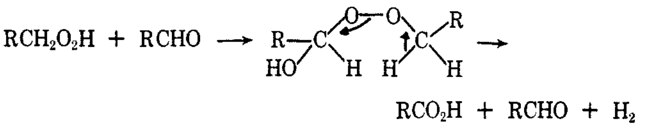
experimental techniques convinces us that they were misled by incomplete separation of decomposition products from the solvent.

Decompositions of n-BuO$_2$H and *sec*-BuO$_2$H in Toluene at 170–180°

Thermal decompositions of dilute solutions of n-BuO$_2$H and *sec*-BuO$_2$H in toluene were carried out to determine the extent of homolysis and to gain some information on cleavage reactions of primary and secondary alkoxy radicals under these conditions. Although both hydroperoxides were slightly contaminated with their parent alcohols, this was not expected to invalidate the results. Rate constants and products are shown in Table IV.

Decompositions of n-BuO$_2$H were autocatalytic, even at 0.01 M in toluene. Plots of per cent of RO$_2$H *vs.* time were linear, and the first-order rate constants in Table IV are calculated from the initial rates of hydroperoxide decomposition determined from such plots. Values of k_1 so determined were approximately proportional to $[n\text{-BuO}_2\text{H}]^{1/2}$ and suggested induced decomposition, although the rates of lowest initial concentration and the yields of bibenzyl were not much different from those for t-BuO$_2$H under similar circumstances.

Autocatalysis for n-BuO$_2$H was not surprising in view of the Mosher[35] reaction for primary hydroperoxides, but the absence of butyric acid in the products



appeared to eliminate any large contribution from this reaction. The evolved gases were not analyzed.

sec-BuO$_2$H gave reasonably good first-order plots for decomposition and gave as much or more bibenzyl as n-BuO$_2$H did.

In product studies on completely decomposed solutions, only 79% of n-BuO residues and 74% of *sec*-BuO residues from the respective hydroperoxides were accounted for. Up to 21% n-BuO· radicals could have been lost through cleavage to Pr· + CH$_2$O·. *sec*-BuO· radicals can cleave in two ways. While the production of methane in the thermal decomposition of *sec*-Bu$_2$O$_2$ in toluene at 100° (part II[1b]) suggests that at 180° CH$_3$· radicals and EtCHO are being formed, we were unable to find the expected propionaldehyde or carboxylic acids in the products. Thus, there appear to be many opportunities for further experimental work on thermal decomposition of primary and secondary hydroperoxides, but little possibility of obtaining clean reactions and high yields of single products.

Registry No.—t-BuO$_2$H, 75-91-2; t-Bu$_2$O$_2$, 110-05-4; α-cumyl O$_2$H, 80-15-9; n-BuO$_2$H, 4813-50-7; s-BuO$_2$H, 13020-06-9.

Acknowledgment.—Mr. Brian Guilbert assisted with part of the experimental work.

[35] H. S. Mosher and L. J. Durham *J. Amer. Chem. Soc.* **82**, 4537 (1960).

Strained Organic Molecules. I. 1,5,6-Triphenyltricyclo[3.1.0.0^{2,6}]hexan-3-one[1-3]

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The synthesis of 1,5,6-triphenyltricyclo[3.1.0.0^{2,6}]hexan-3-one (I) from 1-(1,2,3-triphenylcycloprop-2-enyl)-3-diazopropan-2-one (II) is described. Upon heating I rearranges quantitatively to 3,4,5-triphenylphenol. In base, I readily gives 4,5,6-triphenylbicyclo[3.1.0]hex-3-en-2-one (IV). Upon irradiation with ultraviolet light I rearranges almost exclusively to 2,4,5-triphenylphenol, whereas IV gives substantial amounts of both 3,4,5-triphenylphenol and 2,4,5-triphenylphenol. Compound I reacts with methylmagnesium iodide to give 3-methyl-1,5,6-triphenyltricyclo[3.1.0.0^{2,6}]-3-hexanol (V).

Since 1961 the intramolecular cyclization of "carbenes"[4] has been used to synthesize a number of strained ring compounds. We wish to report on such a synthesis of 1,5,6-triphenyltricyclo[3.1.0.0^{2,6}]hexan-3-one (I) and some of its reactions. Masamune and coworkers[5] have communicated the results of extensive studies on an analogous compound, 1,6-diphenyltricyclo[3.1.0.0^{2,6}]hexan-3-one, and the next lower homolog, 1,5-diphenyltricyclo[2.1.0.0^{2,5}]pentan-3-one.

Compound II, (1,2,3-triphenylcycloprop-2-enyl)acetic acid, was prepared in good yield by the hydrolysis of the crude reaction product from treatment of triphenylcyclopropenyl bromide with ethyl bromoacetate in the presence of zinc in refluxing benzene–ether. It had the typical uv spectrum of a diphenylcyclopropene double bond[6] and the infrared spectrum and analysis also supported the proposed structure (see Experimental Section).

