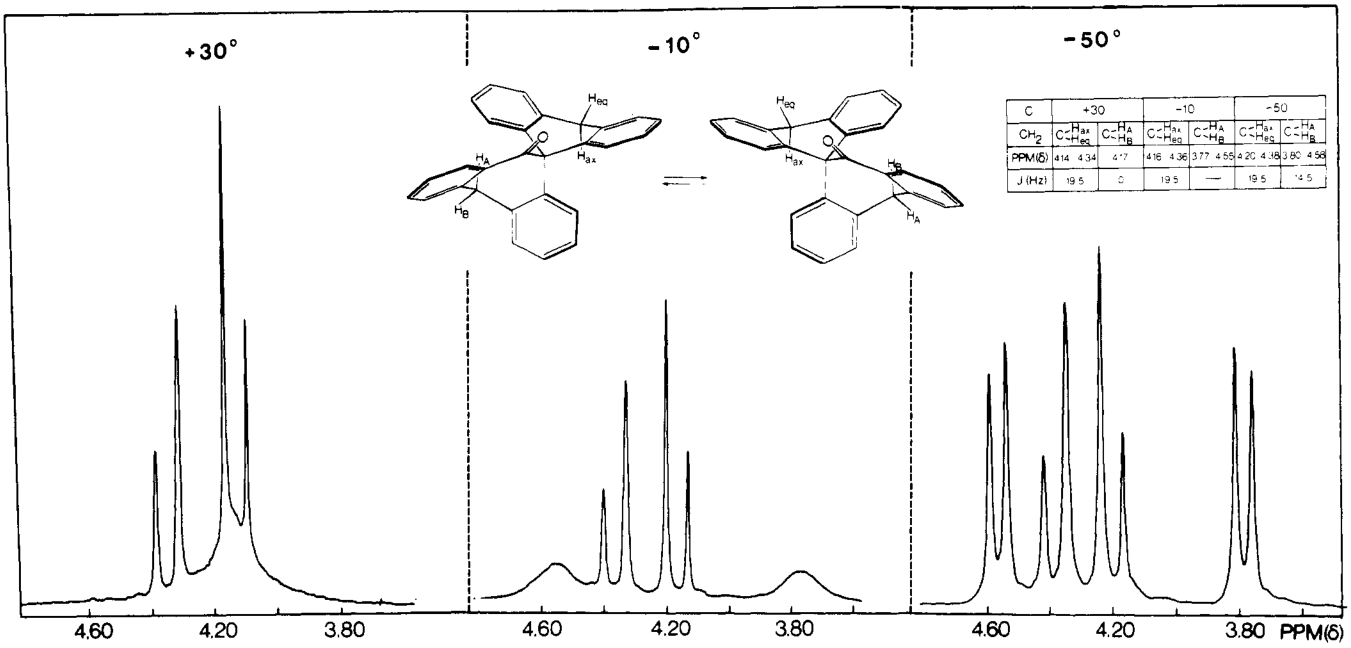

C	+30		-10		-50	
CH_2	$C{<}^{H_{ax}}_{H_{eq}}$	$C{<}^{H_A}_{H_B}$	$C{<}^{H_{ax}}_{H_{eq}}$	$C{<}^{H_A}_{H_B}$	$C{<}^{H_{ax}}_{H_{eq}}$	$C{<}^{H_A}_{H_B}$
PPM(δ)	4.14 4.34	4.17	4.16 4.36	3.77 4.55	4.20 4.38	3.80 4.58
J (Hz)	19.5	0	19.5	—	19.5	14.5

Figure 2. 270-MHz ^{1}H NMR spectra of anthrapinacolin **5** in $CDCl_3$ at 30 °C, −10 °C, and −50 °C.

room-temperature NMR spectrum of the nonaromatic protons in anthrapinacolin (see Figure 2) reveals that an absorption by two protons coincides with the upfield half of an AB spectrum (J = 19.5 Hz). When the temperature is lowered, the overlapping two-proton absorption first separates into two broad bands which finally give rise to an additional AB spectrum (J = 14.5 Hz). This finding leaves no doubt that anthrapinacolin actually has the previously rejected dibenzocycloheptadienone structure **5** in which the methylene protons of the seven-membered ring become magnetically nonequivalent as the intramolecular mobility of the ring system decreases. From the observed coalescence temperature of about 5 °C, the free energy of activation for the folding motion of the cycloheptadienone ring was calculated[9] to be 13 kcal/mol.

