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(13) G. Zon, J. A. Brandt, and W. Egan, *J. Natl. Cancer Inst.*, **58**, 1117 (1977).
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# Photochemical Conversion of Methoxy-Substituted 6/6-Fused Cross-Conjugated Cyclohexadienones into Isomeric Tricyclodecenones[1]

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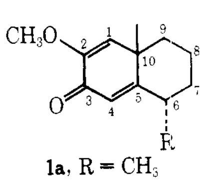
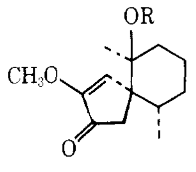
2-Methoxy 6/6-fused cross-conjugated cyclohexadienones of type 1 were irradiated in anhydrous dioxane. In addition to the expected lumiproducts, novel isomeric tricyclodecenone derivatives of type 5 were obtained as primary photoproducts. Phenolic compounds tentatively assigned structures of type 6 were also produced as primary photoproducts. The structure of the *p*-iodobenzoate **14**, a heavy-atom derivative of the tricyclodecenone **5b**, was established by x-ray crystallography. Possible modes of formation of enones of type 5 are discussed.

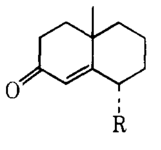
Recently, we reported the synthesis of the 2-methoxy 6/6-fused cross-conjugated cyclohexadienone **1a** and investigated its photochemical behavior on irradiation in protic solvents such as glacial and aqueous acetic aicd.[2] The expected spiro acetoxy- and spiro hydroxyenones **2a** and **2b**, respectively, were obtained and shown to be useful intermediates for the total synthesis of $(\pm)$-$\alpha$-vetispirene.[2] We have now carried out irradiations of **1a** and the related normethyldienone **1b** in the aprotic solvent dioxane and wish to report these results.



**1a**, R = CH$_3$
**b**, R = H

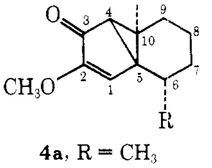


**2a**, R = Ac
**b**, R = H

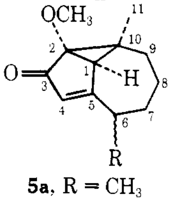


**3a**, R = CH$_3$
**b**, R = H

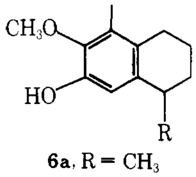
Dienone **1b** was prepared from the octalone **3b** by a route similar to that employed for the synthesis of **1a** from the corresponding octalone **3a**.[2] Dilute solutions (ca. 0.5%) of **1a** or **1b** in anhydrous dioxane were irradiated for 6.0 h at room temperature with a 7-W Hanau NK-20 low-pressure mercury lamp. Analysis of the photolysis mixtures by gas–liquid chromatography (GLC) using an internal standard showed that two tricyclic enones and a phenol were produced in ca. 25, 15, and 15% yields each from each of the dienones. In each case ca. 15% of the starting dienone remained at the end of the irradiation period. On the basis of the evidence presented below, the major enones were assigned the normal lumiproduct structures **4**, while the minor enones were assigned the tricyclic structures **5**. The phenolic products have been tentatively assigned structures **6**.



**4a**, R = CH$_3$
**b**, R = H



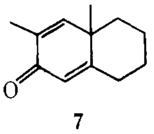
**5a**, R = CH$_3$
**b**, R = H



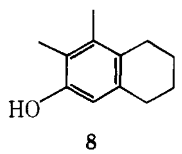
**6a**, R = CH$_3$
**b**, R = H

The phenolic products appeared to be primary photoproducts based on experiments in which a mixture of the isolated enones **4b** and **5b** were irradiated under similar conditions to the dienones **1**. In neither case were detectable amounts of the phenol **6b** formed. Enone **5b** was essentially unchanged under the irradiation conditions, whereas **4b** was almost completely destroyed, being largely converted into nonvolatile material. In one run the course of the photolysis of dienone **1b** was monitered carefully by GLC analysis. This revealed that after a short irradiation period, before **4b** was further rearranged, the kinetic ratio of primary photoproducts **4b** and **5b** was 4.4:1.