Compound III, 1-(1,2,3-triphenylcycloprop-2-enyl)-3-diazopropan-2-one, was synthesized from the acid chloride of II and diazomethane in the usual manner. Its spectra and analysis supported its structure. When this diazo ketone was treated with copper in refluxing benzene, a good yield of compound I was obtained after chromatography. The structure of I was indicated by analysis and by spectral and chemical properties. The infrared spectrum showed a carbonyl

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[1] Preliminary communications of this work have been published: A. Small, *J. Amer. Chem. Soc.*, **86**, 2091 (1964); A. M. Small, *Chem. Commun.*, 243 (1965).

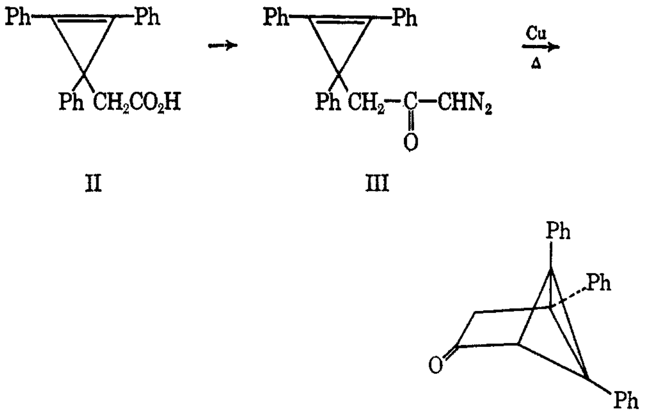
[2] This compound was previously named 4,5,6-triphenyltricyclo-[2.1.1.0^{5,6}]hexan-2-one but renamed to follow the IUPAC rules as pointed out by Meinwald.[3]

[3] J. Meinwald and J. K. Crandall, *J. Amer. Chem. Soc.*, **88**, 1292 (1966).

[4] The first example of such a cyclization was reported by G. Stork and J. Ficini, *ibid.*, **83**, 4678 (1961).

[5] (a) S. Masamune, *ibid.*, **86**, 735 (1964); (b) S. Masamune, *Tetrahedron Lett.*, 945 (1965); (c) S. Masamune and N. T. Castellucci, *Proc. Chem. Soc.*, 298 (1964). (d) S. Masamune, *et al.*, *Tetrahedron Lett.*, 193 (1966).

[6] R. Breslow and C. Yuan, *J. Amer. Chem. Soc.*, **80**, 5991 (1958), and subsequent papers by R. Breslow and coworkers.

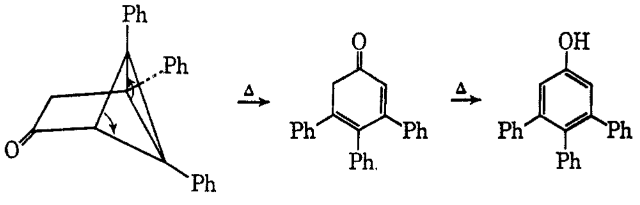


II III

I

band at 1750 cm^{-1} typical of a five-membered ring ketone.[7] The ultraviolet spectrum showed a shoulder at 243 mμ (log ε 4.23). Thus, this compound shows a strong chromophore, typical of other diphenylbicyclobutyl derivatives.[8] The intensity of the ultraviolet absorption is not surprising in view of the large amount of π character in the 1–3-carbon bridge of bicyclobutanes.[9] The nmr spectrum and analysis also agreed with the proposed structure, showing only a 15-proton multiplet centered at 7.2 for the phenyl hydrogens, a one-proton singlet at 3.2 for the bridgehead hydrogen, and a two-proton singlet at 2.6 ppm for the methylene hydrogens. In comparison 1,6-diphenyltricyclo[3.1.0.0^{2,6}]hexan-3-one has the following chemical shift values: phenyl, 7.1; bridgehead hydrogens, 3.4 and 3.2; methylene hydrogens, 2.0 ppm.[5b] Since Silverstein and Bassler[10] indicate a chemical-shift change of 0.35 ppm for adding a phenyl β to a methylene group, the nmr spectra of the two tricyclic compounds agree rather closely.