Experimental Section

Melting points were determined on a hot-stage microscope and are not corrected. NMR spectra were recorded on a Bruker 270 instrument, and chemical shifts are given in parts per million downfield from Me_4Si. Absorption spectra were obtained on a Beckman Acta III spectrophotometer.

Preparation of Anthrapinacolin (5) from Anthrone. A solution of anthrone (2 g) in acetic acid (10 mL) containing concentrated hydrochloric acid (1.2 mL) and granulated zinc (1.2 g) was refluxed for 2.5 h. After cooling the reaction mixture to room temperature, the crystalline precipitate was removed by filtration, washed successively with acetic acid, dilute hydrochloric acid, and water, and then dried (yield 1.69 g). Column chromatography (SiO_2/CH_2Cl_2) gave 0.60 g of 9,9′-bianthryl (33%), and 0.84 g (43%) of anthrapinacolin (**5**): mp 218–219 °C (lit.[1] mp 219 °C; ^{13}C NMR at 60 °C in $CDCl_3$) 35.8 (CH_2), 40.9 (CH_2), 69.7 (C), 125.9, 126.3, 126.4, 127.1, 127.31, 127.32, 127.6, 128.3, 128.6, 130.3, 130.6, 134.6, 136.8, 138.4, 139.1, 139.7, 139.9, 144.3 (aromatic C), 202.5 ppm (CO). The aromatic carbons of the 9,10-dihydroanthracene moiety are pairwise equivalent.

Preparation of Anthrapinacolin (5) from Anthrapinacol. A solution of anthrapinacol[10] (**4**, 1 g) in thionyl chloride (15 mL) was refluxed for 2 h. Vacuum evaporation of solvent left a solid residue which was dissolved in methylene chloride. Acidic material was removed from the organic solution by extraction with water. Column chromatography (SiO_2/CH_2Cl_2) of the organic portion gave 760 mg (80%) of anthrapinacolin, mp 218–219 °C.

Acknowledgment. We are gratefully indebted to Mr. Gunnar Svensson for skillful technical assistance and to Mr. Reine Torberntsson for recording the NMR spectra.

Registry No. 1, 90-44-8; **2**, 1055-23-8; **3**, 161-84-2; **4**, 4393-30-0; **5**, 79483-37-7.

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cis-1,2-Bis(9-anthryl)ethylene: Preparation and Photochemical Properties

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1,2-Bis(9-anthryl)ethylene (**1**) was first found to be formed by pyrolysis of poly-9-thioanthraldehyde,[1] and it was subsequently reported to be accessible by reacting 9-anthraldehyde with sodium diphenylphosphine oxide at 200 °C.[2] The yellow compound obtained by these two methods is characterized by its low solubility and by its high melting point (~335 °C), and it has tacitly been assumed to be the trans isomer. Concerning the seemingly more straightforward formation of **1** from 1,2-bis(9-anthryl)ethanol reported in 1966,[3] the structures of all compounds involved in that sequence of reactions were recently revised and shown to be derivatives of 9,10-dihydroanthracene.[4] We have found during the course of the present investigation that *trans*-1,2-bis(9-anthryl)ethylene is most conveniently prepared by the Wittig re-

