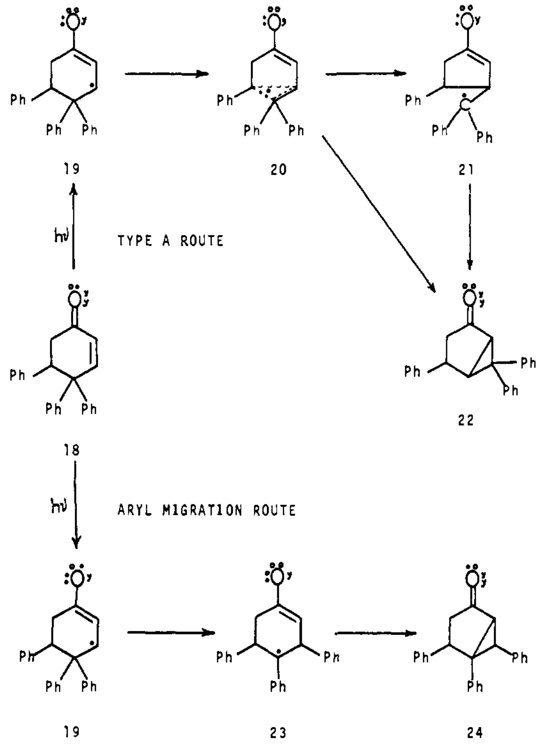
Table I. Summary of Structural Effects Expected in the Rearrangements of 4,4-Diphenyl-, 4,5-Diphenyl-, and 4,4,5-Triphenyl-2-cyclohexen-1-one

Factor in type-A rearr	4,4-Diphenyl[b]	4,5-Diphenyl[a]	4,4,5-Triphenyl
Stabilization at C-4	Yes	Yes	Yes
Stabilization at C-5	No	Yes	Yes
Relief of van der Waals repulsion	No	Minor	Minor

Factor in aryl migration	4,4-Diphenyl[b]	4,5-Diphenyl[a]	4,4,5-Triphenyl
Stabilization at C-4	Yes	No	Yes
Stabilization at C-5		Not a factor	
Relief of van der Waals repulsion	Yes	Minor	Yes

[a] Type-A process preferred for this compound. [b] Aryl migration preferred in this compound.

Chart IV. Type-A and Aryl Migration Routes for 4,4,5-Triphenyl-2-cyclohexen-1-one



Synthesis of 4,4,5-Triphenyl-2-cyclohexen-1-one Reactant. The synthesis of 4,4,5-triphenyl-2-cyclohexen-1-one was carried out as delineated in Chart V starting with the known 2,2-diphenylacetophenone.[15] The condensation of 2,2-diphenylacetophenone with methyl vinyl ketone afforded, after chromatography, 3,4,4-triphenyl-2-cyclohexen-1-one (**25**), mp 145–146°, which was reduced to 3,4,4-triphenylcyclohexanone (**26**), mp 171–172°, with lithium in liquid ammonia. Bromination of 3,4,4-triphenylcyclohexanone with molecular bromine in carbon tetrachloride followed by dehydrobromination in refluxing dimethylformamide in the presence of lithium chloride and lithium carbonate gave, after chromatography, the desired starting material, 4,4,5-triphenyl-2-cyclohexen-1-one (**18**), mp 172.5–174.5°.

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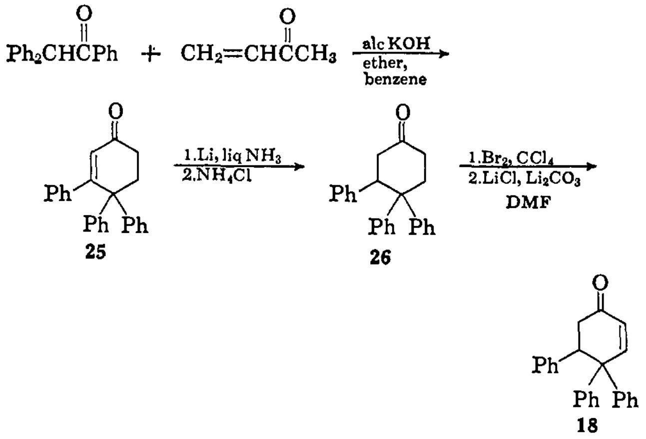
(12) Evidence is available which suggests that the following step of 2,4 bonding is concerted with migration in the photochemical reactions of 2-cyclohexenones.[10,13] Nevertheless, focusing attention on the idealized species is conceptually helpful.

(13) (a) H. E. Zimmerman and K. G. Hancock, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, Abstract O-130; (b) unpublished results.

(14) Another factor could be steric. It seems likely that an axial C-4 phenyl is needed for migration. This may or may not be available in the ground state of *trans*-4,5-diphenyl-2-cyclohexen-1-one. Due to sp^2 hybridization at all but one of the carbons 1,3 related to the phenyl groups, it is not certain that the axial–axial conformation is higher in energy.

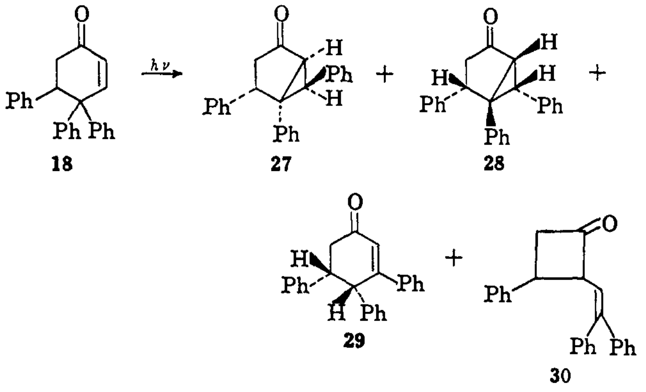
(15) C. F. Koelsch, *J. Amer. Chem. Soc.*, **54**, 2051 (1932).

Chart V. Synthesis of 4,4,5-Triphenyl-2-cyclohexen-1-one



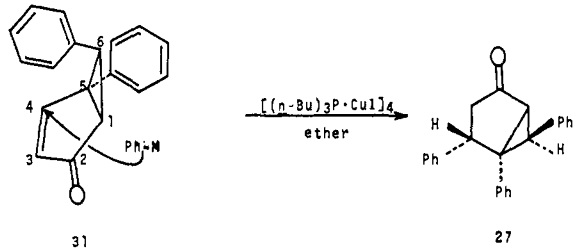
Photolysis of 4,4,5-Triphenyl-2-cyclohexen-1-one. In a typical run, 5.00 g of 4,4,5-triphenyl-2-cyclohexen-1-one (**18**) was irradiated for 1.75 hr in 1 l. of 3:1 *t*-butyl alcohol–benzene using a 450-W, medium-pressure mercury lamp and a Pyrex filter. This afforded a mixture of four products (see Chart VI) that were separated by chromatography on silica gel. These conditions gave the isomeric ketones **27**, mp 157.5–160°, 2.028 g (40.6%); **28**, mp 138–140°, 1.028 g (20.6%); **29**, mp 190–193°, 0.669 g (13.4%), and **30**, mp 101–103°, 0.017 g (0.3%), in addition to recovered starting material **18**, mp 171.5–174°, 0.296 g (5.9%).

Chart VI. Photolysis of 4,4,5-Triphenyl-2-cyclohexen-1-one



Elucidation of Structures. Photoketone 27. Elemental analysis showed the photoproduct **27** to be isomeric with starting material **18**. The infrared spectrum in chloroform exhibited 5.83-μ carbonyl absorption similar to that of 5,6-diarylbicyclo[3.1.0]hexan-2-ones (5.80–5.83 μ)[7,8,10] and the carbonyl absorption of dihydroumbellulone (5.81 μ)[16] and can be considered characteristic of the bicyclo[3.1.0]hexan-2-one system. The nmr spectrum of photoketone **27** had a doublet of doublets at τ 6.27 that was assigned to the benzylic hydrogen at C-4 (bicyclo[3.1.0] numbering). Base-catalyzed treatment with deuterium oxide exchanged two hydrogens and the τ 6.27 quartet collapsed to a singlet. This corresponds to loss of the methylene hydrogens at C-3, and the lack of any further CH–CH coupling suggested the presence of a phenyl rather than a hydrogen at C-5. The cyclopropyl hydrogens appeared as a two-hydrogen singlet at τ 7.03 due to the fortuitous identity of chemical shifts. From these data and the expectation of a type-A or aryl migration product, it seemed that photoketone **27** was most likely a 4,5,6-triphenylbicyclo[3.1.0]hexan-2-one stereoisomer. The infrared carbonyl absorption at 5.83 μ gave the first hint that the phenyls on the cyclopropane ring were *trans* related. Previous photoketones[8,10] with *cis* aryl groups exhibited 5.80–5.81-μ carbonyl absorption while the *trans* isomers had 5.82–5.83-μ absorption. The structure of photoketone **27** was proved by synthesis. Thus 1,4 addition of phenylmagnesium bromide to *trans*-5,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**31**) led to **27** as shown in Chart VII. Photoketone **27** was obtained in good yield and proved identical in all respects with the photochemically obtained material. This synthesis unambiguously defined the stereochemistry at C-5 and C-6. Additionally, the assignment of configuration at C-4 was based on the reasonable assumption that the Grignard reagent approached from the less hindered side, the side not blocked by the C-6 phenyl. Thus, **27** was *cis,trans*-4,5,6-triphenylbicyclo-[3.1.0]hexan-2-one.

Chart VII. Synthesis of *cis,trans*-4,5,6-Triphenylbicyclo[3.1.0]hexan-2-one



M ≡ Cu or MgX

Photoketone 28. Photoketone **28** also had 5.83-μ infrared carbonyl absorption characteristic of a bicyclo[3.1.0]hexan-2-one. Inspection of the nmr spectra of **28** before and after base-catalyzed deuterium oxide treatment was quite helpful. After deuteration there was revealed an AB quartet between τ 6.53 and 7.60 (J_{AB} = 10 cps) which was assigned to two cyclopropyl hydrogens. The coupling constant of 10 cps compared well with the values reported[8,10,17] for *cis*-cyclopropane hydrogens.

The nmr spectrum before deuterium oxide treatment had a one-hydrogen triplet (overlapping doublet of doublets, J = 11, 10 cps) at τ 5.73 which was assigned to a benzylic hydrogen at C-4 (bicyclo[3.1.0] numbering). After deuterium oxide treatment, the benzylic hydrogen appeared as a doublet (J = 11 cps) and there was loss of one hydrogen in the τ 7.20–8.15 region leaving a clear doublet (J = 11 cps) at τ 7.87. This was interpreted to signify that only one of the C-3 methylene hydrogens had been exchanged. The fact that only one of the methylene hydrogens at C-3 could be exchanged for deuterium indicated that approach from one side of **28** must be more hindered than for *cis,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one (**27**), in other words, that **28** had phenyls at C-4 and C-6 which were both blocking approach to C-3 from the same side. The lack of any coupling between the benzylic hydrogen at C-4 and the cyclopropyl hydrogens confirmed the presence of a phenyl rather than a hydrogen at C-5. The above data, collectively, indicated

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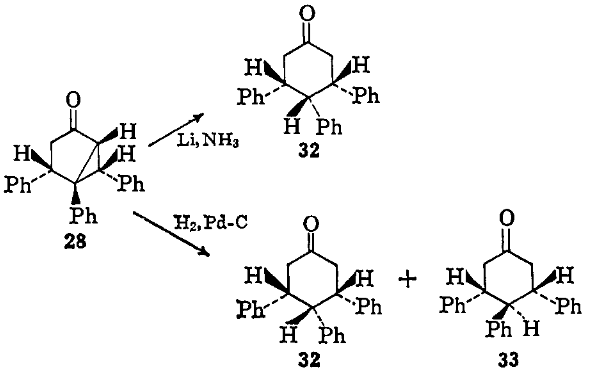
(16) R. H. Eastman and J. C. Selover, *J. Amer. Chem. Soc.*, **76**, 4118 (1954).

(17) J. D. Graham and M. T. Rogers, *ibid.*, **84**, 2249 (1962).

28 to be *trans,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one.

