(m, 4), 2.1–2.7 (m, 4), 7.0–7.4 (m, 5); exact mass calcd for $C_{12}H_{13}Br$ 236.0201, found 236.021.

Likewise, benzylidenecyclohexane[25] was converted in 84% yield into **5c**: bp 135–137 °C (0.2 torr); NMR δ 1.47 (m, 6), 2.08 (m, 2), 2.52 (m, 2), 7.0–7.3 (m, 5); exact mass calcd for $C_{13}H_{15}Br$ 250.0357, found 250.038.

(25) Seyferth, D.; Hughes, W. B.; Heeren, J. K. *J. Am. Chem. Soc.* **1965**, *84*, 2847.

Registry No. **1a**, 68275-02-5; **1b**, 3416-75-9; **1c**, 57718-13-5; **1d**, 35843-78-8; **1e**, 42049-41-2; **1f**, 16664-48-5; **1g**, 57718-12-4; **1h**, 92078-64-3; **1i**, 42049-47-8; **1j**, 92078-65-4; **1k**, 57718-14-6; **1l**, 57718-15-7; **1m**, 92078-66-5; **1n**, 92078-67-6; **1o**, 92078-68-7; **3** (R = n-C_4H_9, n = 4), 53366-55-5; **3** (R = C_6H_5, n = 4), 4410-77-9; **3** (R = C_6H_5, n = 5), 1608-31-7; **3** (R = p-FC_6H_4, n = 4), 92078-69-8; **3** (R = p-$CH_3C_6H_4$, n = 4), 92078-70-1; **3** (R = p-$CH_3OC_6H_4$, n = 4), 20758-63-8; **3** (R = C_6H_5, n = 3), 5244-75-7; **5a**, 82833-97-4; **5b**, 57718-23-7; **5c**, 92078-71-2; $Cr(ClO_4)_2$, 13931-95-8; Bu_3SnH, 688-73-3.

1,4-Addition to Tetracyclone. Kinetic vs. Thermodynamic Product Distribution

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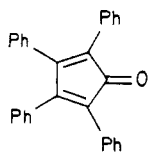
The Michael addition of cyanide ion to tetracyclone produces an enolate (**4a**) which, when protonated, affords a diastereomeric mixture of *cis*- (**5a**) and *trans*-4-cyano-2,3,4,5-tetraphenyl-2-cyclopenten-1-one (**6a**) in varying ratios depending upon the conditions employed. Quenching the enolate at low temperatures affords mainly the cis isomer, the kinetic product, while high temperature quench favors the trans isomer, the thermodynamic product. Base, acid, and heat were used to interconvert the cis and the trans isomers into a thermodynamic equilibrium ratio of products. Protonation of the enolate (**4b**) of 4-methoxy-2,3,4,5-tetraphenyl-2-cyclopenten-1-one gave similar results. Methylation of both enolates **4a** and **4b** is also reported as well as the structure elucidation of the isomers obtained from the above reactions.

Introduction

Reports in the literature concerning 1,4-addition to tetracyclone (**1**) are rare. In 1943, Allen and VanAllan[2] reported that the Michael addition of phenylmagnesium bromide to tetracyclone afforded 2,3,3,4,5-pentaphenyl-1,4-cyclopentadien-1-ol (**2**). However, reinvestigation of



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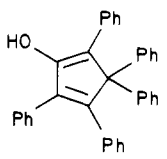

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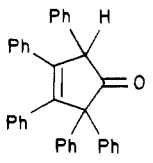
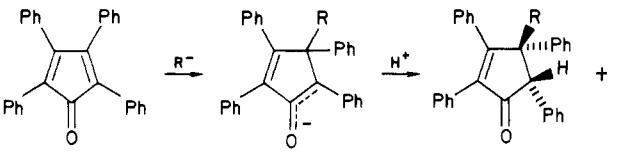


3

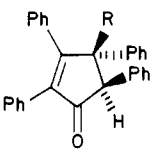
this reaction in our laboratories[3] in 1972 demonstrated that this reaction actually proceeded by a 1,2-addition of phenylmagnesium bromide followed by a thermally allowed [1,5]-sigmatropic rearrangement affording 2,2,3,4,5-pentaphenyl-3-cyclopenten-1-one (**3**). 1,4-Addition has also been reported[4] in the reaction of tetracyclone with 1-indenyl- and 9-fluorenyllithium, and these results are currently under reinvestigation in our laboratories.

In 1971, Gallagher and Jenkins[5] described the Michael addition of selected organophosphorus compounds to tetracyclone and since then, several other papers[6-8] have appeared describing similar additions. However, due to the contradictory nature of these papers, it appears that the true nature of these reactions is still not completely understood.