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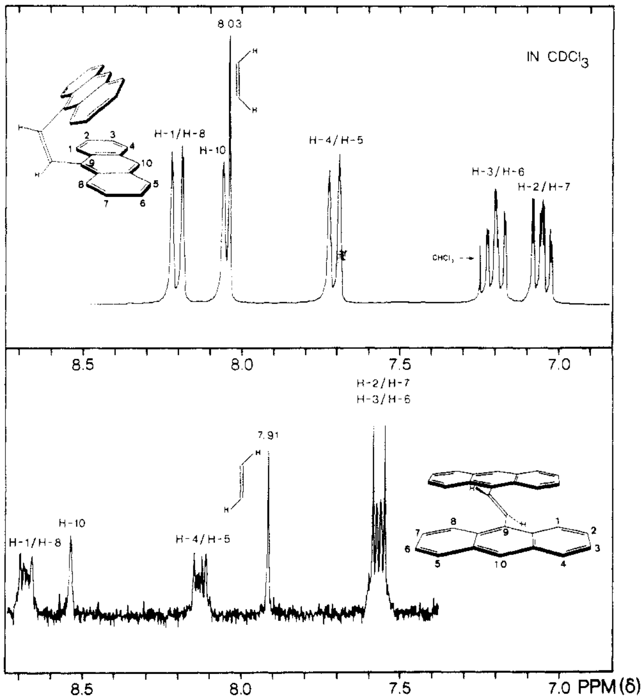


Figure 1. 270-MHz ^{1}H NMR spectra of dianthrylethylenes **1** and **2**.

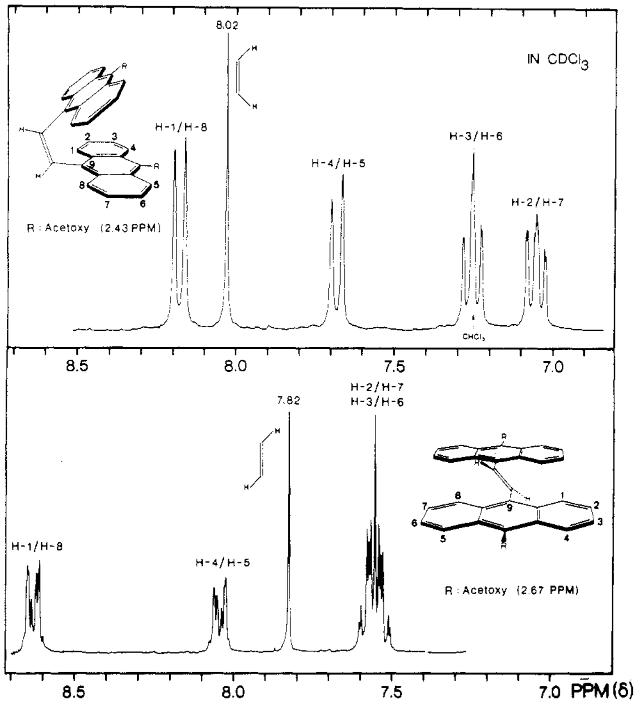
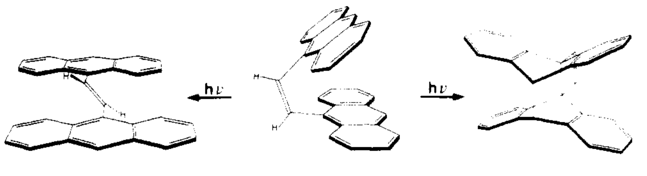


Figure 2. 270-MHz ^{1}H NMR spectra of *cis*- and *trans*-1,2-bis(10-acetoxy-9-anthryl)ethylenes.

action (see Experimental Section).

Our interest in the cis isomer of 1,2-bis(9-anthryl)ethylene (**2**) originates from the conceivable electron



1 2 3

spectral and photochemical implications of its unique molecular geometry in which two anthracene units are facing each other in a virtually fixed arrangement perpendicular to the plane of the linking ethylene double bond. The geometry of *trans*-dianthrylethylene is rather different. The two anthracene moieties may be aligned parallel as the molecule deviates from planarity by twists of about 50° around the anthryl–ethylene single bonds in order to accommodate the hydrogens H-1/H-8 and the hydrogens of the *trans*-ethylene moiety at an intramolecular distance of about 2 Å. The effects of molecular geometry on the excited-state properties of *trans*-dianthrylethylene have been discussed previously in an emission spectroscopic study.[5]