Chart VIII. Degradation of Photoketone **28**



Confirmation of this assignment was obtained by degradation. Reaction of **28** with lithium in liquid ammonia (Chart VIII) gave *cis,cis*-3,4,5-triphenylcyclohexanone (**32**) and catalytic hydrogenation of **28** afforded both *cis,cis*- (**32**) and *trans,trans*-4,5,6-triphenylcyclohexanones (**33**). (The structures and stereochemistry of the triphenylcyclohexanones are discussed below.) Of the four possible 4,5,6-triphenylbicyclo[3.1.0]hexan-2-one stereoisomers, only the *cis,cis* and *trans,trans* isomers could give the observed degradation products. Therefore, the degradation results coupled with the nmr data showing the presence of *trans*-related phenyls (*cis*-related hydrogens, *vide supra*) on the cyclopropane ring firmly established photoketone **28** to be *trans,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one.

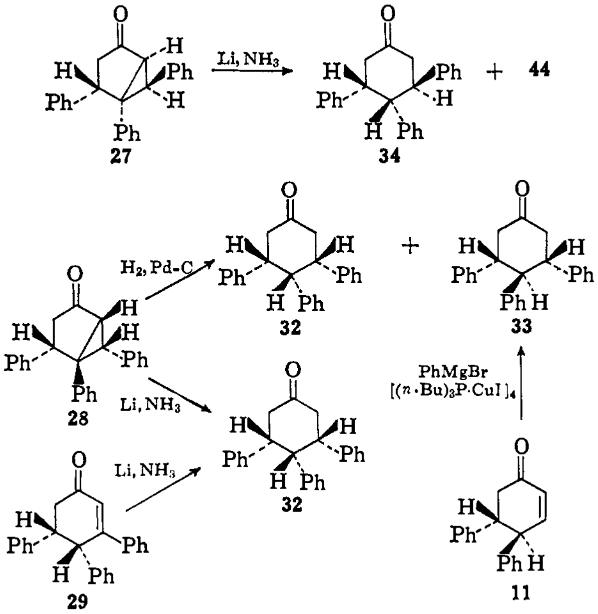
Photoketone 29. Photoketone **29** was shown by spectral, melting point, and mixture melting point comparisons to be identical with 3,4,5-triphenyl-2-cyclohexen-1-one prepared by the method of Chapurlat and Dreux.[18] Further stereochemical evidence was obtained from lithium in liquid ammonia reduction to give *cis,cis*-3,4,5-triphenylcyclohexanone (note below) showing that the phenyls at C-4 and C-5 of **29** were *cis* related and that photoketone **29** was *cis*-3,4,5-triphenyl-2-cyclohexen-1-one.

Photoketone 30. Photoketone **30** exhibited a 5.63-μ carbonyl band in the infrared which is characteristic[19] of a cyclobutanone and compared with the 5.62-μ band observed by Zimmerman and Sam[7] for 2-(*cis*-styryl)-3-phenylcyclobutanone. The nmr spectrum showed an ethylenic hydrogen at τ 3.90 as a doublet, J = 9 cps; this may be compared with the reported[20] chemical shift at τ 3.90 for the ethylenic hydrogen of 1,1-diphenylpropene. The ultraviolet spectrum (ethanol), λ_{max} 258 mμ (ϵ 16,000) and λ_{min} 243 mμ (ϵ 11,000), was similar to that reported[20] for 1,1-diphenylpropene, λ_{max} 248 (ϵ 17,600) and λ_{min} 234 (ϵ 10,000). These data and analogy to the rearrangement of 4,5-diphenyl-2-cyclohexen-1-one[7] (**11**) suggested that photoketone **30** is 2-(2,2-diphenylvinyl)-3-phenylcyclobutanone.

Stereochemistry of the 3,4,5-Triphenylcyclohexanones. The above stereochemical assignments to **28** and **29** (but not to **27**) depend on knowledge of the configurations of the 3,4,5-triphenylcyclohexanones. The assignment of the configuration of *cis,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one (**27**) was independent of these cyclohexanones and provided a starting point. Thus, lithium–liquid ammonia reduction of *cis,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one (**27**) (note Chart IX) afforded a 3,4,5-triphenylcyclohexanone, mp 175–176°, that must be *cis,trans*-3,4,5-triphenylcyclohexanone since only the configuration at C-4 (cyclohexane numbering) was affected in the reaction, and either stereochemical course at C-4 would lead to *cis,trans*-3,4,5-triphenylcyclohexanone (**34**).

trans,trans-Triphenylcyclohexanone was considered next. The 1,4 addition of phenylmagnesium bromide to *trans*-4,5-diphenyl-2-cyclohexen-1-one (**11**) afforded another 3,4,5-triphenylcyclohexanone, mp 200–202° (Chart IX). *A priori*, the addition could give either the *cis,trans* or *trans,trans* isomer. However, the *cis,trans* isomer **34** was already known and different, signifying that the 200–202° compound was *trans,trans*-3,4,5-triphenylcyclohexanone (**33**). This stereochemical course is reasonable on the basis of the less hindered approach to C-3 being *trans* to the C-4 phenyl group; models do confirm this.

Chart IX. Synthesis of 3,4,5-Triphenylcyclohexanone Stereoisomers



The third isomer, mp 145–146°, was obtained from lithium–liquid ammonia reduction of **28** and **29** (note Chart IX) and as one isomer from catalytic hydrogenation of **28**. By the process of elimination, the *cis,cis*-3,4,5-triphenylcyclohexanone (**32**) stereochemistry can be assigned. There is additional evidence for this assignment. Malhotra, Moakley, and Johnson[21] have reported that 3,4-diphenyl-2-cyclohexen-1-one exists with the C-4 phenyl axial because of unfavorable $A^{(1,2)}$ strain (caused by van der Waals repulsion between the C-3 and C-4 phenyls when the C-4 phenyl is equatorial). They found that when 3,4-diphenyl-2-cyclohexen-1-one is treated with lithium in liquid ammonia the C-3 phenyl becomes equatorial and *cis* to the C-4 phenyl. Using the same argument the more stable stereoisomer of 3,4,5-triphenyl-2-cyclohexen-1-one (**29**) should be

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[18] R. Chapurlat and J. Dreux, *Bull. Soc. Chim. France*, 349 (1962).

[19] L. J. Bellamy, "The Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958.

[20] A. Jung and M. Brini, *Bull. Soc. Chim. France*, 697 (1964).

[21] S. K. Malhotra, D. F. Moakley, and F. Johnson, *Tetrahedron Letters*, 1089 (1967).

Table II. Sensitized and Direct Irradiations of 4,4,5-Triphenyl-2-cyclohexen-1-one

	Per cent[a]		Product ratio	
Compound	Control runs	Sensitized run	Control runs	Sensitized run
4,4,5-Triphenyl-2-cyclohexen-1-one (**18**)	74.5 ± 0.6[b]	47.1 ± 1.5[b]		
	1.8 ± 0.1[c]			
cis,trans-4,5,6-Triphenylbicyclo[3.1.0]hexan-2-one (**27**)	12.4 ± 0.6[b]	27.6 ± 0.3[b]	1.00[b]	1.00[b]
	53.2 ± 2.7[c]		1.00[c]	
trans,trans-4,5,6-Triphenylbicyclo[3.1.0]hexan-2-one (**28**)	6.8 ± 0.3[b]	15.2 ± 0.8[b]	0.55 ± 0.05[b]	0.55 ± 0.04[b]
	28.8 ± 1.4[c]		0.54 ± 0.07[c]	
cis-3,4,5-Triphenyl-2-cyclohexen-1-one (**29**)	4.9 ± 2.0[b]	9.0 ± 0.4[b]	0.40 ± 0.18[b]	0.33 ± 0.02[b]
	16.2 ± 3.6[c]		0.31 ± 0.08[c]	

[a] Based on near 100% mass balance. [b] 300–375-mμ filter. [c] 322–387-mμ filter.

cis with the C-4 phenyl axial. The preparation of 3,4,5-triphenyl-2-cyclohexen-1-one[18] involves refluxing methanol–sodium methoxide. These conditions seem likely to be equilibrating and hence should give the *cis* product. Lithium–liquid ammonia reduction of the preferred conformer would then afford *cis,cis*-3,4,5-triphenylcyclohexanone (**32**).

Multiplicity of the Reaction. Evidence on the multiplicity of the rearranging species was gained through acetophenone sensitization. A solution of 4,4,5-triphenyl-2-cyclohexen-1-one (**18**) was irradiated at 300–370 mμ for 25 min in a control run followed by another run of 25 min, identical with the control except for the presence of acetophenone. The concentration of the acetophenone was such that it absorbed over 96% of the light. The product analyses by silica gel chromatography and nmr are shown in Table II; details are given in the Experimental Section. Table II also contains the results of a second direct irradiation for 2.0 hr using a 322–387-mμ solution filter.

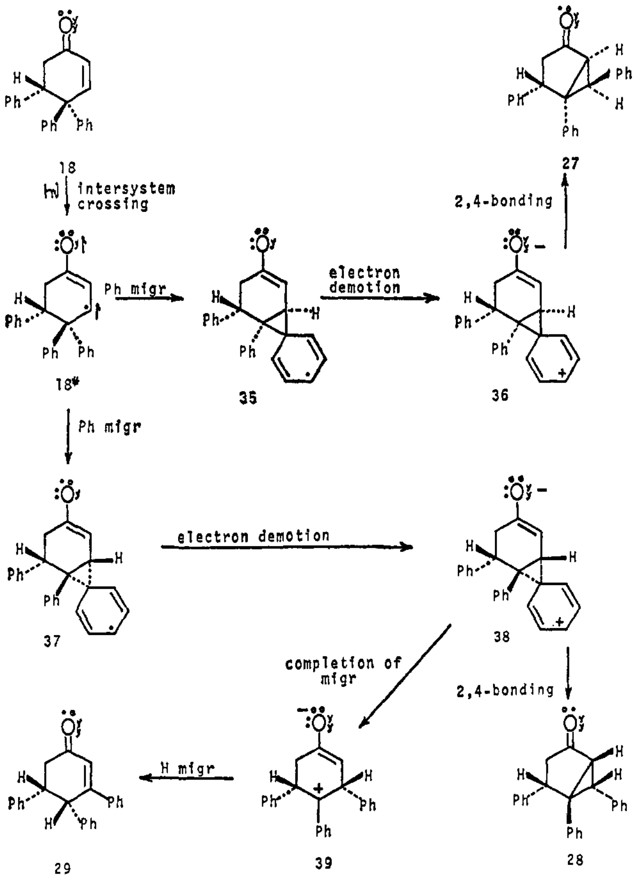
The enone **18** concentration, 4.35 × 10^{-3} *M*, was sufficiently low that acetophenone singlet could not survive long enough to collide with enone molecules but large enough to allow acetophenone triplet to collide with enone prior to spontaneous decay.[6]

The increased consumption of reactant in the sensitized run compared to the direct one might merely arise from more complete light capture with acetophenone present under the conditions used, and we cannot conclude that intersystem crossing is necessarily inefficient for 4,4,5-triphenyl-2-cyclohexen-1-one. However, the formation of the usual products starting with preformed triplet (*i.e.*, in the sensitized run) shows that the rearrangement by the triplet is possible. Additionally, the product distribution in such sensitized runs provides a "fingerprint" characteristic of the triplet. We note in Table II (columns 3 and 4) that the product distribution in the direct runs is the same within experimental error as in the sensitized case. It would be exceedingly fortuitous for another species to give the same "fingerprint," and we can conclude that the triplet is the reacting species in the direct runs as well.

This brings up a more general point, namely one of the kind of evidence providing valid proof of a triplet reaction. Mere quenching by high concentrations of dienes can no longer be accepted as sufficient evidence where the rate of unimolecular singlet decay (most often controlled in ketones by intersystem crossing) is unknown. Recently Hammond and coworkers[22] have noted destruction of naphthalene singlets by dienes at rates which approach diffusion control despite the singlet diene energies being higher than that of naphthalene. With quenching then being potentially a singlet process, it is much safer to rely on the "fingerprint method" presently described.[23,24]

Mechanistic Conclusions. The mechanism for the formation of the photoketones **27**, **28**, and **29** consists of initial n–π* excitation to a singlet excited state which then undergoes intersystem crossing to an excited triplet state depicted by species **18*** (Chart X). Migra-

Chart X. Mechanism of 4,4,5-Triphenyl-2-cyclohexen-1-one Photorearrangement



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[22] L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *J. Amer. Chem. Soc.*, 88, 3665 (1966).

