A Formylation-Cyclization Method of Synthesis of Cycloalkenones from Unsaturated Ketones. 2.[1] Simple Synthesis of Some Functionalized Bicyclo[3.3.1]nonane Derivatives

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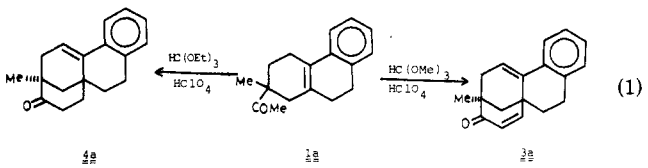
The potential generality of formylation-cyclization of a variety of γ,δ-unsaturated methyl ketones as a route to some functionalized bicyclo[3.3.1]nonane derivatives has been examined. Thus, perchloric acid catalyzed reactions of β-diethoxyethyl ketones **2a-c** and **14a-c**, derived from the 2-acetyl-2-methylhexahydrophenanthrenes and tetrahydrofluorenes **1a-c** and **13a-c**, respectively, in the absence and presence of triethyl orthoformate, afforded the corresponding bridged dienones **3a-c** and **15a-c** and enones **4a-c** and **16a-c** in excellent yields. The bridged enones **4b-c** and **16a-c** are also formed by direct reaction of the methyl ketones **1b,c** and **13a-c** with triethyl orthoformate and perchloric acid, similar to that with **1a**, reported earlier. While similar perchloric acid catalyzed reaction of **2b** and **13a,b** with trimethyl orthoformate gives the dienones **3b** and **15a,b**, the respective *p*-methoxystyrenoid derivatives **1c** and **13c** under identical conditions lead to the bicyclo[2.2.2]octanones **22** and **23**. Unlike the aforementioned 2-methyl 2-acetyl substrates, the desmethyl ketones **18a,b** and **20** and the respective β-diethoxyethyl derivatives **24a,b** and **25** on reaction with triethyl orthoformate and perchloric acid give only the respective bridged cyclodienones **26a,b** and **27** in good yield. Similarly, perchloric acid catalyzed reactions of β-diethoxyethyl ketones **31a-d** derived from 1-acetyl-4-arylcyclohex-3-enes (**30a-d**) in the presence or absence of triethyl orthoformate lead to the respective 6-arylbicyclo[3.3.1]nona-3,6-dien-2-ones (**32a-d**). The carbonyl conjugated double bond in the dienones **3a-c**, **15a-d**, and **32c,d** undergoes chemoselective catalytic hydrogenation using piperidine and palladium-charcoal, affording the respective enones **4a-c**, **16a-c**, and **33c,d**.

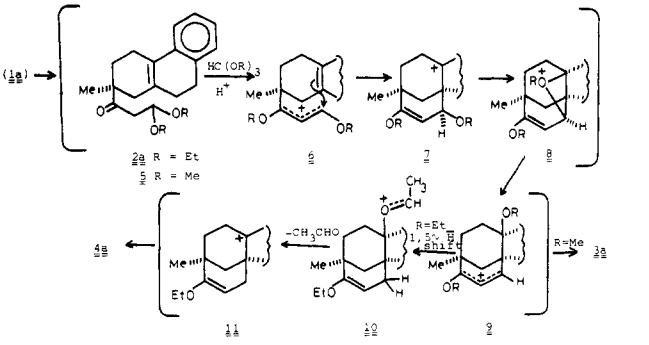
The carbon-oxygen bond formation involving ortho esters with aldehydes or ketones is a well-established reaction.[2] On the other hand, carbon-carbon bond formations by ortho esters, for examples, ethyl and methyl orthoformates, have only been occasionally used.[3,4] Recently we reported[1] a perchloric acid catalyzed formylation-cyclization reaction of the rigid γ,δ-unsaturated methyl ketone **1a** to the bridged dienone **3a** and the enone **4a**, respectively (eq 1), with methyl and ethyl orthoformates in



(1)

