ments were made by following the change in ultraviolet spectra. Additionally we have examined the reaction in deuteriosulfuric acid. Results are summarized in Table I.

TABLE I

DECARBOXYLATION OF AROYLACETIC ACIDS IN SULFURIC ACID AT 25.0°

Substituted acetic acid	% H_2SO_4	$10^5k_{-CO_2}$, sec^{-1}
p-Anisoyl	23.62	2.9
	23.63	3.1
	25.62	3.20
	27.03	2.9
	27.12	2.8
	33.05	2.55
	33.33	2.4
	33.36	2.5
	36.05	2.38
	37.75	2.36
	48.61	1.45
	30.29[a]	2.2
	34.83[a]	2.00
	40.10[a]	1.64
	41.44[a]	1.54
	42.65[a]	1.31
	44.34[a]	1.36
p-Toluoyl	37.50	2.68
	42.00	2.2
	48.84	1.6
	52.72	1.4
	53.69	1.2
	61.37	0.732
	60.70[a]	0.730
Benzoyl	62.33	0.43
	67.40	0.406
	70.36	0.347
	65.85[a]	0.33
	66.68[a]	0.524
	68.64[a]	0.39
	71.71[a]	0.279
m-Chlorobenzoyl	74.38	0.230
	76.72	0.190
	78.11	0.170

[a] $ArCOCD_2CO_2D$ in D_2O-D_2SO_4; wt % D_2SO_4.

These results show that, in common with acetoacetic acid, the rates of decarboxylation of aroylacetic acids likewise are relatively insensitive to strong mineral acid concentration. The modest decrease in the rate of decarboxylation of anisoylacetic acid in changing from 25 to 48% sulfuric acid as the medium is very similar to the decrease observed by Pedersen with acetoacetic acid in sulfuric or perchloric acid solutions. Even in the higher concentrations of sulfuric acid, 60–70%, used with **3** and **4**, the observed behavior is similar.

Additionally, the reactivity of this group of compounds shows little sensitivity to the nature of the substituent in the aromatic moiety. Where the data are overlapping, **1** and **2** show very similar rates of decarboxylation; **3** and **4** appear to be slightly less reactive, but within a factor of 2. Swain, *et al.*,[5] concluded that ρ was about -1 in benzene solution for the decarboxylation of the aroylacetic acids.

In deuteriosulfuric acid, the decarboxylating species is the trideuterio analog. The decarboxylation of anisoylacetic acid in deuteriosulfuric acid shows only a very slightly depressed rate of reaction, which represents the combination of the factors discussed previously by Swain, *et al.*,[5] which are involved in the proton-transfer process concomitant with the decarboxylation; our system also includes secondary isotope effects from the CD_2 moiety, as bonding changes from tetrahedral to trigonal. In the case of **1**, the isotope effect is normal, though small. Swain found similar values for **1** and **3** but a slightly inverse value (k_H/k_D = 0.85) for **2** in benzene solution.[5]

Experimental Section

Materials.—***p*-Anisoylacetic acid** (1) was prepared following the procedure of Swain, *et al.*,[5] mp 80–81° dec (lit.[5] mp 80°, 81–82° dec). ***p*-Toluoylacetic acid** (2) was prepared by saponification of ethyl *p*-toluoylacetate. On purification by reprecipitation from carbonate solution and drying, **2** was obtained, mp 87–88° dec (lit.[5] 85–87° dec). A small sample was further purified to mp 89.7–90.2° dec.

Kinetic Procedures. A.—The appropriate β-keto acid was dissolved in 95% sulfuric acid, and a small volume of this solution was added to more dilute sulfuric acid to make a solution of the desired concentration (5×10^{-5} *M*) in sulfuric acid of the appropriate concentration. Measurements were made using a Beckmann DU spectrophotometer at an appropriate wavelength (260–280 mμ). Stock solutions of **1** and **2** were reasonably stable in 95% acid for 2 weeks.

B.—The β-keto acid was generated *in situ* by the hydration of the appropriate arylpropiolic acid.[8] The conversion of the β-keto acid into the acetophenone was followed spectrophotometrically.

