72691-75-9; (±)-50, 39663-75-7; (±)-51, 90-81-3; C_6H_5CHO, 100-52-7; p-$CH_3OC_6H_4CHO$, 123-11-5; $C_6H_5CH_2CHO$, 122-78-1; CCl_3CHO, 75-87-6; n-$C_5H_{11}CHO$, 66-25-1; propionic acid, 79-09-4; (β-methoxyethoxy)methyl chloride, 3970-21-6; 2,2-dimethyl-3-pentanol, 3970-62-5; 1-adamantanecarboxylic acid, 828-51-3; 2-ethyl-2-(trimethylsilyl)-1,3-dithiane, 72658-48-1; 2-ethyl-1,3-dithiane, 6007-23-4; mesitylene, 108-67-8; propionyl chloride, 79-03-8; diisopropylamine, 108-18-9; lithium diisopropylamide, 4111-54-0; tetra-n-butylammonium fluoride, 429-41-4; lithium hexamethyldisilylazide, 4039-32-1; 2-phenylpropanal, 93-53-8; methyl acrylate, 96-33-3; methyl 4-formylpentanoate, 40630-06-6; 2-hydroxybutyronitrile, 4476-02-2; ethylmagnesium bromide, 925-90-6; 2-methyl-2-[(trimethylsilyl)oxy]-3-pentanone, 72507-50-7; diazomethane, 334-88-3; 3-hydroxy-2,4-dimethylbenzenebutanoic acid, 72691-76-0.

A Formylation–Cyclization Method of Synthesis of Cycloalkenones from Unsaturated Ketones

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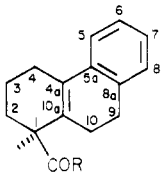
The acid-induced reaction of rigid β,γ- or γ-δ-unsaturated methyl ketones with methyl orthoformate is shown to yield alkenylcyclopentenones and -cyclohexenones, respectively. The use of ethyl orthoformate leads to more complex ring structures incorporating an ethoxy unit in both carbon–oxygen and carbon–carbon bonded form. The new structures are determined by ^{13}C NMR spectroscopy and their formation is justified on the basis of mechanistic arguments.

In continuation of studies of diterpene synthesis[1] it was important to obtain enol ethers of the methyl ketones **1b** and **2b**, which could be prepared from acids **1a**[2] and **2a**,[3]



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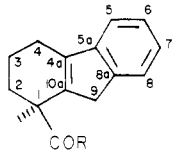

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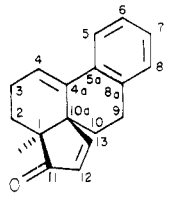
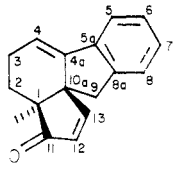


3

a, R = OH; b, R = Me



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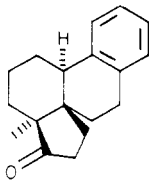

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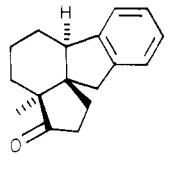
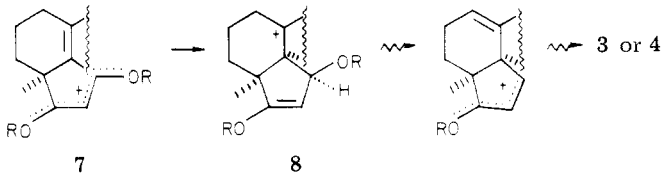


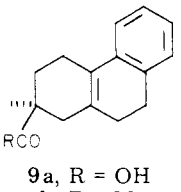
6

respectively, by consecutive treatments with oxalyl chloride, diethyl ethoxymagnesium malonate, and aqueous acid. Since the ketones were inert to orthoformic ester and acid catalysts under a variety of enol ether forming conditions,[4] they were exposed to an excess of trimethyl orthoformate in the presence of perchloric acid in the hope of forcing the desired reaction to occur, in spite of the possibility of α-formylation, a condensation known to take place under these reaction conditions.[5] The products were shown to be tetracyclic enones **3** and **4** by their spectral analyses and those of their tetrahydro products,[6] **5** and **6**, respectively. Whereas the forcing conditions had led to the enol ethers, these had interacted with dimethoxycarbonium perchlorate, the electrophilic product of the reaction of trimethyl orthoformate with perchloric acid, and subsequently lost methanol under acid catalysis. Even though the resultant 1,3-dialkoxyallyl cation should be stable until workup and then yield a β-alkoxyacrolein,[5] in **7** it faces a vicinal styrene double bond and thus reacts further, yielding styrene and cyclopentenone nuclei on workup.

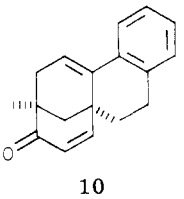


7 8 3 or 4

This simple formylation–cyclization procedure for cyclopentenone synthesis could be envisaged to be applicable to the construction of cyclohexenones by replacement of the starting β,γ-unsaturated ketone by a γ,δ-unsaturated one. As a consequence, the reaction was undertaken with methyl ketone **9b**, prepared from acid **9a** in the manner



9a, R = OH
b, R = Me



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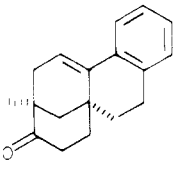

11

(1) U. R. Ghatak, S. K. Alam, and J. K. Ray, *J. Org. Chem.*, **43**, 4598 (1978).