Scheme I



1 → **4a**, R=CN; **b**, R=OMe → **5a**, R=CN; **b**, R=OMe



6a, R=CN; **b**, R=OMe

The only unquestioned report of Michael addition to tetracyclone was published in 1975 by Muckenstrum,[9] who studied the addition of various bases to tetracyclone. In this paper, we wish to extend the series of nucleophiles

(1) Presented at the 35th Southeastern Regional Meeting of the American Chemical Society, Charlotte, NC, Nov 10, 1983.
(2) Allen, C. F. H.; VanAllan, J. A. *J. Am. Chem. Soc.* **1943**, *65*, 1384.
(3) Youssef, A. K.; Ogliaruso, M. A. *J. Org. Chem.* **1972**, *37*, 2601.
(4) Bergman, E. D.; Berthier, G.; Ginsburg, D.; Hirshberg, Y.; Lavie, D.; Pinchas, S.; Pullman, B.; Pullman, A. *Bull. Soc. Chim. Fr.* **1951**, *18*, 661.
(5) Gallagher, M. J.; Jenkins, I. D. *J. Chem. Soc. C* **1971**, 210.
(6) Miller, J. A.; Stevenson, G. M.; Williams, B. C. *J. Chem. Soc. C* **1971**, 2714.
(7) Arbuzov, B. A.; Fuzhenkova, A. V.; Galyautdinov, N. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1978**, 440; *Chem. Abstr.* **1978**, *89*, 6366h.
(8) Fuzhenkova, A. V.; Galyautdinov, N. I.; Arbuzov, B. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1132; *Chem. Abstr.* **1978**, *89*, 109762p.
(9) Muckenstrum, B. *Tetrahedron* **1975**, *31*, 1933.

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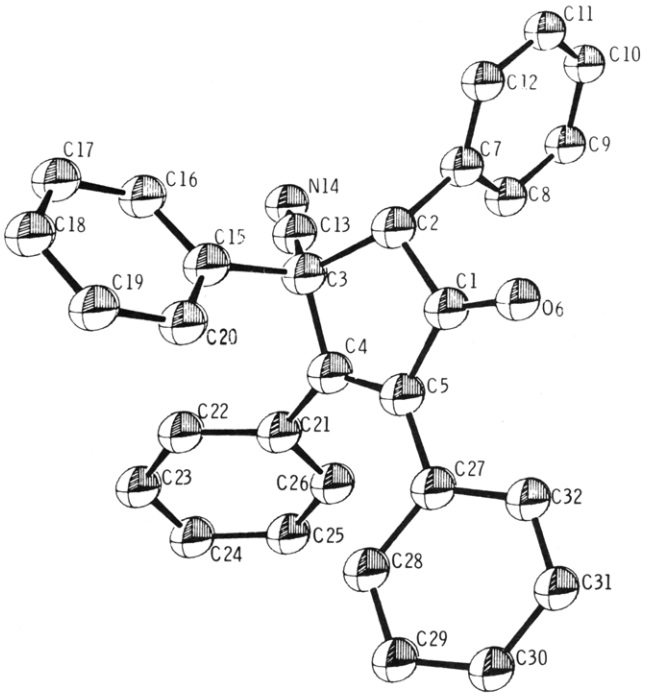


Figure 1. Computer-generated drawing of one of the independent molecules of *trans*-4-cyano-2,3,4,5-tetraphenyl-2-cyclopenten-1-one (**6a**) derived from the X-ray coordinates with hydrogens omitted for clarity.

which react with tetracyclone in a 1,4-manner to include cyanide ion and to report on the kinetic versus thermodynamic products which result from this addition.

Results and Discussion

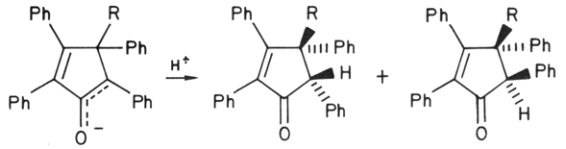
Treatment of tetracyclone (**1**) with potassium cyanide, followed by protonation of the intermediate enolate **4a**, afforded a pair of diasteromeric enones resulting from 1,4-addition of cyanide (Scheme I) The structures of the *cis*-**5a** and *trans*-**6a** isomers were assigned on the basis of their IR, ^{1}H NMR, ^{13}C NMR, and X-ray spectral data.