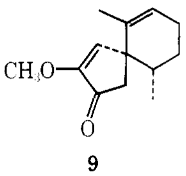
The tentative assignments of the structures of the phenols **6** were by analogy to the work of Kropp,[3] in which the 2-methyldienone **7** was shown to yield the phenol **8** as a primary photoproduct on irradiation in methanol or acetic acid. Phenol **8** was produced by a photochemically induced 1,2-methyl shift. This was a novel rearrangement pathway since cross-conjugated cyclohexadienones do not generally yield phenols as primary photoproducts. Phenolic products are often observed in dienone photolysis, but they normally arise by secondary processes in which initially formed lumiproducts are further rearranged.[4] Since phenols are formed as primary products from the irradiation of the 2-methoxydienones, it seems likely that they are also derived from a simple 1,2-methyl shift.



**7**



**8**



**9**

The spectral properties of the lumiproducts **4a** and **4b** were consistent with the assigned structures (see the Experimental Section). In addition, compound **4a** was converted into the known spiro dienone **9**[2] by cleavage of the external bond of the cyclopropane ring with sulfuric acid in acetic anhydride under the conditions described by Marshall and Johnson[5] for the conversion of the related normethoxy lumiproduct into the corresponding spiro dienone. This information seemed to provide excellent evidence for the structural assignments.

The spectral properties of the enones **5a** and **5b** as well as

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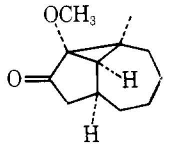
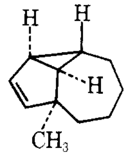
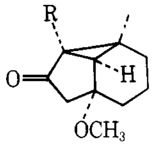
those of the dihydro derivative **10** of **5b** were also consistent with the assigned structures (see the Experimental Section), but they did not permit positive assignment of the relative stereochemistry at C-1 and C-10. Clearly, if the stereochemical assignment at C-10 were reversed, a much more highly strained system would result. However, strained systems such as the tricyclodecene derivative **11** which has trans-fused three- and seven-membered rings have been produced in photochemical reactions.[6] This raised the possibility that isomers of **5a** and **5b** with the 10-methyl groups $\beta$ could have been produced in the irradiations of the corresponding dienones.



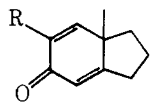
**10**



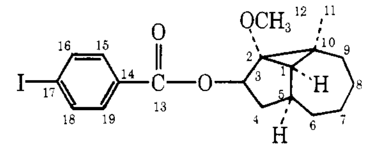
**11**



**12a**, R = H
**b**, R = CH$_3$



**13a**, R = H
**b**, R = CH$_3$



**14**

Irradiations of unsubstituted and methyl-substituted 6/6-fused dienones of type **1** and related compounds in dioxane normally yield lumiproducts of type **4** and derived secondary photolysis products,[4,7] but no isomeric primary photoproducts related to **5** have been observed in these systems.[8] Likewise, irradiations of $\alpha$-halosantonin derivatives in nonprotic media have been reported to yield only lumisantonin derivatives related to **4**.[9] However, the tricyclononanones such as **12**, which we obtained upon irradiation of 6/5-fused dienones of the type **13** in methanolic acetic acid, were considered to arise via 1,4 addition of methanol to strained tricyclononenones related to **5**.[10]

Since the stereochemistry of compounds of the type **5** was of crucial importance with regard to their mechanism of formation, a derivative of **5b** was prepared for use in a single-crystal x-ray crystallographic analysis. Catalytic hydrogenation of **5b** gave the tricyclodecanone **10**. Reduction of the carbonyl group in **10** with lithium tri(*tert*-butoxy)aluminum hydride in tetrahydrofuran (THF) and reaction of the alcohol with *p*-iodobenzoyl chloride in pyridine gave the crystalline *p*-iodobenzoate derivative **14**. The details of the determination of the structure of **14** by x-ray analysis are given in the Experimental Section. The molecular structure of **14** (with the *p*-iodobenzoate group deleted) is shown in Figure 1. This provided unambiguous proof of the structural assignment of **5b** and the structure of **5a** except for the assignment of the configuration at C-6 (see below) followed by analogy.