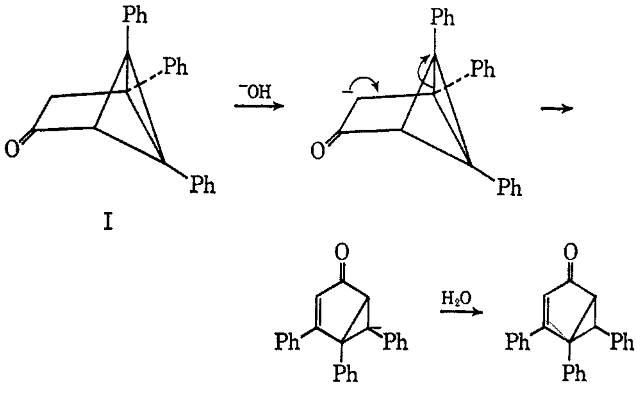
Further evidence for the structure of compound I are the following reactions. Upon melting or heating briefly at 180° this compound rearranges quantitatively to 3,4,5-triphenylphenol, identified by comparison with an authentic sample. The rearrangement simply involves a bond reorganization to the keto form of the phenol which then tautomerizes. This



reaction could have been predicted from the facility and mechanism of the thermal rearrangement of bicyclobutane and simple derivatives.[9,11] Stabilization by the phenyl substituents of the transition state for this reaction should also enhance the reactivity. Masamune[5c] has also observed the facile thermal isomerization of 1,6-diphenyltricyclo[3.1.0.0^{2,6}]hexan-3-one to 3,4-diphenylphenol.

In the presence of base the tricyclic ketone rearranges readily to 4,5,6-triphenylbicyclo[3.1.0]hex-3-en-2-one. (IV). This reaction can take place by the mechanism shown in Scheme I. The driving force for the reaction is relief of strain and formation of the phenyl and carbonyl conjugated double bond.

Scheme I



I

IV

The structure of IV was ascertained from its spectral and photochemical properties. Its carbonyl band at 1690 cm^{-1} in the infrared and its λ_{max} 281 mμ (log ε 4.14) in the ultraviolet are in the region expected for a 3-phenylcyclopent-2-en-1-one.[12] The nmr spectrum also agreed with the structure (see Experimental Section). The low value (J = 4 cps) of the coupling constant between the cyclopropyl protons suggests that these two hydrogens are *trans*.[13] This would mean that in the ring opening of compound I, the cyclopropyl anion is protonated before it has a chance to epimerize.[14] This is not surprising in view of the high exchange *vs.* racemization rate of cyanocyclopropanes[15] and the stereospecific opening in base of 1,5-diphenyltricyclo[2.1.0.0^{2,5}]pentan-3-one to a bicyclobutyl derivative.[5b]

Ultraviolet irradiation of compound IV in a Pyrex vessel gave a small amount of acidic material which was not characterized, a 50% yield of crude 2,4,5-triphenylphenol, and a 20% yield of crude 3,4,5-triphenylphenol. Both products were characterized by comparison with samples prepared by a different route. This photochemical behavior is readily explained on the basis of the mechanism proposed by Zimmerman for the rearrangement of 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one and related compounds.[16] The photo-

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[7] K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p 42.

[8] For example, 1,5-diphenyltricyclo[2.1.0.0^{2,5}]pentan-3-one showed λ_{max} 242 mμ (log ε 4.16),[5a] 1,6-diphenyltricyclo[3.1.0.0^{2,6}]hexan-3-one showed λ_{max} 255 mμ (log ε 4.08),[5b] and methyl 1,3-diphenylbicyclobutane-2-carboxylate showed λ_{max} 270 mμ (log ε 3.95).[5b]

[9] See M. Pomerantz and E. W. Abrahamson, *J. Amer. Chem. Soc.*, **88**, 3970 (1966), and references cited therein.

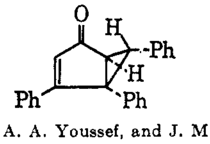
[10] R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," 1st ed, John Wiley and Sons, Inc., New York, N. Y., 1962, p 83.

[11] See K. B. Wiberg and J. M. Lavanish, *J. Amer. Chem. Soc.*, **88**, 5272 (1966), and references cited therein.

[12] See examples in C. F. H. Allen and J. A. VanAllen, *ibid.*, **77**, 2315 (1955); P. Yates, N. Yoda, W. Brown, and B. Mann, *ibid.*, **80**, 202 (1958); B. Eistert and A. Langbein, *Ann.*, **678**, 78 (1964).

[13] J. D. Graham and M. T. Rogers, *J. Amer. Chem. Soc.*, **84**, 2249 (1962).

[14] These considerations lead to the tentative formulation of the stereochemistry of IV as



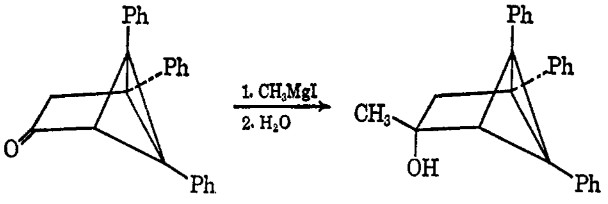
[15] H. M. Walborsky, A. A. Youssef, and J. M. Motes, *J. Amer. Chem. Soc.*, **84**, 2466 (1962).

