Oxidation of *s*-Dodecahydrotriphenylene with Peroxytrifluoroacetic Acid–Boron Fluoride and the Photoisomerization of the Resulting Cyclohexadienones[1]

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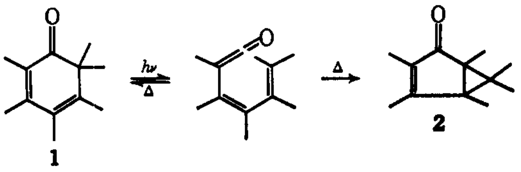
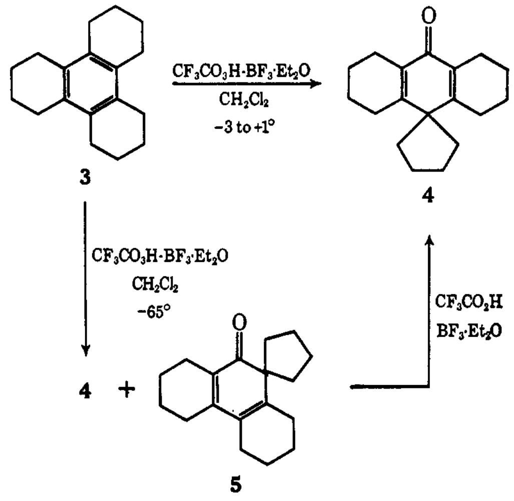
Oxidation of symmetrical dodecahydrotriphenylene (**3**) with peroxytrifluoroacetic acid and boron fluoride etherate at 0° afforded cross-conjugated cyclohexadienone **4** rather than the anticipated conjugated dienone **5**. At −65°, however, both dienones were produced. Dienone **5** isomerized to **4** unusually rapidly (when compared with similar hexaalkyl-2,4-cyclohexadienones) in the presence of trifluoroacetic acid. Irradiation of cross-conjugated dienone **4** in methanol gave the bicyclo[3.1.0]hexenone **9**, but in ether **4** or **9** were further converted into the conjugated dienone **5**. Possible reasons for the difference between the photochemical behavior of these fused ring dienones and that of the related hexaalkyldienones are discussed.

Peroxytrifluoroacetic acid–boron fluoride has proved to be an excellent electrophilic oxidizing agent which can convert aromatic compound directly into phenols,[3] alkenes into ketones[1] and certain aromatics into 2,4-cyclohexadienones.[4] In the present work, our goal was to extend this reaction to the preparation of a 6-spiro-2,4-cyclohexadienone, and to investigate its photoisomerization. It is now known[5] that hexamethyl-2,4-cyclohexadienone (**1**) photoisomerizes to a ketene which, in the absence of a strong nucleophile, thermally rearranges either to the starting dienone or to a bicyclo[3.1.0]hexenone (**2**). These thermal reactions of the diene–ketene are influenced, amongst other factors, by the substituents, although our present state of knowledge about the reaction does not permit many predictions. We were interested in determining whether the spirodienone **5** behaved photochemically in a manner analogous to that of the hexamethyl- (and hexaethyl-[4b]) dienones.



Oxidation Studies.—*s*-Dodecahydrotriphenylene (**3**) is readily available through the trimerization of cyclohexanone.[6] A methylene chloride solution of **3** was oxidized at −3 to +1°, using a more than 100% excess of peroxytrifluoroacetic acid and 47% boron fluoride etherate. Under these conditions, all of the starting material was consumed, which simplified product isolation. There was obtained in 45% yield a crystalline product, mp 115–117°, which was not the desired 6-spiro compound, but whose structure is considered to be that of the 4-spiro-2,5-dienone **4**.[7]

SCHEME I



The structure of **4** follows from its analysis, spectral properties, and mode of formation (Scheme I). Spectroscopic data are summarized in Table I.

TABLE I

SPECTRAL PROPERTIES OF THE DIENONES

	Nmr spectra		Ir spectra[c]		Ultraviolet spectra[d]	
Compd	Chemical shift[a]	Assignment[b]	$\nu_{C=O}$, cm^{-1}	$\nu_{C=C}$, cm^{-1}	λ, mμ	ϵ
4	7.79	Allylic methylenes	1655	1627	253	18,300
	8.17	Spiro ring methylenes			280 (sh)	6,800
	8.40	Nonallylic methylenes in six-membered rings				
5	7.78	Allylic methylenes	1644	1580	332	5,100
	8.37	All remaining protons				

[a] Measured in CCl_4, relative to TMS as an internal reference. [b] All areas are consistent with the assignments. [c] Measured in CCl_4 solution; calibrated against polystyrene. [d] In methanol.