The abnormal enones **5a** and **5b** may be considered to arise by a symmetry-allowed 1,4-sigmatropic rearrangement in a cyclopropyl intermediate of type **15** produced by electronic excitation and $\beta,\beta$ bonding in the dienone system[4,11] or by a photo-induced [$\sigma$2a + $\pi$2a] cycloaddition process involving the 5,10-$\sigma$ and the 1,2-$\pi$ bond of the dienone.[11b] The former process would occur with retention of configuration at C-10, while the latter would involve inversion at C-10.[11b] Since either or both of these pathways may be involved, a prediction of the relative stereochemistry of the C-6 methyl group ($\alpha$ or $\beta$) in **5a** is not possible. Also, the spectral data for **5a** do not allow an unambiguous assignment of the C-6 configuration to be made. In addition, since C-6 is possibly an epimerizable center, the product actually isolated may have arisen as a result of thermodynamic rather then kinetic control under the condition of the photolysis and isolation. For this reason it does not seem that unambiguous evidence for the mode of rearrangement of methoxydienones such as **1** would be obtained even if the structure of **5a** were fully established.

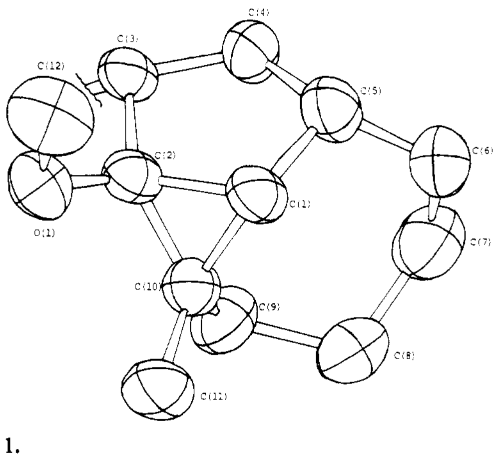
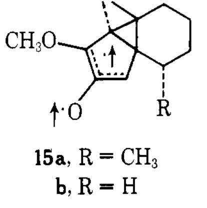


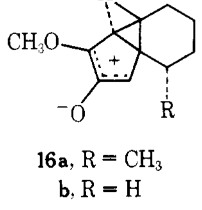
**Figure 1.**

In the two methoxydienones studied, the abnormal rearrangement pathway competes only to a minor, although significant, extent with the normal mode of rearrangement involving either electron demotion in **15** to produce the ground-state dipolar species **16**, followed by a symmetry-allowed 1,4-sigmatropic shift, or a photo-induced [$\sigma$2a + $\pi$2a] cycloaddition involving the 1,10-$\sigma$ and the 4,5-$\pi$ bonds of the dienone.[11] Both of these pathways predict inversion of configuration at C-10 in the formation of the normal lumiproducts, and they are not distinguishable for that reason.[11b] In order to be allowed on orbital-symmetry grounds, cleavage of the 5,10 bond and formation of a 1,10 bond in the ground-state intermediate **16** would have to occur with inversion of configuration at C-10. This would necessarily lead to photoproducts with a trans fusion of the three- and seven-membered rings; such products were not observed.

The exact manner in which the methoxyl group influences these rearrangements is not clear. Its presence may increase the lifetime of triplet species such as **15** to allow time for rearrangement prior to election demotion, or it may cause selective excitation of the 1,2-$\pi$ bond of the dienone. It is known that $\alpha$-methoxy substituents and other polar groups may influence the energy of the lowest lying excited states of $\alpha,\beta$-unsaturated ketones.[12]



**15a**, R = CH$_3$
**b**, R = H



**16a**, R = CH$_3$
**b**, R = H

## Experimental Section[13]

**Preparation of 2-Methoxy-3-keto-10-methyl-$\Delta^{1,4}$-hexahydronaphthalene (1b).** To a solution of 41.0 g (0.093 mol) of lead tetraacetate in 200 mL of glacial acetic acid and 20 mL of acetic anhydride was added 10.0 g (0.061 mol) of 3-keto-10-methyl-$\Delta^{4,5}$-octahydronaphthalene (**3b**).[14] The reaction mixture was stirred under nitrogen at 70–80 °C for 24 h. The bulk of the solvent was removed under reduced pressure and the residue was partitioned between ether and water. The ether layer was extracted with saturated sodium bicarbonate and dried, and the solvent was removed in vacuo. Distillation of the residue yielded 5.22 g (39%) of a mixture of 2$\alpha$- and 2$\beta$-acetoxy-3-keto-10-methyl-$\Delta^{4,5}$-octahydronaphthalene: bp 100–130