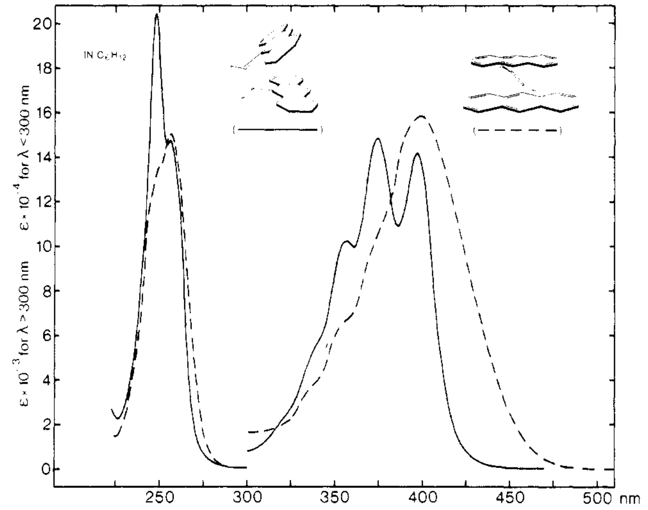


Figure 3. Electronic absorption spectra of dianthrylethylenes **1** and **2** in cyclohexane solution.

The existence of two geometrical isomers of dianthrylethylene was first mentioned in a spectroscopic context in 1963 when *cis*-dianthrylethylene was reported to be formed in the thermal decomposition of 9-anthralazine at 270–290 °C and when its spectral properties were described.[6-8] However, we have recently pointed out that both the reported melting point of 176 °C and the electronic absorption and emission spectra attributed to *cis*-dianthrylethylene are identical with those of 9-cyanoanthracene, and we concluded that the decomposition product of 9-anthralazine described to be *cis*-dianthrylethylene actually is 9-cyanoanthracene.[9]

We have now prepared *cis*-1,2-bis(9-anthryl)ethylene in an uncontroversial fashion by catalytic hydrogenation of the known[10] 1,2-bis(9-anthryl)acetylene.[11] The present report deals with its physical and chemical properties

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(11) Bis(9-anthryl)acetylene was obtained according to ref 10 from 9-anthroyl chloride and triphenyl(9-anthrylmethylene)phosphorane. Our attempt to prepare bis(9-anthryl)acetylene by way of conventional dehydrohalogenation was unsuccessful insofar as the 1,2-dibromo-1,2-bis(9-anthryl)ethane of the literature[1] was found to be *trans*-1,2-bis(10-bromo-9-anthryl)ethylene: ^{1}H NMR δ 8.69–8.59 (m, 8 arom H), 7.78 (s, 2 ethylenic H), 7.68–7.48 (m, 8 arom H).

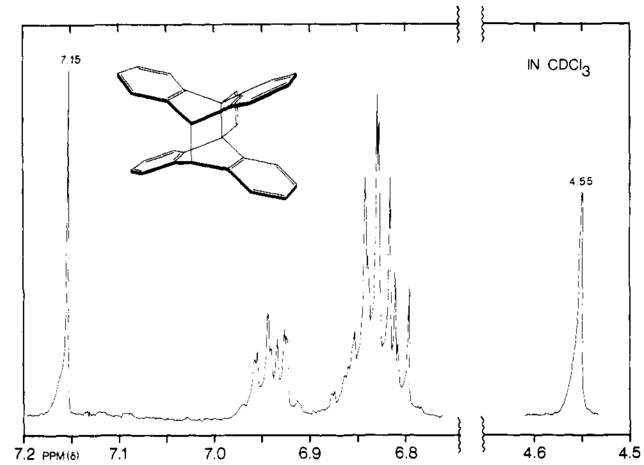


Figure 4. 270-MHz ^{1}H NMR spectrum of photoisomer **3**.

which we find to be such as to vindicate our earlier conclusion that *cis*-dianthrylethylene has not been synthesized before. As far as its melting point is concerned, we find *cis*-dianthrylethylene to be thermally labile. Upon being heated to about 215 °C, it smoothly isomerizes to give its trans isomer **1**.

