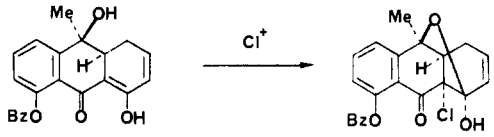

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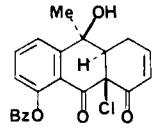
imental modifications that considerably improved the yields and purification methods. A brief outline of this synthesis is shown in Scheme I. When the diketone **6** is chromatographed over silica gel, it is converted into the Shemyakin ketone **5**, although we found **6** to be entirely equivalent to **5** in its response to chlorinating agents. Treatment of **6** with *N*-chlorosuccinimide in dimethoxyethane at 20 °C gave a single crystalline monochloro derivative, **7**. Its structure was not readily apparent from



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spectral data; consequently, a single-crystal X-ray analysis was conducted[4] and the results are shown in Figure 1. Other chlorination reagents such as *tert*-butyl hypochlorite and chloramine T gave similar results although not so cleanly.

The exclusive formation of the *trans*-11a-chloro adduct **7** strongly suggests that for the tetracyclines **1** (X = H or OH) an intramolecular association of the electrophilic chlorinating agent and the 12a-hydroxyl group takes place, thereby directing the chlorine atom into the 11a-position from the same side (α) as the 12a-hydroxyl group. The 5-hydroxyl group cannot be responsible for this effect since tetracycline itself **1** (X = H) gives the 11aα-chloro compound **3** (X = H). It appears likely that in the case of **6** the chlorine atom enters the more hindered concave side by prior hydrogen bonding to the 6-hydroxyl group.

Experimental Section

4,10-Dioxo-4aβ-chloro-5-(benzyloxy)-9β-hydroxy-9α-methyl-1,4,9,9aα,10-pentahydroanthracene (7). The dienolone **6** (100 mg, 0.287 mmol) in dimethoxyethane (3 mL) was treated with *N*-chlorosuccinimide (28 mg, 0.287 mmol) at 20 °C. After 1 h the solvent was removed in vacuo and the residue added to ethanol (0.25 mL) and water (15 mL). The aqueous solution was extracted with chloroform (3 × 10 mL), and the combined extracts were dried (Na_2SO_4) and evaporated under reduced pressure. The residue was dissolved in hot dichloromethane and cooled to 4 °C to give crystals of **7**: 84 mg (77%); mp 124–126 °C dec; IR ($CHCl_3$) ν_{max} 3570, 1720, 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.61 (3 H, s), 2.60–3.20 (3 H, m), 5.16 (2 H, s), 6.14 (1 H, d, J = 7.5 Hz), 6.80–7.56 (9 H, m); ^{13}C NMR (20.1 MHz, $CDCl_3$) 188.3, 186.2, 157.7, 149.2, 148.0, 136.5, 134.6, 128.7, 127.8, 126.9, 119.3, 113.5, 70.8, 70.6, 65.7, 48.9, 30.0, 22.3. Anal. Calcd for $C_{22}H_{19}O_4Cl$: C, 69.02; H, 5.00; Cl, 9.26. Found: C, 69.27; H, 5.06; Cl, 8.99.

Registry No. 5, 67122-45-6; **6**, 82494-99-3; **7**, 82495-00-9; **8**, 73794-49-7; **9**, 73794-50-0; **10**, 82495-01-0; **11**, 82495-02-1; **12**, 82495-03-2; 5-hydroxy-1,4-naphthalenedione, 481-39-0; 1,3-butadien-1-ol acetate, 1515-76-0.

Supplementary Material Available: Experimental procedures and data for compounds **6** and **8–12**, line drawings of the molecules, and fractional coordinates, anisotropic thermal parameters, and bond distances and angles for compound **7** (8 pages). Ordering information is given on any current masthead page.

(3) Inhoffen, H. H.; Muxfeldt, H.; Schaefer, H.; Kramer, H. *Croat. Chem. Acta.* **1957**, *29*, 329. Kolosov, M. N.; Popravko, S. A.; Gurevich, A. I.; Korobko, V. G.; Vasina, I. V.; Shemyakin, M. M. *Zh. Obshch. Khim.* **1964**, *34*, 2534. Kolosov, M. N.; Popravko, S. A.; Korobko, V. G.; Shemyakin, M. M. *Ibid.* **1964**, *34*, 2540. Kolosov, M. N.; Popravko, S. A.; Korobko, V. G.; Karapetyan, M. G.; Shemyakin, M. M. *Ibid.* **1964**, *34*, 2547. Kolosov, M. N.; Popravko, S. A.; Shemyakin, M. M. *Justus Liebigs Ann. Chem.* **1963**, *86*, 668. For a recent modification see: Stork, G.; Hagedorn A. A., III *J. Am. Chem. Soc.* **1978**, *100*, 3609. These authors show that the $BF_3{\cdot}Et_2O$-catalyzed cyclization of juglone with 1-acetoxybutadiene gives almost exclusively the single regioisomer shown in Scheme I.