Both **5a** and **6a** show a carbonyl absorption at 1720 cm^{-1} which is indicative of a five-membered ring α,β-unsaturated ketone; however, the isomers differ in the position of the methine proton in the NMR. The methine proton of **5a** has a chemical shift of 4.81 ppm, while the methine proton of **6a** occurs at 4.16 ppm. Likewise, in the ^{13}C NMR, the chemical shift of the nitrile carbon differs for both isomers. The ^{13}C spectrum for **5a** shows a singlet at 120.4 ppm for this carbon, while **6a** shows a singlet at 118.0 ppm for the same carbon.

On the basis of these observations, the assignment of cis and trans can be rationalized upon shielding and deshielding arguments. In the cis case (**5a**), the proton is above the triple bond of the nitrile in a deshielding environment which produces the downfield chemical shift. In the trans case (**6a**), the proton and nitrile carbon are both located above an aromatic ring in a shielding environment. This shielding effect results in an upfield chemical shift for the methine proton as well as the nitrile carbon. In addition, the structure of the trans isomer (**6a**) was confirmed by X-ray crystallographic analysis (Figure 1).

Initial studies of the reaction of **1** with potassium cyanide resulted in varying ratios of **5a** to **6a** depending upon the temperature at which protonation of the enolate **4a** occurred. As can be seen in Table I, protonation at lower temperatures (i.e., 0 or 27 °C) resulted in the cis isomer (**5a**) being the major isomer, while at elevated

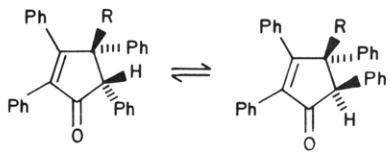
Table I. Effect of Temperature and Solvent on Protonation of Enolates 4a and 4b



4a, R=CN **b**, R=OMe **5a**, R=CN **b**, R=OMe **6a**, R=CN **b**, R=OMe

enolate	temp, °C	solvent	ratio **5**/**6**
4a	0	DMF	91/9
	0	Me_2SO/C_6H_6	91/9
	27	DMF	84/16
	27	Me_2SO/C_6H_6	84/16
	90	Me_2SO/C_6H_6	30/70
4b	0	Me_2SO/C_6H_6	59/41
	27	Me_2SO/C_6H_6	60/40
	90	Me_2SO/C_6H_6	58/42

Table II. Thermodynamic Isomerization of Ketones 5 and 6



5a, R=CN **b**, R=OMe **6a**, R=CN **b**, R=OMe

isomerization mode	starting isomer	time	temp, °C	ratio **5**/**6**
base (CN^-)	**5a**	3 h	27	29/71
	6a	4 h	27	27/73
	5a	5 min	27	61/39
	5b	2 h	27	81/19
	6b	2 h	27	81/19
acid (H^+)	**5a**	3 h	27	57/43
	5a	5 min	90	33/67
	6b	6 h	27	23/77
	6b	98 h	27	81/19
heat	**5a**	15 min	90	82/18
	5a	3 h	90	32/68

temperatures (i.e., 90 °C), the trans isomer (**6a**) was the major isomer.

Clearly, what was occurring was a change from a kinetic protonation of the enolate **4a** to a thermodynamic protonation of the same enolate, affording **5a** as the kinetically controlled product and **6a** as the thermodynamically controlled product. It appears logical that the cis isomer (**5a**) represents the kinetic product, since it is the product obtained by protonation from the least hindered side (i.e., the same side on which the cyanide group is located), while the trans isomer (**6a**) represents the more stable thermodynamic product which positions the two bulky phenyl groups on opposite sides of the ring.

To test the validity of this hypothesis, a series of experiments (Table II) were performed to determine if **6a** was, indeed, the thermodynamically more stable isomer and the extent to which this isomer was favored when different isomerization modes were used. The three isomerization methods employed to convert a single pure isomer, either **5a** or **6a**, into its thermodynamic equilibrium composition were base, acid, and heat.

In the base-catalyzed mode, the pure isomers were separately subjected to potassium cyanide at room temperature, and regardless of which isomer was chosen as the starting material, the isomer ratio obtained was approximately 30 to 70 with the trans isomer (**6a**) dominating. (The 5-min entry simply demonstrates that equilibrium