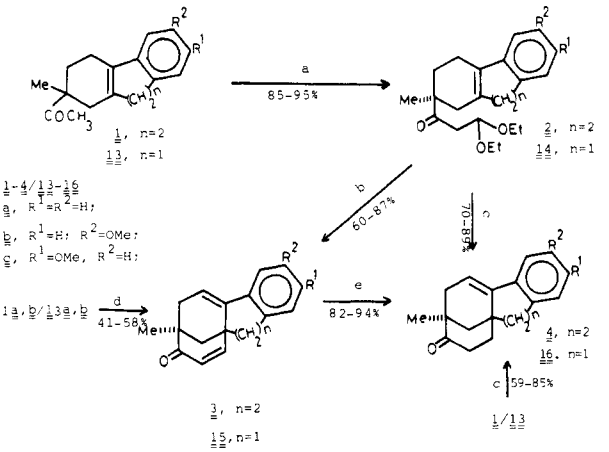
4a **1a** **3a**

a one-pot operation, presumably proceeding through a complex sequence of reactions **2a**/**5** → **9** → **11** (eq 2) involving the intermediate dialkoxyethyl ketone **2a** or **5**. Since the annulation reaction appeared quite attractive as a general method for the construction of functionalized bicyclo[3.3.1]nonane derivatives,[5] a study of its versatility and limitations has been undertaken. The initial phase of this investigation leading to the development of a highly



(2)

Scheme I[a]



[a] (a) $CH(OEt)_3$, $Et_2O{\cdot}BF_3$, $(i\text{-}Pr)_2NEt$, CH_2Cl_2; (b) $HClO_4$, C_6H_6; (c) $HClO_4$-$CH(OEt)_3$, C_6H_6; (d) $HClO_4$-$CH(OMe)_3$, C_6H_6; (e) H_2 Pd(C), $C_5H_{11}N$.

efficient two-step formylation-cyclization route to such compounds is described here.[6] The present work also

† Neé Dasgupta.

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(3) (a) Sathe, V. R.; Venkataraman, K. *Curr. Sci.* **1949**, *18*, 373. (b) Becket, G. J. P.; Ellis, G. P.; Trindade, M. I. *J. Chem. Res. Synop.* **1978**, 47; *J. Chem. Res. Miniprint* **1978**, 0865-0884, (c) Dorofeenko, G. N.; Mezheritskii, V. V. *J. Org. Chem. USSR (Engl. Transl.)* **1968**, *4*, 1260. (d) Dorofeenko, G. N.; Tkachenko, V. V. *Chem. Heterocycl. Compd.* **1972**, *8*, 935. (e) Treibs, W. *Tetrahedron Lett.* **1967**, 4707. (f) Kirby, E. C.; Reid, D. H. *J. Chem. Soc.* **1961**, 1724. (g) Hafner, K.; Pelster, H.; Schneider, J. *Ann.* **1961**, *650*, 62. (h) Gross, H.; Rieche, A.; Matthey, G. *Ber.* **1963**, *96*, 308. (i) Dusza, J. P.; Joseph, J. P.; Bernstein, S. *J. Am. Chem. Soc.* **1964**, *86*, 3908. (j) Pettit, G. R.; Knight, J. C.; Herald, C. L. *J. Org. Chem.* **1970**, *35*, 1393. (k) Morita, K.; Nishimura, M.; Suzuki, Z. *J. Org. Chem.* **1965**, *30*, 533. (l) Morita, K.; Slomp, G.; Jensen, E. V. *J. Am. Chem. Soc.* **1962**, *84*, 3779. (m) Morita, K.; Suzuki, Z. *Tetrahedron Lett.* **1964**, 263. (n) Mukaiyama, T.; Hayashi, N. *Chem. Lett.* **1974**, 15. (o) Miller, B. *J. Org. Chem.* **1981**, *46*, 2795. (p) Takazawa, O.; Mukaiyama, T. *Chem. Lett.* **1982**, 1307. (q) Suzuki, M.; Yanagisawa, A.; Noyori, R. *Tetrahedron Lett.* **1982**, *23*, 3595.

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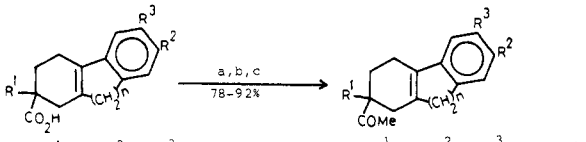
Scheme II[a]



12b, R^1=Me, R^2=H, R^3=OMe, n=1
17a, R^1=R^2=R^3=H, n=2
17b, R^1=R^3=H, R^2=OMe, n=2
19, R^1=R^3=H, R^2=OMe, n=1

13b, R^1=Me, R^2=H, R^3=OMe, n=1
18a, R^1=R^2=R^3=H, n=2
18b, R^1=R^3=H, R^2=OMe, n=2
20, R^1=R^3=H, R^2=OMe, n=1

[a] (a) NaOMe–MeOH, $(COCl)_2$-C_6H_5N-C_6H_6; (b) $(EtO)MgCH(CO_2Et)_2$, Et_2O; (c) AcOH–H_2SO_4–H_2O (8:1:5).

provides direct evidence in support of the proposed mechanism.