(4) A single crystal of **7** of dimensions 0.25 × 0.35 × 0.35 mm was cooled to −165 °C on a computer-automated Picker goniostat. Complete details of the low-temperature device, goniostat, and contorl system are given in: *Inorg. Chem.*, **1980**, *19*, 2755. Crystal data are as follows: space group $P2_1/c$, a = 11.124 (13) Å, b = 11.105 (14) Å, c = 14.438 (19) Å, β = 95.21 (5) Å, and d_{calcd} = 1.432 g cm^{-3} d_{calcd} for Z = 4. Data was collected for $+h$, $+k$ $\pm l$ in the range $5 \le 2\theta < 50°$ by using graphite monochromated Mo Kα radiation (λ = 0.710 69 Å). A scan speed of 4° min^{-1} over a range of 2° in 2θ with a 5-s stationary background were used for the $\pm 2\theta$ continuous scan. The structure was solved by direct methods, and the 1491 data with $F > 3\sigma(F)$ (out of 2318 unique data) were used in the refinement. All hydrogen atoms were located and refined isotropically, with anisotropic thermal parameters for the nonhydrogen atoms. Final residual are $R(F)$ = 0.083 and $R(wF)$ = 0.068. Fractional coordinates, thermal parameters, bonded distances, and bonded angles are available as supplementary data. Complete crystallographic details are also available from the Chemistry Library, Indiana University, Bloomington, IN 47405. Request IUMSC Report 8043.

Organoiron Complexes in Organic Synthesis. 25.[1] Complete Stereocontrol in the Synthesis of 4,4,5-Trisubstituted Cyclohexenones

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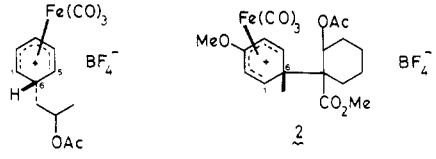
Received March 2, 1982

We recently described[2-4] approaches to the synthesis of 6-exo-substituted tricarbonylcyclohexadienyliumiron cationic complexes **1** and **2** using thallium (III) or $FeCl_3$/silica



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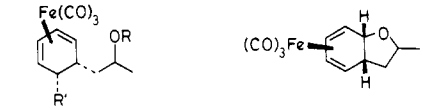
gel promoted cyclization of hydroxy-substituted compounds such as **3a** to give tetrahydrobenzofuran complexes



3a R = R' = H 4

3b R = Ac, R' = SPh, $CH(CO_2Me)_2$

of type **4**. Treatment of **4** with acid (HBF_4) in the presence of acetic anhydride caused opening of the tetrahydrofuran ring and concomitant acetylation of the hydroxy group to give the dienylium complexes. In our earlier work the latter complexes were produced having rather bulky 6-exo substituents, so that addition of nucleophiles to the dienylium ligand to give complexes of structure **3b** occurred either in very poor yield (ca. 40%) or not at all in cases with very bulky substituents, the nucleophile preferring instead to attack a carbonyl ligand or to cause decomplexation of the dienylium ligand (mechanism unknown). However, despite our early lack of success and in view of

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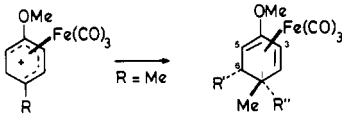
the facility with which dienylium–$Fe(CO)_3$ complexes of structure **5** may be converted to 4,4-disubstituted cyclo-



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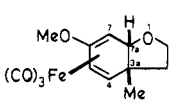
6a R' = H, R'' = $CH(CO_2Me)_2$
6b R' = H, R'' = CH_2CO_2Me
6c R' = H, R'' = CH_2CH_2OH
6d R' = $CH(CO_2Me)_2$, R'' = CH_2CH_2OAc
6e R' = Me, R'' = CH_2CH_2OAc

hexenones[5] of considerable synthetic utility, we considered it a worthwhile exercise to further investigate the reactivity of complexes related to **2** but having sterically less demanding 6-exo substituents. The results of our initial investigation are described in the present paper.