°C (0.005 mm); IR ($CHCl_3$) 1740, 1686, and 1619 $cm^{-1}$; NMR $\delta_{Me_4Si}$ ($CCl_4$) 1.25 (s, 0.6 H), 1.38 (s, 0.4 H), 2.07 (s, 3 H), 5.23 (br t, 1 H), 5.62 (br s, 0.4 H), and 5.67 (br s, 0.6 H). Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.09; H, 8.16.

The mixture of acetoxyenones (2.26 g, 0.0102 mol) was dissolved in 150 mL of methanol, and a solution of 1.2 g (0.022 mol) of potassium hydroxide in 10 mL of water was added. While a slow stream of oxygen was being passed through the solution, it was stirred for 24 h at room temperature. The excess methanol was removed in vacuo and the residue partitioned between ether and water. The aqueous layer was extracted with two 50-mL portions of ether and the ether extracts were discarded. The aqueous layer was acidified with concentrated hydrochloric acid and extracted thoroughly with ether. The combined ether extracts were dried and the solvent was removed in vacuo. The viscous yellow residue was dissolved in 100 mL of dry *tert*-butyl alcohol and stirred under nitrogen, and a solution of potassium *tert*-butoxide [prepared from 0.45 g (0.115 g-atom) of potassium] in 50 mL of dry *tert*-butyl alcohol was added rapidly. After stirring for 0.5 h, 4.0 g (0.028 mol) of methyl iodide was added in one portion and the reaction mixture was then heated under reflux. After ca. 20 min the excess *tert*-butyl alcohol was removed by distillation and 50 mL of water added. Extraction with ether, drying, and removal of the solvent in vacuo gave 0.98 g (50%) of a yellow oil which crystallized on standing. Recrystallization from ether yielded pure **1b:** mp 106.5–107.0 °C; UV $\lambda_{max}$ (95% EtOH) 250 nm ($\epsilon$ 10 000); IR ($CHCl_3$) 1658, 1635, and 1615 $cm^{-1}$; NMR $\delta_{Me_4Si}$ ($CCl_4$) 1.25 (s, 3 H, $C_{10}$-$CH_3$), 3.58 (s, 3 H, $C_2$-$OCH_3$), 5.58 (s, 1 H, $C_4$-H), and 5.93 (br s, 1 H, $C_1$-H). Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.96; H, 8.39. Found: C, 74.75; H, 8.23.

**Irradiation of 1a.** A solution of 1.00 g of 6$\alpha$-methyl-2-methoxydienone **1a**[2] in 150 mL of dry dioxane was irradiated for 6.0 h. The solvent was removed in vacuo and the residue subjected to GLC analysis (column A)[13] using acetophenone as an internal standard. Response factors were calculated from GLC analysis of mixtures of the pure components [isolated by preparative GLC (column B)[13]] and acetophenone. In one run, the results of this analysis were compound **4a,** 28%; compound **5a,** 15%; phenolic compound **6a,** ~15%; starting compound **1a,** 14%.

The residue from three separate irradiations using a total of 2.8 g of dienone was combined and chromatographed on acetone-washed silica gel (60–200 mesh). Elution with 5% ether in hexane yielded an acidic compound tentatively assigned structure **6a** (0.07 g, 6%) which showed IR ($CCl_4$) 3550, 3410, 2925, 2860, and 1600 $cm^{-1}$; NMR $\delta_{Me_4Si}$ ($CCl_4$) 1.23 (d, $J$ = 6 Hz, 3 H, $C_6$-$CH_3$), 2.08 (s, 3 H, $C_1$-$CH_3$), 3.68 (s, 3 H, $C_2$-$OCH_3$), 5.48 (br s, 1 H, $C_3$-OH), and 6.57 (s, 1 H, $C_4$-H). Further elution with 10% ether in hexane yielded 1.16 g (41%) of a mixture of enones **4a** and **5a** (fraction A). Continued elution with 15% ether in hexane yielded a crystalline solid which had identical spectral properties with that of the starting dienone **1a.**