(23) The "fingerprint method" has had earlier use in our laboratory by Zimmerman and Hancock[18] and Zimmerman, Rieke, and Scheffer.[10]

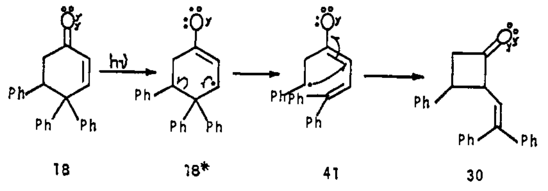
(24) One can rely on diene quenching in those cases where the diene after quenching is converted to a product deriving only from the diene triplet and not from the singlet or *vice versa*. Alternatively, if the rate of reactant singlet decay is so rapid that the diene cannot diffuse to the singlet, quenching again is a safe criterion.

tion of the C-4 phenyl which is *trans* to the C-5 phenyl forms species **35** which on demotion and concerted 2,4 bonding with inversion at C-4 gives *cis,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one (**27**). This inversion has precedent in the earlier work of Zimmerman, Rieke, and Scheffer[10] and Zimmerman and Hancock.[13] Species **37** arises from similar migration of the C-4 phenyl *cis* related to the C-5 phenyl; demotion and 2,4 bonding, again with C-4 inversion, then gives *trans,-trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one (**28**). Electron demotion may take place during or after migration. It cannot precede the rate-limiting stage of the reaction as has been shown by Zimmerman, Rieke, and Scheffer.[10] Thus, earlier evidence[10] indicates that if **36** and **38** are reached they cannot revert to enone **18**. The fact that neither of the isomeric bicyclo[3.1.0] ketones with *cis*-phenyls on the cyclopropane ring was observed supports the previous evidence[10,13] that 2,4 bonding is concerted with the aryl migration step in cyclohexenone photolyses. Figure 1 showing species **40** (*i.e.*, **35**, **36**, **37**, or **38**) is helpful in visualizing the concerted migration and 2,4 bonding with inversion at C-4.

The formation of *cis*-3,4,5-triphenyl-2-cyclohexen-1-one (**29**), but not its stereoisomer, suggests **39** as the precursor. This pathway might be forced on the molecule as a competitor since 2,4 bonding leads to the strained *trans,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one (**28**) in which the phenyls at C-4 and C-6 (bicyclo[3.1.0] numbering) are severely forced together. It should be noted that **29** does not arise from secondary photolysis of **28** since **28** was found to react much too slowly under the reaction conditions. It was also shown that **29** was stable under the conditions of the photolysis and, therefore, was not an intermediate leading to any of the other observed photoketones.

The 2-(2,2-diphenylvinyl)-3-phenylcyclobutanone (**30**) probably arose through cleavage of the carbon–carbon bond between C-4 and C-5 (Chart XI) by a reaction similar to that observed by Zimmerman and Sam[7] in the irradiation of 4,5-diphenyl-2-cyclohexen-1-one (**11**).

Chart XI. Cyclobutanone Formation



Neither of the isomeric 4,6,6-triphenylbicyclo[3.1.0]-hexan-2-ones which would result from a type-A rearrangement was found although the *trans* isomer was synthesized (note Experimental Section) and, with its nmr spectrum at hand, 1% of it in the appropriate chromatographic fraction could have been detected.

Further Photochemical Interconversions. Although the only bicyclic photoketones observed in the initial irradiation had *trans*-related phenyls on the cyclopropane ring, it was anticipated that further photolysis of *cis,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one (**27**) and *trans,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one (**28**) might cause isomerization to the corresponding *cis* isomers in analogy to the findings of Zimmerman, *et al.*,[8,10] Moreover, should this isomerization occur, it would directly answer the question posed earlier,[8,10] namely which of the three ring bonds are broken and re-formed in such bicyclic ketone stereoisomerizations. For example, as shown for **27** in Chart XII, peripheral bond (a or c) fission, free rotation, and reclosure lead to a different stereoisomer than the internal bond (b) scission route.

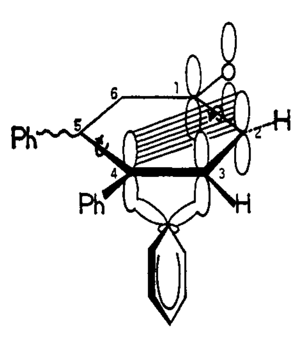
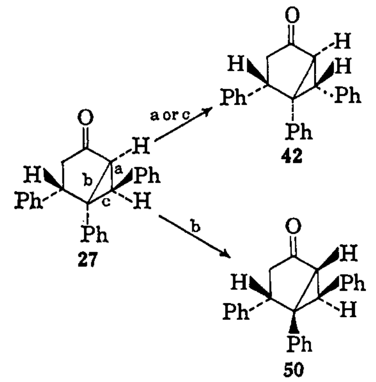


Figure 1. Stereoselectivity rationalized by 2,4 bonding concerted with phenyl migration.

Chart XII. Stereoisomerization Routes of Photoketone 27



The photolysis of *cis,trans*-4,5,6-triphenylbicyclo-[3.1.0]hexan-2-one (**27**) for 13.75 hr in 3:1 *t*-butyl alcohol–benzene using a Pyrex filter gave, after chromatography on silica gel and recrystallization, 46.5% recovered starting material (**27**), 41.7% of a new photoketone **42**, mp 157.5–159.5°, and 2.4% of a mixture containing **42** and another photoketone, **43**.

Photoketone **42** had a 5.81-μ infrared carbonyl peak which suggested it to be an isomeric bicyclo[3.1.0]-hexan-2-one. Catalytic hydrogenation of **42** gave 3-benzyl-*cis*-3,4-diphenylcyclopentanone (**44**), independently obtained from lithium–liquid ammonia reduction of **27** (Chart XIII). This showed that **42** and **27** were identical except for their configuration at C-6 and, therefore, photoketone **42** was *cis,cis*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one. Thus the expected stereoisomerization was realized.

The second new ketone, **43**, could not be isolated. However, comparison of the infrared and nmr spectra of the mixture of **42** and **43** with authentic material confirmed that photoketone **43** was *trans*-3,4,5-triphenyl-2-cyclohexen-1-one (note Experimental Section for synthesis).

It seemed of interest to study the reverse reaction, namely the irradiation of *cis,cis*-4,5,6-triphenylbicyclo-

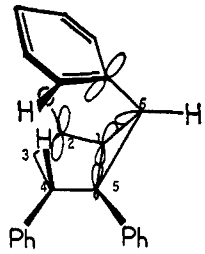
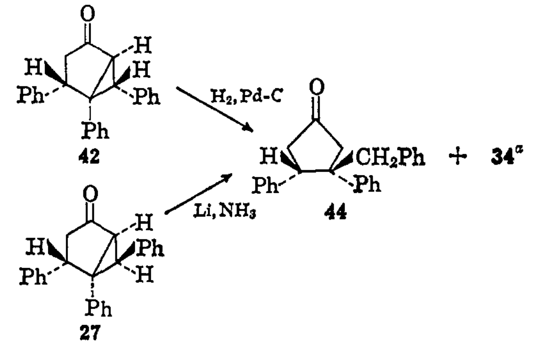


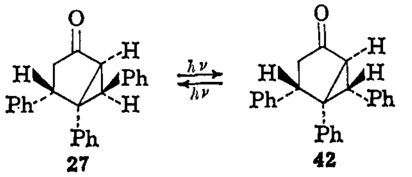
Figure 2. Overlap and steric interactions in photoketone **27**.

[3.1.0]hexan-2-one (**42**). Irradiation of **42** for 16.5 hr afforded mainly *cis,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one (**27**) and starting material. Hence, the photochemical stereoisomerization was shown to be reversible (eq 1).

Chart XIII. Degradation of *cis,cis*- and *cis,trans*-4,5,6-Triphenylbicyclo[3.1.0]hexan-2-ones



ᵃOnly from **27**.

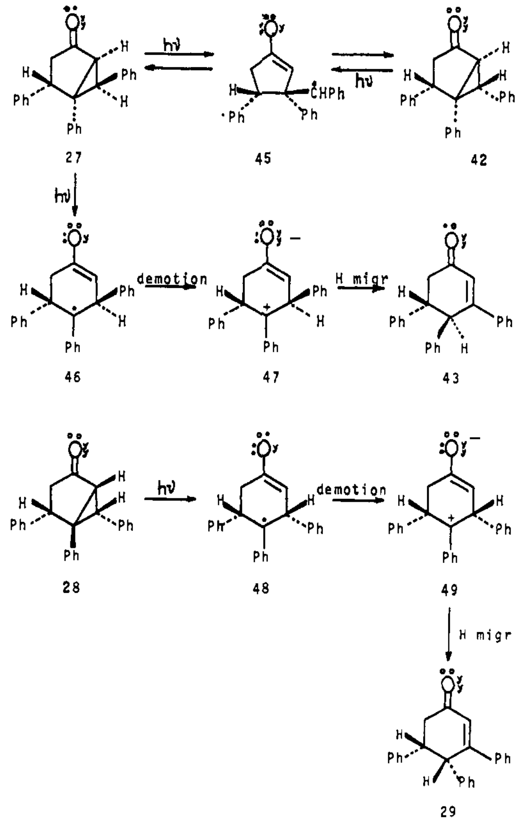


(1)

In similar fashion *trans,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one (**28**) was photolyzed to give mostly *cis*-3,4,5-triphenyl-2-cyclohexen-1-one (**29**); however, there was evidence (note Experimental Section) for formation of some isomeric bicyclic ketone (probably **50**). We note that normally stereoisomerization in the three-membered ring predominates, although in the case of *trans,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one (**28**), the major reaction course is six-membered-ring product (*i.e.*, **29**) formation.

Mechanism of the Bicyclic Ketone Photoreactions. Chart XIV summarizes in mechanistic detail the observations described above. It can be deduced from the stereochemistry observed that the isomerization of *cis,trans*- and *cis,cis*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-ones (**27** and **42**) must occur through peripheral (bond a)[25] rather than internal (bond b) fission. Where products were obtained by internal bond (bond b) scission, the intermediates (*e.g.*, **47** and **49**) appear to be unable to reclose to bicyclic product but undergo hydrogen migration to afford six-membered-ring enones **29** and **43**.

Chart XIV. Irradiation of *cis,trans*- and *trans,trans*-4,5,6-Triphenylbicyclo[3.1.0]hexan-2-ones



Models show that there is better overlap between the p orbital at C-2 and the orbital of the external C-1, C-6 bond (bond a) of the cyclopropane ring than with the orbital of the internal C-1,C-5 bond (bond b); this is shown in Figure 2.[26] To the extent that the C-6 phenyl orients itself to overlap with bond a, fission of bond a will be facilitated. However, in photoketone **28** the bulky phenyl group at C-4 does not allow the C-6 phenyl to assume a favorable conformation for overlap with bond a (note Figure 2 with C-4 stereochemistry reversed). As a result, there is little stabilization for the impending external bond fission and the internal bond (bond b), which does have phenyl overlap, is broken. Thus, phenyl stabilization is even more important than overlap of the cyclopropane bond with the carbonyl π system.

Conclusion

We note in the preceding that the reactions observed have been understood even in stereochemical detail using excited-state structures and ground-state type reasoning. Thus we have assumed the requirement for continuous electron redistribution which we postulated

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(25) Inspection shows that fission, rotation, and reclosure of bond c will also account for the observed stereochemistry. This cannot be ruled out rigorously. However, fission of the α,β bonds of cyclopropyl ketones is a facile process (*e.g.*, note Zimmerman and Hancock, ref 13) while a process paralleling diphenylcyclopropane stereoisomerization (*i.e.*, fission of bond c) would most likely involve a nonvertical process (note G. S. Hammond, P. Wyatt, C. D. Deboer, and N. J. Turro, *J. Amer. Chem. Soc.*, **86**, 2532 (1964)) due to the high vertical excitation energy required and a nonvertical process probably would be less efficient. Additionally, positive evidence is available for internal α,β bond fission (*i.e.*, b) which should be less favorable than bond a scission. This leads us to expect bond a fission to be even more prevalent. Definitive experiments are presently in progress.

(26) In Figure 2 the carbonyl group is pictured as planar for simplicity, although in fact it is likely to be pyramidal with a low inversion barrier (note (for the formaldehyde case) J. C. D. Brand and D. G. Williamson *Advan. Phys. Org. Chem.*, **1**, 365 (1963)). This provides less stringent requirements for overlap with the cyclopropyl orbitals. Additionally, these orbitals are "banana-like." Bond b orbitals are out of the five-ring plane and overlap of the carbonyl carbon p orbital with the orbitals of bond b is appreciable although less than with the orbitals of bond a.

earlier.[27–29] This requirement is an energetic one, which assumes utilization of low-energy pathways.

