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REACTION OF THE ISOMERS OF FEIST'S ESTER (DIMETHYL-METHYLENECYCLOPROPANE-2,3-DICARBOXYLATE) WITH DIIRON ENNEACARBONYL

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Summary

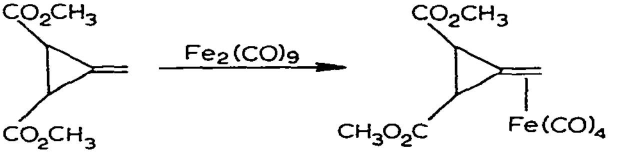
The reaction of diiron enneacarbonyl with the isomers of Feist's ester leads first to the formation of the corresponding iron tetracarbonyl olefin complexes, and then predominantly to the cleavage of the strained sp^2—sp^3 bond of the three-membered ring. This cleavage is followed by a stereospecific series of reactions leading eventually to diene—iron tricarbonyl complexes of dimethyl *cis*- and *trans*-1,3-butadiene-1,2-dicarboxylate. A minor pathway involves cleavage of the sp^3—sp^3 ring bond, and leads to the diiron species (IV). Photochemically, the iron complexes follow rather different pathways, the *cis* isomer giving products paralleling the thermal products, while the *trans* isomer gives a new product tentatively assigned an acyl (π-allyl) structure.

Introduction

The reactions of compounds containing strained carbon—carbon σ bonds with transition metals have been the subject of intensive investigation [1 - 22]. In particular, certain methylenecyclopropanes were observed by Noyori, Nishimura and H. Takaya [23] to give rise to trimethylenemethane complexes on treatment with diiron enneacarbonyl [$Fe_2(CO)_9$]. Since this reaction is of a type which conceivably could involve a concerted, electrocyclic rearrangement occurring in the coordination sphere of a transition metal, we undertook a detailed investigation of the reaction of the isomers of Feist's ester, dimethyl *cis*- and *trans*-1-methylenecyclopropane-2,3-dicarboxylate [25], [(I)-*cis* and (I)-*trans*] with $Fe_2(CO)_9$. These substrates were chosen because of their ready availability and well-defined stereochemistry, since we expected that stereochemical probes of the reaction mechanism would be most helpful.

Results

Reaction of (I)-*trans* or (I)-*cis* with an excess of $Fe_2(CO)_9$ in hexane at room temperature leads to the formation of the corresponding iron tetracarbonyl olefin complexes (II)-*trans* (88%; m.p. 45 - 46°) and (II)-*cis* (65%; m.p. 99 - 100°). The structures of these compounds were assigned on the basis of elemental analysis, spectral data, and chemical reactivity. In particular, an $Fe(CO)_4$ fragment was suggested by the observation of four metal carbonyl bands in the IR spectrum of each compound [(II)-*trans*: 2107, 2020, 2015, and 2005 cm^{-1}; (II)-*cis*: 2107, 2020, 2015, 2005 cm^{-1}] and confirmed by successive loss of up to four carbonyls in the mass spectrum. That the ring remained intact was indicated by the NMR spectra (vide infra), and by the fact that ceric ion oxidation of (II)-*trans* led to recovery of (I)-*trans*. In the NMR spectrum, (II)-*cis* exhibited a sharp singlet at δ 3.65 ppm, due to the six equivalent methyl ester protons. The isomer, (II)-*trans*, showed two three-proton singlets at δ 3.64 and 3.66 ppm confirming the unsymmetrical nature of the compound. The remainder of the spectra were likewise consistent with the proposed structures: (II)-*cis*: δ 2.45 (2H, singlet, complexed $=CH_2$) and 2.00 ppm (2H, singlet, ring protons); (II)-*trans*: δ 2.60 (2H, singlet, complexed $=CH_2$) and 2.25 (1H, doublet, J 3 Hz), and 2.15 ppm (1H, doublet, J 3 Hz, nonequivalent ring protons)*.



(I)-*cis*
(I)-*trans*

(II)-*cis*
(II)-*trans*

With the structures of the two tetracarbonyl complexes thoroughly established, we proceeded to investigate the thermal and photochemical behavior of the two isomers, in the hope that creation of a vacant coordination site would stimulate rearrangement. Thermally, the species are surprisingly stable. For example, (II)-*trans* can be recovered in 80% yield after refluxing in hexane for 72 h. At higher temperatures, e.g., refluxing toluene, the compound was destroyed, and formation of the diene complex (III)-*syn* was observed (see Scheme 1).