[16] H. E. Zimmerman and D. I. Schuster, *ibid.*, **84**, 4527 (1962), and later papers.

chemistry of a similar compound, 1,3,4,5-tetraphenylbicyclo[3.1.0]hex-3-en-2-one has been studied by Durr.[17] The fact that this compound gives a 91% yield of 2,3,4,6-tetraphenylphenol where phenyl migration has not occurred is again not surprising in terms of the Zimmerman mechanism. Thus the similarity of these photochemical rearrangements also lends support to the structure proposed for IV.

In contrast to the photochemical behavior of the bicyclic ketone IV, the tricyclic ketone I undergoes rearrangement almost exclusively to 2,4,5-triphenylphenol. Masamune and coworkers have proposed and substantiated a mechanism for this photochemical reaction in the case of 1,6-diphenyltricyclo[3.1.0.0^{2,6}]hexan-3-one.[5d]

Ketone I reacts typically with methylmagnesium iodide to give the corresponding tertiary alcohol (V) whose spectra and analysis agreed with its structure. Compound I also gives derivatives with hydroxylamine, 2,4-dinitrophenyhydrazine, tosylhydrazine, and bromine in carbon tetrachloride, but these products were not fully characterized.



V

We do not intend to explore the chemistry of the title compound further.

Experimental Section

The nmr spectra were run on a Varian A-60 spectrometer in deuteriochloroform with tetramethylsilane as an internal standard. Ultraviolet spectra were determined either on a Beckman DK or Cary 14 spectrophotometer with 95% ethanol as the solvent unless otherwise indicated. Infrared spectra were taken as potassium bromide disks on either a Beckman IR-9 or Perkin-Elmer Infracord. Melting points are uncorrected.

(1,2,3-Triphenylcycloprop-2-enyl)acetic Acid (II).—Triphenylcyclopropenyl bromide was prepared by the method of Breslow and Chang[18] and recrystallized from acetonitrile before use.

In a 200-ml, three-necked flask equipped with stirrer, pressure equalizing dropping funnel, and reflux condenser topped with a calcium chloride tube was placed 11 g (0.17 g-atom) of small pieces of zinc which had been sandpapered and then cut and rolled. The system was flamed out and 35 ml of solvent (20 ml of dry benzene and 15 ml of anhydrous diethyl ether) was added. In the dropping funnel was placed 20 ml (30 g, 0.18 mol) of ethyl bromoacetate (Eastman Kodak) in 20 ml of benzene and 10 ml of ether. An iodine crystal was added to the stirred mixture which was heated to reflux. Part of the ethyl bromoacetate solution was added and the reaction mixture turned cloudy after 10 min. Then 5.93 g (0.017 mol) of triphenylcyclopropenyl bromide was added. The remainder of the ethyl bromoacetate solution was added over the course of 30 min. The mixture was allowed to reflux for 3–5 hr. During this time the ether was allowed to evaporate. The homogeneous reaction mixture was poured into water and 6 *N* hydrochloric acid added to dissolve the zinc salts. The reaction mixture was extracted three times with ether; the combined ether layers were washed to neutrality with water, dried over magnesium sulfate, filtered, and removed under reduced pressure to give a reddish oil. This was hydrolyzed directly with 20 g of potassium hydroxide in 250 ml of methanol by refluxing for 100 min. The mixture was poured into water and filtered to collect the fairly insoluble acid salt. The filtrate was extracted two times with ether (discarded), then neutralized with hydrochloric acid and extracted three times with ether which was combined and washed with water, dried over magnesium sulfate, filtered, and removed under reduced pressure. The acid obtained in this manner was combined with the acid obtained by stirring the acid salt overnight with 30 ml of concentrated hydrochloric acid, pouring the mixture into water, extracting with ether, and washing, etc. The crude solid was recrystallized from 50 ml of ethanol to give 3.6 g (59%) of pale yellow crystals, mp 182–184 dec. The yield of acid can be improved slightly by running the reaction under nitrogen. A sample, recrystallized for analysis from ethyl acetate, was colorless and had mp 183° dec.

The infrared spectrum showed a carbonyl band at 1730 and a cyclopropene band at 1835 cm^{-1}. The ultraviolet spectrum had λ_{max} 330 (log ϵ 4.39), 313 (4.47), and a shoulder at 300 mμ (4.34).

Anal. Calcd for $C_{23}H_{18}O_2$: C, 84.63; H, 5.56. Found: C, 84.65; H, 5.55.