The ultraviolet absorption maximum and conjugated C=O and C=C absorptions in the infrared spectrum are consistent with the assigned structure and are typical for 2,5-cyclohexadienones.[8] In particular, the uv maximum appears at much shorter wavelength than would be expected for the anticipated 2,4-cyclohexadienone **5**. The uv maximum of **4** does appear, however, at a slightly higher wavelength than has been reported for other 2,5-cyclohexadienones,[8] but this can

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[1] Paper X in a series on oxidations with peroxytrifluoracetic acid–boron fluoride; for paper IX, see H. Hart and L. Lerner, *J. Org. Chem.*, **32**, 2669 (1967).

[2] Taken from the M.S. Thesis of D. C. L., Michigan State University, 1967.

[3] C. A. Buehler and H. Hart, *J. Amer. Chem. Soc.*, **85**, 2177 (1963); H. Hart and C. A. Buehler, *J. Org. Chem.*, **29**, 2397 (1964); H. Hart, C. A. Buehler, A. J. Waring, and S. Meyerson, *ibid.*, **30**, 331 (1965).

[4] (a) A. J. Waring and H. Hart, *J. Amer. Chem. Soc.*, **86**, 1454 (1964); (b) H. Hart, P. M. Collins, and A. J. Waring, *ibid.*, **88**, 1005 (1966); (c) H. Hart and R. M. Lange, *J. Org. Chem.*, **31**, 3776 (1966); (d) P. M. Collins and H. Hart, *J. Chem. Soc.*, 895 (1967); (e) H. Hart and R. K. Murray, Jr., *J. Org. Chem.*, **32**, 2448 (1967).

[5] J. Griffiths and H. Hart, *J. Amer. Chem. Soc.*, **90**, 3297 (1968).

[6] C. Mannich, *Chem. Ber.*, **40**, 153 (1906).

[7] Named spiro[1,2,3,4,5,6,7,8,9,10-decahydroanthracen-10-one-9,1′-cyclopentane]; see "Definitive Rules for Nomenclature of Organic Chemistry," *J. Amer. Chem. Soc.*, **82**, 5545 (1960).

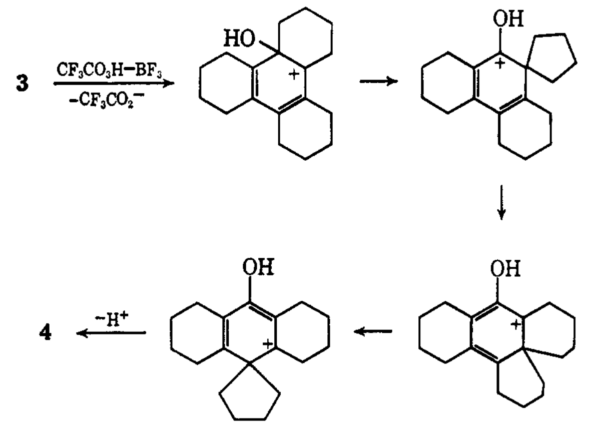
[8] A. J. Waring, *Advan. Alicyclic Chem.*, **1**, 184 (1966).

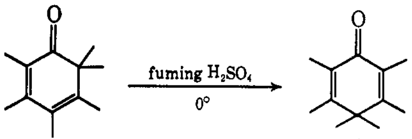
readily be accounted for by comparison with model compounds.[9-12]

The nmr spectrum of **4** consists of three rather broad and unstructured bands, equal in area. The lowest field band (τ 7.79) is assigned to the allylic methylene protons.[13] The high-field band (τ 8.40) is due to the remaining protons in the six-membered ring, whereas the protons in the spiro five-membered ring appear at τ 8.17.[14]

This the first case we have observed where the major product of aromatic oxidation is a 2,5- rather than a 2,4-cyclohexadienone. Even hexaethylbenzene, which is closely related structurally to **3**, but without the "ears" pinned back, gave only the conjugated dienone.[4b] It is likely that **4** is formed by a sequence of three Wagner-Meerwein rearrangements as shown in Scheme II. Normally the carbonium ion from the first of these migrations would be expected to lose a proton to give conjugated dienone **5**. With hexamethyl-2,4-cyclohexadienone, further rearrangement to the 2,5-dienone is not observed under oxidation conditions, although the rearrangement can be brought about by concentrated (and more rapidly by fuming) sulfuric acid.[12] For some reason, in the present instance, further migrations occur in preference to proton loss.