Experimental Section[30]

2,2-Diphenylacetophenone. This was prepared by the method of Koelsch[15] using desyl chloride obtained by the procedure of Fieser.[31,32]

3,4,4-Triphenyl-2-cyclohexen-1-one. In a typical preparation 40.0 g (0.147 mol) of 2,2-diphenylacetophenone was dissolved in 700 ml of benzene and 250 ml of ether, and 20.0 g (0.303 mol) of potassium hydroxide (reagent, 85%) in 85 ml of 95% ethyl alcohol was added. A solution containing 20 ml of methyl vinyl ketone in 50 ml of ether was introduced dropwise over *ca.* 1 hr with stirring. After 17, 41, and 53 hr, 7-, 10-, and 10-ml portions of methyl vinyl ketone, each dissolved in 50 ml of ether, were added over *ca.* 1 hr, for a total of 47 ml (40.6 g, 0.563 mol) of methyl vinyl ketone. After 72 hr of stirring, 200 ml of 95% ethyl alcohol was added. It was found that inclusion of the additional alcohol at the beginning of the reaction, or failure to add any, decreased the yield of 3,4,4-triphenylcyclohexenone significantly. After 90 hr the mixture was diluted with ether. The benzene–ether solution was washed with dilute hydrochloric acid and then with water. The aqueous extracts were washed with ether. After drying, the combined ether–benzene solution was concentrated *in vacuo* to give a deep red viscous material that was chromatographed on a 7.0 × 120 cm column slurry packed in 5% ether–hexane with 60–200 mesh silica gel (Davison, grade 950). Elution was with 4 l. of 5%, 6 l. of 10%, 10 l. of 15%, and 8 l. of 20% ether–hexane, and 1-l. fractions were collected: fractions 1–4, 0.040 g of hydrocarbon impurity; 5–6, 2.14 g of diphenylmethane; 7–8, 0.075 g of a yellow oil; 9–13, 7.87 g (19.7%) of recovered 2,2-diphenylacetophenone; 14–20, 6.73 g of an unidentified orange solid; 21–28, 19.88 g (41.7%) of 3,4,4-triphenyl-2-cyclohexen-1-one as a yellow oil which after recrystallization from hexane–methylene chloride with Norit treatment gave 14.46 g (30.4%) of colorless crystals, mp 145–146°.

The infrared spectrum ($CHCl_3$) showed bands at 3.32, 6.03 (s), 6.27, 6.70, 6.92, 7.51, 7.91, 10.07, 11.10 (s), and 14.24 μ; nmr ($CDCl_3$): τ 2.50–3.03 multiplet (15 H, aromatic), 3.40 singlet (1 H, CH=), 7.03–7.88 multiplet (4 H, CH_2–CH_2).

Anal. Calcd for $C_{24}H_{20}O$: C, 88.85; H, 6.21. Found: C, 88.81; H, 6.20.

3,4,4-Triphenylcyclohexanone. To a flame-dried apparatus equipped with a Dry Ice condenser and a potassium hydroxide drying tube was added 15.0 g (0.0463 mol) of 3,4,4-triphenyl-2-cyclohexen-1-one in 400 ml of anhydrous tetrahydrofuran and 100 ml of anhydrous ether. Ammonia was distilled into the flask until the total volume of the solution was 1500–1600 ml. Lithium metal (1.00 g, 0.144 g-atom) was added over 10 min and the deep-colored solution was stirred for 45 min before careful addition of 15.0 g (0.280 mol) of anhydrous ammonium chloride. The ammonia was evaporated with stirring and the resulting mixture diluted with ether and washed with dilute hydrochloric acid and water. The aqueous layer was ether extracted and the combined ether solution dried. Solvent removal *in vacuo* yielded 14.16 g of a white solid, mp 115–182°. Recrystallization from hexane–methylene chloride after filtering a small amount of insoluble impurity gave 9.70 g of colorless crystals, mp 165–169°. Concentrating the mother liquors, filtering a further small amount of insoluble material, and cooling gave another crop of 1.95 g, mp 165.5–169.5°, totaling 78.0%. Crystallization from ethyl acetate–hexane gave colorless needles, mp 171–172°.

The infrared spectrum ($CHCl_3$) showed bands at 3.32, 5.87 (s), 6.25, 6.70, 6.92, 7.12, 9.25, and 14.35 μ; nmr ($CDCl_3$): τ 2.28–3.47 multiplet (15 H, aromatic), 5.75 broad doublet (1 H, J = 7 cps, PhCH), 6.57–7.80 multiplet (6 H, methylene).

Anal. Calcd for $C_{24}H_{22}O$: C, 88.31; H, 6.79. Found: C, 88.01; H, 6.94.

4,4,5-Triphenyl-2-cyclohexen-1-one. Bromine (4.40 ml, 12.88 g, 0.0805 mol) was added with stirring to a solution of 25.0 g (0.0767 mol) of 3,4,4-triphenylcyclohexanone in 750 ml of carbon tetrachloride at such a rate that the solution maintained a light orange color. The solvent and hydrogen bromide were removed *in vacuo* leaving an amber, viscous material whose infrared spectrum showed a sharp carbonyl band at 5.80 μ. Attempts to isolate the 2-bromo-4,4,5-triphenylcyclohexanone by column chromatography on silica gel were unsuccessful so the crude product was dehydrobrominated without further purification. The crude bromination product was refluxed gently with stirring under nitrogen for 17 hr in 625 ml of dimethylformamide containing 10.7 g (0.254 mol) of lithium chloride and 24.4 g (0.330 mol) of lithium carbonate. The dark brown suspension was cooled, diluted with ether, and washed with dilute hydrochloric acid and water. The aqueous washings were ether extracted and these extracts were washed with water. The combined ethereal layers were dried and the solvent removed *in vacuo* giving a dark brown viscous material that was subjected to chromatography on a 5.0 × 135 cm column, slurry packed with 60–200 mesh silica gel (Davison, grade 950) in 5% ether–hexane. Elution with 18 l. of 10% and 7 l. of 15% ether–hexane and collection of 1-l. fractions gave: fractions 1–2, 0.054 g of a colorless oil; 3–12, 2.707 g of a mixture of 3,4,4-triphenylcyclohexanone and an unidentified ketone; 13–17, 6.18 g (24.9%) of 4,4,5-triphenyl-2-cyclohexen-1-one as a yellow solid; 18, 0.837 g of overlap; 19–25, 13.45 g (54.2%) of 3,4,4-triphenyl-2-cyclohexen-1-one as a yellow oil.

The synthesis using the same quantities of reagents was repeated twice to give, after chromatography, 4.88 (19.7%) and 7.35 g (29.6%) of the crude 4,4,5-triphenyl-2-cyclohexen-1-one. The combined 4,4,5-triphenyl-2-cyclohexen-1-one (18.31 g) from the three preparations was treated with Norit in hexane–methylene chloride, concentrated, and cooled to give 13.62 g of pale yellow crystals that were recrystallized from ethyl acetate to give 12.32 g (16.5% based on 75.0 g of 3,4,4-triphenylcyclohexanone) of colorless crystals, mp 172.5–174.5°.

Spectral data were as follows: infrared ($CHCl_3$) 3.32, 5.97 (s), 6.70, 6.92, 7.23, 11.17–11.27 (w), and 14.34 μ; nmr ($CDCl_3$): τ 2.40–3.50 multiplet (15 H, aromatic; 1 H, CH=), 3.74 doublet (1 H, J = 10 cps, CH=), 5.53 doublet of doublets (1 H, J = 8.5, 6.5 cps, PhCH), 7.27 doublet (1 H, J = 8.5 cps, CH_2), 7.30 doublet (1 H, J = 6.5 cps, CH_2); ultraviolet λ_{max} (3:1 *t*-butyl alcohol–benzene): 327 mμ (n–π^*, ϵ 42).

Anal. Calcd for $C_{24}H_{20}O$: C, 88.85; H, 6.21. Found: C, 88.80; H, 6.28.

Photolysis of 4,4,5-Triphenyl-2-cyclohexen-1-one. The photolysis was carried out on a solution of 5.000 g (15.43 mmol) of 4,4,5-triphenyl-2-cyclohexen-1-one in 1 l. of 3:1 *t*-butyl alcohol–benzene for 1.75 hr. Purified nitrogen[33] was bubbled through the solution for 3 hr before and then during the photolysis. The light source was a 450-W Hanovia medium-pressure mercury lamp with a Pyrex filter, all in a water-cooled immersion well. The photolysis was monitored by examining the infrared spectra of aliquots. The 5.97-μ carbonyl band of the starting material disappeared and was replaced by two new bands at 5.83 and 6.03 μ. Solvent removal *in vacuo* afforded an amber, viscous oil that was subjected to chromatography on a 5.0 × 135 cm column, slurry packed with 60–200 mesh silica gel (Davison, grade 950) in 5% ether–hexane. Elution with 22 l. of 7%, 4 l. of 10%, and 2.5 l. of 15% ether–hexane and the collection of 500-ml fractions yielded: fractions 1–16, nil; 17–22, 0.0449 g of an oil containing strong hydroxyl absorption and a 5.65–5.90-μ carbonyl band in the infrared (decomposition product of 2-(2,2-diphenylvinyl)-3-phenylcyclobutanone on the column); 23, 0.0144 g of overlap; 24–32, 2.1256 g of *cis,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one; 33–37, 0.7374 g of *trans,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one; 38–46, 1.1506 g of a mixture of *trans,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one and 4,4,5-triphenyl-2-cyclohexen-1-one; 47–48, 0.0800 g of a mixture of *trans,-trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one, 4,4,5-triphenyl-2-cyclohexen-1-one, and *cis*-3,4,5-triphenyl-2-cyclohexen-1-one; 49–57, 0.7989 g of *cis*-3,4,5-triphenyl-2-cyclohexen-1-one. Fractions 24–32 were crystallized from hexane–methylene chloride to give 2.028 g (40.8%) of *cis,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one, mp 157.5–160°, and an nmr spectrum of the material remaining in the mother liquors showed no other product. Hexane–methylene chloride crystallization of fractions 33–37 gave 0.6057 g, mp

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[27] H. E. Zimmerman, 17th National Organic Symposium, Bloomington, Ind., June 1961, Abstracts, p 31.

[28] H. E. Zimmerman and D. I. Schuster, *J. Amer. Chem. Soc.*, **84**, 4527 (1962).

[29] H. E. Zimmerman, *Science*, **153**, 837 (1966).

[30] All melting points were taken on a hot-stage apparatus and are corrected.

[31] L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath and Co., Boston, Mass., 1955, p 180.

[32] G. Schroeter, *Chem. Ber.*, **42**, 2348 (1909).

[33] Purified by vanadous sulfate removal of oxygen by the method of L. Meites and T. Meites, *Anal. Chem.*, **20**, 984 (1948).

136.5–139°, and fraction 38 gave 0.0897 g, mp 138–141°. Further recrystallization of the combined product yielded 0.6492 g (13.0%) of *trans,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one, mp 138–140°. Crystallization of fractions 42–47 first from ether and then from hexane–methylene chloride gave 0.1521 g (3.1%) of recovered starting material, mp 171.5–174°. Fractions 49–57 were recrystallized from ethyl acetate–hexane yielding 0.6689 g (13.6%) of *cis*-3,4,5-triphenyl-2-cyclohexen-1-one, mp 190–193°.

The mother liquors from the recrystallization of fractions 33–38 and 42–47 were combined with fractions 39–41 and rechromatographed on a 3.5 × 96 cm column, slurry packed in 5% ether-hexane with 60–200 mesh silica gel (Davison, grade 950). The column was eluted with 8 l. of 8% ether–hexane and 250-ml fractions were collected. Fractions 20–29 gave 0.9432 g of a mixture which was fractionally crystallized to give 0.3791 g (7.6%) of *trans,-trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one, mp 137–140°, and 0.1438 g (2.9%) of recovered starting material, mp 172–174.5°. An nmr spectrum of the material remaining in the mother liquors showed no new products.

The photolysis product from another run using the same amount of 4,4,5-triphenyl-2-cyclohexen-1-one starting material (5.000 g) was chromatographed on a 3.5 × 95 cm column, slurry packed in 5% ether–hexane with deactivated silica gel (Davison, grade 950, 60–200 mesh, washed with water and dried at 60–65° for 100 hr with periodic stirring), and eluted with 1 l. of hexane. Elution with 8 l. of 3% and 2 l. of 4% ether–hexane with the collection of 250-ml fractions gave 42.6 mg of 2-(2,2-diphenylvinyl)-3-phenylcyclobutanone in fractions 23–29 that was recrystallized from ether–hexane to give 0.0170 g (0.3%), mp 101–103°. This photoketone was not isolated on the previous column because of its instability on silica gel; however, deactivated silica gel gave very poor separation of the other photoproducts.