The same transformation may be accomplished much more cleanly at 40° in the presence of $Fe_2(CO)_9$. Thus, in 4 h (hexane solvent), approximately 50% of (II)-*trans* was destroyed, and a 78% yield of (III)-*syn* was obtained, together with a 3% yield of a new species (IV). The *cis* isomer behaved similarly; thermolysis in refluxing toluene gave (III)-*anti*, while treatment of (II)-*cis* with excess $Fe_2(CO)_9$ in hexane at 40° for 4 h led to destruction of 86% of the starting material and the formation of (III)-*anti* (88% yield) and (IV) (1.5% yield). Interestingly, the formation of the diene complexes (III)-*syn* and (III)-

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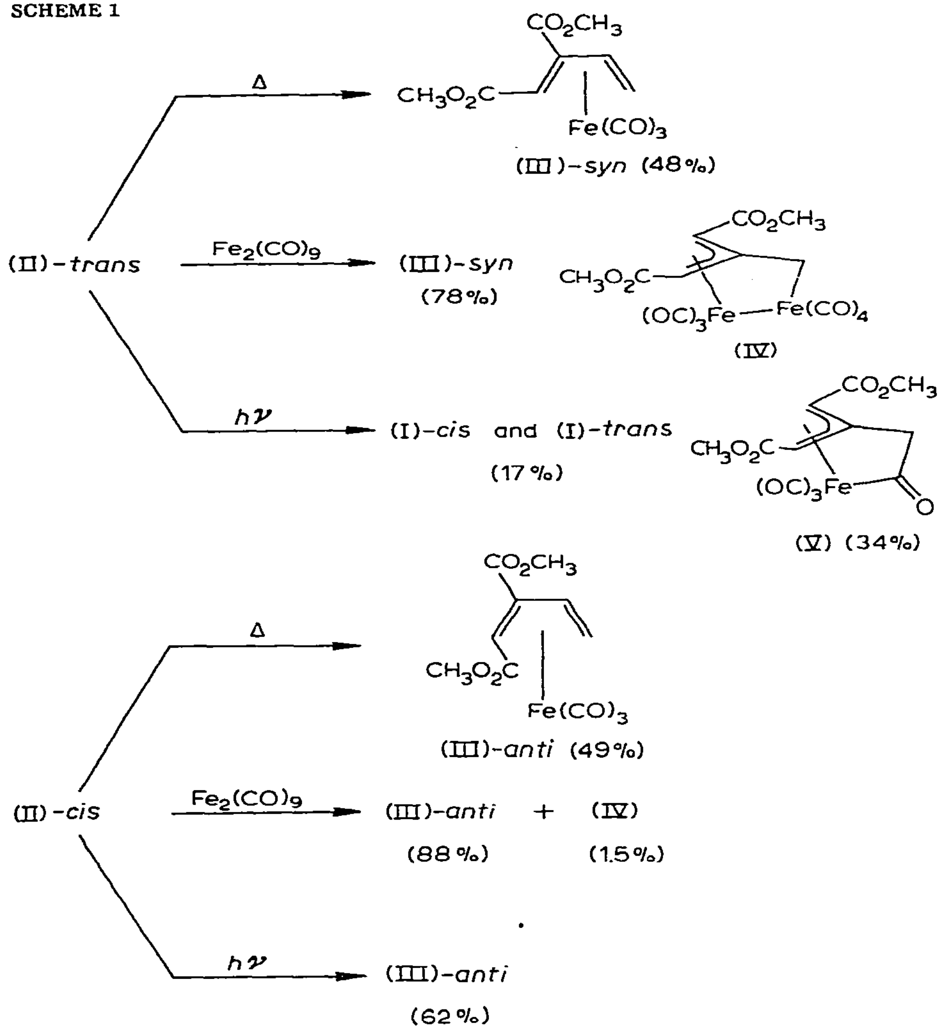
* *Note added in proof:* Experiments with Eu shift reagents indicate that the assignments of the ring and olefin protons are opposite to those suggested here [29].