SCHEME II





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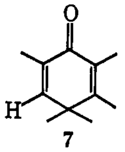
To provide support for this mechanism, the oxidation was carried out at a lower temperature, with the hope that the conjugated dienone might be isolated. When **3** was oxidized at −67 to −65°, there was obtained, in addition to unchanged **3** and 2,5-dienone **4**, a third product which proved to be the desired conjugated dienone **5**. It was isolated by preparative thin layer chromatography, and, though the yield was not determined, substantial amounts were produced.

The structure of **5** follows from its spectral properties (see Table I), mode of formation, and reactions. Elemental analysis and mass spectrum confirm that the product is an isomer of **4**. The uv and ir data are typical for a 2,4-cyclohexadienone.[8] In the nmr spectrum, the spiro five-membered ring protons have shifted upfield relative to their position in the spectrum of **4**.[15] Thus there are only two broad bands centered at τ 7.78 and 8.37, assigned to the allylic protons and all the remaining methylene protons, respectively.

To seek evidence that protonated **5** is an intermediate in the formation of **4** when the oxidation is performed at 0° or above, samples of **5** were treated, in separate experiments, with either boron fluoride etherate or trifluoroacetic acid in methylene chloride at room temperature. Rearrangement of **5** → **4** was complete in 3 hr and in 20 min, respectively. Thus protonic acids are more effective than Lewis acids in bringing about the rearrangement, and the results are consistent with the proposed Scheme II.

At the moment, we have no satisfactory explanation for the fact that **5** rearranges to a cross-conjugated dienone so much more rapidly than **1** or its hexaethyl analog. The only related observation is the formation of **7** (7% yield) as a minor product during the oxidation of pentamethylbenzene.[4d] Presumably the precursor is **8**, one of the major oxidation products.



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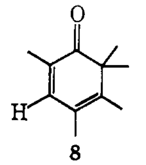

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Photochemical Studies.—Since it was difficult to obtain appreciable quantities of the conjugated spirodienone **5** directly from the oxidation of s-dodecahydrotriphenylene (*vide supra*), we first studied the photoisomerization of the more readily available cross-conjugated dienone **4**. Irradiation of **4** in methanol using a Vycor filter lead to a smooth and steady decrease in the absorption at 253 mμ and the appearance of three new maxima. The photoproduct is considered

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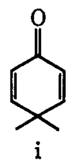
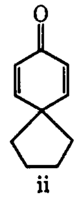
[9] The maxima of i and ii appear at 234.5[10] and 242 mμ,[11] respectively. The difference, 7.5 mμ, is attributed to the spiro ring.[8] If this value is added



i



ii

to 246 mμ reported[12] for **6**, one predicts a λ_{max} of 253.5 mμ for a tetraalkylspirodienone such as **4**. Agreement with the experimental value (Table I) is excellent.

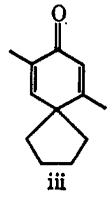
[10] E. W. Garbisch, *J. Org. Chem.*, **30**, 2109 (1963).

[11] S. Winstein and R. Baird, *J. Amer. Chem. Soc.*, **84**, 788 (1962).

[12] H. Hart and D. W. Swatton, *ibid.*, **89**, 1874 (1967).

[13] D. W. Mathieson, "Interpretation of Organic Spectra," Academic Press, New York, N. Y., 1965, pp 51-58.

