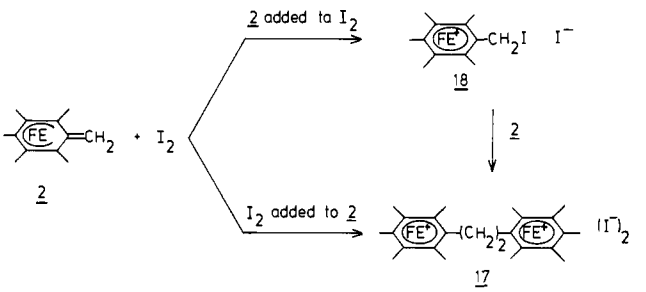
Scheme I



Now reaction of **2** with $CpFe(CO)_2(C_2H_4)^+$ at −80 °C in THF specifically gives the nucleophilic addition product (**15**) onto the ethylene ligand,[17b] crystallized as the PF_6 salt[15] (eq 6).

$$2 + CpFe(CO)_2(C_2H_4)^+ \xrightarrow{-78\ °C} CpFe^+\text{-}\eta^6\text{-}C_6Me_5(CH_2)_3Fe(CO)_2Cp \quad (6)$$
15

While nucleophilic substitution fails with free or complexes halogenoarenes, **2** adds to $CpFe(\eta^6\text{-}PhCl)$ mostly ortho to Cl[21] in 5 min at −18 °C to give **16**, the nucleophilic addition product[15] (eq 7).

$$2 + CpFe(\eta^6\text{-}PhCl) \xrightarrow[THF]{-18\ °C} CpFe^+\text{-}\eta^6,\eta^5\text{-}C_6Me_5CH_2\text{-}o\text{-}C_6H_5ClFeCp \quad (7)$$
16

The reaction of **2** with TCNQ in THF also provides electron transfer followed by H· abstraction from the solvent giving the green salt 1^+ $TCNQ^-$· (eq 8) identified by its characteristic Mössbauer (1^+)[22] and optical spectra ($TCNQ^-$·).[23]

$$2 + TCNQ \xrightarrow{THF} 2^+TCNQ^-\cdot \xrightarrow[(solvent)]{H\cdot} 1^+TCNQ^-\cdot \quad (8)$$

These electron-transfer reactions of **2** are consistent with the low-ionization potential (6.21 V from He(I) PES) recorded by J. Green.[16] Their synthetic goal—the coupling of **2** via the radical $CpFe^+(\eta^6\text{-}C_6Me_5CH_2)$·—was frustrated by the abstraction of H·. However, when a THF solution of I_2 is added to **2** at 20 °C, the sparingly soluble binuclear bication **17**[15] is obtained immediately and quantitatively. If, on the other hand, a solution of **2** in THF is added to I_2 at 20 °C, the iodo complex **18** is formed quantitatively [Scheme I, similar reactions with Cl_2 and Br_2 in the same conditions give $CpFe(\eta^6\text{-}C_6Me_5Ch_2Cl)$(**19**), and $CpFe(\eta^6\text{-}C_6Me_5CH_2Br)$ (**20**)];[15] further reaction of **2** with **18** gives **17**. Thus the formation of **17** from **2** and I_2 is not a coupling of two radicals but a double nucleophilic substitution of I^-.

Since **2** is easily accessible by short contact of **1** with air, the chemistry presented here can be achieved in a straightforward manner from the readily available complex $CpFeC_6Me_6$.[22,24]

Acknowledgment. We thank Dr. M. L. H. Green for helpful discussions, Dr. J. C. Green (Oxford) for communicating the IP value of **2**, P. Michaud and J. P. Mariot from Professor F. Varret's group (Le Mans) for providing the fitted Mössbauer spectra, and D. Catheline for skillful experimental assistance. Financial support by the CNRS (ATP No. 3801) is also gratefully acknowledged.

Supplementary Material Available: Atomic and thermal parameters (1 page). Ordering information is given on any current mashead page.

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Photochemical Formation of the Ketone Tautomer of 3,4-Dihydro-9-hydroxy-2(1*H*)-anthracenone from 2,3-Benzospiro[4.5]deca-2,6-diene-1,8-dione

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Although the ketone tautomer of 1-naphthol (**4**) has been detected by IR spectroscopy at 77 K as an intermediate in the photoreaction of naphthalene 1,2-oxide,[1] most ketone tautomers of phenols are not isolable at room temperature because of the strong driving force for rearomatization.[2] We now report the first isolation of the ketone tautomer of a naphthol derivative as an intermediate for the unique photochemical formation of 3,4-dihydro-9-hydroxy-2(1*H*)-anthracenone (**2**) from 2,3-benzospiro[4.5]deca-2,6-diene-1,8-dione (**1**).