SCHEME 1

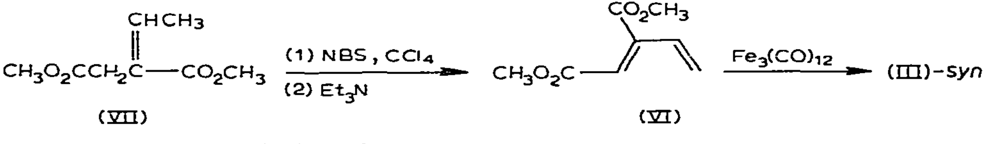


anti were completely stereospecific (to within 5%), (II)-*trans* leading to (III)-*syn* only and (II)-*cis* to (III)-*anti*.

The structures of (III)-*syn*, (III)-*anti*, and (IV) were assigned by a combination of their elemental analyses, physical properties, and independent synthesis. The major products, (III)-*syn* and (III)-*anti*, showed absorptions in the IR typical of diene—iron tricarbonyl complexes. [(III)-*syn*: 2075, 2020 and 2004 cm^{-1}; (III)-*anti*: 2075, 2020 and 2000 cm^{-1}.] In the NMR spectra, (III)-*syn* showed resonances at δ 0.45 (1H, doublet of doublets, *J* 3, 8 Hz, "internal" C_4H); 1.22 (1H, singlet, C_1H); 1.95 (1H, doublet of doublets, *J* 3, 6 Hz, "external" C_4H); 3.65 (3H, singlet) and 3.85 (3H, singlet, ester OCH_3); and 5.70 ppm (1H, doublet of doublets, *J* 6, 8 Hz, C_3H), while (III)-*anti* had peaks at δ 1.80 (1H, doublet of doublets, *J* 2, 10 Hz, "internal" C_4H); 2.20 (1H, doublet of doublets, *J* 2, 8 Hz, "external" C_4H); 2.65 (H, singlet, C_1H);

3.55 (3H, singlet) and 2.85 (3H, singlet, ester OCH_3); and 6.38 ppm (1H, doublet of doublets, J 8, 10 Hz, C_3H). The stereochemistry of the complexes is assigned on the basis of the higher field resonance of C_1H in (III)-*syn* than (III)-*anti*. Previous workers [25] have shown that protons in diene—iron tricarbonyl complexes which are on the "inside" of the complex resonate at higher field than those on the "outside". Further, (III)-*syn* was independently synthesized by the route shown in Scheme 2. The starting material for this synthesis was obtained by the method of Trost and Melvin [26].