The over-all yields of the photoproducts were: 2.028 g (40.6%) of *cis,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one, mp 157.5–160°, 1.028 g (20.6%) of *trans,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one, mp 138–140°, 0.669 g (13.4%) of *cis*-3,4,5-triphenyl-2-cyclohexen-1-one, mp 190–193°, and 0.017 g (0.3%) of 2-(2,2-diphenylvinyl)-3-phenylcyclobutanone, mp 101–103°, in addition to 0.296 g (5.9%) of recovered starting material, mp 171.5–174°.

Characterization of *cis,trans*-4,5,6-Triphenylbicyclo[3.1.0]hexan-2-one. Recrystallization from methylene chloride–hexane gave a constant melting point of 158–158.5°. The infrared spectrum ($CHCl_3$) showed bands at 3.32, 5.83 (s), 6.24, 6.70, 6.91, 7.11, 7.58, 8.64, 9.28, 9.71, 10.36, and 14.35 μ; ultraviolet (3:1 *t*-butyl alcohol-benzene) 290 mμ (ϵ 65), 300 (36), 310 (21), and 320 (5); nmr ($CDCl_3$): τ 2.50–3.20 multiplet (15 H, aromatic), 6.27 doublet of doublets (1 H, J = 8.0, 1.5 cps, PhCH), 7.03 singlet (2 H, cyclopropyl CH–CH), 7.63, 7.65, 7.94, 7.96, 8.15, 8.28, 8.46, and 8.59 AB portion of an ABX pattern (2 H, J_{AB} = 19, J_{AX} = 1.5, J_{BX} = 8.0 cps, CH_2).

The methylene hydrogens at C-3 were exchanged for deuteriums by stirring 187 mg (0.576 mmol) of ketone in 10 ml of anhydrous *p*-dioxane and 1.0 ml of deuterium oxide containing 0.010 ml of 4.9 *N* sodium deuterioxide for 3 hr at room temperature. Nmr showed the exchange to be only partial so the above procedure was repeated for 2.83 hr. After concentration *in vacuo* and crystallization from ether the nmr spectrum ($CDCl_3$) showed an exchange of the two methylene hydrogens: τ 2.50–3.20 multiplet (15 H, aromatic), 6.27 singlet (1 H, PhCH), 7.03 singlet (2 H, cyclopropyl CH–CH).

Anal. Calcd for $C_{24}H_{20}O$: C, 88.85; H, 6.21. Found: C, 88.70; H, 6.20.

Characterization of *trans,trans*-4,5,6-Triphenylbicyclo[3.1.0]hexan-2-one. Further recrystallization of the 138–140° product (*vide supra*) from hexane–methylene chloride gave a constant melting point of 139–140°. Prominent peaks in the infrared spectrum ($CHCl_3$) were at 3.32, 5.83 (s), 6.24, 6.79, 6.90, 7.57, 9.28, 9.71, 9.90, 10.57, 10.86, and 14.35 μ; ultraviolet (3:1 *t*-butyl alcohol-benzene) 290 mμ (ϵ 200), 300 (106), 310 (49), and 320 (6); nmr ($CDCl_3$): τ 2.40–3.60 multiplet (15 H, aromatic), 5.75 triplet (1 H, J = 10 cps, PhCH), 6.60 doublet (1 H, J = 10 cps, cyclopropyl PhCH), and 7.20–8.15 multiplet (3 H, CH_2 and CH).

Deuterium exchange of one methylene hydrogen was effected in 10 ml of anhydrous *p*-dioxane and 1.0 ml of deuterium oxide containing 0.010 ml of 4.9 *N* sodium deuterioxide and 50.0 mg (0.154 mmol) of ketone. After 3.25 hr of stirring at room temperature the solvent was removed *in vacuo* and a nmr spectrum ($CDCl_3$) showed τ 2.40–3.60 multiplet (15 H, aromatic), 5.73 doublet (1 H, J = 11 cps, PhCH), 6.53, 6.68, 7.45, 7.60 AB pattern (2 H, J_{AB} = 10 cps, cyclopropyl methine), and 7.87 doublet (1 H, J = 11 cps, methylene). The value of 10 cps for the AB coupling constant agrees well with the value of 8.4 cps for *cis*-cyclopropane CH–CH coupling observed by Graham and Rogers.[17]

Anal. Calcd for $C_{24}H_{20}O$: C, 88.85; H, 6.21. Found: C, 88.87; H, 6.16.

Characterization of *cis*-3,4,5-Triphenyl-2-cyclohexen-1-one. This material was recrystallized from benzene to a constant melting point of 189–191° using a rapid increase in melting point block temperature and with a slow increase in temperature there was a change in crystalline form above 189° with melting at 215–218° (lit.[18] mp 188°). The oxime was prepared and recrystallized from ethanol–water to a constant melting point of 220–223° (lit.[18] mp 211–213°). The infrared spectrum ($CHCl_3$) showed bands at 3.32, 6.03 (s), 6.25, 6.36, 6.70, 6.91, 7.29, 7.40, 7.50, 7.70, 7.93, 9.70, 11.10, 11.42, 14.40, and 15.85 μ; nmr ($CDCl_3$): τ 2.45–3.50 (15 H, aromatic; 1 H, CH=), 5.67 doublet (1 H, J = 5 cps, C-4 methine), 6.12 doublet of triplets (1 H, J = 13, 5 cps, C-5 methine), 6.83, 7.05, 7.13, 7.33, 7.37, 7.44, 7.64, and 7.72 AB portion of an ABX pattern (2 H, J_{AB} = 17, J_{AX} = 13, J_{BX} = 5 cps, methylene).

Anal. Calcd for $C_{24}H_{20}O$: C, 88.85; H, 6.21. Found: C, 88.87; H, 6.03.

The ketone proved identical with authentic *cis*-3,4,5-triphenyl-2-cyclohexen-1-one prepared by the method of Chapurlat and Dreux[18] as shown by infrared, nmr, and mixture melting point comparisons and also the infrared and a mixture melting point of the oximes. The stereochemical assignment derives from the present study (*vide infra*).

Characterization of 2-(2,2-Diphenylvinyl)-3-phenylcyclobutanone. This material was recrystallized to a constant melting point of 102–104° from ether–hexane. The infrared spectrum ($CHCl_3$) showed bands at 3.32, 5.63 (characteristic[18] of cyclobutanone C=O), 6.24, 6.69, 6.91, 9.30, 9.71, and 14.38 μ; nmr ($CDCl_3$): τ 2.75 singlet (15 H, aromatic), 3.90 doublet (1 H, J = 9 cps, CH=), 5.90 triplet (1 H, J = 9 cps, CH), 6.27–6.92 multiplet (3 H, CH_2, PhCH). The reported[20] chemical shift (CCl_4) of the ethylenic proton of 1,1-diphenylpropene is τ 3.90. The ultraviolet spectrum (ethanol) showed λ_{max} 258 mμ (ϵ 16,000), λ_{min} 243 mμ (ϵ 11,000) (lit.[20] ultraviolet spectrum (cyclohexane) of 1,1-diphenylpropene λ_{max} 248 mμ (ϵ 16,600), λ_{min} 234.5 mμ (ϵ 10,000)).

Anal. Calcd for $C_{24}H_{20}O$: C, 88.85; H, 6.21. Found: C, 88.75; H, 6.38.

***trans*-5,6-Diphenylbicyclo[3.1.0]hex-3-en-2-one.** A solution of 7.78 g (0.0312 mol) of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one[8] and 3.45 g (0.0312 mol) of selenium dioxide (freshly sublimed from concentrated nitric acid) in 75 ml of 75% *p*-dioxane–water was refluxed with stirring for 17.5 hr and cooled in ice and the precipitated selenium metal filtered from the deep red solution. The filtrate was diluted with ether, washed with water, dried, and concentrated *in vacuo* giving 9.70 g of a dark red-orange, viscous material. Presence of the desired enone was shown by thin layer chromatography and comparison with an authentic sample.[1] The crude product was chromatographed on a 2.5 × 110 cm column slurry packed with 100–200 mesh silicic acid (Mallinckrodt, SilicAR, CC-7) in 5% ether–hexane. Elution was with 8% ether–hexane and 250-ml fractions were collected. All of the fractions were contaminated with varying amounts of red selenium. Fractions 1–5 gave 0.028 g of yellow oil; 6–11, 3.489 g of a 1:1 mixture of the desired enone and starting material as shown by infrared and nmr spectra; 12–15, 1.416 g of a mixture containing decreasing amounts of the ketones and unidentified hydroxyl-containing material.

Liquid–liquid partition chromatography of fractions 6–8 (1.890 g) and fractions 9–12 (1.987 g) was achieved on a 4.0 × 140 cm water-jacketed column (28°) dry packed with a mixture prepared from 750 g of Celatom FW-80 (Eagle-Picher Co.) and 310 ml of the lower phase of a two-phase system consisting of 1000 ml of cyclohexane, 400 ml of dimethylformamide, 250 ml of ethyl acetate, and 30 ml of water. The column was eluted with 1 l. of upper phase and then the 1.890-g sample, from fractions 6–8 above, was added in a minimum of upper phase. Fractions of 40 ml were collected, and an ultraviolet scanner set at 280 mμ was used to follow the chromatography. A repeat separation was run on fractions 9–12 (1.987 g) of the silica gel chromatogram. The two chromatographies were worked up together by combining the appropriate fractions, dilution with ether, washing with water, drying, and concentrating *in vacuo*. Fractions 31–36 gave 0.1161 g of yellow-orange oil; 37–40, 1.5537 g (20.0%) of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one; 41, 0.0861 g of overlap; and 42–49, 1.5116 g (19.6%) of *trans*-5,6-diphenylbicyclo[3.1.0]hex-3-en-2-one.

The enone was crystallized from ether–hexane to give 0.8944 g of colorless crystals, mp 71–80°, and a second crop of 0.2044 g of slightly yellow crystals, mp 65–97.5°, from methanol. Further recrystallization from ether–hexane gave a constant melting point of 71–90° but when the melted sample was allowed to solidify and then melted again its melting point was 71–72°. The infrared spectrum (CCl_4) showed bands at 3.24, 3.27, 5.86 (s), 6.24, 6.78, 6.90, 7.60, 8.62, 9.30, 9.70, 9.80, 10.83, 10.96, and 14.35 μ; nmr (CCl_4): τ 2.53–2.91 multiplet (10 H, aromatic; 1 H, CH=), 4.43 doublet of doublets (1 H, J = 5.5, 1.0 cps, COCH=), 6.44 doublet (1 H, J = 9.0 cps, cyclopropyl PhCH), 7.40 doublet of doublets (1 H, J = 9.0, 1.0 cps, cyclopropyl CH).

Anal. Calcd for $C_{18}H_{14}O$: C, 87.80; H, 5.73. Found: C, 87.85; H, 5.68.

***cis,trans*-4,5,6-Triphenylbicyclo[3.1.0]hexan-2-one.** A solution of phenylmagnesium bromide prepared from 0.785 g (5.00 mmol) of bromobenzene and 0.122 g (5.00 mg-atoms) of magnesium in 3.0 ml of ether was added to 0.502 g of *trans*-5,6-diphenylbicyclo-[3.1.0]hex-3-en-2-one and 0.7504 g (0.490 mmol) of tetrakis[iodo-(tri-*n*-butylphosphine)copper(I)][34,35] in 5.0 ml of anhydrous ether; a closed system was used. The resulting intense green solution was stirred for 20 min before dilution with ether and worked up with 25% ammonium chloride solution. After washing with water the ether solution was dried and concentrated *in vacuo* yielding 1.389 g of a yellow solid that was chromatographed on a 2.25 × 115 cm column, slurry packed in 5% ether–hexane with 100–200 mesh silica gel (Davison, grade 923). Elution with 1 l. of 5%, 3.5 l. of 8%, and 1 l. of 50% ether-hexane and collection of 250-ml fractions gave: fraction 1, nil; 2–4, 252.2 mg of a brown oil; 5–9, nil; 10–13, 519.7 mg (78.5%) of *cis,trans*-4,5,6-triphenylbicyclo-[3.1.0]hexan-2-one as a colorless solid; 14, 20.2 mg of overlap; 15, 11.4 mg of unreacted starting material; and 16–18, 33.9 mg of a mixture of unreacted starting material and a hydroxyl-containing compound. Fractions 10–13 were combined and crystallized from methylene chloride–hexane to give 429.7 mg (65.1%), mp 152–159°. Recrystallization gave a constant melting point of 158–159°. The infrared and nmr spectra were identical with those of the *cis,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one obtained photolytically. A mixture melting point was undepressed.