When a solution of spiro diketone **1**[7,8] in benzene or methanol was irradiated through a Pyrex filter with a medium-pressure mercury lamp (Hanovia 450W) for 80 min at 25 °C, an air-labile product **2** (mp 122-123 °C) was obtained in 13 and 20% yields, respectively (Scheme I). The structure of **2**, 3,4-dihydro-9-hydroxy-2(1*H*)-anthracenone, was determined from its spectral characteristics and elemental analysis.[8] The elemental analysis and mass spectrum (70 eV, M^+, *m/e* 212) suggested that it was formulated as $C_{14}H_{12}O_2$. Its UV (C_2H_5OH) spectrum shows strong absorption bands at 243 (log ε, 4.40), 275 (3.74), and 325 nm (sh). This absorption pattern is similar to that of **4**.[3] In its ^1H NMR ($CDCl_3$) spectrum, the resonances of three methylene groups, the hydroxyl group, and aromatic ring protones appear at 2.73 (t, 2 H, J = 6.5 Hz), 3.18 (t, 2 H, J = 6.5 Hz), 3.70 (s, 2 H), 6.07 (s, 1 H, exchangeable with D_2O), and 7.23-8.20 ppm (m, 5 H).[9] The chemical shifts and coupling pattern of the resonances of aromatic ring protones are similar to that of **4**.[4] Its ^{13}C NMR (50% Me_2SO-d_6 in $CDCl_3$) spectrum shows the presence of 14 carbon atoms at 210.0, 149.1, 135.6, 132.9, 126.9, 125.6, 124.1 (×2), 121.9, 117.1, 114.9, 38.9, 38.3, and 28.7 ppm.[9] Its IR (Nujol) spectrum shows carbonyl absorption band at 1695 cm^{-1}. These results support **2** or **2'** for the structure. The method using a NMR shift reagent [$Eu(fod)_3$] allows us to assign the structure as **2**.[5] On the other hand, when a ether solution of **1** was irradiated through a Pyrex filter under nitrogen bubbling with a medium-pressure mercury lamp (Hanovia 450W) at 0 °C for 80 min, colorless compound **3** was crystallized out on the reaction tube: 23% yield; colorless fine needles, mp 132-133 °C. The structure of **3** is evident from elemental analysis[8] and spectral data: mass spectrum (70 eV), M^+, *m/e* 212; IR (Nujol) 1712, 1640

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(6) The rate of the thermal reaction of **3** to **2** was measured in a chloroform-ethanol (10:1) solution. The Arrhenius plot of the first-order rate constants provides a straight line from which activation parameters were calculated as follows: E_a = 10.18 kcal/mol, log A = 5.27, $\Delta S^{\ddagger}$ = −36.4 (eu, 295 K).
(7) **1** was prepared by the treatment of 2-(hydroxymethyl)-1-indanone with methyl vinyl ketone and followed by acid (HCl) catalyzed aldol condensation of 2-formyl-2-(3-oxobutyl)-1-indanone formed: 13.6%; mp 84-85 °C; IR (Nujol) 1705, 1665 cm^{-1}; ^1H NMR ($CDCl_3$) 1.80-3.30 (m, 4 H), 3.27 (s, 2 H), 6.10 (d, 1 H, J=10.3 Hz), 6.61 (d, 1 H, J=10.3 Hz), 7.23-7.90 ppm (m, 4 H);[9] UV λ_{max} (ethanol) 206 (log ε, 4.30), 250 (4.16), 290 nm (3.37).[8]
(8) Satisfactory CHN elemental analyses were obtained for **1-3**.
(9) Tetramethylsilane (Me_4Si) is used for an internal standard.

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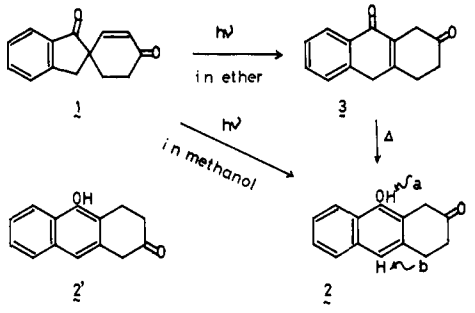
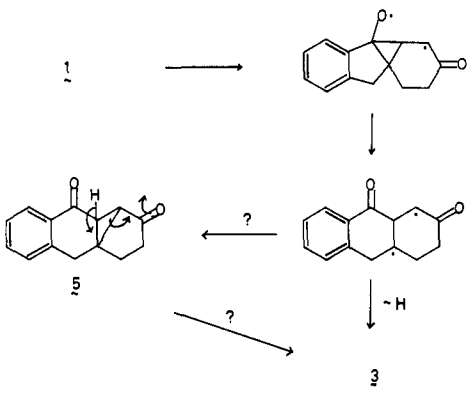
Scheme I