The two geometrical isomers of dianthrylethylene are clearly distinguishable by ^{1}H NMR spectroscopy. In the ^{1}H NMR spectrum of *cis*-dianthrylethylene, the ethylenic protons and the H-10 protons give rise to singlets at 8.03 and 8.05 ppm, respectively. In the spectrum of the trans isomer, by contrast, the ethylenic protons give rise to a singlet at 7.91 ppm while the singlet due to the H-10 protons is shifted downfield to 8.52 ppm. As for the remaining, pairwise-equivalent protons H-1/H-8, H-2/H-7, H-3/H-6, and H-4/H-5, their chemical shifts and coupling patterns are diagnostically useful since they are characteristic for each of the geometrical isomers. Thus, the 270-MHz ^{1}H NMR spectrum of *cis*-dianthrylethylene looks strikingly simple, exhibiting two doublets and two "triplets" (see Figure 1). *trans*-Dianthrylethylene **1**, in contrast to its cis isomer **2**, lacks the mirror plane symmetry element, and chemically equivalent protons of the 9-anthryl moiety are no longer magnetically equivalent because of hindered rotation around the anthryl–ethylene single bond. Consequently, the 270-MHz ^{1}H NMR spectrum of *trans*-dianthrylethylene exhibits three multiplets whose shapes are indicative of four-spin systems. The same differentiation between geometrical isomers is exhibited in the ^{1}H NMR spectra of *cis*- and *trans*-1,2-bis(10-acetoxy-9-anthryl)ethylenes[5] (see Figure 2).

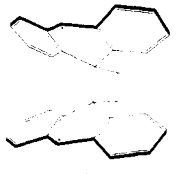
In accord with the differences in their molecular geometry, *cis*- and *trans*-dianthrylethylenes **2** and **1** are also distinguishable by their electron spectral properties. The impairment of conjugation in *cis*-dianthrylethylene is borne out in the electronic absorption spectrum by the exhibition of fine structure in conjunction with the hypsochromic shift relative to the absorption spectrum of the trans isomer (see Figure 3).

Upon photoexcitation in cyclohexane solution at room temperature, *cis*-dianthrylethylene undergoes geometrical isomerization to **1** with a remarkably low quantum yield (7×10^{-4}). In a competing process of equally low quantum yield (7×10^{-4}), photoexcited *cis*-dianthrylethylene deactivates by intramolecular [4 + 4] cycloaddition to give the heretofore unknown dianthracene derivative **3**. The ^{1}H NMR spectrum of the photoisomer is in agreement with this structure. Thus, the presence of the ethylenic protons is verified by the singlet at 7.15 ppm (see Figure 4), and the singlet at 4.55 ppm due to the bridgehead protons is similar to that of the bridgehead protons in the dianthrylethane photoisomer (4.51 ppm). Furthermore, as is typical of dianthracenes, photoisomer **3** undergoes cycloreversion at elevated temperature (~230 °C) to give the thermodynamically stable trans isomer **1**.

The quantum yield data for the deactivation of photoexcited **2** by chemical product formation as mentioned above apply to low (5%) conversions of 10^{-4} M solutions. A preparative experiment involving total consumption of *cis*-dianthrylethylene afforded the cycloaddition product **3** in about 10% chemical yield only, suggesting that other reactions may occur when, because of their strongly overlapping electron spectra, both the cis and the trans isomers absorb the incident light.

Interestingly, the quantum yield for the photochemical formation of **1** from **2** was found to be solvent dependent. Compared to the photochemical isomerization in cyclohexane solution, the quantum yield of cis–trans isomerization in benzene solution increases by about one order of magnitude. The more drastic quantum yield increase to 1.5×10^{-2} observed in chloroform solution is probably explicable in terms of intersystem crossing enhancement due to an external heavy-atom effect and suggests that the geometrical isomerization of **2** proceeds via the excited triplet state. In support of this assumption, we find that the photochemical isomerization of **2** to give **1** can be sensitized by biacetyl.