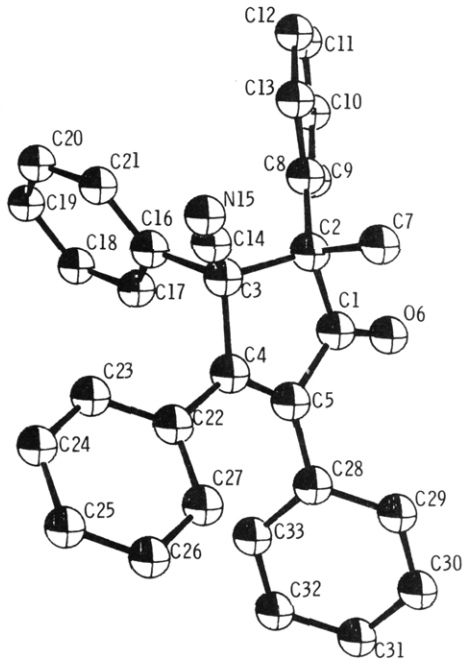
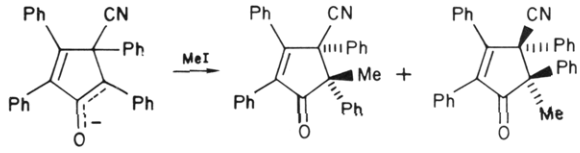


Figure 2. Perspective drawing of one of the independent molecules of *cis*-1,2,3,4-tetraphenyl-4-cyano-5-methyl-2-cyclopenten-1-one (**7**) derived from the X-ray coordinates with hydrogens omitted for clarity.

Table III. Effect of Temperature and Solvent upon Methylation of 4a



temp, °C	solvent	ratio 7/8
0	DMF	92/8
0	Me_2SO/C_6H_6	92/8
27	DMF	89/11
27	Me_2SO/C_6H_6	90/10

had not yet been established.)

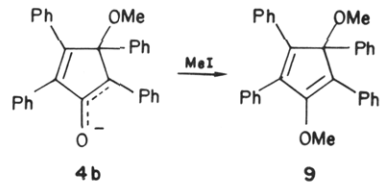
Acid-catalyzed isomerization of the cis isomer (**5a**) at 90 °C produced an isomer ratio of 33 to 67, for **5a** to **6a**, respectively, within 5 min, while at room temperature (ca. 27 °C), equilibrium had not been established at the end of 3 h.

Finally, thermal-catalyzed isomerization of the cis isomer (**5a**) at 90 °C for 3 h resulted in a 32 to 68 ratio of **5a** to **6a**, respectively. Thus, approximately the same ratio of **5a** to **6a** was obtained by the three different modes of isomerization.

Due to the reversible nature of the protonation of enolate **4a**, it was decided to investigate the irreversible kinetic quench of the enolate using methyl iodide (Table III). As expected, methylation of enolate **4a** at either room temperature (27 °C) or 0 °C afforded the kinetic cis isomer (**7**) as the most abundant product. Confirmation of the structure of this product was again obtained by X-ray crystallographic analysis (Figure 2).

As a result of these findings, an investigation of the kinetic and thermodynamic protonation of enolate **4b**, as well as a study of the products obtained upon quenching enolate **4b** with methyl iodide, was undertaken. Enolate **4b** was obtained via the literature[9] method by treating tetracyclone (**1**) with either a solution of Triton B or potassium methoxide in a 1:1 benzene/Me_2SO solvent system. Although both bases gave identical results, the product obtained from the Triton B experiment was more difficult to analyze because of the benzyl methyl ether present which also interfered with the ^1H NMR analysis of the isomer mixtures obtained. For this reason, only reactions of potassium methoxide in methanol were used on all runs in which ratios of **5b** to **6b** were to be determined.

Scheme II



As can be seen from Table I, there appears to be no temperature dependence for protonation of enolate **4b**. All three temperatures (0, 27, and 90 °C) gave approximately the same ratio of *cis*-**5b** to *trans*-**6b** of 60 to 40. Thus, the cis isomer (**5b**) appears to be the kinetically favored product, but not by much, and the kinetic protonation of either enolate **4a** or **4b** resulted in the formation of the cis isomer (**5a** or **5b**) as the major product. The temperature dependence of the **5a** to **6a** ratio can be attributed to the ease of enolizability of this isomer pair over the **5b** and **6b** isomer pair, which show no temperature dependence of their ratio. This ease of enolizability, especially at the higher temperatures, results in the formation of the more stable thermodynamic isomer of the pair.

However, the isomerization experiments (Table II) of ketones **5b** and **6b** did provide some interesting results. The base-catalyzed isomerization of either the cis isomer (**5b**) or the trans isomer (**6b**) resulted in the same isomer ratio (**5b** to **6b**) of 81 to 19. Likewise, the acid-catalyzed isomerization of the trans isomer (**6b**) gave exactly the same ratio after equilibrating for 98 h. Unfortunately, both isomers decomposed to tetracyclone (**1**) and methanol under thermal conditions before equilibration could occur. As a result, the data from the thermal isomerization cannot corroborate the data obtained from the base- and acid-catalyzed rearrangements.