SCHEME 2



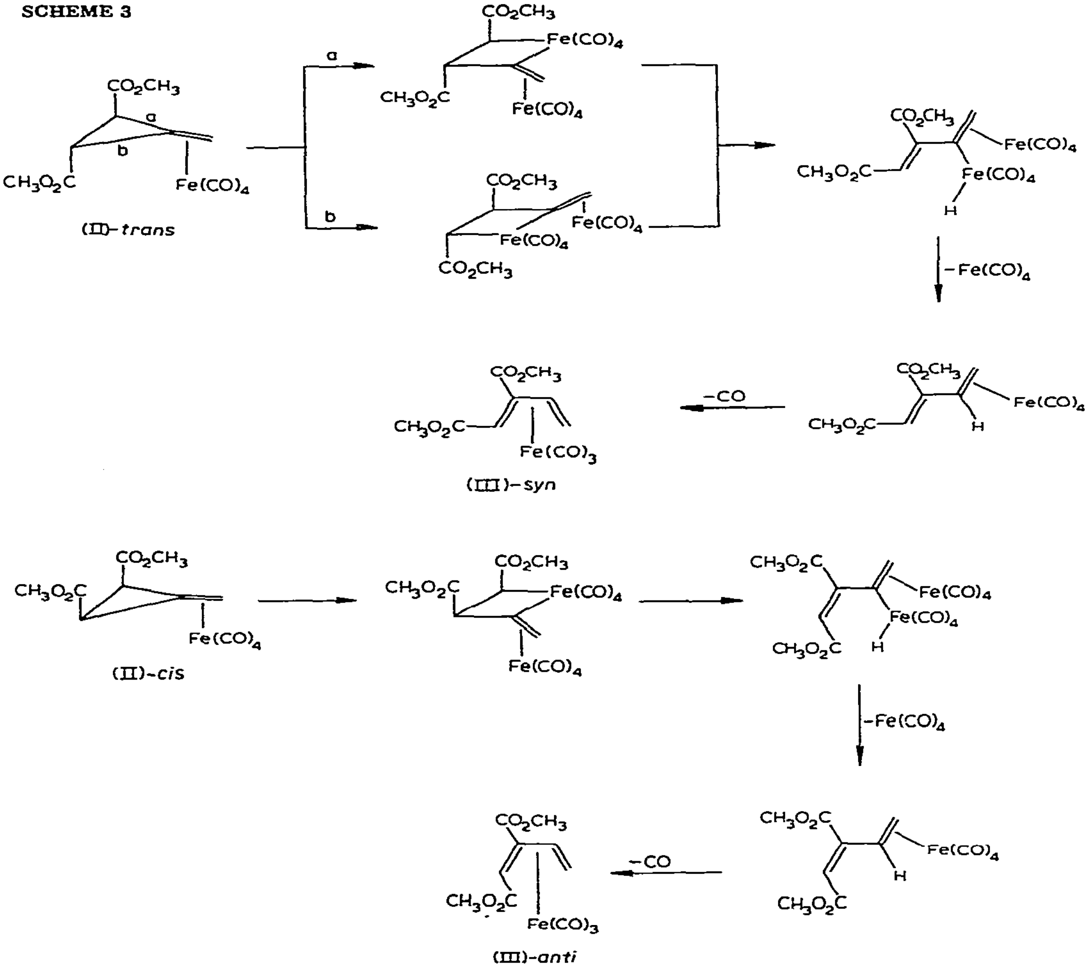
The compound (IV), formed in low yield from either (II)-*cis* or (II)-*trans*, was a deep red solid, m.p. 71 - 72°. It displayed two different methyl resonances at δ 3.55 and 3.68 ppm. The two protons on the π-allyl position of the ligand appeared as singlets at δ 3.70 and 4.10 ppm. The geminal protons were an AB quartet with a coupling constant of 17.5 Hz ($\Delta\nu$ 32 Hz) centered at δ 2.40 ppm. Five metal carbonyls could be distinguished in the IR and the elemental analysis was consistent with the formula $C_{15}H_{10}Fe_2O_{11}$. The large geminal coupling indicates substantial rehybridization at C_4.

While the thermal chemistry of (II)-*cis* and (II)-*trans* is analogous, the photochemical behavior of these compounds is quite distinct. Under irradiation with UV light, (II)-*cis* again rearranged predominantly to (III)-*anti* (62%) in a stereospecific manner. In contrast, (II)-*trans* underwent a completely different reaction to give as the principal product an unstable, yellow oil (34%) which has been tentatively assigned the structure (V), together with a 17% yield of a mixture of (I)-*cis* and (I)-*trans*. Neither of the diene complexes were found. The NMR spectrum of (V) displays two methyl singlets at δ 3.30 and 3.45 ppm. The protons on the π-allyl ligand gave two doublets (J 2 Hz) at δ 4.6 and 5.45 ppm, while the geminal protons consisted on an ABX pattern at δ 4.0 ppm (J_{AB} 9, J_{AX} 0, J_{BX} 2 Hz, $\Delta\nu$ 39 Hz). The IR of (V) consisted of three metal carbonyl absorptions (2123, 2070, 2024 cm^{-1}), two separate ester absorptions at 1739 and 1709 cm^{-1} and an absorption at 1670 cm^{-1} attributed to the metal acyl carbonyl stretch. Unfortunately, the instability of the species precluded accurate elemental analysis.

Discussion

The principle novel feature of this work involves the stereospecific rearrangement of (II)-*cis* and (II)-*trans* to give the diene complexes (III)-*anti* and (III)-*syn*, respectively. Noyori and coworkers [16] detected butadiene iron tricarbonyl as a product from the reaction of methylenecyclopropane itself with $Fe_2(CO)_9$, but this product was formed in relatively low yield, and no information concerning the stereochemistry or molecularity of the process was available. Our results strongly suggest that the rearrangement observed involves more than one metal center. The stereochemistry of the process can be conveniently rationalized by the following sequence (Scheme 3): *1*, oxidative addition of the strained sp^2—sp^3 bond to a coordinatively unsaturated $Fe(CO)_4$ fragment; *2*, *cis*-elimination of metal hydride; *3*, reductive elimination of alkene; and *4*, elimination of CO and formation of the diene complex. It should be noted that it makes no difference which of the sp^3—sp^2 bonds is attacked in (II)-*trans*; the predicted stereochemistry is the same.