Results and Discussion

The diester complex **6a**, readily available by our previously published method,[6] was a suitable starting point for our investigation and was readily decarbomethoxylated in good yield to give monoester **6** by using tetramethylammonium acetate in hexamethylphosphoramide or sodium cyanide in wet dimethyl sulfoxide.

At this point we attempted to convert **6b** to the dienylium complex **8a** by treatment with triphenylmethylium



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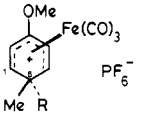
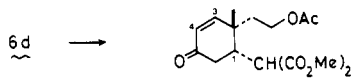


8a R = CH_2CO_2Me
8b R = CH_2CH_2OAc

hexafluorophosphate, the standard hydride-abstracting reagent.[7] However, prolonged reaction in refluxing dichloromethane gave no observable conversion (infrared spectroscopy) to the desired cation. Consequently, we decided to use the aforementioned oxidative cyclization technique. Accordingly, the monoester **6b** was reduced with *i*-Bu_2AlH to the primary alcohol **6c**. Attempts to effect the cyclization of this compound to the tetrahydrobenzofuran complex **7** by using either buffered thallium(III) trifluoroacetate or ferric chloride supported on silica gel, successful in our earlier studies,[2-4] gave disappointing yields (ca. 30%) of the desired product. Birch and co-workers had previously described[8] manganese dioxide promoted cyclizations of enol derivatives into diene–$Fe(CO)_3$ groups, so we decided to investigate the use of this reagent for our system. Treatment of complex **6c** with excess manganese dioxide in refluxing benzene resulted in smooth conversion to the desired complex **7**, in 75–80% yield. This material was readily transformed into the dienylium complex **8b** by treatment with hexafluorophosphoric acid in acetic anhydride, giving an overall yield upwards of 65% **8b** from the alcohol **6c**.

Reaction of the cationic derivative **8b** with dimethyl sodiomalonate occurred instantaneously to give a single product in 78% yield, after chromatographic purification, readily identified from its spectral data as the cyclohexadiene complex **6d**. Thus, the IR spectrum showed the usual $Fe(CO)_3$ bands at 2060 and 1980 cm^{-1}, the ester absorptions at 1763 and 1742 cm^{-1}, and a strong absorption at 1488 cm^{-1} which we have found to be characteristic of diene–$Fe(CO)_3$ complexes bearing a methoxy substituent at C-2 of the diene system.[9] We have previously demonstrated that nucleophile addition to similar 6-exo-substituted dienylium–$Fe(CO)_3$ complexes occurs exclusively at the exo face,[2] in agreement with the known stereoelectronic control exerted by the $Fe(CO)_3$ group.[10] That addition of the malonate nucleophile to complex **8b** also occurs in the exo mode is evidenced by the observation of the CH_2OAc group as two ABXY patterns (1 H each) centred at δ 4.25 and 4.10 in the 250-MHz NMR spectrum of **6d** (see Experimental Section). Since this methylene group is somewhat remote from the asymmetric grouping, the dissimilarity is unlikely to be due to a diastereotopic effect. A plausible explanation is that the presence of the malonate substituent cis to the acetoxyethyl group leads to restricted rotation in the latter substituent.[11] Furthermore, a doublet of doublets is observed at δ 2.56, corresponding to H-6, which shows a coupling of 2.28 Hz with H-5. The similarity of this value to the coupling between H-7 and H-7a in the tetrahydrobenzofuran complex **7** (3.3 Hz) indicates a very similar dihedral angle between these protons in both complexes, again indicating the exo stereochemistry for the malonate suubstituent. Reaction of **8b** with lithium dimethylcuprate[12] again resulted in stereospecific addition of nucleophile to give the complex **6e**, but in somewhat lower yield.

Treatment of the dimethyl malonate adduct with ceric ammonium nitrate effected its direct conversion to the 4,4,5-trisubstituted cyclohexenone **9**. This compound did



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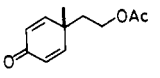
not show such a complex NMR spectrum for the acetoxyethyl group, since this substituent has an axial–equatorial relationship to the malonate group and is therefore not in such close proximity. Thus, the overall conversion corresponds to a stereospecific conjugate addition to the 4,4-disubstituted cyclohexadienone **10**, cis to the more



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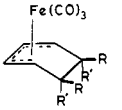
bulky substituent. This transformation is interesting in