(2) U. R. Ghatak, N. R. Chatterjee, A. K. Banerjee, J. Chakravarty, and R. E. Moore, *J. Org. Chem.*, **34**, 3739 (1969).

(3) U. R. Ghatak, R. Dasgupta, and J. Chakravarty, *Tetrahedron*, **30**, 187 (1974).

(4) A. Serini and H. Köster, *Chem. Ber.*, **71**, 1766 (1938); H. H. Inhoffen, G. Kölling, G. Koch, and I. Nebel, *Chem. Ber.*, **84**, 361 (1951); U. Schmidt and P. Grafen, *Justus Liebigs Ann. Chem.*, **656**, 97 (1962).

(5) J. P. Dusza, J. P. Joseph, and S. Bernstein, *J. Am. Chem. Soc.*, **86**, 3908 (1964).

(6) The stereochemistry depicted in **5** and **6** is based on analogy with the steric course of hydrogenation of styrenes structurally related to **3** and **4**.[1]

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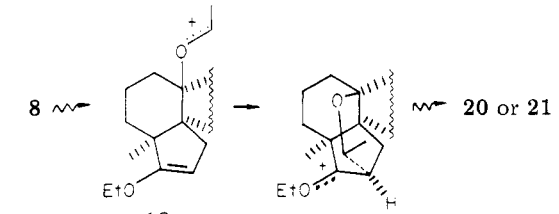
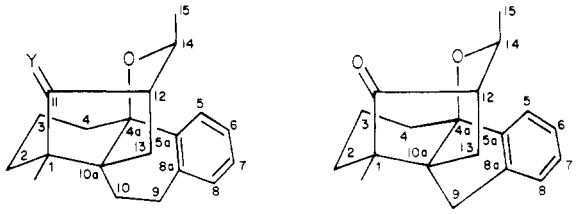
of the above **1a** → **1b** and **2a** → **2b** conversions. Treatment of the ketone with trimethyl orthoformate and perchloric acid afforded tetracyclic ketone **10**. Thus a potentially general cycloalkenone synthesis was available.

When the formylation–cyclization processes were carried out with triethyl orthoformate acting as the ortho ester reagent, unexpected products were obtained, which, however, were important for gaining some understanding of the mechanistic subtleties of the complex reaction sequences. Acid-catalyzed condensation of ketones **9b** and **1b** with triethyl orthoformate led to tetracycle **11** and a $C_{20}H_{24}O_2$ product, respectively, in excellent yields, while a similar reaction of ketone **2b** gave a $C_{19}H_{22}O_2$ compound in lower yield. The formation of ketone **11**, the dihydro derivative of the expected conjugated ketone **10**, indicated that a reduction had accompanied the formylation–cyclization process. Since such a reaction somewhere along an extended, carbonium ion producing pathway usually requires a hydride transfer, the ortho ester is the prime candidate as a reducing agent in view of the resultant liberation of the stable trialkoxycarbonium ion. However, the absence of any reduction during the reactions with trimethyl orthoformate and the known tendency for carbonium ion reductions to be preferably intramolecular and of a 1,5-hydride transfer nature[7] mitigated against the idea of the ortho ester itself acting as the reducing species and favored the involvement of an ethoxy group in the unusual reaction by intramolecular donation of a hydride from its oxymethylene component. The greater stability of the resultant oxycarbonium ion $(R'O{=}CHR)^+$ emanating from an ethoxy group (R = Me) than one from a methoxy function (R = H), therefore, could be the basis for the different reaction behavior of triethyl orthoformate and the trimethyl orthoester. The presumed ethoxy group involvement in the reactions of the methyl ketones with triethyl orthoformate was favored also by the production of ketones **1b** and **2b**, whose molecular formulas (vide supra) corresponded to those of the products of the trimethyl orthoformate reactions (**3** and **4**, respectively) plus the elements of ethanol. The following picture represents a mechanistic portrayal of the proposed reaction pathways.

If it is assumed that the intermediate 1,3-dialkoxyallyl cation is formed during the initial formylation process in the stable all-trans configuration, e.g., **7** or **12**, its cyclization leads to γ-alkoxyallyl ether, e.g., **8** or **13**, whose spatial orientation places the saturated alkoxy group in close proximity to the benzyl cation center, permitting the intramolecular transfer of the alkoxy unit to the latter via an oxetane cation intermediate (e.g., **13** → **14** → **15**).[8] In the case of the trimethyl orthoformate reactions the resultant benzyl methyl ethers, e.g., **15** (R = Me), merely lose methanol and yield styrene products, whereas the benzyl ethyl ether intermediate (e.g., **16**) of the triethyl orthoformate reactions donates a hydride in a 1,5-hydrogen shift to the ethoxyallyl cation species (**16** → **17**), which subsequently loses acetaldehyde, with the reliberation of a benzyl cation (**18**), en route to the ketostyrene **11**.