Registry No.—**1,** 13422-77-0; **2,** 13422-78-1; benzoylacetic acid, 614-20-0; *m*-chlorobenzoylacetic acid, 13422-80-5; sulfuric acid, 7664-93-9.

Photochemical Reaction of 1,3,4,6-Tetraphenylhexa-1,3,5-triene[1]

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Theis and Dessy have reported that 1,3,4,6-tetraphenyl-1,3,5-hexatriene (1) upon irradiation with light of wavelengths above 280 mμ gave one photoproduct which could be isolated in 87% yield.[3] The photoproduct was postulated to be 1,2,3,5-tetraphenyl-1,4-cyclohexadiene (2).[3] This result is contrary to the previous results in the photochemistry of conjugated cyclohexadienes[4] and, in particular, of phenyl-substituted cyclohexadienes.[5] In these cases, the first formed photoproduct is either a hexatriene[4,5] or a bicyclo[2.2.0]hexene.[6] When the examples which form

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(1) This work was supported in part by PHS Grant No. AM-709, National Institute for Arthritis and Metabolic Diseases, U. S. Public Health Service.

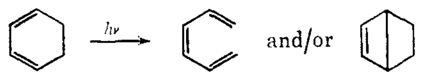
(2) NASA Predoctoral Trainee, 1964–1967.

(3) R. J. Theis and R. E. Dessy, *J. Org. Chem.*, **31**, 4248 (1966).

(4) (a) W. G. Dauben and W. Todd Wipke, *Pure Appl. Chem.*, **9**, 539 (1964); (b) J. Meinwald and P. H. Mazzocchi, *J. Am. Chem. Soc.*, **89**, 1755 (1967), and references therein.

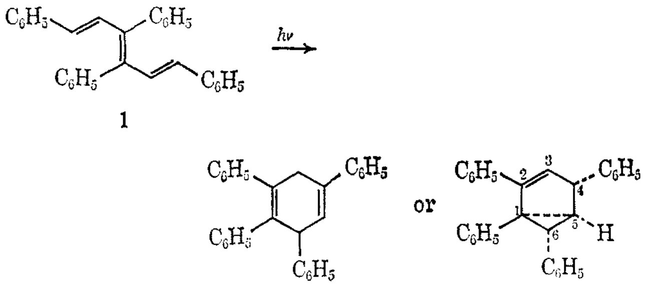
(5) (a) G. R. Evanega, W. Bergman, and J. English, Jr., *J. Org. Chem.*, **27**, 13 (1962); (b) W. G. Dauben and J. H. Smith, Abstracts of the 19th National Organic Chemistry Symposium, Tempe, Ariz., June 13–17, 1965, p 30.

(6) (a) W. G. Dauben and R. M. Coates, *J. Am. Chem. Soc.*, **86**, 2490 (1964); (b) G. J. Fonken and K. Mehrotra, *Chem. Ind.* (London), 1025 (1964).



trienes are irradiated for a longer time, bicyclo[3.1.0]hexenes are frequently formed.[4,5] To our knowledge, there are no published cases of 1,4-cyclohexadiene formation. Therefore, we would expect *a priori* that

the photoproduct of **1** should be 1,2,4,6-tetraphenylbicyclo[3.1.0]cyclohex-2-ene (**3**), a compound that Theis and Dessy[3] suggested as a possible transient intermediate. Both **2** and **3** would be expected to be dehydrogenated in the presence of palladium on charcoal to give 1,2,3,5-tetraphenyl benzene (**4**).[3,5a] This reaction was used by the previous workers[3] to determine