SCHEME 3



Reactions somewhat similar to these have been observed for the reaction of certain cyclopropene derivatives with platinum [27] or silver [28] derivatives. The formation of the diiron species (IV) in low yield seems to be completely non-stereospecific. Apparently, the ease of cleavage of the sp^3—sp^3 bond of the methylenecyclopropane is a sensitive function of the substituents on the ring, since Noyori et al. [23], who studied aryl-substituted methylenecyclopropanes predominantly, observed the cleavage of this bond to be the major reaction pathway.

The remaining interesting feature of our reactions is the differing photochemical behavior of (II)-*cis* and (II)-*trans*. The photochemical behavior of (II)-*cis* parallels its thermal behavior in its principle characteristics. The reaction of (II)-*trans*, on the other hand, takes a completely different course, the absorption of light resulting in formation of (I)-*cis*, (I)-*trans* and (V). The pathway(s) by which *both* (I)-*cis* and (I)-*trans* are formed is obscure. Presumably, the unique reactivity of (II)-*trans* is due in some fashion to the ester function which must be *cis* to the metal in (II)-*trans*. Such a function need not be *cis* to the metal in (II)-*cis*; indeed, for steric reasons, the stereochemistry of (II)-*cis* is probably as shown in Scheme 3.

Experimental

General

All reactions were carried out under a nitrogen atmosphere. Hydrocarbon solvents were stirred with concentrated H_2SO_4 and distilled. Ethereal solvents were refluxed with benzophenone dianion and distilled under nitrogen. All solvents were degassed before use by passing a stream of nitrogen through them for several minutes. Infra-red spectra were obtained on hydrocarbon or CS_2 solutions with a Beckman IR-8, and NMR spectra were obtained on Varian T-60 or A60A spectrometers. Analyses were performed by Gailbraith Laboratories, Inc., Knoxville, Tenn.

Preparation of (II)-trans

Diiron enneacarbonyl (5.5 g, 15 mmol) and 40 ml hexane were placed in a 100 ml flask equipped with a magnetic stirrer and nitrogen inlet. After purging with nitrogen, 1.00 g (5.9 mmol) of (I)-*trans* was added and the reaction stirred at room temperature for 4 h. The excess $Fe_2(CO)_9$ was filtered off and the solvent evaporated to yield 1.62 g (88%) of light tan crystals. Vacuum sublimation gave (II)-*trans* as off-white crystals, m.p. 45 - 46°, NMR (CS_2): δ 3.66 (3H, s); 3.64 (3H, s); 2.60 (2H, s); 2.25 (1H, d, J 3Hz); 2.15 ppm (1H, d, J 3Hz). IR (CS_2): 2107 (m), 2020 (s), 2015 (s), 2005 (s) and 1730 cm^{-1}. UV(cyclohexane) 190 nm (ϵ 11,000). (Found: C, 42.66; H, 2.81; Fe, 16.34. $C_{12}H_{10}FeO_8$ calcd.: C, 42.65; H, 2.96; Fe, 16.53%.)

Preparation of (II)-cis

The complex (II)-*cis* was prepared using (I)-*cis* in a manner analogous to the preparation of (II)-*trans*: off-white crystals, 65% yield, m.p. 99 - 100°; NMR (CS_2), δ 3.65 (6H, s); 2.45 (2H, s); and 2.00 ppm (2H, s); IR (CS_2), 2107, 2020, 2015, 2005 and 1730 cm^{-1}. UV (Cyclohexane) 189 nm (ϵ 10,700).(Found: C, 42.56; H, 2.88; 16.37. $C_{12}H_{10}FeO_8$ calcd.: C, 42.65; H, 2.96; Fe, 16.53%.)

Oxidation of (II)-trans with $Ce(NH_4)_2(NO_3)_6$ [CAN]

Complex (II)-*trans* (100 mg, 0.296 mmol) was dissolved in 1 ml of methanol. A solution of CAN (2 mmol in 8 ml methanol) was added dropwise until gas evolution ceased (approximately 4.3 ml). The solution was diluted with water and extracted with ether which was dried, filtered and evaporated.