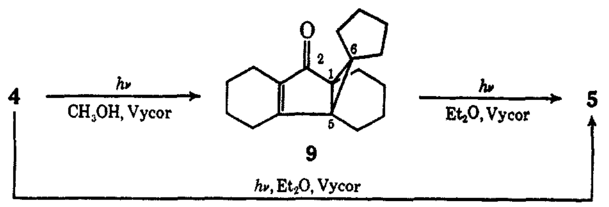
[14] The spiro protons in ii appear as a weakly split singlet at τ 8.17 (S. Winstein, private communication); similarly, those in iii occur as a narrow band at τ 8.13 (P. J. Kropp, private communication).



iii

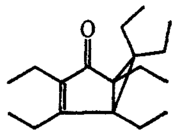
[15] A similar upfield shift, from τ 8.79 to 8.89, is observed in the *gem*-dimethyl group of **1** relative to **6**.

SCHEME III



to be **9**, spiro[tetracyclo[7.4.1.0^{1,9}0^{3,8}]tetradec-3-en-2-one-14,1′-cyclopentane] (Scheme III).

The structure of **9** rests on its spectral properties, method of synthesis, and further conversions. The mass spectrum showed a parent peak at *m/e* 256, consistent with formulation of **9** as an isomer of **4**. The carbonyl and carbon–carbon double bond bands at 1685 and 1639 cm^{-1}, respectively, may be compared with similar bands at 1680 and 1638 cm^{-1} reported for the closely related **10**.[4b] The ultraviolet spectrum of **9** [λ_{max} 240 mμ (ϵ 6440), 275 (2735), and 330 (580)] also closely resembles that of **10** [λ_{max} 239 mμ (ϵ 5300), 270 (2660), 332 (850)]. The nmr spectrum of **9** was complex and not helpful in the structural assignment. The formation of **9** from **4** has ample precedent.[16]



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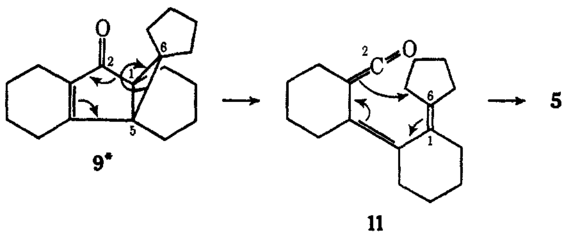
Compound **9** was relatively inert to further irradiation in methanol; *i.e.*, it was a simple matter to obtain **9** in high yield from **4** without having to be overcautious about the irradiation time. Irradiation of **9** in ether, however, proceeded smoothly; the bands at 240 and 275 mμ diminished in intensity, and the band at 330 mμ grew and shifted slightly. The reaction was worked up after the band at 332 mμ reached maximum intensity. The crystalline product was the conjugated dienone **5**. The same product was obtained by irradiation of **4** in ether, and, if this photoisomerization was monitored by uv, **9** could be detected as an intermediate. The structure of **5** was established by comparison with an authentic sample prepared by the low temperature oxidation of *s*-dodecahydrotriphenylene.

Continued irradiation of **5** in ether resulted in a gradual decay of the band at 332 mμ until eventually the only remaining band of any significance had a maximum at 205 mμ. The product had ir bands at 1720 and 1705 cm^{-1}. The ir data suggest that the product was an acid,[17] probably from reaction of the diene–ketene with water present in the ether used as solvent.

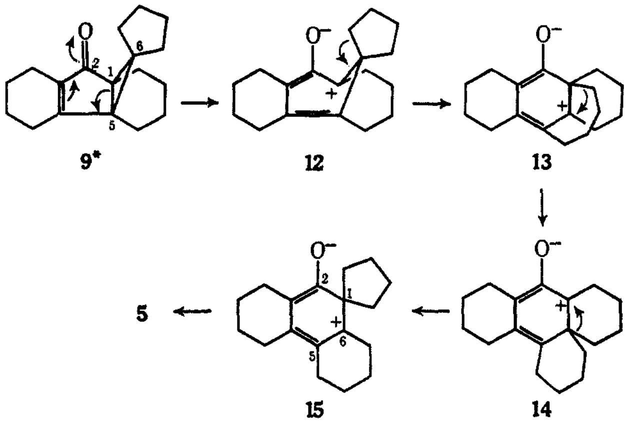
The contrast between the photochemical reactions in the hexamethyldienone series (**1**, **2**, and **6**) and the fused ring series (**4**, **5**, and **9**) is striking. Whereas the conjugated dienone **1** is converted into bicyclic ketone **2**, the analogous ketone **9** is under similar conditions, converted into the conjugated dienone **5**. The reasons for this difference are not yet clear, but several features of the reactions are worth noting. Whereas the conversion **1** → **2** is favored by polar solvents,[4b,5] the reverse type of reaction, **9** → **5**, proceeds only very slowly in methanol and is particularly favored by nonpolar solvents. The effect is sufficiently large that the photolysis of **4** to either **9** or **5** can be controlled by choice of solvent.