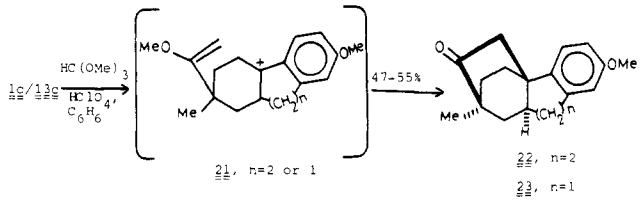
Results and Discussion

In order to probe the intermediacy of the dialkoxyethyl ketones (**2a**/**5**) in the acid-catalyzed orthoformate-induced annulation, detailed study was first undertaken with the methyl ketone **1a**. The interaction of **1a** with diethoxycarbonium fluoroborate according to Mock and Tsou,[4] afforded the β-diethoxyethyl ketone **2a** in excellent yield (Scheme I). This relatively unstable intermediate, characterized by spectral data, on cyclization with perchloric acid (70%) in benzene gave the dienone **3a** in 87% yield, which was obtained only in 41% yield[1] in the one-pot sequence (eq 1). In contrast, repeating the cyclization of **2a** with an excess of ethyl orthoformate under identical conditions gave the enone **4a** in 89% yield. Obviously, in the perchloric acid catalyzed reaction of **1a**, the dienone **3a** originates by the normal electrophilic cyclization followed by elimination of the β-ethoxy group from the cyclized ketone, whereas in the presence of ethyl orthoformate the sequence of reactions involving the alkoxy transfer and 1,5-hydride shift, for example **7** → **8** → **9** (R = Et) → **10** (eq 2) can only account for the formation of **4a**. Thus, the present observations clearly support the mechanism depicted in eq 2.

Having ascertained the optimal conditions for synthesis of the dienone **3a** and enone **4a** by the two-step process, we investigated this sequence on the rigid hexahydrophenanthrene and tetrahydrofluorene methyl ketones **1b,c**, **18a,b** and **13a–c**, **20** respectively. The preparations of **1b,c** and **13a,c** were reported earlier.[7] The ketones **13b**, **18a,b**, and **20** were readily available in good yields by condensation of the acid chlorides, prepared from the known acids **12b**,[8] **17a,b**,[9] and **19**,[8] with diethyl ethoxymagnesium malonate[10] followed by hydrolytic decarboxylation with acetic acid and dilute sulfuric acid (Scheme II).

Initially, each of the *gem*-acetylmethyl substrates **1b,c** and **13a–c** (structurally related to **1a**) was converted to the respective β-diethoxyethyl derivaties **2b,c** and **14a–c** and submitted to cyclization with perchloric acid (70%) in benzene to afford the corresponding cyclodienones **3b,c** and **15a–c** in excellent yields. Repeating the cyclizations of **1b,c** and **13a–c** with excess triethyl orthoformate in the presence of perchloric acid gave the respective cycloalkenones **4b,c** and **16a–c** in good yields (Scheme I). Direct formylation–cyclization[1] of the methyl ketones **1b,c** and **13a–c** with ethyl orthoformate in benzene in the presence of perchloric acid also furnished the respective enones **4b,c** and **16a–c** in comparable yields. The IR and ^1H NMR spectra of these compounds (see the Experimental Section) are in complete agreement with the assigned structures. The carbonyl conjugated double bond in the dienones **3a–c** and **15a–c** underwent highly chemoselective hydrogenation[11] in the presence of Pd–C (10%) in piperidine to afford the respective enones **4a–c** and **16a–c** in excellent yields. Each of the solvents such as *N*-methylpiperidine, pyrrolidine, pyridine, γ-picoline, or collidine was also equally effective. However, hydrogenation in pyridine required a relatively longer time.

Scheme III



21, n=2 or 1

22, n=2
23, n=1

In accord with the previous finding[1] (cf. eq 1), the methyl ketones **1a,b** and **13a,b** on reaction with excess trimethyl orthoformate in the presence of perchloric acid afforded the expected dienones **3a,b** and **15a,b** in 41–58% yields (Scheme I). In contrast, the *p*-methoxy ketones **1c** and **13c**, under identical reaction conditions, gave the known[7] bridged ketones **22** and **23** in 55% and 47% yields, respectively, evidently through intramolecular C-alkylation of the corresponding protonated enol ether intermediates (e.g., **21**) (Scheme III) in preference to the alternative formylation–cyclization sequence. The enhanced facility for intramolecular alkylation in enol ethers similar to **21** has been utilized in this laboratory[7] in the syntheses of **22** and **23**.