A preliminary spectral inspection of the products of the reactions of ketones **1b** and **2b** with triethyl orthoformate showed them to be saturated (with the exception of the benzene ring) keto ethers of the cyclopentanone variety, whose incorporation of ethanol manifested itself in the form of a methylated oxymethine system (R'OCHRMe) (vide infra). Were it to be assumed that the orthoformate ester condensation (**1b** or **2b** → **7**), cyclization (**7** → **8**), intramolecular ethoxy group transfer, and 1,5-hydrogen shift were to follow the pathway outlined above for the reactions of ketone **9b**, cation **19**, the oxycarbonium ion





20a, Y = O
b, Y = α-H, β-OH

21

equivalent of **17**, would be produced. Instead of the oxidized, benzylic ethoxy unit of **19** losing acetaldehyde, the carbocation can interact with the proximate enol ether, furnishing a new carbon–carbon bond as well as an extra ring. This added feature of the chemistry of ketones **1b** and **2b** indicated the structure of their products to be **20a** and **21**, respectively.[9] These structures were in accord with the results of the full spectral analysis of the substances (vide infra).

Spectral Analyses. In order to facilitate the ^{13}C NMR analysis of the structurally complex products of the reactions of ketones **1b** and **2b**, the carbon shift assignments were initiated with the parent ketones. In the spectra of hydrophenanthrene **1b** the methyl signals were differentiated from each other by the dissimilarity of the magnitude of their residual coupling. Among the methylenes C(9) was identified by its shift similarity with the benzyl carbon of 9,10-dihydrophenanthrene[10] and the C(2) and

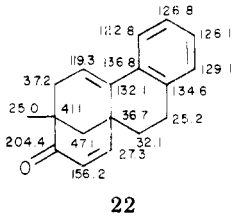
(7) For a recent example see J. G. D. Schulz and A. Onopchenko, *J. Org. Chem.*, **43**, 339 (1978).

(8) Whereas the alkoxylation of the benzyl cation (**13**) could occur, in principle, also by intermolecular interaction with the orthoformic ester or the alcohol, liberated in the reaction sequence, such reaction can be expected to be slow and to lead preponderantly to benzyl ethers epimeric with intermediates **15** at the benzyl carbon site and thus to substances unable to engage in the subsequent intramolecular oxidation–reduction process.

(9) The stereochemistry of the methyl group attached to the oxymethine unit is based on the assumption of the methyl function assuming an equatorial stance in the final carbon–carbon bond-forming reaction.

C(3) shifts were designated in analogy with the ^{13}C NMR spectral identification of structurally similar carbons among hydrophenanthrenic and decalinic diterpenes.[11] The aromatic methines could be classified as belonging to either the α or β types by their fingerprints,[11a,12] the α carbons showing shift differences analogous to those of 9,10-dihydrophenanthrene.[10] Finally, the nonprotonated, sp^2-hybridized carbons could be distinguished from each other by their second-order coupling characteristics in certain sford spectra. In the case of the decoupler being set at 2.5 ppm of the ^1H NMR spectral region and its power at ca. 1.0 W the signals above 135 ppm were less intense and broader ($\nu_{1/2}$ = 5 Hz) than those below 135 ppm ($\nu_{1/2}$ = 2–3 Hz), whereas with the decoupler at 7.2 ppm under the same power the signal intensity and width were reversed, i.e., $\nu_{1/2}$ = 8–10 Hz for signals below 135 ppm and $\nu_{1/2}$ = 4–5 Hz for those above that limit. These observations revealed the two >135-ppm signals to belong to the nonprotonated aromatic carbons, in view of their coupling with aromatic methines, and the <135-ppm resonances to be associated with the olefinic carbons. Finally, both coupling information and neighboring group effects permitted the differentiation of each carbon within the two sets of nonprotonated carbon centers. All carbon shifts of ketones **1b** and **2b** are listed in Table I.

With the ^{13}C NMR spectral analysis of the starting ketones as background, a priori ^{13}C NMR principles permitted the shift assignment of their formylation–cyclization products **3** and **4** as well as of the tetrahydro derivatives **5** and **6**, respectively. A Yb(dpm)$_3$ shift study on ketones **3** and **5** confirmed the signal designations and was in agreement with the stereochemistry assignment for tetracycle **5**. All resonances are depicted in Table I. Those for compounds **10** and **11** are portrayed on formulas **22** and **23**, respectively.



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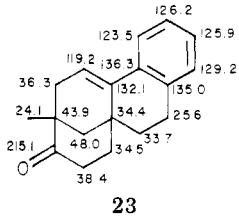

23

The $C_{20}H_{24}O_2$ product of acid-catalyzed condensation of ketone **1b** with triethyl orthoformate revealed unconjugated alkylbenzene and five-membered-ring ketone chromophores through its ultraviolet absorption maxima at 266 (log ϵ 2.66) and 273 nm (2.65) and carbonyl infrared absorption band of 1740 cm^{-1} (potassium bromide pellet), respectively. Its ^1H NMR spectrum exhibited a methyl group on a nonprotonated carbon center, another methyl function attached to an oxymethine unit, two benzylic hydrogens, and three normal aromatic hydrogens and one appreciably deshielded in the form of the following signals: a three-hydrogen 0.89-ppm singlet, a three-hydrogen 1.27-ppm doublet (J = 6 Hz) and a one-hydrogen 3.68-ppm quartet (J = 6 Hz), a two-hydrogen 2.8–3.0-ppm multiplet, a three-hydrogen 7.0–7.3-ppm multiplet, and a one-hydrogen 7.4–7.5-ppm multiplet, respectively. Whereas these data were in agreement with formula **20a**, they were not structurally conclusive.