Thus we found the cis isomer (**5b**) to be both the kinetic and thermodynamic product from protonation of **4b**, and that the literature[9] claim that the ratio of **5b** to **6b** for the kinetic protonation of **4b** was identical with that obtained for thermodynamic protonation was incorrect.

Last, we investigated the methylation of **4b** (Scheme II). Treatment of **4b** with excess methyl iodide produced a 95% yield of the O-methylated product **9**, while methylation of **4a** afforded a 90% yield of C-methylated products (**7** plus **8**). It appears that steric and/or electronic effects are responsible for this observed difference in the site of methylation, since in **4a**, it appears that there is more electron density on the carbon atom of the enolate than on the oxygen atom, while in **4b**, the electron density resides mainly on the oxygen atom of the enolate. This can be accounted for by interaction of the methoxide oxygen lone pairs with the adjacent p orbital of the enolate, thus increasing the electron density of the enolate oxygen atom. As a result, O-methylation predominates in this system.

Experimental Section

General Procedures. Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. The infrared spectra were recorded on a Perkin-Elmer 710B spectrophotometer with salt plates. ^1H NMR spectra were determined at 90 MHz on a Varian EM-390, while ^{13}C NMR spectra

were recorded at 50 MHz on a JEOL FX-200 and on a Bruker NP200. NMR chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (Me_4Si) as the internal standard. Mass spectra and exact mass determinations were obtained on a Varian Mat 112 mass spectrometer at 70 eV ionizing voltage. Elemental analyses were performed by Multi Chem Laboratories, Inc., Lowell, MA. All solvents were purified by standard methods prior to use and all reactions were run in oven-dried glassware under an atmosphere of dry nitrogen. Tetracyclone (1) was prepared by the method of Johnson and Grummitt[10] and was used without further purification.

Crystallographic Analysis. Crystals of **6a** formed in symmetry space group $P\bar{1}$ with a = 14.428 (3) Å, b = 15.954 (1) Å, c = 10.609 (4) Å, α = 104.40 (2)°, β = 109.48 (2)°, and γ = 84.16 (1)° for Z = 4. An automatic four circle diffractometer equipped with Cu radiation (λ 1.5418 Å) was used for data collection. Of the 6021 reflections measured with $2\theta \leq 114°$, 4970 were observed and corrected for Lorentz and polarization effects. A multisolution tangent formula approach[11a,b,d] with recycling[12] of initially found fragments gave positions for a majority of the non-hydrogen atoms. Subsequent least-squares refinements and difference Fourier analysis gave positions for the remainder of the atoms. The function $\sum\omega(|F_o| - |F_c|)^2$ with $\omega = (1/\sigma F_o)^2$ was minimized to give an unweighted residual of 0.045. Figure 1 is a perspective drawing showing one of the independent molecules of **6a**; the other molecule has essentially the same conformation. There are no close intermolecular contacts. The phenyl groups at C2 and C3 in Figure 1 are trans to one another and, because of crowding, the five-membered rings are somewhat distorted from planarity.

Suitable crystals of **7** for X-ray diffraction studies were formed from an ethyl alcohol solution. The space groups symmetry was $P2\ 1/c$ with a = 8.983 (1) Å, b = 16.254 (2) Å, c = 15.988 (2) Å, and β = 98.22 (1)° for Z = 4. Of the 3105 reflections measured with an automatic four circle diffractometer equipped with Cu radiation, 2119 were observed ($I > 3\sigma I$). The structure was solved with a multisolution tangent formula approach and difference Fourier analysis and refined with full-matrix least-squares techniques.[11a,c,d] Hydrogens were assigned isotropic temperature factors corresponding to their attached atoms. The function $\sum\omega(|F_o| - |F_c|)^2$ with $\omega = (1/\sigma F_o)^2$ was minimized to give an unweighted residual of 0.039. Figure 2 is a perspective drawing showing one of the independent molecules of **7**; the other molecule has essentially the same conformation. Tables IV–IX (supplementary material) contain the final fractional coordinates, temperature parameters, bond distances, and bond angles for **6a** and **7**.