Fraction A was readily separated into two components by preparative GLC (column B).[13] The first material eluted from the column was **5a** which showed the following properties: UV $\lambda_{max}$ (95% EtOH) 240 nm ($\epsilon$ 5900); IR ($CHCl_3$) 2930, 1682, and 1585 $cm^{-1}$; NMR $\delta_{Me_4Si}$ ($CCl_4$) 1.18 (d, $J$ = 6 Hz, 3 H, $C_6$-$CH_3$), 1.27 (s, 3 H, $C_{10}$-$CH_3$), 2.33 (s, 1 H, $C_1$-H), 3.47 (s, 3 H, $C_2$-$OCH_3$), and 5.47 (s, 1 H, $C_4$-H). Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 75.41; H, 8.94.

The longer retention time component was assigned structure **4a:** UV $\lambda_{max}$ (95% EtOH) 234 nm ($\epsilon$ 7800) and 285 (2200) shoulder); IR ($CHCl_3$) 2940, 1695, and 1618 $cm^{-1}$; NMR $\delta_{Me_4Si}$ ($CCl_4$) 1.15 (s, 3 H, $C_{10}$-$CH_3$), 1.22 (d, $J$ = 6 Hz, 3 H, $C_6$-$CH_3$), 1.67 (s, 1 H, $C_4$-H), 3.65 (s, 3 H, $C_2$-$OCH_3$), and 6.15 (s, 1 H, $C_1$-H). Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 75.41; H, 9.01.

**Acid-Catalyzed Cleavage of 4a.** To a solution of 220 mg (2.07 mmol) of lumiproduct **4a** in 3.7 mL of acetic acid and 0.073 mL of acetic anhydride was slowly added 0.073 mL of concentrated sulfuric acid. The reaction mixture was stirred for 24 h and then poured into cold 10% sodium hydroxide. Ether was added, the ether layer was separated, washed with saturated aqueous sodium chloride, and dried, and the solvent was evaporated in vacuo. This yielded 173 mg (79%) of a yellow oil which by GLC was mostly **9.** Preparative GLC (column B)[13] gave a pure sample of **9** which showed essentially identical spectral properties with those previously reported.[2]

**Irradiation of 1b.** A solution of 1.00 g of 2-methoxydienone **1b** in 250 mL of dry dioxane was photolyzed for 6.0 h. The solvent was removed in vacuo and the residue subjected to GLC (column A)[13] analysis using acetophenone as an internal standard. In one run, the results of this analysis were compound **4b,** 31%; compound **5b,** 18%; compound **6b,** 12%; compound **1b,** ~15%. In another run the photolysis mixture was analyzed after 15 min and showed that the ratio of **5b** to **4b** was 4.4 to 1.0 with about 96% of dienone **1b** remaining.

The products of five, separate photolysis runs were combined and chromatographed on silica gel. Elution with 15% ether in hexane gave a product (496 mg, 9.9%) tentatively identified as the phenol **6b:** IR ($CCl_4$) 3550, 3420, 2930, 2860, and 1597 $cm^{-1}$; NMR $\delta_{Me_4Si}$ ($CCl_4$) 1.70 (m, 4 H, $C_7$-H, $C_8$-H), 2.05 (s, 3 H, $C_1$-$CH_3$), 2.50 (m, 4 H, $C_6$-H, $C_9$-H), 3.65 (s, 3 H, $C_2$-$OCH_3$), 5.50 (br s, 1 H, $C_3$-OH), and 6.42 (s, 1 H, $C_4$-H). Further elution with 25% ether in hexane gave a 1.65-g (33%) mixture of **4b** and **5b** (fraction A). Continued elution with pure ether yielded a crystalline solid that had identical spectral properties with those of the starting dienone **1b.**