The ^{13}C NMR spectra showed the compound to possess two methyl groups, six methylenes, one methine, one oxymethine, four aromatic methines, two quaternary carbon sites, one oxygenated and two aromatic nonprotonated carbon centers, and a carbonyl group. Inspection of the two-bond, carbon–hydrogen coupling characteristics of the methyl groups in a gated spectrum differentiated them and indicated their respective attachments to a quaternary carbon center and methine. One methylene unit was shielded strongly and thus under the influence of several γ effects, reminiscent of the spectral behavior of C(2) in labdanic and related diterpenes.[11] Specific decoupling experiments showed the nonprotonated, aromatic carbons to be adjacent to a methylene group and a nonprotonated carbon center.

In order to explore the substitution pattern around the carbonyl group of the cyclopentanone moiety, whose presence in the compound had been demonstrated by the infrared spectrum (vide supra), the δ values were compared with those of an alcohol (**20b**), prepared by reduction of **20** with lithium aluminium hydride, which reverted to the initial ketone on Collins oxidation. Since a keto function strongly deshields its α carbons, the reduction was expected to cause appreciable upfield shifts of two signals. This change was observed for a quaternary carbon and methine, implying that the pentacyclic $C_{20}H_{24}O_2$ ketone, derived from **1b** and structurally based on tetracycle **5**, had one of the termini of its fifth ring attached to its α-keto carbon C(12) in conformity with proposed structure **20a**. However, complete structure analysis and signal assignment required a lanthanide shift study on the ketone and its reduction product. These data are compiled in Table I.

The lanthanide shift differences for the ketone are in full accord with the mechanistically derived structure **20a**, the anomalous $\Delta\delta$ values for C(14) and C(15) being due to minor coordination of the lanthanide with the ether oxygen. In view of the much greater complexation difference between a hydroxy and ether unit than keto vs. ether moieties, no unexpected phenomena were observed in the lanthanide shift investigation of the alcohol. Not only did it prove structure **20b** for the alcohol, but it also revealed the stereochemistry at the hydroxycarbon site. Whereas hydride reduction of the cage-like ketone **20a** might have been predicted to occur from outside the cage, structure **20b** for the product suggested aluminum hydride coordination with the ether oxygen and subsequent intramolecular hydride transfer to the carbonyl group from the inside of the cavity.

Experimental Section

Melting points observed in capillary tubes are uncorrected. Infrared spectra of chloroform solutions were recorded on Beckman IR-20A and Acculab-4 spectrophotometers and ultraviolet spectra of ethanol solutions were recorded on a Beckman DU spectrophotometer. ^1H NMR spectra of deuteriochloroform solutions with tetramethylsilane acting as internal standard (δ = 0 ppm) were taken on Varian T-60A and XL-100 spectrometers and ^{13}C NMR spectra were obtained on a Varian XL-100-15 spectrometer operating at 25.2 MHz in the Fourier transform mode. The δ values on formulas **22** and **23** are in parts per million downfield from Me_4Si; $\delta(Me_4Si) = \delta(CDCl_3) + 76.9$ ppm.

1-Acetyl-1-methyl-1,2,3,4,9,10-hexahydrophenanthrene (1b). The dry sodio salt of acid **1a**[2] (prepared from 2.5 g (10.4 mmol) of the acid[2]) and 0.25 mL of dry pyridine were suspended in 50 mL of anhydrous benzene and cooled in an ice bath, and 2.8 mL (32.5 mmol) of oxalyl chloride was added slowly with

(10) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, 1972, p 99.

(11) (a) E. Wenkert, B. L. Buckwalter, I. R. Burfitt, M. J. Gašić, H. E. Gottlieb, E. W. Hagaman, F. M. Schell, and P. M. Wovkulich, in G. C. Levy, "Topics in Carbon-13 NMR Spectroscopy", Vol. 2, Wiley-Interscience, New York, 1976, pp 81–121; (b) B. L. Buckwalter, I. R. Burfitt, A. A. Nagel, E. Wenkert, and F. Näf, *Helv. Chim. Acta*, **58**, 1567 (1975).

(12) H. Günther, H. Schmickler, and G. Jikeli, *J. Magn. Reson.*, 11, 344 (1973); H. Günther, G. Jikeli, H. Schmickler, and J. Prestien, *Angew. Chem.*, **85**, 826 (1973).