1-(1,2,3-Triphenylcycloprop-2-enyl)-3-diazopropan-2-one (III).—Compound II, (1,2,3-triphenylcycloprop-2-enyl)acetic acid, was covered with excess oxalyl chloride and allowed to stand overnight at room temperature. The excess oxalyl chloride was removed under reduced pressure; the resulting solid was dissolved in dry benzene which was then removed under reduced pressure. The acid chloride, dissolved in dry benzene or ether, was added to a stirred solution of a 2-mole excess of diazomethane in ether. The addition (using 1 g of acid chloride in 10 ml of benzene) took about 0.5 hr and the mixture was allowed to stand at room temperature for 2 hr. Removal of the solvent under reduced pressure (do not heat) gave the diazo ketone which was used directly in the synthesis of I. A sample was purified for analysis by recrystallization from carbon tetrachloride. The infrared spectrum showed strong peaks at 2120 (diazo compound), 1820 (cyclopropene), and 1650 cm^{-1} (carbonyl). The ultraviolet spectrum in dioxane had λ_{max} 330 mμ (log ϵ 4.42), 313 (4.50), and 227 (4.59) and a shoulder at 299 mμ (4.41), The nmr spectrum had a 15-proton multiplet centered at 7.5 (phenyl hydrogens), a one-proton singlet at 5.1 (methine hydrogen), and a two-proton singlet at 3.3 ppm (methylene hydrogens).

Anal. Calcd for $C_{24}H_{18}N_2O$: C, 82.26; H, 5.18; N, 8.00. Found: C, 82.05; H, 5.21; N, 7.91.

1,5,6-Triphenyltricyclo[3.1.0.0^{2,6}]hexan-3-one (I).—A 150-ml, three-necked flask was flamed out and equipped with a reflux condenser, dropping funnel, and nitrogen inlet tube. To the flask was added 30 ml of benzene and 0.9 g of copper powder and the system flushed with nitrogen and brought to reflux. Positive nitrogen pressure was maintained throughout the period of heating. In the dropping funnel was placed 0.992 g of the crude diazo compound III, dissolved in 30 ml of benzene. This was dropped into the refluxing benzene over a period of 10 min and refluxed for 1 hr more. The solution was cooled and filtered free of copper; the benzene was removed under reduced pressure. Chromatography on Fisher alumina (80–200 mesh) gave, in benzene, 0.51 g (57%) with mp 155.5–156° and 0.068 g (7%), with mp 148–156°. A sample prepared for analysis by recrystallization from ethyl acetate had mp 155–157°. The compound rapidly resolidified at its melting point. The infrared spectrum showed a strong carbonyl band at 1750 and a weaker peak at 1710 cm^{-1}. The ultraviolet spectrum (dioxane) showed a shoulder at 243 mμ (log ϵ 4.34). The nmr spectrum had a 15-proton multiplet centered at 7.2 (phenyl hydrogens), a one-proton singlet at 3.2 (bridgehead hydrogen), and a two-proton singlet at 2.6 ppm (methylene hydrogens).

Anal. Calcd for $C_{24}H_{18}O$: C, 89.42; H, 5.63; mol wt, 322. Found: C, 89.24; H, 5.68. mol wt, 318 (thermoelectric osmometer).

Thermal Reaction of 1,5,6-Triphenyltricyclo[3.1.0.0^{2,6}]hexan-3-one (I).—A 40-mg sample of the tricyclic ketone was heated for 1 min under nitrogen in a test tube immersed in an oil bath at 180°. The sample quickly melted and resolidified. The product had mp 227–229. A mixture melting point with an authentic sample of 3,4,5-triphenylphenol[19] which had mp 227–229° was 228–230°. An infrared spectrum was identical with the infrared spectrum of authentic 3,4,5-triphenylphenol.

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(17) H. Durr, *Tetrahedron Lett.*, 5829 (1966).

(18) R. Breslow and H. W. Chang, *J. Amer. Chem. Soc.*, **83**, 2374 (1961).

(19) Prepared by the method of A. Smith [*Chem. Ber.*, **26**, 65 (1893)] as modified by J. B. Garner [*Amer. Chem. J.*, **31**, 143 (1904)]; B. Prager, *et al.*, "Beilsteins Handbuch der Organischer Chemie," Vol. VI, 4th ed, Julius Springer, Berlin, Germany, 1923, p 721; Vol. VIII, p 220.

Rearrangement of I to 4,5,6-Triphenylbicyclo[3.1.0]hex-3-en-2-one (IV).—To 15 ml of purified dioxane and 10 ml of water was added 1.0 g (0.003 mol) of tricyclic ketone I and 1.0 g (0.025 mol) of sodium hydroxide. The resulting mixture was refluxed for 1 hr, then poured into water. The water layer was extracted three times with ether which was washed with water, dried over magnesium sulfate, filtered, and removed under reduced pressure to give an oily solid which was recrystallized from ethanol to give 0.77 g with mp 150–152° and 0.06 g with mp 149–153°. These crops were recombined and recrystallized to give 0.70 g (70%) of colorless, feathery crystals, mp 155–156°. A sample recrystallized for analysis had mp 157–158°. The compound is not stable on silica gel and is sensitive to light.