***cis*-1,2,3,4-Tetraphenyl-4-cyano-2-cyclopenten-1-one (5a).** Into a 250-mL three-necked flask equipped with a magnetic stirring bar was placed 2.0 g (5.2 mmol) of tetracyclone (**1**), 0.50 g (7.7 mmol) of potassium cyanide, 60 mL of benzene, and 60 mL of dimethyl sulfoxide (Me_2SO). This mixture was stirred at room temperature (27 °C) for 5 h and was then placed into an ice bath for an additional 30 min. It was then quenched with 50 mL of a 1 M HCl solution previously cooled to 0 °C. The benzene layer was then separated, washed three times with 50-mL portions of water, and dried over anhydrous magnesium sulfate. Removal of the benzene on a rotary evaporator left a yellow oil which was dissolved in 10 mL of hot benzene, and 20 mL of petroleum ether (bp 30–60 °C) was then added. This afforded 1.58 g (3.84 mmol, 75%) of white needles: mp 174–176 °C; IR (CCl_4) 2260 cm^{-1} (CN); ^1H NMR ($CDCl_3$) δ 6.6–7.8 (m, 20 H), 4.81 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 120.4 (CN); M_r found (mass spectrometry) 411. Anal. Calcd for $C_{30}H_{21}NO$: C, 87.56; H, 5.14; N, 3.40. Found: C, 87.80; H, 5.43; N, 3.15.

***trans*-1,2,3,4-Tetraphenyl-4-cyano-2-cyclopenten-1-one (6a).** The procedure used for the preparation of this isomer was exactly the same as described for **5a** to the point of stirring at room temperature for 5 h. At the end of this time, concentrated HCl was added dropwise until the color changed from deep red to light yellow. The resulting mixture was allowed to stir at room temperature for 18 additional h. The contents of the flask were then transferred to a separatory funnel containing 50 mL of water, and the benzene layer was separated, washed twice with 50-mL portions of water, and dried over anhydrous magnesium sulfate. Removal of the solvent on a rotary evaporator afforded a yellow oil which was dissolved in 10 mL of hot benzene and treated with 20 mL of petroleum ether (bp 30–60 °C). This afforded 1.4 g (3.40 mmol, 65%) of a mixture of the cis (**5a**) and trans (**6a**) isomers. The off-white, denser-packed crystals of the trans isomer (**6a**) were separated from the slightly yellow needles of the cis isomer (**5a**) by hand. This separation afforded 1.1 g (2.67 mmol, 51%) of the trans isomer (**6a**), which upon recrystallization from benzene/petroleum ether (1/2) gave an analytically pure sample of the trans isomer: mp 195–197 °C dec; IR (CCl_4) 2260 (CN), 1720 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.6–7.8 (m, 20 H), 4.16 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 118.0 (CN); M_r found (mass spectrometry) 411. Anal. Calcd for $C_{30}H_{21}NO$: C, 87.56; H, 5.14; N, 3.40. Found: C, 87.68; H, 5.36; N, 3.40.

***cis*-1,2,3,4-Tetraphenyl-4-cyano-5-methyl-2-cyclopenten-1-one (7).** The procedure used for the preparation of this compound was exactly the same as that described for **5a** to the point of stirring at room temperature for 5 h. At the end of this time, 2 mL of methyl iodide were added to the deep red solution of the enolate **4a** which was then allowed to stir at 27 °C for an additional 30 min. The contents of the flask were then transferred to a separatory funnel containing 50 mL of water, and the benzene layer was separated and dried over anhydrous magnesium sulfate. Removal of the benzene on a rotary evaporator afforded a yellow oil which was dissolved in 8 mL of hot benzene and treated with 16 mL of petroleum ether (bp 30–60 °C). This afforded 1.58 g (3.7 mmol, 71%) of off-white crystals: mp 198–199 °C; IR (CCl_4) 2260 (CN), 1720 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.8–7.5 (m, 20 H), 2.17 (s, 3 H); M_r found (mass spectrometry) 425. Anal. Calcd for $C_{31}H_{23}NO$: C, 87.50; H, 5.45; N, 3.29. Found: C, 87.44; H, 5.70; N, 3.30.

***trans*-1,2,3,4-Tetraphenyl-4-cyano-5-methyl-2-cyclopenten-1-one (8).** Column chromatography on silica gel with carbon tetrachloride as eluent of the mother liquor obtained from the crystallization of the cis isomer (**7**) above afforded several fractions. Like fractions as determined by NMR were combined, the solvent was removed on a rotary evaporator, and the resulting light yellow oil was dissolved in 2 mL of hot benzene and treated with 4 mL of petroleum ether (bp 30–60 °C). Cooling afforded 0.22 g (0.5 mmol, 10%) of off-white crystals: mp 170–171 °C; IR (CCl_4) 2260 (CN), 1720 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.6–7.4 (m, 20 H), 2.4 (s, 3 H); M_r found (mass spectrometry) 425. Anal. Calcd for $C_{31}H_{23}NO$: C, 87.50; H, 5.45; N, 3.29. Found: C, 87.46; H, 5.55; N, 3.28.