There are several alternative mechanisms which one can envision for the photochemical conversion of **9** → **5**. Perhaps the most plausible is the isomerization of an excited state of **9** (**9***) to a ketene (**11**), followed by cyclization to **5**.[18] The closure of highly substituted diene–ketenes such as **11** to 2,4-cyclohexadienones in nonpolar solvents is particularly facile,[5,19] whereas their reaction with nucleophiles can be quite slow.[5,19] In this mechanism the 5,6 bond of the three-membered ring in **9*** is broken. Thus atoms 6 and 1 interchange positions during the reaction (*i.e.*, in **9**, atom 2 is connected to atom 1, whereas, in **5**, atom 2 is connected to atom 6). It is not essential that the ketene be a discrete intermediate to accomplish the same result; cleavage of the 5,6 bond followed by acyl migration and rebonding has the same net effect.



There are several examples in the literature where the exocyclic bond (5,6) of a bicyclo[3.1.0]hexenone breaks in a photochemical reaction,[16,20,21] but much more frequently it is the endocyclic or 1,5 bond which breaks.[16] If this were to happen with **9**, one could envision the sequence given in Scheme IV to complete the reaction. Three Wagner–Meerwein rearrangements follow the initial ring opening (**9*** → **12**). Atoms 2, 1, and 6 which are joined consecutively in **9** remain in the

SCHEME IV



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[16] For a general discussion, see P. J. Kropp in "Organic Photochemistry," Vol. I, O. L. Chapman, Ed., Marcel Dekker, Inc., New York, Chapter 1.

[17] K. Nakanishi, "Practical Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1964, p 43.

[18] For a related example, see J. S. Swenton, E. Saurborn, R. Srinivasan, and F. I. Sonntag, *J. Amer. Chem. Soc.*, **90**, 2990 (1968). In a low temperature study, we have observed a ketene from the irradiation of a tetramethylbicyclo[3.1.0]hexenone; unpublished observation of J. Griffiths and H. Hart.

[19] J. D. Hobson, M. M. Al Holly, and J. R. Malpass, *Chem. Commun.*, 764 (1968).

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

[21] B. Miller and H. Margulies, *ibid.*, **89**, 1678 (1967).

same sequence throughout the mechanistic scheme. Thus one could, by a carbon-labeling experiment, distinguish between these alternatives. Only carbon labeling will do, however; the spiro ring in **9** becomes the spiro ring in **5** by either path. Thus the labeling experiment will be quite difficult indeed.

It will be noted that the first intermediate (**12**) in the latter mechanism contains five sp^2 hybridized carbons in a bridged system with six-, seven-, and nine-membered rings. Two of these carbons are at bridgehead positions. Although models of **12** (and **13**, which at first glance also seems unduly strained) can be constructed we currently are inclined to favor a mechanism in which bond 5,6 (rather than 1,5) is broken. One reason for this preference (other than that it is simpler) is that the reaction is favored by nonpolar solvents; this would seem to be inconsistent with the dipolar intermediates **12–15**. It may be the strain in **12**, as contrasted with the corresponding intermediate derived from **2**, which causes the two bicyclo[3.1.0]hexenones to exhibit different photochemical behavior.[12,22]

Experimental Section

General Procedures.—Spectra were determined as follows: ir, CCl_4 solution, Unicam SP200; uv, CH_3OH solution, Unicam SP800; nmr, CCl_4 solution, Varian HA-100; mass spectra, CEC21-103C operating at 70 V. Elemental analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. Melting points are uncorrected. Analysis by tlc involved 1 × 4 in. microscope slides coated with Brinkmann silica gel H as the adsorbent, eluted with $CHCl_3$ and developed with iodine vapor. Separations by preparative tlc used 8 × 8 in. glass plates coated with Brinkmann silica gel PF_{254}, 2 mm thick, eluted with $CHCl_3$.