Fraction A was separated into two components by careful column chromatography on silica gel. Elution with 30% ether in hexane yielded 405 mg (8.1%) of pure **4b:** UV $\lambda_{max}$ (95% EtOH) 237 nm ($\epsilon$ 8000) and 285 (2200) (shoulder); IR ($CHCl_3$) 2935, 1700, and 1620 $cm^{-1}$; NMR $\delta_{Me_4Si}$ ($CCl_4$) 1.17 (s, 3 H, $C_{10}$-$CH_3$), 1.61 (s, 1 H, $C_4$-H), 3.60 (s, 3 H, $C_{10}$-$OCH_3$), and 5.90 (s, 1 H, $C_1$-H); MS *m/e* (70 eV) 192.117 (EMC = 192.115). Further elution with 40% ether in hexane yielded 425 mg (8.5%) of pure **5b:** UV $\lambda_{max}$ (95% EtOH) 241 nm ($\epsilon$ 5400); IR ($CHCl_3$) 2930, 1682, and 1590 $cm^{-1}$; NMR $\delta_{Me_4Si}$ ($CCl_4$) 1.26 (s, 3 H, $C_{10}$-$CH_3$), 2.32 (s, 1 H, $C_1$-H), 3.48 (s, 3 H, $C_2$-$OCH_3$), and 5.50 (s, 1 H, $C_4$-H); MS *m/e* (70 eV) 192.113 (EMC = 192.115). Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.96; H, 8.39. Found: C, 74.72; H, 8.45.

**Irradiation of 4b and 5b.** A mixture of 45 mg of **4b** and 5 mg of **5b** was dissolved in 100 mL of dry dioxane and photolyzed for 0.5 h. The solvent was removed in vacuo and the residue analyzed by GLC. This analysis showed that **4b** had completely disappeared, whereas the amount of **5b** remained essentially unchanged. Only trace amounts of other volatile components were produced. No volatile photoproduct with a retention time corresponding to phenol **6b** was obtained.

**Hydrogenation of 5b.** A solution of 425 mg of **5b** in 100 mL of 95% ethanol was mixed with 400 mg of 10% palladium on carbon in a pressure bottle and shaken on a Parr apparatus at 40 psi of hydrogen pressure for 4.0 h. The catalyst was removed by filtration and the solvent removed in vacuo. This yielded 362 mg (85%) of **10** (pure by GLC analysis) which showed mp 52–53 °C (from pentane); IR ($CHCl_3$) 2930 and 1718 $cm^{-1}$; NMR $\delta_{Me_4Si}$ ($CCl_4$) 1.18 (s, 3 H, $C_{10}$-$CH_2$), 1.73 (d, $J$ = 6 Hz, 1 H, $C_1$-H), three peaks at 2.00, 2.03, and 2.17 ($J$ = 8.8 and 10.0 Hz, 2 H, $C_4$-$CH_2$, geminal coupling not observable), 2.67 (m, 1 H, $C_5$-H), and 3.34 (s, 3 H, $C_2$-$OCH_3$); MS *m/e* (70 eV) 194.131 (EMC = 194.131).

**Preparation of the *p*-Iodobenzoate 14.** To a mixture of 107 mg (2.81 mmol) of lithium aluminium hydride and 50 mL of dry tetrahydrofuran (THF) was added 0.79 mL (625 mg, 8.43 mmol) of dry *tert*-butyl alcohol with stirring under nitrogen. A solution of 362 mg (1.87 mmol) of **10** in 4 mL of dry THF was added dropwise with stirring over a 10-min period, and stirring was continued at room temperature for 1.0 h. The reaction mixture was poured into excess hydrochloric acid and extracted with three 50-mL portions of ether. The combined ether extracts were back extracted with saturated aqueous sodium bicarbonate and saturated aqueous sodium chloride and then dried, and the solvent was removed in vacuo. This gave 370 mg (101%) of material which did not have significant infrared absorption at 1718 $cm^{-1}$. This material (370 mg, 1.89 mmol) was dissolved in 5 mL of dry pyridine and 755 mg (2.83 mmol) of *p*-iodobenzoyl chloride (Eastman 9541, mp 63–65 °C) was added with stirring over a 10-min period. This mixture was allowed to stand for 48 h at room temperature and then poured into a mixture of 50 g of ice and 10 mL of concentrated hydrochloric acid. After stirring for ca. 5 min, the mixture was extracted with three 50-mL portions of ether. The ether extracts were washed with water and dried, and the solvent was removed in vacuo. This yielded a yellow oil that was chromatographed on silica gel. Elution with 20% ether in hexane gave 415 mg (52%) of crystalline iodobenzoate **14** which showed mp 110–111 °C (from hexane); NMR $\delta_{Me_4Si}$ ($CCl_4$) 1.17 (s, 3 H, $C_{10}$-$CH_3$), 3.28 (s, 3 H, $C_2$-$OCH_3$), 5.90 (t, $J$ = 8 Hz, 1 H, $C_3$-H), and 7.67 (s, 4 H, aromatic H). Anal. Calcd for $C_{19}H_{23}O_3I$: C, 53.53; H, 5.44. Found: C, 53.43; H, 5.47.