The residue (44 mg, 88%) was shown by NMR and TLC to be (I)-*trans* with no evidence of (I)-*cis* or any other isomer.

Reaction of (II)-cis with $Fe_2(CO)_9$

In a typical experiment a flask equipped with a nitrogen inlet and a magnetic stirrer was charged with 60 ml of degassed hexane, 100 mg (0.296 mmol) of (II)-*cis* and 200 mg (0.55 mmol) of $Fe_2(CO)_9$. The reaction was warmed to 40° and stirred under nitrogen for 4 h. The solution was cooled and filtered, and the hexane evaporated under reduced pressure. The residue was subjected to column chromatography on silica gel. Elution with hexane gave a red band [(IV), 1.5%]. Elution with benzene gave a broad yellow band (mixture of (II)-*cis*, 12%, and (III)-*anti*, 88%). (III)-*anti* was subsequently purified by preparative thick layer chromatography (Silica Gel PF 254, 5% Et_2O, C_6H_6 eluant, repeated development). Complex (IV) is a deep red solid, m.p. 71 - 72°. NMR (CS_2), δ 2.40 (2H, AB quartet, J_{AB} 17.5 Hz, $\Delta\nu$ 32 Hz); 3.55 (3H, s); 3.68 (3H, s); 3.70 (1H, s); and 4.10 ppm (14, s). IR (CS_2), 2079, 2032, 2008, 1992, 1972 and 1739 cm^{-1}. (Found: C, 37.59; H, 2.24; Fe, 23.09. $C_{15}H_{10}Fe_2O_{11}$ calcd: C, 37.70; H, 2.11; Fe, 23.38%.)

(III)-*anti* is a yellow solid, m.p. 60 - 61°. NMR (CS_2), δ 1.80 (1H, dd, J 2, 10 Hz); 2.20 (1H, dd, J 2, 8 Hz); 2.65 (1H, s); 3.55 (3H, s); 3.85 (3H, s); and 6.38 ppm (1H, dd, J 8, 10 Hz). IR (CS_2) 2075, 2020, 2000, and 1710 cm^{-1}. (Found: C, 42.80; H, 3.34; Fe, 17.81. $C_{11}H_{10}FeO_7$ calcd.: C, 42.63; H, 3.23; Fe, 18.02%.)

Reaction of (II)-trans with $Fe_2(CO)_9$

This reaction was performed in a manner analogous to that described for (II)-*trans*. Chromatography as before gave 55% recovered (II)-*trans*, 3% [based on recovered (II)-*trans*] (IV), and 78% [based on recovered (II)-*trans*] (III)-*syn*.

(III)-*syn* is a yellow solid, m.p. 62°. NMR (CS_2), δ 0.45 (1H, dd, J 3, 8 Hz); 1.22 (1H, s); 1.95 (1H, dd, J 3, 6 Hz); 3.65 (3H, s); 3.85 (3H, s); and 5.70 ppm (1H, dd, J 6, 8 Hz). IR (CS_2) 2075, 2020, 2004, 1724—1694 cm^{-1} (br). (Found: C, 42.78; H, 3.23; Fe, 17.93. $C_{11}H_{10}FeO_7$ Calcd.: C, 42.63; H, 3.23; Fe, 18.02%.)

Attempted thermal isomerization of (II)-trans in hexane

Complex (II)-*trans* (50 mg, 0.147 mmol) was dissolved in 50 ml of hexane and the solution placed in a 100 ml flask equipped with a reflux condenser, magnetic stirrer, and nitrogen inlet. After purging with nitrogen the reaction was heated under reflux. The progress of the reaction was checked periodically by IR. No appreciable change was observed. After 72 h the reaction was cooled, filtered under nitrogen and the solvent evaporated. The residue was an oil (40 mg) whose NMR was identical with starting material (80% recovery).

Thermal rearrangement of (II)-trans in refluxing toluene.

(II)-trans (400 mg; 1.18 mmol) was dissolved in 70 ml of dry, degassed toluene in a 100 ml flask equipped with a magnetic stirrer, reflux condenser and nitrogen inlet. After purging with nitrogen, the solution was heated under

reflux for 90 min. After cooling, the solution was filtered under nitrogen and the toluene evaporated. The residue was subjected to preparative thick layer chromatography (Silica Gel PF-254, 5% Et_2O/benzene eluant). One major band was collected and shown to be (III)-*syn* (175 mg, 48%).