Lithium in Liquid Ammonia Reduction of *trans,trans*-4,5,6-Triphenylbicyclo[3.1.0]hexan-2-one. Into a dried apparatus equipped with a Dry Ice condenser and a potassium hydroxide drying tube and containing 91.0 mg (0.281 mmol) of *trans,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one in 15 ml of ether was distilled 85 ml of liquid ammonia. Lithium metal (12.0 mg, 1.73 mg-atoms) was added and the resulting deep blue solution was stirred for 30 min before addition of excess anhydrous ammonium chloride. The ammonia was evaporated to give a white suspension that was diluted with ether and washed with water. Solvent removal *in vacuo* left 94.8 mg of a white solid whose infrared spectrum showed both hydroxyl and 5.87-μ carbonyl absorption. The crude product was chromatographed on a 1.5 × 60 cm column, slurry packed in 5% ether–hexane with 100–200 mesh silica gel (Davison, grade 923), and the column was eluted with 250 ml of 5% ether–hexane, 500 ml of 10% ether–hexane, 500 ml of 15% ether–hexane, 500 ml of 30% ether-hexane, and 375 ml of ether. Collection of 125-ml fractions yielded: fractions 1–5, nil; 6–8, 71.3 mg (77.9%) of *cis,cis*-3,4,5-triphenylcyclohexanone; 9–13, nil; and 14–17, 20.3 mg of an unidentified hydroxyl compound.

The ketone from fractions 6–8 was recrystallized to a constant melting point of 145.5–146.6° (53.5 mg, 58.8%) from hexane-methylene chloride. The infrared spectrum ($CHCl_3$) showed bands at 3.32, 3.43, 3.47, 5.87 (s), 6.24, 6.69, 6.89, 7.03, 7.50, 9.23, 9.68, 11.00, and 14.40 μ; nmr ($CDCl_3$): τ 2.80–3.25 multiplet (15 H, aromatic), 6.00–7.46 complex multiplet with peaks at 6.00, 6.08, 6.13, 6.23, 6.32, 6.36, 6.43, 6.54, 6.66, 6.90, 7.15, 7.20, 7.36, and 7.44 (3 H, methine; 4 H, methylene).

Anal. Calcd for $C_{24}H_{22}O$: C, 88.31; H, 6.79. Found: C, 88.24; H, 6.91.

The product proved identical with authentic (*vide infra*) *cis,cis*-3,4,5-triphenylcyclohexanone by nmr, infrared, and mixture melting point comparisons.

Catalytic Hydrogenation of *trans,trans*-4,5,6-Triphenylbicyclo-[3.1.0]hexan-2-one. Atmospheric catalytic hydrogenation of 76.1 mg (0.232 mmol) of *trans,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one was effected in 15.5 ml of 95% ethyl alcohol using 45.5 mg of 10% palladium on carbon. After 1.75 hr at 22°, an equimolar amount of hydrogen had been consumed; the catalyst was filtered and the solvent removed *in vacuo* leaving 73.0 mg of a colorless, oily solid that was chromatographed on a 1.5 × 60 cm column, slurry packed in 5% ether-hexane using 100–200 mesh silica gel (Davison, grade 923). Elution with 500 ml of 8% ether-hexane, 500 ml of 15% ether-hexane, 500 ml of 50% ether-hexane, and 250 ml of ether with 125-ml fractions being collected gave: fractions 1–2, 9.3 mg of unidentified compound whose infrared showed strong aromatic absorption but no hydroxyl or carbonyl absorption; 3–4, nil; 5-6, 26.7 mg (35.1%) of *cis,cis*-3,4,5-triphenylcyclohexanone; 7–8, 30.5 mg (40.2%) of *trans,trans*-3,4,5-triphenylcyclohexanone; 9–14, 12.5 mg of a hydroxyl-containing compound.

The material from fractions 5–6 (26.7 mg) was crystallized from hexane–methylene chloride to give 15.3 mg (20.1%), mp 144–145°, and was shown to be identical with authentic *cis,cis*-3,4,5-triphenylcyclohexanone and the lithium in liquid ammonia reduction product by infrared, nmr, and mixture melting point comparisons.

The material from fractions 7–8 (30.5 mg) was crystallized from hexane–methylene chloride to give 14.1 mg (18.5%), mp 201–205°. The infrared spectrum ($CHCl_3$) showed bands at 3.32, 5.87 (s), 6.25, 6.70, 6.88, 7.61, 9.31, 9.70, 10.95 (br), and 14.40 μ; nmr ($CDCl_3$): τ 2.94 singlet (10 H, aromatic), 3.16 singlet (5 H, aromatic), 6.25–7.50 multiplet with no distinct peaks (3 H, methine; 4 H, methylene).

Anal. Calcd for $C_{24}H_{22}O$: C, 88.31; H, 6.79. Found: C, 88.18; H, 6.90,

The infrared and nmr spectra and melting point of this reduction product were identical with those for authentic *trans,trans*-3,4,5-triphenylcyclohexanone.

Lithium in Liquid Ammonia Reduction of *cis,trans*-4,5,6-Triphenylbicyclo[3.1.0]hexan-2-one. Liquid ammonia (300–350 ml) was distilled into a dried apparatus equipped with a Dry Ice condenser and potassium hydroxide drying tube and containing 0.5028 g (1.536 mmol) of *cis,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one in 50 ml of anhydrous ether. Lithium metal (0.0524 g, 7.55 mg-atoms) was added, and the resulting deep blue solution was stirred for 1 hr before work-up with excess anhydrous ammonium chloride. The ammonia was evaporated and the resulting suspension diluted with ether and washed with dilute hydrochloric acid and water. After drying, solvent removal *in vacuo* afforded 0.5095 g of an amber, viscous material whose infrared spectrum ($CHCl_3$) showed carbonyl bands at 5.77 and 5.87 μ. This material was subjected to chromatography on a 3 × 70 cm column, slurry packed with 60–200 mesh silica gel (Davison, grade 950) in 5% ether–hexane. The column was eluted with 0.5 l. of hexane, 3 l. of 5% ether–hexane, 6.25 l. of 7% ether–hexane, and 1 l. of 20% ether–hexane, and 250-ml fractions were collected: fractions 1–2, nil; 3–7, 7.5 mg of hydrocarbon residues; 8–12, 18.3 mg of a colorless oil whose infrared spectrum showed a 5.77-μ carbonyl band; 13–14, nil; 15–18, 4.8 mg of colorless oil; 19–31, 352.5 mg (69.7%) of 3-benzyl-*cis*-3,4-diphenylcyclopentanone as a colorless oil; 32–43, 135.0 mg (26.7%) of *cis,-trans*-3,4,5-triphenylcyclohexanone, mp 153–164°.

All attempts to crystallize the 3-benzyl-*cis*-3,4-diphenylcyclopentanone from fractions 19–31 were unsuccessful. An analytical sample was prepared by gradient temperature molecular distillation in an 8 × 100 mm tube (33–100°, 0.025 mm). The infrared spectrum showed bands at 3.32, 3.42, 5.77 (s), 6.25, 6.79, 6.91, 7.11, 8.58, 9.27, 9.70, and 14.35 μ; nmr (CCl_4): τ 2.80–3.45 multiplet (15 H, aromatic), 6.20–7.69 multiplet with peaks at 6.20, 6.37, 6.50, 6.58, 6.92, 7.02, 7.15, 7.30, 7.42, 7.48, 7.62, 7.65, and 7.69 (2 H, benzylic; 5 H, ring hydrogens). A solid oxime derivative was prepared,[36] mp 104–108°.

Anal. Calcd for $C_{24}H_{22}O$: C, 88.31; H, 6.79. Found: C, 88.12; H, 6.83.

The *cis,trans*-3,4,5-triphenylcyclohexanone from fractions 32–43 was recrystallized from methylene chloride–hexane to a constant melting point of 175–176°. The infrared spectrum ($CHCl_3$) showed bands at 3.32, 3.43, 5.87 (s), 6.24, 6.70, 6.89, 7.09, 7.51, 9.30, 9.71, 9.82, and 14.35 μ; nmr ($CDCl_3$): τ 2.70–3.50 multiplet (15 H, aromatic), 5.28–6.72 multiplet (3 H, methine), 6.89–7.32 multiplet (4 H, methylene).

Anal. Calcd for $C_{24}H_{22}O$: C, 88.31; H, 6.79. Found: C, 88.34; H, 6.74.

Independent Synthesis of *cis,cis*-3,4,5-Triphenylcyclohexanone. Into a solution of 0.500 g (1.54 mmol) of *cis*-3,4,5-triphenyl-2-

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(34) H. O. House, W. L. Respess, and G. M. Whitesides, *J. Org. Chem.*, **31**, 3128 (1966).

(35) G. B. Kaufman and L. A. Teter, *Inorg. Syn.*, 7, 9 (1963).

(36) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1964, p 189.

cyclohexen-1-one in 20 ml of tetrahydrofuran and 20 ml of ether in a dried apparatus equipped with a Dry Ice condenser and a potassium hydroxide drying tube was distilled 300–350 ml of liquid ammonia. Addition of 0.0685 g (9.86 mg-atoms) of lithium metal gave a deep blue solution that was stirred for 3 hr before addition of excess anhydrous ammonium chloride and evaporation of the ammonia with stirring. The resulting suspension was acidified with dilute hydrochloric acid and ether extracted. The ether extract was washed with water, dried, and concentrated *in vacuo*, yielding 0.496 g of a light pink solid whose infrared spectrum showed a 5.87-μ carbonyl in addition to some hydroxyl absorption. The crude product was chromatographed on a 2.0 × 65 cm column, slurry packed with 60–200 mesh silica gel (Davison, grade 950) in 5% ether–hexane. Elution was with 2 l. of 8% ether–hexane and 2.63 l. of 12% ether–hexane with 125-ml fractions being collected: fractions 1–4, 15.7 mg of a colorless oil; 5–9, nil; and 10–17, 343.2 mg (68.6%) of *cis,cis*-3,4,5-triphenylcyclohexanone. The material from fractions 10–17 was recrystallized from methylene chloride–hexane to give 287.1 mg (57.4%) with a constant melting point of 145–146°. Infrared, nmr, and mixture melting point comparisons showed it to be identical with the *cis,cis*-3,4,5-triphenylcyclohexanone obtained from the lithium in liquid ammonia reduction and catalytic hydrogenation of *trans,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one.

Independent Synthesis of *trans,trans*-3,4,5-Triphenylcyclohexanone. Phenylmagnesium bromide prepared from 1.648 g (10.5 mmol) of bromobenzene and 0.252 g (10.5 mg-atoms) of magnesium in 30 ml of ether, under N_2, was added to 1.303 g (5.25 mmol) of *trans*-4,5-diphenyl-2-cyclohexen-1-one[7] and 2.011 g (1.31 mmol) of tetrakis[iodo(tri-*n*-butylphosphine)copper(I)][34,35] in 20 ml of ether. The resulting suspension was stirred at room temperature, under N_2, for 0.5 hr before pouring into 20% ammonium chloride and ether extracting. The ether extract was washed with water, dried, and concentrated *in vacuo* to give a yellow solid whose infrared spectrum showed weak hydroxyl absorption and a strong 5.87-μ carbonyl band. Crystallization first from hexane–methylene chloride and then treatment with Norit and recrystallization from ethanol–water gave 0.741 g (43.8%), mp 199–206°. Further recrystallization from 95% ethanol gave a constant melting point of 200–202°. The infrared and nmr spectra and melting point were identical with the *trans,trans*-3,4,5-triphenylcyclohexanone obtained from the catalytic hydrogenation of *trans,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one.

Stereochemical Assignment of 4,5-Diphenyl-2-cyclohexen-1-one.[7] For the above synthesis it was necessary to know the stereochemistry of 4,5-diphenyl-2-cyclohexen-1-one prepared by the route of Zimmerman and Sam.[7] In previous work in this laboratory[37] 4,5-diphenyl-2-cyclohexen-1-one was reduced by catalytic hydrogenation to give a 3,4-diphenylcyclohexanone, mp 106.5–107°. In the same study[37] 3,4-diphenyl-2-cyclohexen-1-one was reduced by catalytic hydrogenation to afford both 3,4-diphenylcyclohexanone stereoisomers, mp 70.5–71.5° and 106.5–107°.