***cis*- (5b) and *trans*-1,2,3,4-Tetraphenyl-4-methoxy-2-cyclopenten-1-one (6b).** Into a 250-mL three-necked flask equipped with a magnetic stirring bar was placed 2.0 g (5.2 mmol) of tetracyclone (**1**), 60 mL of benzene, and 60 mL of Me_2SO. To this solution at room temperature was added 4 mL of a 40% solution of benzyltrimethylammonium hydroxide in methanol (Triton B) and the resulting red solution of enolate **4b** was stirred at 27 °C for 50 min and then 5 mL of concentrated HCl was added. The contents of the flask were then transferred to a separatory funnel containing 50 mL of water, and the benzene layer was separated, washed twice with 50 mL of water, and dried over magnesium sulfate. Removal of the solvent on a rotary evaporator afforded a pink oil which was dissolved in 10 mL of hot benzene and treated with 20 mL of petroleum ether (bp 30–60 °C). Within 1 h at room temperature the cis isomer (**5b**) began crystallizing in the form of fine white needles, and after 2 h the crystals were filtered and washed with cold petroleum ether to afford 0.91 g (2.18 mmol, 42%): mp 208–210 °C dec (lit.[9] mp 193–203 °C dec); IR (CCl_4) 1720 cm^{-1} (CO); ^1H NMR ($CDCl_3$) δ 6.8–7.8 (m, 20 H), 4.63 (s, 1 H), 3.35 (s, 3 H); M_r found (mass spectrometry) 416. Anal. Calcd for $C_{30}H_{24}O_2$: C, 86.51; H, 5.81. Found: C, 86.51; H, 5.99.

Allowing the mother liquor to stand overnight at room temperature afforded white salt-like crystals which were filtered and washed with cold petroleum ether producing 0.23 g (0.55 mmol,

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(11) The following libraries of crystallographic programs were used: (a) MULTAN 80, University of York, York, England (1980). (b) Structure Determination Package V17.0, Enraf-Nonius Corporation, Delft, Holland (1981). (c) Structure Determination Package Plus VI.1, B. A. Frenz and Associates, College Station, TX (1983). (d) ORTEP-II, Oak Ridge National Laboratory, Oak Ridge, TN (1970).

(12) Karle, J. *Acta. Crystallogr., Sect. B* **1968**, *B24*, 182.

11%) of the trans isomer (**6b**): mp 126–130 °C dec; IR (CCl_4) 1720 cm^{-1} (CO); ^1H NMR ($CDCl_3$) δ 6.8–7.8 (m, 20 H), 4.27 (s, 1 H), 3.07 (s, 3 H); M_r found (mass spectrometry) 416. Anal. Calcd for $C_{30}H_{24}O_2$: C, 86.51; H, 5.81. Found: C, 86.62; H, 6.04.

1,3-Dimethoxy-1,2,4,5-tetraphenyl-2,4-cyclopentadiene (9). The procedure used for the preparation of this compound was exactly the same as that described for **5b** to the point of stirring at 27 °C for 50 min. At the end of this time, 2 mL of methyl iodide were added to the deep red solution of enolate **4b** which was then stirred at 27 °C for an additional 45 min. The contents of the flask were then transferred to a separatory funnel containing 50 mL of water, and the benzene layer was separated, washed twice with 50-mL portions of water, and dried over magnesium sulfate. Removal of the solvent on a rotary evaporator afforded a dark red oil which was dissolved in 20 mL of absolute ethanol. The crystals obtained were filtered and washed with cold 95% ethanol affording 1.77 g (4.1 mmol, 79%) of impure material which upon recrystallization from absolute ethanol produced 1.70 g of dazzling yellow needles: mp 160–161 °C; IR (CCl_4) 1650 (C=$COCH_3$), 1085 (COC) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.9–7.6 (m, 20 H), 3.51 (s, 3 H), 3.32 (s, 3 H); M_r found (mass spectrometry) 430. Anal. Calcd for $C_{31}H_{26}O_2$: C, 86.48; H, 6.09. Found: C, 86.31; H, 6.23.

Tables I–III. The data reported in the tables were obtained using the following procedures.

Formation of Enolate 4a. Into a 25-mL three-necked flask equipped with a magnetic stirrer was placed 100 mg of tetracyclone (1), 25 mg of potassium cyanide, 7.5 mL of benzene, and 7.5 mL of Me_2SO (or 15 mL of *N,N*-dimethylformamide) and the reaction was stirred at 27 °C for 3 h.