(1) Part 24: Pearson, A. J.; Chandler, M. *J. Chem. Soc., Perkin Trans. 1*, in press.
(2) Pearson, A. J. *J. Chem. Soc., Chem. Commun.* **1980**, 488.
(3) Pearson, A. J.; Chandler, M. *Tetrahedron Lett.* **1980**, *21*, 3933.
(4) Pearson, A. J.; Ong, C. W. *J. Chem. Soc., Perkin Trans. 1*, **1981**, 1614.
(5) Pearson, A. J. *Acc. Chem. Res.* **1980**, *13*, 463; *Transition Met. Chem. (Weinheim, Ger.)* **1981**, *6*, 67.
(6) Pearson, A. J. *J. Chem. Soc., Perkin Trans 1*, **1977**, 2069; **1979**, 1255.
(7) Fischer, E. O.; Fischer, R. D. *Angew. Chem.* **1960**, *72*, 919.
(8) Birch, A. J.; Chamberlain, K. B.; Thompson, D. J. *J. Chem. Soc., Perkin Trans 1* **1973**, 1900.
(9) Pearson, A. J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1981**, 884.
(10) Pearson, A. J.; Raithby, P. R. *J. Chem. Soc., Perkin Trans. 1*, **1980**, 395. Pearson, A. J.; Mincione, E.; Chandler, M.; Raithby, P. R. *Ibid.* **1980**, 2774.
(11) A useful working model for these complexes, for purposes of investigating steric interactions, is the boat form of a cyclohexene.



This is in agreement with X-ray structure data (see, for example: Pearson, A. J.; Raithby, P. R. *J. Chem. Soc., Perkin Trans. 1* **1980**, 395).
(12) Pearson, A. J. *Aust. J. Chem.* **1976**, *29*, 1101.

view of the difficulties associated with stereochemical control of, e.g., cuprate addition to substituted cyclohexenones.[13] Since the organoiron methodology currently being developed in our laboratories[5] allows the synthesis of a variety of complexes of type **6** in which the *endo*-methyl substituent is replaced by a functionalized group, the work reported here adds a new dimension to the synthetic utilty of these complexes, further studies of which will form the basis of future investigations.

Experimental Section

IR spectra were recorded with a Perkin-Elmer 577, mass spectra with an AEI MS 12 (organometallics) or MS 30 (organic compounds), and ^{1}H NMR spectra with Varian EM 390 or Bruker 250 instruments. Melting points are uncorrected. All reactions and chromatographic operations with iron complexes were conducted under an atmosphere of nitrogen. Solvents were freshly distilled under nitrogen as follows: tetrahydrofuran (THF) from sodium/benzophenone; hexamethylphosphoramide (HMPA) from calcium hydride; benzene from sodium.

Tricarbonyl[2-5-η-4-methoxy-1-methyl-1-[(methoxycarbonyl)methyl]cyclohexa-2,4-diene]iron (6b). The diester complex **6a** (7.0 g) was dissolved in dry HMPA (35 mL) and purged with argon. Tetramethylammonium acetate (24.0 g) was added, and the stirred mixture was heated at 95–100 °C for 21 h. The cooled mixture was diluted with ether (200 mL), and the extract was washed throughly with 10% aqueous hydrochloric acid, water, aqueous sodium bicarbonate, dried ($MgSO_4$), and evaporated to give a yellow solid. Crystallization from pentane afforded the monoester **6b**: 4.27 g (72%); mp 56.5–57.5 °C; IR ($CHCl_3$) ν_{max} 2060, 1960, 1710, 1485 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.05 (1 H, dd, J = 6.5, 2.5 Hz, 3-H), 3.65 (6 H, s), 3.30 (1 H, m, 5-H), 2.48 (1 H, d, J = 6.5 Hz, 2-H), 2.17 (2 H, s), 2.05 (1 H, dd, J = 16, 2.5 Hz, *endo*-6-H), 1.55 (1 H, dd, J = 16, 2.5 Hz, *exo*-6-H), 1.08 (3 H, s). Anal. Calcd for $C_{14}H_{16}FeO_6$: C, 50.03; H, 4.80; m/e 336 (M^+). Found: C, 50.06; H, 4.81; m/e 336 (M^+).