The presence or absence of an α′-methyl group in the methyl ketone substrates seems to have an influence on the course of the formylation–cyclization reactions. Thus, perchloric acid catalyzed cyclizations of the diethoxyethyl derivatives **24a,b** and **25** from the ketones **18a,b** and **20** having no α′-methyl group, in the presence or absence of triethyl orthoformate, gave only the respective dienones **26a,b** and **27** in good yields (Scheme IV). Direct reaction of **18a,b** and **20** with triethyl orthoformate and perchloric acid again produced the dienones **26a,b** and **27** as the only isolable products in comparable yields. That alkoxy hydride transfer is retarded in this series is supported by the isolation of the β-methoxy ketone **28** (R^1 = OMe; R^2 = H, X = Me, *n* = 1) in perchloric acid catalyzed reaction of **20** with trimethyl orthoformate. This was smoothly converted to the respective dienone **27** by treatment with *p*-toluenesulfonic acid in boiling benzene.

In order to explore the synthetic potentiality of the formylation–cyclization reactions, we have also investigated the structurally related monocyclic, γ,δ-unsaturated methyl ketones **30a–d**. These were obtained in excellent yields

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(5) For comprehensive review, see: Peters, J. A. *Synthesis* **1979**, 321.
(6) A part of the work has been reported in a communication: Dasgupta, R.; Ranu, B.; Ghatak, U. R. *Indian J. Chem.* **1983**, *22B*, 619.
(7) Kanjilal, P. R.; Sarkar, M.; Patra, S. K.; Ghosh, S.; Ghatak, U. R. *J. Org. Chem.* **1985**, *50*, 857.
(8) Ranu, B. C.; Sarkar, M.; Chakraborti, P. C.; Ghatak, U. R. *J. Chem. Soc., Perkins Trans. 1* **1982**, 865.
(9) Chakrabortty, P. N.; Dasgupta, R.; Dasgupta, S. K.; Gosh, S. R.; Ghatak, U. R. *Tetrahedron* **1972**, *28*, 4653.
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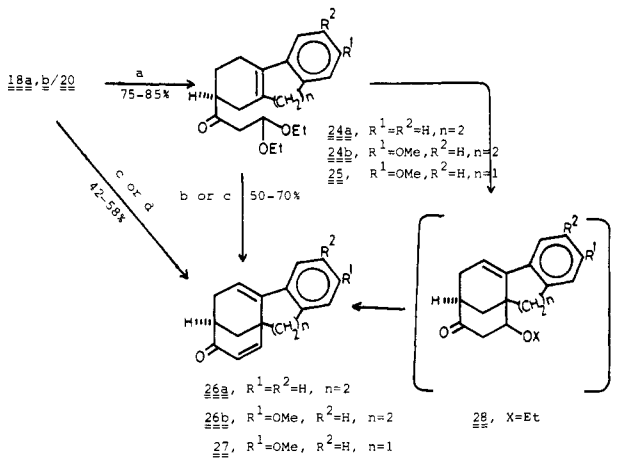
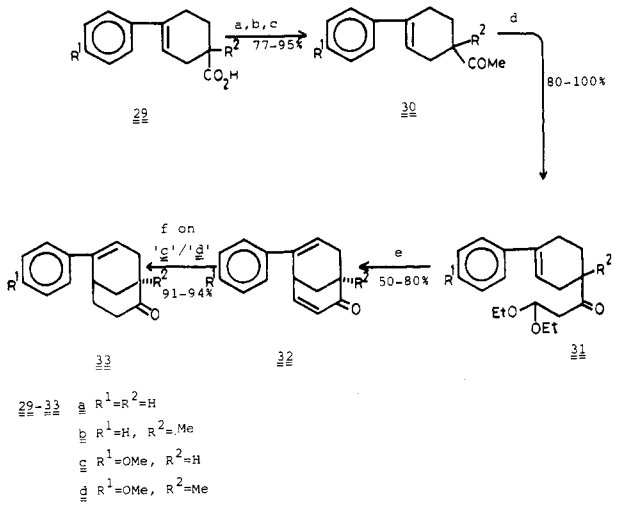
(11) Although the rate of hydrogenation of isolated olefins over a platinum or a palladium catalyst shows a sharp decrease in basic media, the hydrogenation of the double bond of an α,β-unsaturated ketone, however, is unaffected or slightly increased by the addition of moderate amounts of base: Augustine R. L. In "Catalytic Hydrogenation"; marcel Dekker: New York, 1965; p 46. This information has been used only to a limited extent for the selective hydrogenation of a carbonyl conjugated over an isolated double bond: McQuillin, F. J.; Ord, W. O. *J. Chem. Soc.* **1959**, 2902. Loewenthal, H. J. E. *Tetrahedron* **1959**, *6*, 269.