A single crystal suitable for x-ray analysis was prepared by dissolving 50 mg of **14** in 1.0 mL of hexane and 5 drops of toluene. The solid was brought into solution by heating to about 55 °C, and the solution was then allowed to cool overnight in a Dewar flask that contained water heated to 55 °C.

**Crystallographic Data Collection.** A needle-shaped crystal with approximate dimensions 0.2 × 0.2 × 0.4 mm was mounted on a glass fiber using epoxy cement such that the longest crystal dimension was approximately parallel to the fiber axis.

Unit cell parameters and the orientation matrix were determined on a Syntex $P2_1$ four-circle diffractometer equipped with a graphite monochromator (Bragg $2\theta$ angle = 12.2°) using Mo$K\alpha$ radiation at a takeoff angle of 6.5°. Fifteen reflections whose $2\theta$ values ranged from 6.0 to 24.0° were machine centered and used in least-squares refinement of the lattice parameters and orientation matrix. Unit cell parameters obtained were $a = 7.073\ (2)$ Å,[15] $b = 23.354\ (14)$ Å, $c = 11.049\ (7)$ Å, $\alpha = 90.0°$, $\beta = 91.05\ (4)°$, $\gamma = 90.0°$, and $V = 1824\ (2)$ Å$^3$. The calculated density of 1.55 g cm$^{-3}$ for four formula units per unit cell agrees with the experimental density of 1.48 g cm$^{-3}$ measured by the flotation method using aqueous zinc chloride. $\omega$ scans of several low $2\theta$ angle reflections gave peak widths at half-height of less than 0.25°, indicating a satisfactory mosaic spread for the crystal.

Axial photographs indicated that the crystal belonged to the monoclinic system. Intensity data for zero and upper levels were collected at a rapid scan rate and the intensities examined carefully for systematic absences. The absence of $h0l$ with $h + l = 2n + 1$ and $0k0$ with $k = 2n + 1$ reflections is consistent with only space group $P2_1/n$.

Intensity data were collected using $\theta$–$2\theta$ scans with x-ray source and monochromator settings identical with those used for determination of the unit cell parameters. A variable scan rate of from 4.5 to 29.3°/min was used and a scan width of 2° was sufficient to collect all of the peak intensity. Stationary background counts were measured at the beginning (bgd1) and at the end (bgd2) of each scan with a total background to scan time ratio, TR, of 1.0. No significant fluctuations were observed in the intensities of three standard reflections (0,0,10; 0,8,0; 2,0,0) monitored every 100 reflections. Intensities were calculated from the total scan count (CT) and background counts by the relationship

$$I = \mathrm{CT} - (\mathrm{TR})(\mathrm{bdgl} + \mathrm{bgd2})$$

The intensities were assigned standard deviations according to the formula

$$\sigma(I) = [\mathrm{CT} + (\mathrm{TR})^2(\mathrm{bgdl} + \mathrm{bgd2})]^{1/2}$$

from a total of 5223 reflections collected in a complete quadrant of data out to $2\theta = 60°$; 2454 were accepted as statistically above background on the basis that $I$ was greater than $3\sigma(I)$. Lorentz and polarization corrections were made in the usual way.