Lithium–liquid ammonia reduction of 0.505 g (2.03 mmol) of 3,4-diphenyl-2-cyclohexen-1-one was effected with 0.058 g (8.32 mg-atoms) of lithium in a solution of 25 ml of ether and 150 ml of liquid ammonia in a dried apparatus equipped with a Dry Ice condenser. After stirring for 30 min, excess ammonium chloride was added to the deep blue solution and it became colorless. The ammonia was evaporated with stirring and the remaining suspension was diluted with ether, washed with water, and dried. Concentration *in vacuo* gave 0.519 g of a colorless oil that was fractionally crystallized from ether–hexane to give two crops of a hydroxyl compound: 0.137 g, mp 109–120°, and 0.108 g, mp 106–118°. Further concentration of the mother liquors afforded two crops of 3,4-diphenylcyclohexanone: 0.105 g (21.0%), mp 68–69.5°, and 0.066 g (13.2%), mp 69.5–70.6°. Recrystallization from hexane gave a constant melting point, 70–71.5°. A mixture melting point with the 70.5–71.5° 3,4-diphenylcyclohexanone obtained from the catalytic hydrogenation of 3,4-diphenyl-2-cyclohexen-1-one[37] was undepressed.

It has been reported[21] that lithium–liquid ammonia reduction of 3,4-diphenyl-2-cyclohexen-1-one stereoselectively affords *cis*-related phenyls at C-3 and C-4. Thus the 70–71.5° isomer must be *cis*-3,4-diphenylcyclohexanone and the 106.5–107° isomer obtained from catalytic hydrogenation of 4,5-diphenyl-2-cyclohexen-1-one[37] must then be *trans*-3,4-diphenylcyclohexanone. This confirms that the 4,5-diphenyl-2-cyclohexen-1-one[7] was in fact the *trans* isomer as had been suspected.[7]

Photosensitization of 4,4,5-Triphenyl-2-cyclohexen-1-one. A standard photolysis of 324 mg (1.00 mmol) of 4,4,5-triphenyl-2-cyclohexen-1-one in 230 ml of 3:1 *t*-butyl alcohol–benzene was carried out under purified nitrogen[33] through a Pyrex filter and a solution filter with a 450-W Hanovia medium-pressure lamp for 25 min. The filter solution, prepared from 660 g of $NiSO_4\cdot 6H_2O$, 30 g of $CuSO_4.5H_2O$, 20 g of KNO_3, and 40 g of $CoSO_4\cdot 7H_2O$ in 1 l. of water, transmitted light between 285 and 370 mμ with 2.0, 7.5, 26.7, 47.1, 32.2, 12.4, and 1.1% transmittance at 300, 310, 320, 330, 340, 350, and 360 mμ, respectively. The filter solution was unchanged after the irradiation. Solvent removal *in vacuo* gave 327 mg of white solid that was fractionally crystallized from hexane–methylene chloride to give 205 mg (63.3%) of 4,4,5-triphenyl-2-cyclohexen-1-one, mp 173–174°. The mother liquors were concentrated *in vacuo*. The product distribution was determined by nmr analysis in $CDCl_3$ as follows: *cis,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one, 20 ± 1.0 relative area, 12.4 ± 0.6%; *trans,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one, 11.0 ± 0.5 relative area, 6.8 ± 0.3%; *cis*-3,4,5-triphenyl-2-cyclohexen-1-one, 8.0 ± 3.0 relative area, 4.9 ± 2.0%; and 4,4,5-triphenyl-2-cyclohexen-1-one, 18.0 ± 0.8 relative area, 11.2 ± 0.6% of the mixture.

Next, a 25-min acetophenone-sensitized irradiation was run using 324 mg (1.00 mmol) of 4,4,5-triphenyl-2-cyclohexen-1-one and 13.0 g (0.108 mol) of acetophenone, calculated to absorb over 96% of the light, in 230 ml of 3:1 *t*-butyl alcohol–benzene. The filter solution was unchanged. After solvent removal *in vacuo*, the acetophenone was removed by short-path distillation (40–50° (0.5 mm)) and the residue (418 mg) was chromatographed on a 2.0 × 90 cm column, slurry packed with 60–200 mesh silica gel (Davison, grade 950) in 5% ether–hexane. Elution with 1 l. of 7%, 4 l. of 8%, and 0.75 l. of 15% ether–hexane and the collection of 250-ml fractions gave: fractions 1–5, nil; 6–7, 6.2 mg of acetophenone; 8, 20.4 mg of a mixture of *cis,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one and acetophenone; 9–10, 70.8 mg (21.8%) of *cis,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one, mp 155–158°; 11, 18.2 mg of a mixture of *cis,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one and *trans,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one; 12, 25.8 mg of a mixture of *trans,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one and 4,4,5-triphenyl-2-cyclohexen-1-one; 13–14, 90.4 mg of a mixture of *trans,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one and 4,4,5-triphenyl-2-cyclohexen-1-one; 15–17, 72.1 mg (22.2%) of 4,4,5-triphenyl-2-cyclohexen-1-one as shown by its nmr spectrum; 18–19, 14.2 mg of a mixture of 4,4,5-triphenyl-2-cyclohexen-1-one and *cis*-3,4,5-triphenyl-2-cyclohexen-1-one; and 20–23, 21.3 mg (6.6%) of *cis*-3,4,5-triphenyl-2-cyclohexen-1-one, mp 185–188°. The fractions containing mixtures were subjected to nmr analysis with the following results: fraction 8, acetophenone (30.0 ± 1.5 relative area), *cis,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one (18.5 ± 0.9 relative area, 2.4 ± 0.1%); fraction 11, *cis,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one (7.3 ± 0.4 relative area, 3.4 ± 0.2%), *trans,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one (4.5 ± 0.2 relative area, 2.2 ± 0.1%); fraction 12, *trans,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one (11.5 ± 0.6 relative area, 5.0 ± 0.25%), 4,4,5-triphenyl-2-cyclohexen-1-one (7.0 ± 0.3 relative area, 3.0 ± 0.15%); and fractions 13–14, *trans,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one (9.5 ± 0.5 relative area, 8.0 ± 0.4%), 4,4,5-triphenyl-2-cyclohexen-1-one (23.5 ± 1.2 relative area, 19.9 ± 1.0%). Fractions 18–19 contained 4,4,5-triphenyl-2-cyclohexen-1-one (2.0 ± 0.3%) and *cis*-3,4,5-triphenyl-2-cyclohexen-1-one (2.4 ± 0.4%) as estimated from the infrared spectrum of the mixture. The combined product percentages from the chromatography and analyses of the overlapping fractions are: 27.6 ± 1.4% *cis,trans*-triphenylbicyclo[3.1.0]hexan-2-one; 15.2 ± 0.8% *trans,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one; 9.0 ± 0.4% *cis*-3,4,5-triphenyl-2-cyclohexen-1-one; and 47.1 ± 1.5% 4,4,5-triphenyl-2-cyclohexen-1-one starting material.

Another direct run was made using 400 mg (1.23 mmol) of 4,4,5-triphenyl-2-cyclohexen-1-one in 125 ml of 3:1 *t*-butyl alcohol–benzene. The solution was irradiated for 2.0 hr through a filter solution prepared from 227 g of $SnCl_2\cdot 2H_2O$ and 200 g of $NiSO_4\cdot 6H_2O$ in 1000 ml of 5% hydrochloric acid which transmitted light between 322 and 387 mμ with 14, 60, 61, 27, and 5% transmittance at 330, 340, 350, 360, and 370 mμ respectively. After irradiation, the photolysis solution was concentrated *in vacuo* to yield 426 mg of a viscous material that was subjected to nmr analysis. The results are summarized as follows: *cis,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one, 59.0 ± 3.0 relative area, 53.2 ± 2.7%; *trans,*-

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(37) H. E. Zimmerman and R. G. Peterson, unpublished results.

trans-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one, 32.0 ± 1.6 relative area, 28.8 ± 1.4%; *cis*-3,4,5-triphenyl-2-cyclohexen-1-one, 18.0 ± 4.0 relative area, 16.2 ± 3.6%; and 4,4,5-triphenyl-2-cyclohexen-1-one, 2.0 ± 0.1 relative area, 1.8 ± 0.1%.

The nmr analyses were made using the relative areas of the following peaks: τ 7.03, 2 H singlet for *cis,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one; τ 6.60, 1 H doublet for *trans,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one; τ 3.74, 1 H doublet for 4,4,5-triphenyl-2-cyclohexen-1-one; and the relative area of τ 5.67, 1 H doublet of *cis*-3,4,5-triphenyl-2-cyclohexen-1-one, determined by difference from the τ 5.50–5.95 multiplet by subtracting the relative areas of the τ 5.75, 1 H triplet of *trans,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one and the τ 5.53, 1 H doublet of doublets of 4,4,5-triphenyl-2-cyclohexen-1-one from the total area of the multiplet.

Photolysis of *cis*-3,4,5-Triphenyl-2-cyclohexen-1-one. Using the standard procedure described above, 0.402 g (1.24 mmol) of *cis*-3,4,5-triphenyl-2-cyclohexen-1-one in 100 ml of 3:1 *t*-butyl alcohol–benzene was irradiated for 3 hr through a Pyrex filter. Solvent removal *in vacuo* yielded 0.416 g of a light colored solid whose nmr and infrared spectra showed only starting material. Recrystallization from ethyl acetate–hexane gave 0.355 g of *cis*-3,4,5-triphenyl-2-cyclohexen-1-one, mp 190–192°.

***trans*-4,6,6-Triphenylbicyclo[3.1.0]hexan-2-one.** Phenylmagnesium bromide prepared from 1.57 g (10.0 mmol) of bromobenzene and 0.243 g (10.0 mg-atoms) of magnesium in 10 ml of anhydrous ether was added with stirring to a solution of 1.00 g (4.06 mmol) of 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one[28] and 1.555 g (1.02 mmol) of tetrakis[iodo(tri-*n*-butylphosphine)copper(I)][34,35] in 75 ml of anhydrous ether. After stirring at room temperature for 45 min the reaction was poured into 250 ml of 20% aqueous ammonium chloride, diluted with ether, washed with water, dried, and concentrated *in vacuo* leaving 2.70 g of a viscous amber oil that was subjected to chromatography on a 3.0 × 75 cm column slurry packed with 60–200 mesh silica gel (Davison, grade 950) in 5% ether–hexane. Elution with 2 l. of 5%, 3 l. of 8%, and 1 l. of 15% ether–hexane and collection of 250-ml fractions gave: fractions 1–7, 1.134 g of oil residues from the catalyst; 8–9, nil; 10–17, 0.779 g (59.1%) of *trans*-4,6,6-triphenylbicyclo[3.1.0]hexan-2-one; 18–24, 0.043 g of a hydroxyl compound. The material from fractions 10–17 was crystallized from methylene chloride–hexane to give 0.6857 g (52.1%) of *trans*-4,6,6-triphenylbicyclo[3.1.0]hexan-2-one, mp 137.5–140°. Further recrystallization from methylene chloride–hexane gave a constant melting point of 138–140°. The infrared spectrum ($CHCl_3$) showed bands at 3.32, 5.83 (s), 6.24, 6.79, 6.90, 7.11, 8.43, and 14.36 μ; nmr ($CDCl_3$): τ 2.40–2.94 multiplet (15 H, aromatic), 6.48 doublet of doublets (1 H, J = 8, 2 cps, PhCH), 7.20 singlet (2 H, CHCH), 7.80, 7.85, 8.13, 8.17, 8.30, 8.43, 8.63, and 8.76 AB portion of an ABX pattern (2 H, J_{AB} = 20 cps, J_{AX} = 2 cps, J_{BX} = 8 cps, CH_2).

Anal. Calcd for $C_{24}H_{20}O$: C, 88.85; H, 6.21. Found: C, 88.66; H, 6.10.

Photolysis of *cis,trans*-4,5,6-Triphenylbicyclo[3.1.0]hexan-2-one. Using the standard procedure, 2.103 g (6.49 mmol) of *cis,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one was photolyzed in 230 ml of 3:1 *t*-butyl alcohol–benzene, under purified nitrogen, for 13.75 hr through a Pyrex filter. The solvent was removed *in vacuo* leaving 2.176 g of white solid that was chromatographed on a 3.5 × 95 cm column, slurry packed with 60–200 mesh silica gel (Davison, grade 950) in 5% ether–hexane. Elution was with 2 l. of 8%, 10 l. of 10%, and 2 l. of 20% ether–hexane, and 500-ml fractions were collected. Fraction 1 yielded 6 mg of aliphatic solvent residues: 2–7, nil; 8–14, 1.050 g (50.1%) of *cis,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one as a white solid; 15, 0.019 g of overlap; 16–23, 0.951 g (45.2%) of a new photoketone, mp 140–150°, which was shown (*vide infra*) to be *cis,cis*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one; 24–28, 0.051 g of a colorless oil.