The compound had a carbonyl band at 1690 cm^{-1} in the infrared and a peak at 1.68 μ in the near infrared. In the ultraviolet it showed λ_{max} 281 mμ (log ϵ 4.14). The nmr spectrum showed a 15-proton multiplet centered at 7.1, a one-proton doublet with some fine structure (J = 1 cps) centered at 5.9 (vinyl proton), a one-proton doublet with some fine structure (J = 4 cps) at 3.1 (cyclopropyl proton), and a one-proton pair of doublets (J = 1 cps, J = 4 cps) at 2.7 ppm (cyclopropyl proton).

Anal. Calcd for $C_{24}H_{18}O$: C, 89.42; H, 5.63; mol wt, 322. Found: C, 89.15; H, 5.68; mol wt, 324 (thermoelectric osmometer).

Photoreaction of IV.—A solution of 0.295 g of IV in 500 ml of 60% dioxane–water in a Pyrex gas bubbler was flushed with nitrogen for 45 min. The system was irradiated in a Srinivasan–Griffin reactor containing 2537-Å lamps for 14 hr. The reaction mixture was reduced in volume to 100 ml by reduced pressure distillation. Water was added and the resulting mixture extracted three times with ether. The ether was extracted with 10% sodium carbonate, acidification of which gave 0.027 g of oil which was not characterized further. The ether was washed with water, dried over magnesium sulfate, filtered, and removed under reduced pressure. Treatment of the resulting oil with ethanol gave 0.027 g (9%) of 3,4,5-triphenylphenol, mp 221–225. Chromatography of the remainder of the material on alumina gave 0.147 g (50%) of crude 2,4,5-triphenylphenol which on recrystallization from petroleum ether (bp 30–60°) gave 0.090 g with mp 97.5–100° and 0.032 g (11%) of 3,4,5-triphenylphenol, mp 195–205°, which on recrystallization from acetonitrile gave 0.011 g, mp 222–224°. The triphenylphenols were characterized by infrared and mixture melting point determinations. Thin layer chromatography revealed that the purified sample of 2,4,5-triphenylphenol contained a trace of 3,4,5-triphenylphenol.

Photoreaction of I.—The photoreaction of 0.290 g of this compound was run the same way as that of compound IV except that it was photolyzed for 22 hr. A slight residue formed (<1%) which was not characterized. A work-up similar to that for the photoreaction of IV gave no acidic fraction. Treatment of the other fraction with ethanol gave 0.143 g (49%) of starting material, mp 155.5–156.5° (identified by mixture melting point and infrared determination). There was left 0.146 g (50%), mp 87–90°, whose infrared spectrum was identical with that of 2,4,5-triphenylphenol. Recrystallization from petroleum ether gave 0.085 g, mp 113–114°. A mixture melting point with authentic 2,4,5-triphenylphenol of mp 114.5–115°[20] was 113.5–115°.

A thin layer chromatogram of the crude reaction product revealed that only starting material and 2,4,5-triphenylphenol were present in large amounts. There were several spots showing traces of other components one of which had the same R_f value as 3,4,5-triphenylphenol. Control reactions, run under the same conditions of temperature, time, concentration, and work-up, revealed that without ultraviolet light neither I nor mixtures of I and 2,4,5-triphenylphenol gave the presumed 3,4,5-triphenylphenol. The other trace spots were present after the photolysis of 2,4,5-triphenylphenol under the same conditions (but not the spot for presumed 3,4,5-triphenylphenol).

Preparation of 2,4,5-Triphenylphenol. 4-Hydroxy-3,4,6-triphenylcyclohex-2-en-1-one.—To a 1-l. round-bottomed, three-necked flask equipped with a mechanical stirrer was added 52 g (0.25 mol) of benzoin, 100 ml of absolute methanol, 100 ml of absolute ethanol, 200 ml of ethylene glycol, and 29 g (0.50 mol) of sodium methoxide. The mixture was stirred until it turned brown. Then 30 g (0.21 mol) of freshly prepared 3-phenyl-3-buten-2-one[21] dissolved in 250 ml of ethanol was added dropwise. As the vinyl compound was added everything dissolved giving a deep reddish purple color. After 14 hr of stirring the reaction mixture was orange and a precipitate had formed. The reaction mixture was poured into a large excess of water and ether and filtered. This gave 50 g (70%) of product, mp 198–201°. A sample recrystallized from ethyl acetate for analysis had mp 212.5–214.5°.

Its infrared spectrum showed a carbonyl band at 1660 cm^{-1}. The ultraviolet spectrum in dioxane had λ_{max} 282 mμ (log ϵ 4.26).

Anal. Calcd for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92. Found: C, 84.39; H. 5.92.