1

2 **3**

the location of the phenyl groups in the rearranged product.[3] However, the spectral data which was used to establish the structure of the photoproduct as **2** is, in our opinion, inconclusive. Dessy reports[3] that the nuclear magnetic resonance (nmr) spectrum of the photoproduct showed twenty phenyl protons, one vinyl proton (doublet) at τ 4.3, one benzylic proton (doublet) at 5.9, and two equivalent methylene protons (singlet) at 7.7.[3] The high-field singlet appears to be at too high a field for normal diallylic protons, which usually appear at about τ 7.1.[7] It is also conceivable that the two protons would not be chemically equivalent and therefore should not have the same chemical shift. The ultraviolet spectrum of the photoproduct is reported to be λ_{max} 238 mμ (ϵ 23,800)[3] (see Figure 1). This spectrum should resemble the additive spectrum of the isolated chromophores, *cis*-stilbene and styrene. For comparison, Figure 1 shows the sum of the ultraviolet spectra of *cis*-stilbene and β-methylstyrene,[8] which exhibits strong absorption above 300 mμ; a similar absorption is not present in the ultraviolet spectrum of the photoproduct. The spectrum of the photoproduct is more compatible with structure **3**. For these reasons we decided to reinvestigate the problem.

Triene **1**, prepared by the method of Dessy,[3] upon irradiation using a high-pressure mercury lamp through a Pyrex filter afforded a single photoproduct in 87% yield. The nmr spectrum of this product showed the two low-field absorptions. However, in our hands, the lower field "doublet" was a broad singlet that could not be resolved even when a 100-MHz spectrometer was employed. The high-field "singlet" possessed small shoulders which could not be resolved. Double resonance proved that the peaks at τ 4.3 and 5.9 were coupled (J = 2.0 cps) and that the lowest field proton was coupled to the protons of the high-field singlet. Irradiation at τ 7.7 collapsed the broad singlet at 4.3 to a doublet (J = 2.0 cps). These results do not establish the structure of the photoproduct since in either **2** or **3** the lower field protons should be coupled.

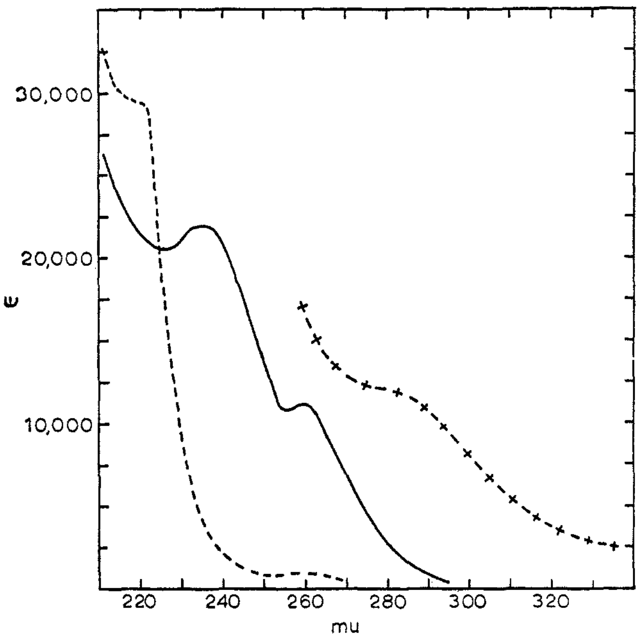
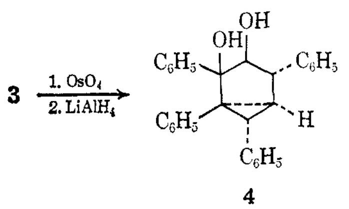


Figure 1.—Ultraviolet spectra: ———, **3**; - - - -, **4**; +—+—+, sum of spectra of β-methylphenylpropene-2 and *cis*-stilbene.[7]

Reaction of the photoproduct with 2.1 equiv of osmium tetroxide followed by reduction of the osmium ester with lithium aluminum hydride and filtration through silica gel gave a white crystalline material. This compound had a molecular weight (determined from the mass spectrum) of 418, corresponding to a molecular formula $C_{30}H_{26}O_2$. These data require that one double bond of the photoproduct (mol wt 384) was oxidized by the osmium tetroxide to yield a diol. The ultraviolet spectrum, λ_{max} 259 mμ (ϵ 880) and λ_{sh} 220 mμ (ϵ 29,000) (see Figure 1), suggests that the major chromophore has been destroyed, leaving only absorption characteristic of a phenylcyclopropane.[9] If the structure of the photoproduct was **2**, the resulting diol from the osmylation reaction should have either a stilbene or a styrene chromophore, which is inconsistent with the ultraviolet spectrum of the diol obtained. Therefore, we conclude that the diol must be structure **4** and that, contrary to the assignment of Theis and Dessy,[3] the photoproduct must be **3**.