Tricarbonyl[2-5-η-1-(2-hydroxyethyl)-4-methoxy-1-methylcyclohexa-2,4-diene]iron (6c). To a stirred solution of the monoester **6b** (1.32 g) in THF (50 mL) at −78 °C was added diisobutylaluminium hydride (10 mL of 1 M solution in hexane). The mixture was stirred overnight and allowed to attain room temperature, after which time methanol (3 mL) and then water (3 mL) were added. Stirring was continued for 15 min, after which time ether (100 mL) was added, and the mixture was filtered through Celite. The organic extract was washed thoroughly with water, dried ($MgSO_4$), and evaporated to give the alcohol **6c**, chromatographically pure, as a yellow oil: 1.10 g (91%); IR ($CHCl_3$) ν_{max} 3575, 3450, 2065, 1970, 1490 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.01 (1 H, dd, J = 7, 2.5 Hz, 3-H), 3.59 (3 H, s, OMe), 3.59 (2 H, t, J = 7.5 Hz, CH_2OH), 3.22 (1 H, m, 5-H), 2.34 (1 H, d, J = 7 Hz, 2-H), 1.73 (1 H, dd, J = 15, 3 Hz, *endo*-6-H), 1.43 (1 H, dd, J = 15, 2.5 Hz, *exo*-6-H), 1.40 (2 H, t, J = 7.5 Hz), 1.31 (1 H, s, exchanges with D_2O, OH), 0.90 (3 H, s, Me); mass spectrum, m/e (relative intensity) 308 (10), 280 (30), 252 (10), 224 (40), 178 (100).

Tricarbonyl(4-7-η-6-methoxy-3aβ-methyl-2,3,3aβ,7aβ-tetrahydrobenzofuran)iron (7). Manganese dioxide (1.0 g) was heated at reflux temperature in benzene overnight using a water separator. The mixture was cooled, and the alcohol complex **6c** (140 mg) in benzene (1 mL) was added. The mixture was boiled for 3 h, after which time TLC examination showed completion of the reaction. The cooled mixture was filtered and evaporated to afford the product **7** (110 mg, 79%), obtained as a pale yellow oil after preparative TLC: IR ($CHCl_3$) ν_{max} 2055, 1975, 1488 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.21 (1 H, dd, J = 7, 2.5 Hz, 5-H), 4.02 (1 H, d, J = 3.3 Hz, 7a-H), 3.80 (2 H, t, J = 7.5 Hz, CH_2O), 3.74 (3 H, s, OMe), 3.15 (1 H, dd, J = 3.3, 2.5 Hz, 7-H), 2.45 (1 H, d, J = 7 Hz, 4-H), 1.56 (2 H, *t*, J = 7.5 Hz), 1.23 (3 H, s); mass spctrum, m/e (relative intensity) 306 (25), 278 (40), 250 (17), 222 (70), 194 (100), 165 (35).

Tricarbonyl[1-5-η-6-*exo*-(2-acetoxyethyl)-3-methoxy-6-*endo*-methylcyclohexa-1,3-dienylium]iron Hexafluorophosphate (8b). The above cyclized complex **7** (160 mg) was dissolved in dichloromethane (2 mL) and acetic anhydride (1 mL) and stirred at 0 °C while hexafluorophosphoric acid (0.2 mL of a 65% aqueous solution) was added dropwise. Stirring was continued for 30 min, after which time the product was precipitated by pouring the reaction mixture into ether (20 mL). The dienylium complex was removed by filtration, washed with ether, and dried in vacuo to give **8b** as a yellow solid: 232 mg (90%); IR (Nujol) ν_{max} 2103, 2050, 1733 cm^{-1}; ^{1}H NMR (CD_3CN) δ 5.87 (2 H, d, J = 7 Hz, 2-H, 4-H), 4.15 (3 H, s, OMe), 3.93 (2 H, t, J = 6 Hz, CH_2OAc), 3.88 (2 H, d, J = 7 Hz, 1-H, 5-H), 1.98 (3 H, s, Ac), 1.67 (3 H, s), 1.27 (2 H, t, J = 6 Hz, CH_2). Anal. Calcd for $C_{15}H_{17}FeO_6PF_6$: C, 36.46; H, 3.47). Found: C, 36.76; H, 3.46.