Table I. Carbon and Lanthanide Shifts of Hydrophenanthrenes and Hydrofluorenes[a,b]

	1b	3		5		20a		20b		2b	4	6	21
	δ	δ	Δδ	δ	Δδ	δ	Δδ	δ	Δδ	δ	δ	δ	δ
C(1)	53.4	51.2	34.4	52.3	30.5	51.1	8.7	43.7	62.0	50.7	49.8	52.9	54.2
C(2)	33.2	33.0	27.2	31.0	21.0	29.3	5.3	29.5	44.5	34.0	36.5	30.5	30.6
C(3)	18.8	22.9	22.9	21.3	9.7	18.6	4.7	20.9	35.0	19.3	22.3	21.9	19.3
C(4)	25.4[c]	123.1	8.4	24.2	7.0	38.1	2.7	37.8	24.5	22.1	120.8	31.2	37.3
C(4a)	128.8	135.8	13.0	39.4	9.0	78.1	2.2	78.9	33.5	137.7	138.6	48.8	85.6
C(5a)	135.4	134.3	5.0	138.4	5.0	141.9	2.0	141.9	17.0	144.7	141.9	147.3	149.3
C(5)	121.7	124.9	3.4	124.9	3.2	125.3	2.0	124.9	11.0	118.0	120.3	123.8	122.5
C(6)	125.8	126.0	2.4	125.4	2.5	126.0	1.3	126.1	6.0	125.9	125.3	126.1	126.6
C(7)	125.8	127.0	2.0	125.4	2.5	126.4	0.3	126.3	4.0	123.1	127.9	126.1	127.1
C(8)	126.7	128.5	4.0	128.4	2.5	127.9	1.3	127.9	8.0	124.2	127.0	124.8	124.7
C(8a)	135.0	134.0	4.6	135.2	4.5	134.8	1.3	135.6	12.0	141.6	140.5	140.1	137.0
C(9)	28.2	26.6	9.0	26.1	5.5	25.3	1.3	26.2	12.0	37.3	38.2	38.8	36.0
C(10)	25.2[c]	34.8	11.6	28.9	12.0	24.7	2.7	25.3	17.5				
C(10a)	134.5	50.6	18.2	43.1	17.3	43.7	5.3	43.7	36.0	142.3	60.2	51.0	49.2
C(11)	208.2	213.2	68.0	221.4	82.0	220.2	22.4	85.1	250.0	211.3	215.4	222.5	223.5
C(12)	25.3	128.8	36.0	32.7	33.5	49.5	11.3	42.0	58.5	26.0	128.6	34.5	51.8
C(13)		165.7	28.4	19.6	15.0	32.8	4.7	34.7	31.0		167.3	30.8	27.5
C(14)						74.1	8.0	74.3	47.0				74.7
C(15)						20.6	8.0	28.0	25.0				21.2
1-Me	21.4	15.9	23.0	13.8	22.0	19.2	5.3	21.5	36.0	23.3	22.6	21.3	23.0

[a] The δ values are in ppm downfield from Me_4Si; δ(Me_4Si) = δ($CDCl_3$) + 76.9 ppm. [b] The Δδ values are Yb(dpm)$_3$-induced molar shifts in ppm [cf. E. Wenkert, G. V. Baddeley, I. R. Burfitt, and L. N. Moreno, *Org. Magn. Reson*, 11, 337 (1978)]. [c] These signals may be reversed.

stirring. The mixture was stirred while cooling for 0.5 h and at 60 °C for 1 h and filtered. The filtrate was evaporated under vacuum and the residue taken up in 100 mL of anhydrous ether. A solution of diethyl ethoxymagnesium malonate,[13] prepared from 2.5 g of magnesium, 16 mL of diethyl malonate, carbon tetrachloride (catalyst), and ethanol in 100 mL of ether, was added slowly to the stirred ether solution of the crude acid chloride with salt–ice bath cooling. Stirring was continued for 2 h with cooling and then for 12 h at room temperature. The mixture was added to 400 mL of ice-cold 2 N sulfuric acid. The combined ether solution and ethereal extracts of the aqueous solution were washed with water, 5% sodium carbonate solution, and again water and dried (Na_2SO_4). A solution of the residue from the distillation of solvent and excess diethyl malonate, 5 mL of concentrated sulfuric acid, and 25 mL of water in 4 mL of acetic acid was refluxed under nitrogen for 7 h. The mixture was added to saturated brine solution and extracted with ether. The extract was washed with 5% sodium carbonate solution and water, dried (Na_2SO_4), and evaporated under vacuum, leaving 1.9 g (77%) of a waxy solid, mp 70–72 °C. Filtration as a pentane solution through neutral alumina and crystallization from pentane yielded ketone **1b**: mp 84–86 °C; IR C=O 1700 (s), C=C 1600 (m) cm^{-1}; UV λ_{max} 265 nm (log ε 4.10); ^{1}H NMR δ 1.29 (s, 3, Me), 1.5–2.0 (m, 4, methylenes), 2.11 (s, 3, Ac Me), 2.4–2.8 (m, 6, allylic, benzylic CH_2), 7.0–7.3 (m, 4, aromatic H's).

Anal. Calcd for $C_{17}H_{20}O$: C, 84.95; H, 8.39. Found: C, 85.06; H, 8.59.