4

If we accept the proposal that the photoproduct of **1** is **3**, on the basis of the chemical and ultraviolet data,

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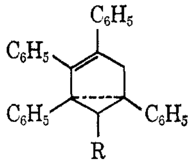
[7] L. M. Jackman, "Applications of Nuclear Magnet Resonance," The Macmillan Co., New York, N. Y., 1959, p 60.

[8] M. Orchin and R. A. Friedel, "The U.V. Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., Spectra No. 24 and 125.

[9] A. L. Goodman and R. H. Eastman, *J. Am. Chem. Soc.*, **86**, 908 (1964).

we are forced to conclude that the two cyclopropyl protons of **3** have the same chemical shift, and therefore the coupling between them cannot be observed.[10] There are two effects which probably combine to cause this coincidence. In general, phenyl substituents cause a downfield shift of adjacent protons.[5] For instance, in other studies in this laboratory, it has been found that the cyclopropyl protons of **5** appear at τ 7.6 and of **6** at τ 6.2.[5] The absence of the C-5 phenyl in **3** must cause an upfield shift of the C-6 proton from its chemical shift in **6**. In **3**, the C-4 and C-6 phenyls must be causing a downfield shift of the C-5 proton.



5, R = H
6, R = C_6H_5

The nmr spectrum of the diol supports our structural assignment. There is a two-proton AB pattern at τ 5.68 and 6.27 (J = 7.5 cps) attributable to the benzylic proton and proton adjacent to the hydroxyl group, a two-proton AB pattern at τ 7.29 and 7.47 (J = 4.0 cps) for the cyclopropyl protons, and a two-proton broad multiplet which is not observed after 1 drop of deuterium oxide was added to the sample tube and is therefore attributed to the hydroxyl protons. The 4.0-cps coupling constant of the cyclopropyl protons is evidence that they are *trans*.[11] The spectra of both **3** and **4** show that the benzylic proton (on C-4) and the bridgehead proton (on C-5) are not coupled. If they are *trans*, molecular models show that the dihedral angle is about 110°; if they are *cis*, it is about 0°. On the basis of the Karplus relation the dihedral angle must be 90° if the coupling constant is zero.[12] In support of this conclusion is the observation of Bergvist and Norin that the coupling constant of the C-4 and C-5 protons of (−)-thujone is zero.[13] Thus, we conclude that the protons must be *trans* and the complete stereochemistry of **3** and **4** is as shown.

In summary, we have shown that irradiation of **1** yields **3**, rather than **2** as was previously proposed.[3] There is insufficient evidence to permit determination of the immediate precursor of **3**. Although it has been assumed that trienes are the precursors of bicyclo[3.1.0]hexenes, this has not been rigorously proven.[4b,14] Presumably the conversion of trienes to dienes and the isomerization of trienes is reversible.[4,5] Careful study may show that the corresponding 2,3,5,6-tetraphenylcyclohexadiene and at least one isomeric triene is present in the photomixture of **1**.

Experimental Section

Melting points were determined in an oil bath and are uncorrected. Infrared spectra were determined in carbon tetrachloride using a Perkin-Elmer Infracord Model 137. Ultraviolet spectra were taken in acetonitrile on a Perkin-Elmer Model 202 spectrometer. Nmr spectra were recorded on Varian A-60 (60 MHz) and HA-100 (100 MHz) instruments. Mass spectra were determined on a Varian Model M-66 instrument.