Significantly, *cis*-dianthrylethylene **2** in cyclohexane solution at room temperature is virtually nonfluorescent ($\Phi_F < 10^{-4}$). Since the quantum yields for the disappearance of **2** by photochemical cis–trans isomerization and by intramolecular [4 + 4] cycloaddition also are low, the major mode of deactivation of electronically excited **2** is nonradiative return to the ground state. Similar excited-state properties had been encountered in the case of the diacetoxy derivative of **2**.[5] We believe, therefore, that the molecular geometry of *cis*-dianthrylethylenes is directly responsible for their inefficient chemical reactivity in the excited state. The closest intramolecular separation of the two aromatic π systems in *cis*-dianthrylethylene **2**, being about 3 Å, is well within the crystallographically documented[12] photochemical contact distance of ~4 Å. Consequently, intramolecular excited-state interaction is bound to occur between C-9 and C-9′. We are inclined to visualize this geometry-induced intramolecular deactivation of photoexcited *cis*-dianthrylethylene **2** as a reversible formation of biradical **4**. The involvement of similar biradicals in the photochemistry of bis(9-anthryl)alkanes is a subject of current debate.[13-16]



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Experimental Section

Melting points were determined on a hot-stage microscope and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker 270

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instrument, and chemical shifts are given in parts per million downfield from Me_4Si.

Starting Materials. Commercially available 9-anthraldehyde was purified by column chromatography (SiO_2/CH_2Cl_2). (9-Anthrylmethyl)triphenylphosphonium bromide was prepared according to ref 10. The Lindlar catalyst was purchased from Fluka, AG.

Photochemical Experiments. Actinometric experiments were carried out as described in ref 5. The quantum yield for the cycloaddition of **2** was calculated by subtracting the quantum yield for the cis–trans isomerization from the quantum yield for the disappearance of **2**, both of which are accessible spectrophotometrically. The formation of **3** was ascertained by subsequent irradiation at 280 nm which regenerated **2** from **3** by photolytic cycloreversion but did not affect the yield of **1**. The sensitized formation of **1** from **2** was accomplished by irradiating a benzene solution (7.8×10^{-5} M) and biacetyl (10^{-2} M) in an optical bench arrangement and using a Corning cut-off filter (Type 3-72; $\lambda >$ 430 nm; high-pressue mercury arc, HPK 125 W). The formation of **1** was established and assayed by absorption spectroscopy.

***trans*-1,2-Bis(9-anthryl)ethylene (1).** A solution of lithium ethoxide (prepared from 30 mg of lithium in 28 mL of ethanol) was added to a warm solution of 9-anthraldehyde (0.58 g, 2.8 mmol) and (9-anthrylmethyl)triphenylphosphonium bromide (1.5 g, 2.8 mmol) in absolute ethanol (40 mL). The color of the solution turned transiently red, and yellow crystals precipitated. After the suspension was stirred for 3 h, the precipitate (0.58 g) was removed by filtration, washed with ethanol, and recrystallized from boiling xylene (200 mL): yield 0.48 g (45%) of yellow crystals; mp 350 °C (lit. mp 338,[1] 335 °C[2]); mass spectrum, *m/e* 380 (100, M^+), 378 (10, M − 2), 303 (18, M − 77), 202 (33, M − 178), 190 (7, M − 190), 178 (28, M − 202); M^+ found by high-resolution mass spectroscopy at *m/e* 380.1529, calcd for $C_{30}H_{20}$ *m/e* 380.1566.

***cis*-1,2-Bis(9-anthryl)ethylene (2).** A solution of 1,2-bis(9-anthryl)acetylene[10] (25 mg) in ethyl acetate (150 mL) was hydrogenated under ambient conditions over Lindlar catalyst (1.0 g). After uptake of 1 molar equiv of hydrogen (45 min), the catalyst was removed by filtration, and the solvent was evaporated under reduced pressure. The crystalline residue was recrystallized from CH_2Cl_2 by addition of cyclohexane to give pale yellow crystals: 18 mg (72%); mass spectrum, *m/e* 380 (100, M^+), 378 (12, M − 2), 303 (20, M − 77), 202 (30, M − 178), 190 (12, M − 190), 178 (25, M − 202); M^+ found by high-resolution mass spectrosopy at *m/e* 380.1515, calcd for $C_{30}H_{20}$ *m/e* 380.1566. Anal. Calcd for $C_{30}H_{20}$: C, 94.70; H, 5.30. Found: C, 95.07; H, 5.33. With respect to melting point of **2**, the crystalline appearance of **2** changes around 215 °C, and the substance melts around 348 °C. The thermal formation of **1** was verified by keeping **2** for 3 min at 240–250 °C. The electronic absorption spectrum (in xylene) of the thermolysis product indicated quantitative isomerization of **2** to **1**.