Reactions of Dienylium Complex 8b with Nucleophiles. (a) With Dimethyl Sodiomalonate. The sodium salt of dimethyl malonate was prepared in THF solution (1 mL) in the usual way from sodium hydride (16 mg of a 50% dispersion in mineral oil) and a slight excess of dimethyl malonate. The reaction vessel was opened briefly while the hexafluorophosphate **8b** (100 mg) was added. Instantaneous reaction was evidenced by rapid dissolution of the salt. The reaction mixture was diluted with ether, washed thoroughly with water, dried ($MgSO_4$), and evaporated to give the crude product which showed a single spot on TLC examination. Preparative TLC afforded the product **6d** as a pale yellow oil: 75 mg (78%); IR (CCl_4) ν_{max} 2060, 1980, 1763, 1742, 1488 cm^{-1}; ^{1}H NMR (CD_2Cl_2, 250 MHz) δ 5.11 (1 H, dd, J = 6.3, 2.1 Hz, 3-H), 4.25 (1 H, ddd, ABXY, J = 10.5, 9.5, 5.8 Hz, CHOAc), 4.10 (1 H, ddd, ABXY, J = 10.5, 9.5, 5.9 Hz, CHOAc), 3.73 (3 H, s), 3.70 (3 H, s), 3.62 (3 H, s), 3.26 (1 H, d, J = 8.7 Hz, malonate CH), 3.11 (1 H, dd, J = 2.28, 2.10 Hz, 5-H), 2.56 (1 H, dd, J = 8.7, 2.28 Hz, 6-H), 2.50 (1 H, d, J = 6.3 Hz, 2-H), 2.01 (3 H, s, OAc), 1.45 (1 H, complex ABXY) and 1.23 (1 H, complex ABXY, CH_2), 1.04 (3 H, s); mass spectrum, m/e (relative intensity) 424 (M − 2CO, 33), 396 (100), 381 (43), 349 (43). Anal. Calcd for $C_{20}H_{24}FeO_{10}$: C, 50.02; H, 5.04. Found: C, 50.15; H, 5.32.

(b) With Lithium Dimethylcuprate. The nucleophile (excess) was prepared in ether solution at 0 °C in the usual way from cuprous iodide (100 mg) by addition of methyllithium (1.4 M solution in hexane) until dissolution of methylcopper was just complete. The reaction vessel was opened briefly while the hexafluorophosphate **8b** was added. Stirring was continued for 10 min, when the reaction mixture was poured into saturated aqueous NH_4Cl and stirred in air for 15 min. Extraction with ether in the usual way followed by preparative TLC afforded the complex **6c** (45 mg, 61%) as a pale yellow oil: IR (CCl_4) ν_{max} 2025, 1960, 1733, 1475 cm^{-1}; ^{1}H NMR (CCl_4) δ 5.05 (1 H, dd, J = 6, 2.5 Hz, 3-H), 4.17 (2 H, complex m, CH_2OAc), 3.57 (3 H, s, OMe), 3.14 (1 H, t, J = 2.5 Hz, 5-H), 2.40 (1 H, d, J = 6 Hz, 2-H), 1.98 (3 H, s, OAc), 1.77 (1 H, qd, J = 7, 2.4 Hz, 6-H), 1.35 (2 H, complex m, CH_2), 1.85 (3 H, s, 1-Me), 1.78 (3 H, d, J = 7 Hz, 6-Me); mass spectrum, m/e (relative intensity) 364 (3), 336 (18), 308 (2), 280 (37), 252 (23), 237 (10), 209 (10), 192 (100).

Dimethyl [2-(2-Acetoxyethyl)-2-methyl-5-oxo-3-cyclohexenyl]malonate (9). The complex **6d** (80 mg) was dissolved in acetone/water (3:1, 2 mL) and stirred at room temperature while ceric ammonium nitrate was added in small portions until no more evolution of carbon monoxide occurred. Stirring was continued for 15 min, when the mixture was poured into water and the product extracted with ether in the usual way. Purification by preparative TLC gave the enone **9** as a colorless oil: 33mg (61%); IR (CCl_4) ν_{max} 1747, 1693, 1620 (vw) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.65 (1 H, d, J = 10 Hz), 5.90 (1 H, d, J = 10 Hz), 4.13 and 4.12 (2 H, 2 t, J = 7.5 Hz, CH_2OAc), 3.75 (3 H, s), 3.68 (3 H, s), 3.70 (1 H, obscured, malonate CH), 2.90–2.30 (3 H, m), 1.96 (3 H, s, OAc), 1.79 (3 H, t, J = 7.5 Hz), 1.18 (3 H, s); mass spectrum, m/e (relative intensity) 326 (5), 311 (2), 295 (7), 281 (2), 264 (5), 253 (7), 239 (22), 206 (8), 179 (30), 135 (100). Anal. Calcd for $C_{16}H_{22}O_7$: C, 58.83; H, 6.80; m/e 326.1365 (M). Found: C, 58.67; H, 6.95; m/e 326.1371 (M).

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