1-Acetyl-1-methyl-1,2,3,4-tetrahydrofluorene (2b). The dry sodio salt (3.0 g, 13.1 mmol) of acid **2a**[3] and 0.30 mL of dry pyridine in 60 mL of dry benzene were treated with 4.0 mL of oxalyl chloride according to the above procedure. This procedure was followed also for the reaction of a solution of the resultant acid chloride in 100 mL of dry ether with diethyl ethoxymagnesium malonate (from 2.5 g of magnesium 16 mL of diethyl malonate and 12 mL of ethanol). Finally, the above method led to the hydrolytic decarboethoxylation of the formed acylmalonate with 2 mL of concentrated sulfuric acid and 10 mL of water in 16 mL of acetic acid. Chromatography of a pentane solution of the crude product on neutral alumina gave 2.1 g (80%) of colorless, liquid ketone **2b**: IR C=O 1700 (s), C=C 1600 (m) cm^{-1}; UV λ_{max} 260 nm (log ε 4.10); ^{1}H NMR δ 1.30 (s, 3, Me), 2.03 (s, 3, Ac Me), 1.5–2.4 (m, 6, methylenes), 3.20 (br s, 2, benzyl CH_2), 7.0–7.4 (m, 4, aromatic H's). Crystallization of its 2,4-dinitrophenylhydrazone from methanol yielded a compound with mp 153 °C.

Anal. Calcd for $C_{22}H_{22}O_4N_4$: C, 65.01; H, 5.46. Found: C, 65.03; H, 5.30.

2-Acetyl-2-methyl-1,2,3,4,9,10-hexahydrophenanthrene (9b). A solution of crude 1-vinyl-1-tetralol (prepared by the interaction of vinylmagnesium bromide with 30.0 g (17 mmol) of α-tetralone in tetrahydrofuran), 0.2 g of iodine, 0.5 mL of quinoline, and 48.0 g (48 mmol) of methyl methacrylate in 200 mL of anhydrous benzene was refluxed for 9 h in the presence of a Dean–Stark water separator.[14] After the usual workup and distillation (140–170 °C (0.2 torr)) of the Diels–Alder adduct (UV λ_{max} 257 nm) a benzene solution (200 mL) of the pale yellow oil was saturated with dry hydrogen chloride gas at 0 °C for 4 h and then evaporated. Distillation (160–170 °C (0.2 torr)) of the residue gave 18 g of liquid ester isomer (UV λ_{max} 260 nm). A methanol (200 mL) solution of this ester containing 19 g of potassium hydroxide and 19 mL of water was refluxed for 8 h. The usual workup yielded 10 g of crude acid mixture, whose anhydrous chloroform solution was saturated with dry hydrogen chloride gas according to a published procedure[15] for the separation of the Diels–Alder regioisomeric adducts. Separation of the neutral product (1.2 g of 4aβ-hydroxy-1α-methyl-1,2,3,4,4a,9,10,10aα-octahydrophenanthrene-1β-carboxylic 4a-lactone (mp, mmp[2] 180–181 °C) and crystallization of the acidic product from ethyl acetate gave 7.5 g (18%) of solid, mp 164–167 °C, whose crystallization from methanol afforded acid **9a**: mp 167 °C; IR C=O 1700 (s) cm^{-1}; UV λ_{max} 260 nm (log ε 4.26).

Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.29; H, 7.50.

A mixture of the dry sodio salt (from 7.0 g of acid **9a**) and 2 mL of pyridine in 250 mL of anhydrous benzene was treated with 8.0 mL of oxalyl chloride according to the above procedure. The crude acid chloride was reacted with ethereal diethyl ethoxymagnesium malonate (from 5 g of magnesium and 32 g of diethyl malonate in 27 mL of ethanol), and the resultant acylmalonate was hydrolyzed and decarboxylated according to the above procedure. Filtration of a pentane solution through neutral alumina yielded 6.8 g (96%) of liquid ketone **9b**: IR C=O 1700 (s) cm^{-1}; UV λ_{max} 262 nm (log ε 4.07); ^{1}H NMR δ 1.10 (s, 3, Me), 2.06 (s, 3, Ac Me), 6.9–7.2 (m, 4, aromatic H's).

Anal. Calcd for $C_{17}H_{20}O$: C, 84.95; H, 8.34. Found: C, 85.01; H, 8.24.

Reactions of Ketones 1b, 2b, and 9b with Methyl Orthoformate. A mixture of 1.50 g (6.20 mmol) of ketone **1b**, 20 mL

(13) J. A. Price and D. S. Tarbell, "Organic Syntheses", Collect. Vol. 4, Wiley, New York, 1963, p 285.

(14) Cf. P. N. Chakrabortty, R. Dasgupta, S. K. Dasgupta, S. R. Ghosh, and U. R. Ghatak, *Tetrahedron*, 28, 4653 (1972).

(15) T. R. Klose and L. N. Mander, *Aust. J. Chem.*, 27, 1287 (1974).

(184 mmol) of methyl orthoformate, and 0.7 mL of 70% perchloric acid in 25 mL of benzene was stirred at room temperature for 1.8 h and then poured into 25 mL of 5% sodium carbonate. The organic solution was washed repeatedly with water, dried (Na_2SO_4), and evaporated under vacuum. Chromatography of the gummy solid residue on 30 g of neutral alumina and elution with pentane gave 650 mg (41%) of a colorless solid, whose crystallization from pentane yielded ketone **3**: mp 96 °C; IR C=O 1695 (s), C=C 1578 (m) cm^{-1}; UV λ_{max} 212 nm (log ϵ 4.50); ^1H NMR δ 1.12 (s, 3, Me), 1.5–2.4 (m, 6, methylenes), 2.8–3.0 (m, 2, benzyl CH_2), 6.01 (d, 1, J = 6 Hz, H-12), 6.23 (t, 1, J = 5 Hz, H-4), 7.1–7.4 (m, 4, aromatic H's), 7.49 (d, 1, J = 6 Hz, H-13).

Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.25; H, 7.29.

A mixture of 0.2 mL of 70% perchloric acid solution in 3 mL of benzene was added dropwise to a stirring solution of 500 mg (2.20 mmol) of ketone **2b** and 7.5 mL (60 mmol) of methyl orthoformate in 12 mL of benzene under nitrogen at 0 °C. Stirring was continued for 0.5 h at 0 °C and then at room temperature for 1.5 h. Workup as for **3** above, slow chromatography on 10 g of neutral alumina, and elution with pentane led to 75 mg of starting ketone and 100 mg of a solid, whose crystallization from pentane gave 60 mg (14% based on **2b** recovery) of ketone **4**: mp 105 °C; IR C=O 1700 (s), C=C 1590 (m) cm^{-1}; UV λ_{max} 220 nm (log ϵ 4.40), 253 (4.20), 290 (3.60); ^1H NMR δ 1.20 (s, 3, Me), 1.3–2.3 (m, 4, methylenes), 2.71, 3.26 (AB q, 2, J = 16 Hz, benzyl CH_2), 6.05 (d, 1, J = 6 Hz, α-keto H), 6.30 (t, 1, J = 4 Hz, olefinic H), 7.1–7.4 (m, 5, H-13, aromatic H's).

Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.55; H, 6.93.

Elution with 3:1 pentane–benzene yielded 85 mg of an incompletely characterized solid dimer: m/e 476 (M^+).

A solution of 0.6 mL of 70% perchloric acid was added dropwise to a stirring solution of 2.0 g (0.83 mmol) of ketone **9b** and 20 mL (184 mmol) of methyl orthoformate in 14 mL of dry benzene under nitrogen at −5 °C. Stirring was continued for 0.5 h at 0 °C and then at room temperature for 2 h. Workup as for **3** above, chromatography of the crude product on neutral alumina, and elution with 20:1 pentane–benzene yielded a solid whose repeated crystallization from pentane–ether afforded 840 mg (41%) of colorless ketone **10**: mp 108 °C; IR C=O 1670 (s) cm^{-1}; UV λ_{max} 235 nm (log ϵ 4.51); ^1H NMR δ 1.20 (s, 3, Me), 1.5–2.1 (m, 4, methylenes), 2.2–3.2 (m, 4, allyl, benzyl methylenes), 5.90 (d, 1, J = 9 Hz, α-keto H), 6.26 (t, 1, J = 4 Hz, olefinic H), 7.0–7.6 (m, 5, aromatic H's, β-keto H).

Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.34; H, 7.05.

Hydrogenations. A mixture of 150 mg of ketone **3** and 40 mg of 10% palladium–charcoal in 10 mL of ethanol was hydrogenated at atmospheric pressure. It was filtered after the uptake of 2 equiv of hydrogen in 1 h and the filtrate evaporated under vacuum. Crystallization of the residual solid, 150 mg (99%), from pentane yielded colorless ketone **5**: mp 102 °C; IR C=O 1725 (s), C=C 1595 (w) cm^{-1}; UV λ_{max} 260 nm (log ϵ 2.50), 266 (2.70), 273 (2.70); ^1H NMR δ 1.04 (s, 3, Me), 1.1–2.4 (m, 12, methylenes), 2.6–3.0 (m, 3, H_2-12, H-4a), 7.0–7.2 (m, 4, aromatic H's).

Anal. Calcd for $C_{18}H_{22}O$: C, 84.99; H, 8.72. Found: C, 84.73; H, 8.86.

A mixture of 130 mg of ketone **4** and 60 mg of 10% palladium–charcoal in 15 mL of ethanol was hydrogenated at atmospheric pressure. It was filtered after 1 h and the filtrate evaporated under vacuum. Crystallization of the solid residue, 110 mg (84%), from pentane gave colorless crystals of ketone **6**: mp 96 °C; IR C=O 1730 (s), C=C 1600 (w) cm^{-1}; UV λ_{max} 260 nm (log ϵ 2.80), 266 (3.09), 272 (3.10); ^1H NMR δ 0.95 (s, 3, Me), 1.0–3.2 (m, 13, methylenes, CH), 7.0–7.2 (m, 4, aromatic H's).

Anal. Calcd for $C_{17}H_{20}O$: C, 84.95; H, 8.39. Found: C, 84.68; H, 8.21.

Reactions of Ketones 1b, 2b, and 9b with Ethyl Orthoformate. An aqueous solution, 10 mL, of 70% perchloric acid was added slowly to a stirring solution of 1.00 g (4.2 mmol) of ketone **1b** and 10 mL of freshly distilled ethyl orthoformate in 7 mL of benzene and the stirring continued for 1 h. Saturated sodium carbonate solution, 20 mL, was added and the mixture extracted with ether. The extract was washed with water, dried (Na_2SO_4), and evaporated under vacuum. Chromatography of the solid residue on neutral alumina and elution with pentane led to 980 mg (80%) of a colorless solid whose crystallization from pentane yielded needles of ketone **20a**, mp 163–165 °C.

Anal. Calcd for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16. Found: C, 80.83; H, 8.20.