1,2,4,6-Tetraphenylbicyclo[3.1.0]cyclohexene (3).—The procedures of Dessy were followed,[3] except that triene **1** was irradiated with a Hanovia high-pressure mercury lamp in an immersion apparatus fitted with a Pyrex filter. The material so prepared possessed all the published properties[3] except details of the nmr spectrum which follow: τ 2.4–3.4 (20 H, multiplet, phenyl H), 4.3 (1 H, broad singlet, vinyl H), 5.9 (1 H, doublet, J = 2.0 cps, allylic H), 7.7 (2 H, singlet which also has unresolved fine structure on both shoulders, cyclopropyl H). A double irradiation was performed: irradiation at τ 4.3 collapsed the doublet at 5.9 to a singlet; irradiation at τ 5.9 narrowed the broad singlet at 4.3; irradiation at τ 7.7 collapsed the broad singlet at 4.3 to a doublet (J = 2.0 cps). The high-field singlet was not noticeably affected by these experiments.

Degradation of 3 by Osmium Tetroxide.—To a 250-ml, round-bottomed flask was added 108 mg (0.281 mmole) of **3**, 10 ml of pyridine, 100 ml of dry ether, and 150 mg (0.59 mmole) of osmium tetroxide. The flask was stoppered, wrapped in aluminum foil, and allowed to stand at room temperature for 1 week.

The solvent was removed and the brown oil was placed in a vacuum oven for 1 hr to remove the last traces of pyridine. The oil was taken up in ether and cooled in an ice bath, and 550 mg (0.68 mmole) of lithium aluminum hydride was added. The slurry was stirred for 1 hr at room temperature and cooled in an ice bath, and the salts were precipitated with saturated ammonium chloride solution. The organic layer was decanted and the salts were washed once with water. The combined ethereal layers were dried over magnesium sulfate and the solvent was removed to yield 61 mg of a brown oil. An attempted crystallization gave impure brown crystals.

The crystals and mother liquors were recombined and filtered through a silica gel column (6 × 0.8 cm). Two fractions were taken: the first, eluted with 10 ml of benzene, contained 3 mg of a colorless oil; the second, eluted with 15 ml of ether, contained 59 mg of a white solid shown to be **4** (50% over-all yield of diol). Two crystallizations from benzene–methylcyclohexane of the second fraction gave the analytical sample: mp 184.8–185.8°; infrared, ν_{max} 3540 cm^{-1}; ultraviolet, λ_{max} 259 mμ (ϵ 880) and λ_{sh} 220 mμ (ϵ 29,000); nmr, τ 2.4–7.4 (20 H, multiplet, phenyl H), 5.68 (1 H, doublet, J = 7.5 cps, C-3 or benzylic H), 6.28 (1 H, doublet, J = 7.5 cps, benzylic or C-3 H), 7.29 (1 H, doublet, J = 4.0 cps, cyclopropyl H), 7.47 (1 H, doublet, J = 4.0 cps, cyclopropyl H), and 7.7–8.1 (2 H, multiplet, hydroxyl H; the signal of these protons disappears when 1 drop of deuterium oxide is added to the sample); mass spectrum, M = 418, 400, and 384 (base peak).

Anal. Calcd for $C_{30}H_{26}O_2$ (418.54): C, 86.09; H, 6.26. Found: C, 85.96; H, 6.22.

Registry No.—**1**, 13573-38-1; **3**, 13573-39-2; **4**, 13573-40-5.

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(10) Reference 7, p 89.

(11) W. G. Dauben and W. T. Wipke, *J. Org. Chem.*, **32**, 2976 (1967).

(12) N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, pp 49–53.

(13) M. S. Bergvist and T. Norin, *Arkiv Kemi*, **22**, 137 (1964).

(14) See E. F. Ullman, W. A. Henderson, Jr., and K. R. Huffman, *Tetrahedron Letters*, 935 (1967). Generalization of their conclusion to polyolefins awaits determination of the multiplicity of the states involved in the various reactions, especially since their bicyclo[3.1.0]hexene can be viewed as arising from a normal photochemical dienone rearrangement [see H. Hart, P. M. Collins, and A. J. Waring, *J. Am. Chem. Soc.*, **88**, 1005 (1966), and references therein].

Ketimine Syntheses. Use of Titanium Tetrachloride in a New Procedure for Their Preparation

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Various preparative procedures for certain ketimines from a variety of cyclohexanones and primary amines were evaluated from the standpoint of yield and con-