Oxidation of *s*-Dodecahydrotriphenylene (3).[23]—To a cooled, vigorously stirred solution of *s*-dodecahydrotriphenylene (**3**, 4.59 g, 1.9×10^{-2} mol) in 200 ml of methylene chloride was simultaneously added (1) a solution of peroxytrifluoroacetic acid prepared by dissolving trifluoroacetic anhydride (9.0 g, 4.3×10^{-2} mol) in 15 ml of methylene chloride, cooling to 0°, and with vigorous stirring adding 1.1 ml of 98% hydrogen peroxide until a homogeneous solution was obtained; (2) 20 ml of distilled 47% boron fluoride etherate. The temperature was maintained at −3 to +1°. Slow addition of the oxidant and acid catalyst was completed after 1.5 hr and the reaction was stirred for an additional 1.5 hr, during which time the temperature rose to 20°. The reaction mixture was analyzed by tlc and it was determined that all of **3** had reacted. The reaction mixture was hydrolyzed with water (200 ml) and the organic layer was successively extracted with two 200-ml portions of water, two 200-ml portions of saturated sodium bicarbonate solution, and two 200-ml portions of water, dried (Na_2SO_4), and concentrated. The residue was dissolved in 20 ml of methanol, concentrated to 5–10 ml, and cooled overnight. Crystallization afforded 2.21 g (45%) of **spiro[1,2,3,4,5,6,7,8,9,10-decahydroanthracen-10-one-9,1′-cyclopentane]**, **4**, mp 115–117°, as colorless crystals. Spectral properties are given in Table I. The compound showed a parent peak in the mass spectrum at *m/e* 256. In several experiments it was necessary to treat the methanol solution with Norit, as the solution was dark and did not lighten during work-up.

Anal. Calcd for $C_{18}H_{24}O$: C, 84.32; H, 9.43. Found: C, 84.26; H, 9.26.

Low Temperature Oxidation of 3.—To a cooled, vigorously stirred solution of **1** (4.74 g, 1.97×10^{-2} mol) in 175 ml of methylene chloride was simultaneously added (1) a solution of peroxytrifluoroacetic acid, made by dissolving trifluoroacetic anhydride (8.7 g, 4.15×10^{-2} mol) in 15 ml of methylene chloride, cooling to 0°, and with vigorous stirring adding 98% hydrogen peroxide (2.9 g, 8.3×10^{-2} mol) until a homogeneous solution was obtained; (2) 15 ml of distilled 47% boron fluoride etherate. The temperature was maintained at −67 to −65° using a Dry Ice-acetone bath. Addition of the oxidant and acid catalyst was completed in 35 min after which the reaction mixture was immediately hydrolyzed by pouring into 750 ml of cold saturated sodium bicarbonate solution. The organic layer was successively washed with two 300-ml portions of water, two 200-ml portions of saturated sodium bicarbonate solution, and two 200-ml portions of water and dried (Na_2SO_4). The reaction mixture was analyzed by tlc and shown to consist of three components. A portion of the reaction mixture was separated by preparative tlc and the three components were identified. Two were shown to be unreacted **3** and dienone **4** by comparison of tlc R_f values and ir and nmr spectra with those of authentic samples. The third component, obtained as pale yellow crystals, mp 69–71° (MeOH), was **spiro[1,2,3,4,5,6,7,8,9,10-decahydrophenanthrene-10-one-9,-1′-cyclopentane]**, **5**. Spectroscopic data are given in Table I. The compound showed a parent peak in the mass spectrum at *m/e* 256.

Anal. Calcd for $C_{18}H_{24}O$: C, 84.32; H, 9.43. Found: C, 84.35; H, 9.44.

The Acid-Catalyzed Isomerization of 5 to 4. A. With Trifluoroacetic Acid.—To a stirred solution of **5** (100 mg, 3.9×10^{-4} mol) in 30 ml of methylene chloride was added 2 ml of trifluoroacetic acid. The reaction mixture was stirred at room temperature for 45 min. The reaction was monitored by tlc after 5, 10, and 20 min, at which time no detectable trace of **5** could be observed. The mixture was hydrolyzed with 150 ml of water, extracted with two 50-ml portions of saturated sodium bicarbonate solution and two 50-ml portions of water, dried (Na_2SO_4), and concentrated. The residue was dissolved in 5 ml of methanol. Tlc analysis of the methanol solution indicated the presence of only one compound. Crystallization afforded 71.4 mg of **4**. The melting point and spectral properties of the rearrangement product were identical with those of authentic material.