A solution of 0.6 mL of 70% perchloric acid in 2.5 mL of benzene was added dropwise to a stirring solution of 1.50 g (6.60 mmol) of ketone **2b** and 17.5 mL (105 mmol) of ethyl orthoformate in 15 mL of benzene under nitrogen at 5 °C. Stirring was continued for 0.5 h at 5 °C and at room temperature for 1.5 h. Workup as above and chromatography of the crude product, 1.8 g, on 30 g of neutral alumina yielded 750 mg of solid whose crystallization from pentane afforded 670 mg (37%) of ketone **21**: mp 121 °C; IR C=O 1730 (s), C=C 1600 (w) cm^{-1}; ^1H NMR δ 1.08 (s, 3, Me), 1.17 (d, 3, J = 6 Hz, H_3-15), 1.0–2.3 (m, 9, methylenes, CH), 2.68 (d, 1, J = 16 Hz, benzyl H), 3.08 (d, 1, J = 16 Hz, benzyl H), 3.39 (q, 1, J = 6 Hz, OCH), 7.1–7.3 (m, 4, aromatic H's).

Anal. Calcd for $C_{19}H_{22}O_2$: C, 80.81; H, 7.85. Found: C, 81.01; H, 8.08.

Perchloric acid, 0.6 mL of 70%, was added dropwise to a stirring solution of 2.00 g (0.83 mmol) of ketone **9b** and 20 mL of ethyl orthoformate in 14 mL of benzene at −5 °C. Stirring was continued for 2 h at −5 °C and then at room temperature for an extra 2 h. Workup as before, chromatography of the crude product on neutral alumina, and elution with pentane gave 1.76 g (85%) of crystalline solid, mp 139–141 °C. Elution with 9:1 pentane–benzene gave 80 mg of an uncharacterized substance. Crystallization of the pentane eluate from pentane yielded ketone **11**: mp 141 °C; IR C=O 1695 (s) cm^{-1}; UV λ_{max} 258 nm (log ϵ 4.27), 288 (3.61); ^1H NMR δ 1.10 (s, 3, Me), 1.4–2.5 (m, 10, methylenes), 2.7–3.1 (m, 2, α-keto CH_2), 6.46 (t, 1, J = 4 Hz, olefinic H), 7.0–7.2 (m, 3, aromatic H's), 7.5–7.8 (m, 1, aromatic H peri to olefin).

Anal. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.81; H, 8.11.

Interconversion of Pentacycles 20. A stirring mixture of 100 mg (0.33 mmol) of ketone **20a** and 300 mg (7.70 mmol) of lithium aluminum hydride in 150 mL of anhydrous ether was refluxed for 4 h and then poured into saturated sodium sulfate solution. The combined ether solution and ether extracts of the aqueous solution were dried (Na_2SO_4) and evaporated to yield 80 mg (79%) of a white solid, mp 120–125 °C. Crystallization of the latter led to colorless needles of alcohol **20b**: mp 125–126 °C; IR OH 3460 (m) cm^{-1}; ^1H NMR δ 0.89 (s, 3, Me), 1.3–2.8 (m, 16, H_3-15, methylenes, CH), 3.56 (q, 1, J = 6 Hz, H-14), 4.00 (br s, 1, H-11), 6.9–7.1 (m, 3, aromatic H's), 7.4–7.5 (m, 1, H-5).

Anal. Calcd for $C_{20}H_{26}O_2$: C, 80.49; H, 8.78. Found: C, 80.20; H, 8.80.

A solution of 50 mg (0.16 mmol) of alcohol **20b** in 5 mL of methylene chloride was added dropwise to a stirring mixture of 1.0 g (10 mmol) of chromium trioxide and 1.56 g of pyridine in 20 mL of methylene chloride at 0 °C. Stirring was continued for 0.5 h at room temperature. The supernatant liquid was decanted from the solid complex and the latter extracted thoroughly with methylene chloride. The combined organic solutions were washed with 5% sodium hydroxide solution, 5% hydrochloric acid solution, 5% sodium bicarbonate solution, and water, dried (Na_2SO_4), and evaporated. Crystallization of the residual, white solid, 35 mg (70%), from pentane gave ketone **20a**, mp 162–164 °C, spectrally identical with the above sample.

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Registry No. 1a, sodium salt, 72610-90-3; **1b**, 72610-91-4; **2a**, sodium salt, 72610-92-5; **2b**, 72610-93-6; **2b** DNP, 72610-94-7; **3**, 72610-95-8; **4**, 72610-96-9; **5**, 72610-97-0; **6**, 72610-98-1; **9a**, 72610-99-2; **9a**, sodium salt, 72611-00-8; **9b**, 69366-28-5; **10**, 72611-01-9; **11**, 72611-02-0; **20a**, 72611-03-1; **20b**, 72611-04-2; **21**, 72611-05-3; 1-vinyl-1-tetralol, 6244-50-4; vinyl bromide, 593-60-2; methyl methacrylate, 80-62-6; α-tetralone, 529-34-0; 4aβ-hydroxy-1α-methyl-1,2,3,4,4a,9,10,10aα-octahydrophenanthrene-1β-carboxylic **4a**-lactone, 72657-63-7; methyl orthoformate, 149-73-5; ethyl orthoformate, 122-51-0.