Scheme II



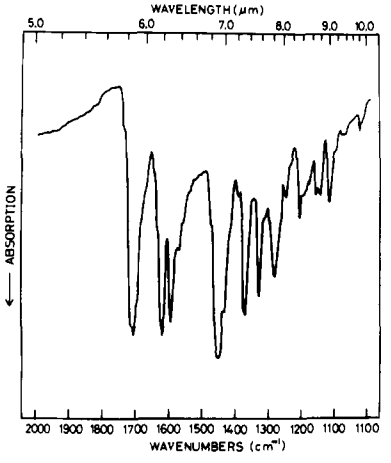


Figure 1. Infrared absorption spectra (25 °C, Nujol) of **3**.

cm^{-1} (see Figure 1); ^1H NMR ($CDCl_3$) 2.40–3.00 (m, 4 H), 3.35 (s, 2 H), 3.77 (s, 2 H), 7.23–7.70 (m, 3 H), 8.20 ppm(m, 1 H);[9] ^{13}C NMR ($CDCl_3$) 208.6, 183.7, 150.9, 139.5, 132.1, 131.3, 130.4, 127.8, 127.2, 126.5, 37.4, 37.2, 35.0, and 30.8 ppm;[9] UV λ_{max} ($CHCl_3$) 253 (log ϵ, 4.10), 268 (4.05), 300 nm (sh). The thermal rearrangement of **3** to **2** was observed during triturating with ethanol or dimethyl-d_6 sulfoxide (Me_2SO).[6] From these results **3** was assigned as 3,4-dihydro-2,9(1*H*,10*H*)-anthracenedione. This is the first example of the photochemical preparation of the ketone tautomer of a naphthol. A plausible mechanism for the photoisomerization from **1** to **3** is shown in Scheme II. This may be an example of the oxa-di-π-methane rearrangement of β,γ-enones.[10]

Acknowledgment. We thank S. Kohara and M. Honjo for some preliminary studies.

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Total Synthesis of Racemic Siccanin

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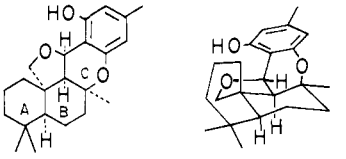
Siccanin (**1**) is a mold metabolite isolated from the culture broth of *Helminthosporium siccans*[1] and exhibits a remarkable antifungal activity against a variety of fungi, in particular, *Trichophyton interdigitale* and *T. asteroids*, that cause fungal infection in skin.[2] This compound is clinically utilized thereby.



1a **1b**

Since its unique structure involving the unusual cis-, syn-, cis-fused A/B/C ring system was revealed as **1b** in 1967 by X-ray crystallographic study,[3] some synthetic approaches to this intriguing target were reported.[4]

Siccanin is regarded as a drimane sesquiterpene combined with orcinol. Herein is described the first total synthesis of racemic siccanin by a novel approach. The synthesis is divided into three major tasks: (a) stereoselective synthesis of *cis*-octalone **10**, (b) development of **10** to the formyldecalol **17** with the drimane structure, (c) subsequent elaboration to the tetracyclic hydrofuran derivative **24**, and acid treatment of **24** to lead to siccanin methyl ether (**26**) (see Schemes I and II).

The known, readily available keto ester **2**[5] was submitted to the Robinson annulation ($MeCOCH{=}CH_2$, NaOMe, MeOH) to yield octalone **3**, mp 121–122 °C (Scheme I). The octalone was smoothly methylated (MeI, *t*-BuOK, *t*-BuOH) to give liquid dimethyl ketone **4**. Reduction of the hindered ketone carbonyl of **4** to methylene group was achieved by reduction [$NaB(CN)H_3$, *p*-TsOH, sulfolane, DMF, 100 °C][6] of its tosylhydrazone **5** ($TsNHNH_2$, MeOH), mp 217 °C (decomp), affording octalin **6**, mp 43–44 °C. Reduction of **6** ($LiAlH_4$, DME) to alcohol **7**, mp 38–40 °C, and methylation (MeI, NaH, DME) of the resulting hydroxy group gave methyl ether **8**, mp 52–54 °C. Acetal exchange reaction of **8** (*p*-TsOH, acetone, 25 °C) gave oily deconjugated octalone **9**.

After a number of attempts for isomerization of **9** to conjugated enone **10**, it was eventually found that treatment of the former with *p*-toluenesulfonic acid (0.5 equiv) in methanol at 50 °C yielded an equilibrium mixture consisting of the ketone **9** and **10** in a 1:4 ratio. The oily enone **10** separated by silica gel chromatography was shown to be a *cis*-octalone as mentioned below, and no formation of its trans isomer was observed.

Unambiguous assignment of the cis stereochemistry was done by transformation of the decalone **18**, quantitatively obtained by hydrogenation of **10** (H_2, 10% Pd-C, EtOH), into the known trimethyl ketone **19**[7] as follows: replacement of the methoxy group

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