B. With Boron Fluoride Etherate.—To a stirred solution of **5** (100 mg, 3.9×10^{-4} mol) in 30 ml of methylene chloride was added 3 ml of distilled 47% boron fluoride etherate. The reaction mixture was stirred at room temperature and monitored by tlc. After 3 hr, no detectable trace of **5** could be observed. The reaction mixture was hydrolyzed with 150 ml of water, the layers were separated, and the organic layer was extracted with two 50-ml portions of water, dried (Na_2SO_4), and concentrated. The residue was dissolved in 5 ml of methanol and analysis of the methanol solution by tlc indicated the presence of only one compound. Crystallization afforded 56.9 mg of **4**, with melting point and spectral properties identical with those of authentic material.

General Photolysis Procedure.—All irradiations were conducted with a Hanovia Type S 200-W mercury vapor lamp placed in a quartz water jacket which was fitted into a Pyrex container of slightly larger diameter. The effective volume of the intervening space, which held the solution being irradiated, was 450 ml. The solution could be agitated with a moderate flow of nitrogen. A Vycor filter was fitted between the lamp and the quartz jacket. The entire system was immersed in a dewar flask filled with cold (15°) water.

Irradiation of 4 in Methanol.—A solution of **4** (691.6 mg, 2.70 mmol) in 400 ml of methanol was irradiated and the reaction was followed by decay of the 253-mμ band. Reaction was complete in 50 min. Overphotolysis for several hours brought about no significant change in the spectrum. The methanol was evaporated, affording 672 mg (97%) of a slightly colored transparent oil which showed only a single spot on tlc, with a different R_f from that of **4**. The product is considered to be **spiro[tetracyclo-[7.4.1.$0^{1,9}0^{3,8}$]tetradec-3-en-2-one-14,1′-cyclopentane]**, **9**.

Anal. Calcd for $C_{18}H_{24}O$: C, 84.32; H, 9.43. Found: C, 83.11; H, 9.29.[24]

The compound showed a parent peak at *m/e* 256. It had principle ir bands (liquid film) at 1685 and 1639 cm^{-1} and a uv spectrum with maxima [mμ (ε)] at 211 (5950), 240 (6440), 275 (2735), and 330 (580). The nmr spectrum consisted of a broad complex between τ 7 and 9, with principle peaks centered at

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[22] We thank one of the referees, who encouraged the somewhat expanded mechanistic discussion presented here, over that in the original manuscript.

[23] Prepared according to ref 6. The nmr spectrum of **3** showed two broad singlets centered at τ 7.55 and 8.3 with areas in the ratio 1:1. These correspond to the benzylic and remaining alicyclic methylenes, respectively.

[24] Analytical samples were purified by tlc or column chromatography; despite several attempts, we could not get a sample which gave an entirely satisfactory carbon analysis.

τ 8.02, 8.43, 8.38 (sh), and 8.72. The peaks overlapped too much to obtain accurate integrations.

Irradiation of 9 in Ether.—A solution of 9 (448.9 mg, 1.78 mmol) in 350 ml of anhydrous ether was irradiated. The photolysis was followed by the appearance of a maximum at 332 mμ, which reached maximum intensity in 2 hr. The ether was evaporated and the residue was dissolved in methanol and concentrated to a volume of 5 ml. On cooling, crystals (347 mg, 77%) of spiro[1,2,3,4,5,6,7,8,9,10-decahydrophenanthren-10-one-9,1'-cyclopentane] (**5**) separated, mp 69–70°. The compound was identical (ir, nmr) with material obtained from the low temperature oxidation of **3**. No other photoproduct was detected (tlc).

Irradiation of 4 in Ether.—A solution of 4 (770.7 mg, 3.00 mmol) in 400 ml of anhydrous ether was irradiated, the reaction being followed by the decay of a maximum at 253 mμ and the appearance of a new band at 332 mμ. After 4.9 hr the latter band reached maximum intensity, and the reaction was terminated. The ether was evaporated, and the residue, taken up in 15 ml of methanol, showed no unreacted **4** and only one product (tlc). The solution was concentrated to 5 ml, cooled, and afforded 438.4 mg (57%) of dienone **5**, identical (melting point, ir, nmr) with an authentic sample. During the photolysis, maxima attributable to **9** appeared, then decayed.