Formation of Enolate 4b. Into a 25-mL three-necked flask equipped with a magnetic stirrer was placed 100 mg of tetracyclone (1), 7.5 mL of benzene, and 7.5 mL of Me_2SO. To this solution was added 0.2 mL of Triton B (or 0.25 mL of 1.2 M potassium methoxide in methanol) and the resulting solution was stirred at 27 °C for 15 min.

Kinetic Protonation of Enolates 4a and 4b. Approximately 5 min prior to protonation, the temperature of the flask containing the enolate was adjusted to the desired level (0 °C by using an ice bath or 90 °C by refluxing the solvent) and at this point, 5 drops of concentrated HCl was rapidly added. The flask contents were then transferred to a separatory funnel containing 10 mL of benzene and 10 mL of water, and the benzene layer was separated, washed twice with 20-mL portions of water, and dried over anhydrous magnesium sulfate. Removal of the solvent with a rotary evaporator afforded a yellow oil which was dissolved entirely in $CDCl_3$ and analyzed by ^1H NMR. The cis–trans ratios were determined by proton integration and recorded in Table I.

Quenching Enolate 4a with Methyl Iodide. At the temperatures specified in Table III, 1 mL of methyl iodide was added to the enolate **4a** and the resulting solution was stirred for 10 min. The remaining purification procedure was identical with that described above.

Equilibration of Isomers 5 and 6. Into a 25-mL three-necked flask equipped with a magnetic stirring bar was placed 100 mg of the starting isomer (either **5** or **6**), 7.5 mL of benzene, and 7.5 mL of Me_2SO. Once the sample had dissolved (ca. 5 min), the particular isomerization mode was employed: (a) Base (for **5a** and **6a**). One drop of a saturated solution of potassium cyanide in Me_2SO was added to the above mixture, the solution was stirred at 27 °C for the amount of time indicated in Table II, and then the solution was analyzed by ^1H NMR. (b) Base (for **5b** and **6b**). One drop of a base solution, prepared by adding 5 drops of Triton B to 1 mL of Me_2SO, was added to the above solution to be equilibrated, the solution was stirred at 27 °C for 2 h, and the solution was analyzed by ^1H NMR to give the results recorded in Table II. (c) Acid. Three drops of concentrated HCl were added to the above solution to be equilibrated and the solution was stirred at the temperature and for the time indicated in Table II. Analysis of the resulting solution by ^1H NMR afforded the results recorded. (d) Thermal. Refluxing the solution at 90 °C for the time specified in Table II, followed by ^1H NMR analysis of the resulting solution, afforded the results recorded.

Registry No. 1, 479-33-4; **4a**, 92011-29-5; **4b**, 92011-30-8; **5a**, 92011-31-9; **5b**, 58008-91-6; **6a**, 92011-32-0; **6b**, 58009-01-1; **7**, 92011-33-1; **8**, 92011-34-2; **9**, 92011-35-3.

Supplementary Material Available: Tables of the atomic positional and thermal parameters, bond distances, and bond angles for **6a** and **7** (12 pages). Ordering information is given on any current masthead page.

Photochemical Synthesis of Decipiene Diterpenes

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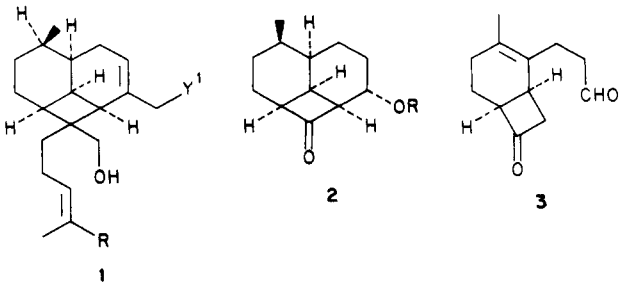
The decipiene diterpene nucleus has been synthesized by an intramolecular [2 + 2] photocycloaddition between an enone and an allene grouping. The process makes use, for the first time, of a stereocontrol element at a remote center in the precursor unit to control the final stereochemistry of the product. A formal total synthesis of (±)-trihydroxydecipiadiene has been achieved.

The decipiane diterpenoids **1**, a new class of diterpenes isolated[1] from the surface coating of *Eremophilia decipiens*, contain the tricyclo[5.3.1.$0^{5,11}$]undecane ring skeleton; the CH_2Y^1 can be a primary alcohol or a methyl group and R can be a primary alcohol or a carboxyl group. A total synthesis of (±)-trihydroxydecipiadiene (**1**, Y^1 = OH, R = CH_2OH) has been reported,[2] a synthetic route which



first prepared the basic tricyclic skeleton **2** by cyclization of **3**. The elaboration of the side chain was performed in

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