(2,4,5-Triphenyl)phenyl Acetate.—To 2.4 g (0.007 mol) of 4-hydroxy-3,4,6-triphenylcyclohex-2-en-1-one, mp 206–209°, was added 25 ml of acetic anhydride and 5 drops of concentrated sulfuric acid. The mixture was refluxed for 10 min, then poured into water. The resulting mixture was extracted three times with ether which was washed with water, 10% sodium carbonate, and water and then dried over magnesium sulfate, filtered, and removed under reduced pressure. This gave 2.8 g (109%) of product smelling of acetic acid, mp 153.5–155°. A sample recrystallized for analysis from ethanol had mp 154.5–155.5°. The infrared spectrum showed a carbonyl band at 1750 cm^{-1}. The ultraviolet spectrum had λ_{max} 244 mμ (log ϵ 4.57). The nmr spectrum showed a 17-proton multiplet (phenyl hydrogens) at 7.3 and a three-proton singlet (methyl hydrogens) at 2.1 ppm.

Anal. Calcd for $C_{26}H_{20}O_2$: C, 85.69; H, 5.53. Found: C, 85.93; H, 5.70.

2,4,5-Triphenylphenol.—To 1.0 g (0.0028 mol) of acetate was added 50 ml of ethanol and 1.5 g (0.026 mol) of potassium hydroxide. The mixture was boiled for 15 min on the steam bath and allowed to cool slowly to room temperature. The reaction mixture was poured into water, neutralized with hydrochloric acid, extracted three times with ether which was washed with water, dried over magnesium sulfate, filtered, and removed under reduced pressure to give 1.0 g (110%) of product, mp 102–104°. One recrystallization from petroleum ether gave colorless crystals, mp 93–94°.[20] The infrared spectrum showed a peak at 3600 cm^{-1} (hydroxyl). The ultraviolet spectrum showed λ_{max} 308 mμ (log 3.97) and 250 (4.61). The nmr spectrum showed a 17-proton multiplet centered at 7.0 (phenyl hydrogens) and a one-proton singlet at 1.4 ppm (phenolic hydrogen).

Anal. Calcd for $C_{24}H_{18}O$: C, 89.42; H, 5.63. Found: C, 89.23; H, 5.58.

3-Methyl-1,5,6-triphenyltricyclo[3.1.0.0^{2,6}]-3-hexanol (V).—To the Grignard reagent prepared from 1.25 g (0.01 mol) of methyl iodide and 0.25 g (0.01 g-atom) of magnesium in 20 ml of anhydrous ether was added dropwise with stirring 0.300 g (0.00093 mol) of tricyclic ketone I dissolved in 5 ml of benzene. The resulting mixture was stirred 2 min longer and poured into water. The mixture was extracted three times with ether which was washed, dried over magnesium sulfate, filtered, and removed under reduced pressure to give a yellow solid, mp 70–160°. The material was taken up in benzene (some material did not dissolve) and chromatographed on Fisher alumina. Elution with benzene gave 0.234 g of crude solid which on recrystallization from petroleum ether gave 0.075 g (24%) mp 84–90°. The melting point depends on the rate of heating. The infrared spectrum showed a peak in the hydroxyl region.

The nmr spectrum showed a 15-proton multiplet centered at 7.2 (phenyl hydrogens), a one-proton singlet at 2.8 (methine hydrogen), a two-proton singlet at 2.2 (methylene hydrogens), and a three-proton singlet at 1.5 ppm (methyl hydrogens). Apparently, the hydroxyl peak was so broad that it could not be detected.

Anal. Calcd for $C_{25}H_{22}O$: C, 88.72; H, 6.55. Found: C, 88.51; H, 6.68.

Registry No.—I, 1731-34-6; II, 15707-53-6; III, 15707-48-9; IV, 15707-49-0; V, 15746-00-6; 4-hydroxy-3,4,6-triphenylcyclohex-2-en-1-one, 15707-50-3; (2,4,5-triphenyl)phenyl acetate, 15707-51-4; 2,4,5-triphenylphenol, 1731-36-8.

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[20] Samples of 2,4,5-triphenylphenol show variable melting points depending on the rate of heating. Rapid heating results in considerably lower melting points. All samples, even those which have been thoroughly dried, show some bubbling on melting. We have not investigated this phenomenon further.

[21] W. Wilson and Z-Y. Kyi, *J. Chem. Soc.*, 1321 (1952).