Irradiation of 5.—A solution of **5** (107 mg, 0.42 mmol) in 300 ml of ether was irradiated through a Pyrex filter with a 200-W Hanovia Type S mercury lamp. The photolysis, followed by the disappearance of the band at 332 mμ, was complete in 6.2 hr. Evaporation of the solvent gave an oil different (ir, uv, tlc) from **9**. The oil, which had characteristic ir bands at 3500, 1720, 1705, and 1452 cm^{-1} and λ_{max}^{MeOH} 205 mμ (ϵ 12,300) in the uv, was an acid which was not further characterized.

Dark Reactions.—A solution of dienone **4** (14 mg) in either 5 ml of methanol or 3 ml of ether was stored in the dark for 27 and 36 days, respectively. Analysis by tlc showed that no reaction had occurred, and evaporation of the solvent afforded quantitative recovery of the starting material. Similarly, a solution of **9** (15 mg) in 3 ml of ether kept in the dark for 15 days gave a quantitative recovery of unchanged starting material.

Registry No.—**3**, 1610-39-5; **4**, 17790-43-1; **5**, 17790-44-2; **9**, 17790-45-3; peroxytrifluoroacetic acid-boron fluoride, 17790-46-4.

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Nitrogen Photochemistry. *syn* and *anti* Isomers of Semicarbazones[1-4]

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The *syn* and *anti* sets of isomers of several different phenyl ketone semicarbazones have been isolated, and the structural formulas have been assigned. Evidence is presented which demonstrates that the phenyl ring is restricted from rotation in the *syn*-phenyl isomers of the semicarbazones as shown by a diminished amount of conjugation of the phenyl group with the imine double bond. The *syn*-phenyl isomers also have a decreased thermal stability, and, with these isomers, the nmr data clearly portrays that one of the hydrogens of the ureido group is strongly shielded by the phenyl ring confirming the structural assignments.

Although the existence of *syn* and *anti* isomers of semicarbazones has been recognized for some time, there are few cases where both isomers of a semicarbazone have been isolated. In these instances, the structural assignments given are open to question. However, from these earlier experiments certain facts have been learned. The early works of Heilbron and Wilson[6] and of Wilson and Macaulay[7] have clearly demonstrated that *syn* and *anti* isomers of semicarbazones exist and can be interconverted by the agency of ultraviolet light.

Another significant contribution to the history of semicarbazones is the work of Ramart-Lucas and Bruzau.[8] Semicarbazones of phenyl ketones were categorized into two types by means of their uv spectra characteristics, *i.e.*, the "forme absorbante" and the "forme transparente." The phenyl ketone semicarbazones studied had uv spectra which nearly superimposed on one of two general type absorption curves (curves a and b, Figure 1). The "forme absorbante" refers to those semicarbazones which absorb at longer wavelengths. Acetophenone, *p*-methylacetophenone, *p*-methoxyacetophenone, and deoxybenzion semicarbazones have uv spectra approximating that of curve a; and α,α-dimethyldeoxybenzoin, β-phenyl-*p*-methylpropiophenone, and β-phenyl-*p*-methoxypropiophenone semicarbazones have spectra similar to that of curve b. The semicarbazone of α-methyldeoxybenzoin is composed of two isomeric forms which were separated by fractional crystallization from the reaction solution. One of the isomers has an uv absorption spectrum similar to that of curve a in Figure 1, and the other to curve b. A conjugated phenylimine structure of the semicarbazone was postulated for the compounds absorbing with longer wavelengths, and either of two nonconjugated cyclic structures were proposed for the other.

A third important contribution to the background of semicarbazones is the nmr studies of Karabatsos, Graham, and Vane.[9] The nmr spectra were obtained from solutions made by dissolving the crystalline isomer mixtures in trifluoroacetic acid. No separation of the isomers was attempted. The relative chemical shielding of the protons on positions adjacent to the semicarbazone substituent (H_α on I) was measured. The necessary assumption was made that the H_α protons *syn* to the ureido group are more shielded than those *anti* to it. The mixtures of isomeric semicarba-

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