**Solution and Refinement of the Structure.** Computations were performed using standard programs;[16] all computations were carried out on the CDC Cyber 74 system. For structure-factor calculations the scattering factors were taken from Cromer and Waber's tabulation[17] for all atoms. The scattering factor for iodine was corrected for the real and imaginary anomalous dispersion components, using the dispersion factors given by Cromer.[18] The agreement factors are defined in the usual way as

$$R = (\Sigma||F_o| - |F_c||)/(\Sigma|F_o|)$$

and

$$R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2]^{1/2}$$

In all least-squares refinements, the quantity minimized was $w(|F_o| - |F_c|)^2$. A weighting scheme based on counting statistics [$w = 4I/\sigma^2(I)^2$] was employed for calculating $R_w$ and in least-squares refinement.

Coordinates for the iodine atom were obtained from a three-dimensional Patterson synthesis; successive cycles of least-squares refinement and electron density calculation revealed the position of all carbon and oxygen atoms; hydrogen atoms were not located. All atoms were refined anisotropically. Least-squares refinement converged to give the residuals $R = 0.056$ and $R_w = 0.050$ (2454 observations, 208 variables). In the final refinement no parameter changed by more than one standard deviation from the previous value.

**Registry No.**—**1a,** 58355-87-6; **1b,** 64761-36-0; **3b,** 40573-28-2; **4a,** 64761-37-1; **4b,** 64761-38-2; **5a,** 64761-31-5; **5b,** 64761-32-6; **6a,** 64761-39-3; **6b,** 64761-40-6; **10,** 64761-33-7; **14,** 64761-34-8; 2-$\alpha$-3-keto-10-methyl-$\Delta^{4,5}$-octahydronaphthalene, 64771-34-2; 2-$\beta$-3-keto-10-methyl-$\Delta^{4,5}$-octahydronaphthalene, 64761-35-9; methyl iodide, 74-88-4; $p$-iodobenzoyl chloride, 1711-02-0.

**Supplementary Material Available:** Table I listing final positional parameters (1 page). Ordering information is given on any current masthead page.

## References and Notes

(1) This investigation was supported by Grant No. CA 12193, awarded by the National Cancer Institute, Department of Health, Education and Welfare.
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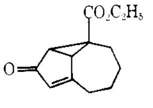
(8) Professor P. J. Kropp has informed us that the tricyclodecenone i is produced as a minor product of irradiation of the angular carboethoxydienone ii in dioxane. However, the stereochemistry of this photoproduct was not established.



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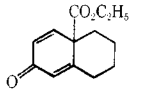

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(13) Melting and boiling points are uncorrected. Infrared spectra were determined using a Perkin-Elmer Model 457 infrared spectrophotometer. Ultraviolet spectra were measured using a Beckman Model 25 recording spectrophotometer using 1-cm matched quartz cells. NMR spectra were determined at 60 MHz with a Varian T-60 spectrometer. Signals are reported in parts per million ($\delta$) downfield from internal tetramethylsilane. Mass spectra were obtained using a Hitachi Perkin-Elmer RMU-7 or a Varian M-66 spectrometer. Microanalyses were obtained by Atlantic Microlab, Inc., Atlanta, Ga. Gas-liquid chromatography was carried out using a Perkin-Elmer 881 or an Aerograph A-90-P3 gas chromatograph. The following columns were used: A (6 ft × 0.125 in. 20% Carbowax K-20M on Chromosorb W); B (10 ft × 0.25 in. 20% Carbowax K-20M on Chromosorb W). Irradiations were conducted using a 7-W Hanau NK 20 low-pressure mercury lamp. Solutions were agitated with a stream of nitrogen for a few minutes preceding and during the irradiation period. Anhydrous magnesium sulfate was employed as the drying agent. Dioxane was distilled from sodium metal prior to use.
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(15) Numbers in parentheses here and elsewhere in this paper indicate estimated standard deviations in the least significant digit(s).
(16) Programs utilized were Zalkin's OFRDAP Fourier summation program, Iber's NUCLS modification of the Busing-Martin-Levy least-squares program, Doeden's RBANG rigid group orientation program, Stewart's ABSORB absorption correction program from the X-Ray 72 system, and Johnson's ORTEP program.
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