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Strained Organic Molecules. II. Rearrangements of 1-(1,2,3-Triphenylcycloprop-2-enyl)-3-diazopropan-2-one and (1,2,3-Triphenylcycloprop-2-enyl)acetyl Azide[1,2]

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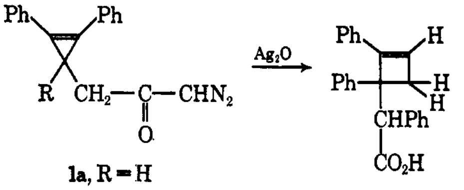
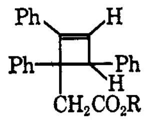
Several reactions are discussed. In the presence of silver benzoate, triethylamine, and ethanol, 1-(1,2,3-triphenylcycloprop-2-enyl)-3-diazopropan-2-one (**1b**) rearranges to two isomers of ethyl (1,2-diphenylcyclobut-2-enyl)phenylacetate (**6a** and **b**). Thermally, (1,2,3-triphenylcycloprop-2-enyl)acetyl azide (**8b**) rearranges to the corresponding isocyanate which was trapped with either dimethylamine or ethanol. With ultraviolet light the azide follows a different pathway.

In the course of our studies on the title rearrangements Masamune and coworkers published several communications[3] on a similar topic. This paper will substantiate and add to the conclusions drawn by his group. The elegant work of Masamune has shown that the product of rearrangement of 1-(1,2,3-triphenylcycloprop-2-enyl)-3-diazopropan-2-one (**1b**) in the presence of silver oxide is to (1,2-diphenylcyclobut-2-enyl)phenylacetic acid (**2**) and not to the tentatively assigned structure, (1,2,4-triphenylcyclobut-2-enyl)acetic acid[1] (**3a**). He also demonstrated that for 1-(2,3-diphenylcycloprop-2-enyl)-3-diazopropan-2-one (**1a**) intermediates in the reaction were 1,2-diphenyltricyclo[2.2.0.0^{2,6}]hexan-3-one (**4a**)[4] and/or phenyl (2-phenylcyclobut-2-enyl)ketene (**5a**).[5]

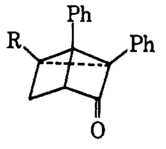


1a, R = H
b, R = Ph

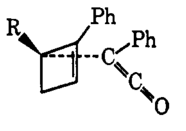
2



3a, R = H
b, R = CH_2CH_3



4a, R = H
b, R = Ph



5a, R = H
b, R = Ph

In addition to the silver oxide conditions for the Wolff rearrangement of **1b**, silver benzoate, triethylamine, and absolute ethanol have also been utilized.[6] Under the latter conditions the rearrangement also takes place and a 48% yield of crude ester **6a** is isolated. The ester was characterized by spectra, which were similar to the corresponding acid, and analysis. In strong base this ester is converted into a new isomeric compound, **6b**. An nmr spectrum of the crude reaction product from the Wolff rearrangement indicates that **6a** and **b** are present in the ratio of roughly 2:1. Under the reaction conditions both **6a** (containing some **6b**) and **6b** remain essentially unchanged so that **6b** must arise from an intermediate and not from **6a**.

The infrared and ultraviolet spectra of **6a** and **b** are very similar. However, the fact that they are different compounds is evidenced in particular by the nmr spectra. First, the chemical-shift values for the various groups are decidedly different for the two compounds. In fact, a weak absorption for the ethyl group in **6b** can be seen clearly in the spectrum of impure **6a**. Moreover, the absorption for the ethyl group in the two compounds is decidedly different. For compound **6a** this absorption is a simple A_2X_3 pattern, whereas for compound **6b** the pattern is that for an ABX_3 system (see Experimental Section). Thus the differing asymmetry of the two molecules affects the nmr pattern for the ethyl group. The conclusion drawn from the spectral and chemical data is that the two compounds must be racemic diastereomers differing in the configuration of the carbon α to the carbonyl group.

The preferential formation of **6a** can be explained by a stereoselective reaction of either 1,2,6-triphenyltricyclo[2.2.0.0^{2,6})hexan-3-one (**4b**) (postulated in analogy

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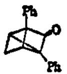
(1) A preliminary communication of part of this work appeared in A. Small, *J. Amer. Chem. Soc.*, **86**, 2091 (1964).

(2) Abstracted in part from the Master's thesis of S. Tang, University of Connecticut, June 1966.

(3) (a) S. Masamune and N. C. Castellucci, *Proc. Chem. Soc.*, 298 (1964); (b) S. Masamune and K. Fukumoto, *Tetrahedron Lett.*, 4647 (1965); (c) N. C. Castellucci, M. Kato, H. Zenda, and S. Masamune, *Chem. Commun.*, 473 (1967).

(4) A referee has suggested 2,4-diphenyltricyclo[2.2.0.0^{2,6}]hexan-3-one (i) as an alternative structure to **4a**. With the information available, the authors cannot unequivocably decide between i and **4a**; the nmr data[3b] and the results of the application of Occam's Razor to the mechanism of formation seem more compatible with **4a**.



i

(5) For convenience only one member of each *dl* pair is drawn.

(6) M. S. Newman and P. F. Beal, *J. Amer. Chem. Soc.*, **72**, 5163 (1950).