Photochemical Isomerization of 2 To Give 1 and Cycloaddition Product 3. A solution of **2** (30 mg) in cyclohexane (85 mL) was irradiated through Pyrex for 45 min (10 °C; immersion well apparatus; nitrogen atmosphere; high-pressure mercury lamp, HPK 125 W). A yellow crystalline precipitate formed during the irradiation. Vacuum evaporation of the solvent gave a solid yellow residue which was triturated with about 3 mL of $CDCl_3$. Filtration gave 21 mg (70%) of insoluble material which consisted mainly (94%) of trans isomer **1** (determined by absorption spectroscopy). Evaporation of solvent from the $CDCl_3$ filtrate gave a yellow residue which was washed with about 1 mL of CD_3COCD_3 to give 3 mg (10%) of **3** as colorless, needle-shaped crystals. Upon being heated, **3** turns yellow at about 230 °C and melts between 340 and 345 °C: mass spectrum, *m/e* 380 (100, M^+), 378 (22, M − 2), 303 (16, M − 77), 202 (23, M − 178), 191 (13, M − 189), 190 (8, M − 190), 178 (17, **M** − 202); M^+ found by high-resolution mass spectroscopy at *m/e* 380.1595, calcd for $C_{30}H_{20}$ *m/e* 380.1566.

Acknowledgment. We are indebted to Dr. Kjell Sandros for the actinometric experiments, to Mr. Reine Torberntsson for 270-MHz ^1H NMR spectra, and to Mr. Weston Pimlott for high-resolution mass spectra.

Registry No. 1, 3849-11-4; 2, 3162-57-0; 3, 79483-07-1; 9-anthraldehyde, 642-31-9.

Dihydrofurans from Hydroxyallenes and Dicarbonyl(η^5-cyclopentadienyl)(η^2-isobutylene)iron Cation

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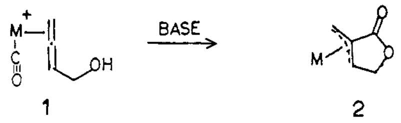
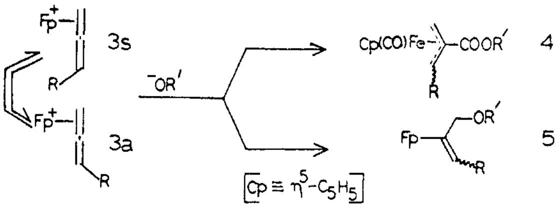
Received February 24, 1981

In our studies on the synthetic approaches to functionalized η^3-allyl transition-metal complexes such as **2**,[1] which could be used as versatile intermediates in the synthesis of biologically active lactone-containing natural products, we envisioned a general route through intermediate **1**. Rearrangement of **1** via carbonylation/lactonization might give **2**, in the presence of a suitable base. Such a rearrangement has been recently reported by us[1a] and others[1b] for M = $CpMo(CO)_2$ [Cp ≡ η^5-C_5H_5].



In the initial stages of the work the analogous iron complex (M = CpFe(CO)) was considered for the **1** to **2** transformation for the following reasons. Fp(η^2-allene) cations without hydroxyl groups [Fp = η^5-$C_5H_5Fe(CO)_2$] are readily prepared via an exchange reaction with the Fp(η^2-isobutylene) cation **8** and a free allene[2] or by protonation of Fp(η^1-propargyl) complex.[3] In addition, certain Fp(η^2-allene) cations (**3**) are known to react with external alkoxides to give carbonylated η^3-allyl complexes **4** and/or products of simple addition to the allene carbon, **5**.[4]



1-Substituted allene complexes exist as syn (**3s**) and anti (**3a**) isomers which slowly interconvert at room temperature.[2] For **1**, which has an internal nucleophile (R = CH_2OH in **3**), it is not clear which mode of attack would predominate. The intermolecular attack of water on Fp(η^2-allene) cations gives only addition to the allene carbon.[5] We report here the results of attempted synthesis of Fp(η^2-hydroxyallene) cations and the chemistry of the observed dihydrofuran products.[6]

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