Thermal isomerization of (II)-cis in refluxing toluene

When (II) *cis* (250 mg, 0.74 mmol) was allowed to react in 50 ml refluxing toluene for 35 min, and worked up as described for (II)-*trans*, 150 mg of a 3/1 NMR mixture of (III)-*anti* and starting material were obtained. This mixture corresponds to a 49% yield of (III)-*anti* based on recovered starting material.

Photolysis of (II)-cis

The photolysis was carried out using a 450 W Hanovia Hg vapor lamp with a pyrex filter. One hundred milligrams (0.296 mmol) (II)-*cis* was dissolved in 75 ml of hexane in a cylindrical photolysis vessel equipped with a nitrogen inlet. After 4 minutes of irradiation the solution was filtered under nitrogen and the solvent evaporated. The residue (92 mg) was identified by NMR as a mixture of (II)-*cis* and (III)-*anti* in a 1/1.15 ratio, corresponding to a 63% yield of (III)-*anti* based on recovered starting material. In similar experiments, these materials were isolated and characterized as before.

Photolysis of (II)-trans

The photolysis of (II)-*trans* (100 mg, 0.296 mmol) was carried out in a manner analogous to that described for (II)-*cis*. Preparative thick layer chromatography (PF-254, 3% Et_2O/benzene eluant) gave 3 bands. The top band gave 9 mg (17% yield) [based on recovered (II)-*trans*] of a mixture of (I)-*cis* and (I)-*trans*. The middle band gave 34 mg (34% recovery) (II)-*trans*. The most polar band gave 34 mg (34% yield) of complex (V).

Complex (V) was obtained as an unstable yellow oil, which changed color on standing under nitrogen in the refrigerator. NMR (benzene-d_6), δ 3.30 (3H, s); 3.45 (3H, s); 4.10 (2H, ABX, J_{AB} 9, J_{AX} 0, J_{BX} 2 Hz, $\Delta\nu$ 39 Hz); 4.6 (1H, d, J 2Hz); 5.45 ppm (1H, d, J 2 Hz). IR (CS_2), 2123, 2070, 2024, 1739, 1709, 1670 cm^{-1}. Because of the instability of this species and the presence of persistant impurities, adequate elemental analysis could not be obtained.

Preparation of diene diester (VI)

In a 500 ml round bottom flask equipped with a magnetic stirrer and reflux condenser was placed 250 ml of CCl_4, 21 g (0.12 mol) of (VII) and 21 g (0.12 mol) of NBS. This mixture was refluxed and irradiated with a 275 W sun lamp. A small amount of benzoyl peroxide was added and the reaction commenced immediately. After 1 h heating and irradiation the reaction was cooled, filtered, and the solvent evaporated, yielding 27 g of red oil. The oil was vacuum distilled and one fraction, b.p. 115°/0.2 mm was collected giving 26 g (83%) of a mixture of mono-bromide isomers, which was used without purification. One gram (4.0 mmol) mono-bromide was dissolved in 10 ml of benzene in a 25 ml flask equipped with reflux condenser and magnetic stirrer and 0.6 g (6.0 mmol) of triethylamine was added. The solution was heated under reflux for 1 h. The reaction was cooled, filtered, and the benzene evaporated. The residue was column chromatographed (Silica Gel). Benzene eluted 300 mg (44%) of diene diester (VI). NMR (CCl_4); δ 3.7 (3H, s); 3.8 (3H, s); 5.50 (1H, d, J 17 Hz); 5.55 (1H, d, J 10 Hz); 5.80 (1H, s); 6.40 ppm (1H, dd, J 10, 17 Hz). IR (CCl_4), 1720—1730 (br), 1640—1600 cm^{-1}.

Preparation of (III)-syn from (VI)

150 mg (0.3 mmol) and 50 mg (0.296 mmol) of (VI) were dissolved in 10 ml of benzene in a 25 ml flask equipped with reflux condenser, magnetic stirrer and nitrogen inlet. After purging with nitrogen the reaction was heated under reflux for 3 h. The reaction was cooled, filtered under nitrogen, and the solvent evaporated. The residue was subjected to preparative thick layer chromatography (Silica Gel PF-254, 5% Et_2O/benzene eluant) and one major band isolated (26 mg). This material was identical to (III)-*syn* in all respects.

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