The starting material, *cis,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one, from fractions 8–14 was crystallized from hexane–methylene chloride to give 0.978 g (46.5%), mp 157.5–159°, and a nmr spectrum of the material remaining in the mother liquors showed no other compounds. The *cis,cis*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one from fractions 16–23 was recrystallized from hexane–methylene chloride to give two crops of fine needle crystals: 0.797 g (37.9%), mp 157.5–159.5°, and 0.079 g (3.8%), mp 158–159°. An nmr spectrum of the material remaining in the mother liquors showed no other compounds. Infrared and nmr spectra of the colorless oil from fractions 24–28 (0.051 g) showed a mixture of *ca.* 70% of *cis,cis*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one and 30% of a second product, *trans*-3,4,5-triphenyl-2-cyclohexen-1-one, as determined by comparison of the infrared and nmr spectra of the mixture with those of authentic material (*vide infra*).

In another run the irradiation of 812 mg of *cis,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one for 6.0 hr gave 478 mg (58.9%) of recovered *cis,trans*-4,5 6-triphenylbicyclo[3.1.0]hexan-2-one, mp 158–160°; 214 mg (26.4%) of *cis,cis*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one, mp 158–160.5°; and 14 mg of a mixture of *cis,cis*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one and *trans*-3,4,5-triphenyl-2-cyclohexen-1-one.

Characterization of *cis,cis*-4,5,6-Triphenylbicyclo[3.1.0]hexan-2-one. This material, as obtained above, was recrystallized to a constant melting point of 158–159.5° from hexane–methylene chloride. The infrared spectrum ($CHCl_3$) showed bands at 3.32, 5.81 (s), 6.24, 6.69, 7.05, 9.30, 9.77, 11.25, and 14.40 μ; ultraviolet (3:1 *t*-butyl alcohol–benzene): 290 mμ (ϵ 143), 300 (89), 310 (26), and 320 (4); nmr ($CDCl_3$): τ 2.80–3.37 multiplet (15 H, aromatic), 6.03 doublet of doublets (1 H, J = 8.5, 1.5 cps, methine), 6.70–7.70 multiplet (4 H, methylene and cyclopropyl methine). An AB quartet (J_{AB} = 3 cps) can be picked out at τ 6.97 7.02, 7.13, and 7.18. This quartet was assigned to the *trans*-cyclopropyl methine hydrogens. The value of 6 cps for *trans*-cyclopropane CH–CH coupling is reported in the literature.[17]

Anal. Calcd for $C_{24}H_{20}O$: C, 88.85; H, 6.21. Found: C, 88.79; H, 6.38.

Catalytic Hydrogenation of *cis,cis*-4,5,6-Triphenylbicyclo[3.1.0]hexan-2-one. An atmospheric hydrogenation was run with 57.3 mg (0.137 mmol) of *cis,cis*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one and 31.1 mg of 10% palladium on carbon in 20 ml of 95% ethanol. After 30 min at 22°, 1 molar equiv of hydrogen had been absorbed. The catalyst was filtered and the solvent removed *in vacuo* to give 56.8 mg (98.4%) of 3-benzyl-*cis*-3,4-diphenylcyclopentanone as a colorless oil. A solid oxime was prepared[36] and recrystallized from methanol–water to mp 104–108.5°.

This material was shown to be identical with the 3-benzyl-*cis*-3,4-diphenylcyclopentanone obtained from the lithium–ammonia reduction (*vide supra*) of *cis,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one by comparison of infrared and nmr spectra and a mixture melting point of the oximes.

***trans*-3,4,5-Triphenyl-2-cyclohexen-1-one.** To a solution of 495 mg (1.528 mmol) of *trans,trans*-3,4,5-triphenylcyclohexanone in 40 ml of carbon tetrachloride was added 293 mg (0.10 ml, 1.83 mmol) of bromine over 2 min. Excess sodium bisulfite was added and after stirring a few minutes, the sodium bisulfite was filtered off and the solvent removed *in vacuo*. The amber bromination product was stirred with 244 mg (5.76 mmol) of lithium chloride and 484 mg (6.56 mmol) of lithium carbonate in 20 ml of dimethylformamide at 140° under nitrogen for 8 hr. The brownish suspension was cooled, diluted with ether, washed with water, and dried and the solvent removed *in vacuo* leaving 416 mg of a brown, glassy solid which was chromatographed on a 2.5 × 60 cm column, slurry packed in 5% ether–hexane with 60–200 mesh silica gel (Davison, grade 950). Elution was with 2 l. of 10%, 1 l. of 15%, and 1 l. of 20% ether–hexane and 250-ml fractions were collected: fractions 1–7, 40 mg of a yellow solid; 8–10, 59 mg of a fluffy, white solid; and 11–16, 228 mg of *trans*-3,4,5-triphenyl-2-cyclohexen-1-one as a yellow oil. The *trans*-3,4,5-triphenyl-2-cyclohexen-1-one was crystallized first from ether and then from methylene chloride–hexane to give 120 mg (24.6%) of colorless needles, mp 118.5–120°. Further recrystallization gave needles that melted at 119.5–121° then resolidified as prisms and melted again at 140.5–141°.

The infrared spectrum ($CHCl_3$) showed bands at 3.32, 6.03 (s), 6.24, 6.70, 6.91, 7.50, 7.93, 8.70, 9.30, 11.10, 11.43, and 14.50 μ; nmr ($CDCl_3$): τ 2.74 singlet (15 H, aromatic), 3.27 singlet (1 H, CH=), 5.50 doublet (1 H, J = 4 cps, C_4–methine), 6.40 quartet from overlapping doublet of triplets (1 H, J = 5, 4 cps, C_5–methine), 7.20 doublet (2 H, J = 5 cps, methylene).

Anal. Calcd for $C_{24}H_{20}O$: C, 88.85; H, 6.21. Found: C, 88.75; H, 6.30.

Photolysis of *cis,cis*-4,5,6-Triphenylbicyclo[3.1.0]hexan-2-one. Using the standard procedure, 298 mg of *cis,cis*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one in 140 ml of 3:1 *t*-butyl alcohol–benzene was irradiated for 16.5 hr with a Pyrex filter. Solvent removal *in vacuo* gave 294 mg of a slightly yellow solid that was chromatographed on a 2.0 × 94 cm column, slurry packed with 60–200 mesh silica gel (Davison, grade 950) in 5% ether–hexane. Elution was with 2 l. of 8% ether–hexane and 3.5 l. of 10% ether–hexane, and 250 ml fractions were collected: fractions 1–2 yielded 1.8 mg of a colorless oil; 3–6, nil; 7–11, 51.0 mg (17.1%) of *cis,trans* 4,5,6-triphenylbicyclo[3.1.0]hexan-2-one; 12, 2.0 mg of overlap; 13–16, 175 mg (58.7%) of *cis,cis*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one;

and 17–21, 52.9 mg (17.8%) of a mixture of *cis,cis*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one and a trace of *cis*-3,4,5-triphenyl-2-cyclohexen-1-one. The *cis,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one from fractions 7–11 was crystallized from hexane–methylene chloride to give 41.5 mg (13.9%), mp 157.5–159°. The recovered starting material from fractions 13–16 was crystallized from hexane–methylene chloride to give 123 mg (41.3%), mp 157–158.5°.

Another photolysis, starting with 223 mg of *cis,cis*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one, for 8.75 hr gave 27 mg (12.1%) of *cis,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one, mp 158–160°, and 135 mg (60.6%) of recovered starting material, mp 157–159°.

Photolysis of *trans,trans*-4,5,6-Triphenylbicyclo[3.1.0]hexan-2-one. Using the standard procedure, 786 mg (2.43 mmol) of *trans,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one was photolyzed in 110 ml of 3:1 *t*-butyl alcohol–benzene for 13.25 hr with a Pyrex filter. The solvent was removed *in vacuo* giving 853 mg of a glassy solid that was chromatographed on a 3.5 × 95 cm column, slurry packed with 60–200 mesh silica gel (Davison, grade 950) in 5% ether–hexane. The column was eluted with 12 l. of 8% ether–hexane and 1.5 l. of 15% ether–hexane and 500-ml fractions were collected: fractions 1–3, 10 mg of aliphatic solvent residues; 4–13, nil; 14–22, 559 mg (71.1%) of starting material, *trans,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one; 23, 19 mg of overlap; 24–31, 192 mg (24.4%) of a mixture of *cis*-3,4,5-triphenyl-2-cyclohexen-1-one and a new photoketone.

The *trans,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one from fractions 14–22 was recrystallized from hexane–methylene chloride to give 496 mg (63.1%), mp 138–139°, and a nmr spectrum of the material remaining in the mother liquors showed no other compound. The material from fractions 24–31 was crystallized from ether to give 90 mg (11.5%) of *cis*-3,4,5-triphenyl-2-cyclohexen-1-one, mp 188–191°. Nmr and infrared spectra of the material remaining in the mother liquors (102 mg) showed it to consist of *ca.* 30% *cis*-3,4,5-triphenyl-2-cyclohexen-1-one and *ca.* 70% of a new photoketone (not *cis,trans*-, *trans,trans*-, or *cis,cis*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one) having a 5.81-μ carbonyl band in the infrared. Attempts to isolate the new photoketone by fractional crystallization and liquid–liquid partition chromatography were unsuccessful.

In another run, the irradiation of 105 mg of *trans,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one for 2.5 hr gave 64.1 mg (61.0%) of starting material, mp 138.5–140.5°, and 16.4 mg (15.6%) of a mixture of *cis*-3,4,5-triphenyl-2-cyclohexen-1-one and the new photoketone.

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Studies in Mass Spectrometry. XXIV.[1] A Study of the Reactions Induced in Triphenylphosphine, Triphenylphosphine Oxide, and Related Substances upon Electron Impact

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Abstract: Some reactions induced by electron impact in triphenylphosphine, triphenylphosphine oxide, methylenetriphenylphosphorane, and triphenylphosphine sulfide have been studied by means of deuterium labeling. Evidence is presented to support the view that the main decomposition pathways occur with the formation of bridged phosphafluorenyl ions (containing trivalent or pentacovalent phosphorus). Some reactions proceed with hydrogen–deuterium scrambling within labeled phenyl rings, while others proceed without randomization.

As part of a program[2,3] to evaluate deuterium–hydrogen scrambling in deuterium-labeled phenyl rings, the reactions induced by electron impact on triphenylphosphine (**1a**), triphenylphosphine oxide (**2a**), methylenetriphenylphosphorane (**3a**, generated within the ion source by pyrolysis of methyltriphenylphosphonium bromide), and triphenylphosphine sulfide (**4a**) have been studied.

$(C_6H_5)_3P$	$(C_6H_5)_3P{=}O$	$(C_6H_5)_3P{=}CH_2$	$(C_6H_5)_3P{=}S$
1a	**2a**	**3a**	**4a**

To permit detailed and secure analysis of the mass spectra, a number of deuterated analogs of **1a–4a** have been synthesized. Bromination of benzene-d_6 gave bromobenzene-d_5 which was converted to the Grignard reagent and treated with phosphorus trichloride[4] to furnish triphenylphosphine-d_{15} (**1d**). This material upon oxidation gave triphenylphosphine-d_{15} oxide (**2d**), or upon quaternization with methyl bromide followed by pyrolysis within the source at 10^{-6} mm gave methylenetriphenylphosphorane-d_{15} (**3b**). Analogous sequences starting from bromobenzene-2,4,6-d_3[5] afforded the triphenylphosphine-d_9 **1b**, the triphenylphosphine-d_9 oxide **2b**, and the methylenetriphenylphosphorane-d_9 **3c**. Alternatively, treatment of **1b** with sulfur in benzene[6] at room temperature furnished the triphenylphosphine-d_9 sulfide **4b**. Reaction of dichlorophenylphosphine with the Grignard reagent derived from bromobenzene-d_5 gave the triphenylphosphine-d_{10} **1c** which on oxidation led to the triphenylphosphine-d_{10} oxide **2c**.

The mass spectra of the unlabeled compounds and those of the deuterated derivatives are summarized in Figures 1a–d, 2a–d, 3a and b, and 4. The isotopic purities of the labeled triphenylphosphines **1b**, **1c**, and **1d** are summarized in Table I; these have been

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