Scheme IV[a]



[a] (a) $CH(OEt)_3$, $Et_2O{\cdot}BF_3$, $(i\text{-}Pr)_2NEt$, CH_2Cl_2; (b) $HClO_4$-C_6H_6; (c) $HClO_4$-$CH(OEt)_3$-C_6H_6; (d) $HClO_4$-$CH(OMe)_3$-C_6H_6.

Scheme V[a]



[a] (a) NaOMe-MeOH, $(COCl)_2$, C_6H_5N, C_6H_6; (b) $(EtO)MgCH(CO_2Et)_2$, Et_2O; (c) AcOH-H_2SO_4-H_2O (8:1:5); (d) $CH(OEt)_3$, $Et_2O{\cdot}BF_3$, $(i\text{-}Pr)_2NEt$, CH_2Cl_2; (e) $HClO_4$-C_6H_6; (f) H_2 Pd(C), $C_6H_{11}N$.

by condensation of the respective acid chlorides from the known acids **29a–d**,[12] prepared in improved yields, with diethyl ethoxymagnesium malonate followed by hydrolytic decarboxylation (Scheme V). While each of **30a** and **30b** was recovered unchanged on reaction with methyl orthoformate and perchloric acid in benzene, identical acid-catalyzed reaction with ethyl orthoformate gave a complex mixture of products in both the cases. However, the β-diethoxyethyl ketones **31a–d**, prepared from **30a–d**, underwent smooth electrophilic cyclization and elimination of ethanol with perchloric acid in benzene to afford bridged dienones **32a–d** in good yields. Repeating the cyclization of **31a–d** with perchloric acid in the presence of triethyl orthoformate also gave only the dienones **32a–d** in good yield, thereby indicating that the ethoxy group does not play any role in this reaction.

While the dienones **32c** and **32d** were smoothly reduced to the respective enones **33c** and **33d** on catalytic hydrogenation over Pd–C (10%) in piperidine or pyridine, the desmethoxy ketones **32a,b** gave some over reduction products along with the respective enones **33a,b**.

In conclusion, the present method provides a simple synthetic entry to some highly functionalized bicyclo-[3.3.1]nonane derivatives and a better understanding of the mechanism of the one-pot formylation–cyclization reaction.[1]

Experimental Section

The compounds described are all racemates. Melting points taken in open capillary tubes, are uncorrected. UV spectra were recorded for solutions in 95% ethanol. ^1H NMR spectra were recorded at 60 and 200 MHz. Column chromatography was performed on neutral alumina (aluminium oxide, active, Brockmann grade 1 for chromatographic analysis). Petroleum ether and light petroleum ether refer to the fractions boiling in the ranges 60–80 and 40–60 °C, respectively.

Preparation of Methyl Ketones 13b, 18a,b, 20, and 30a–d. 2-Acetyl-2-methyl-1,2,3,4-tetrahydro-6-methoxyfluorene (13b). A related procedure was adopted.[1] A solution of diethyl ethoxy magnesium malonate,[10] prepared from magnesium (1.0 g, 0.04 mol), diethyl malonate (6 mL), and ethanol (4.2 mL), in the presence of catalytic amount of CCl_4, in 50 mL of Et_2O was added slowly to the stirred solution of the acid chloride, made from acid **12b** (2.2 g, 8.53 mmol) by treatment with oxalyl chloride (3.04 g, 24.4 mmol) in the usual way[7] in 50 mL of Et_2O with salt ice bath cooling. Stirring was continued for 2 h at 0 °C and then for 12 h at room temperature. The mixture was added to 200 mL of ice-cold 2 N H_2SO_4, the Et_2O layer was separated, and the aqueous layer was extracted with Et_2O (2 × 50 mL). The combined Et_2O extracts were washed with H_2O, 5% aqueous Na_2CO_3, and again with H_2O and dried (Na_2SO_4). After evaporation of Et_2O, the crude mixture was refluxed with CH_3CO_2H (24 mL), concentrated H_2SO_4 (3 mL), and H_2O (15 mL) for 7 h under N_2. The reaction mixture was then diluted to 400 mL with H_2O and extracted with Et_2O (4 × 50 mL). The Et_2O extract was washed with H_2O, with 10% aqueous Na_2CO_3, and again with H_2O and dried (Na_2SO_4). Evaporation of Et_2O left a viscous liquid that on purification through a short column of neutral alumina (15 g) (eluted with petroleum ether) afforded a solid **13b**: (1.7 g (75%); mp 70 °C (light petroleum (ether); IR (KBr) 2930, 1700, 1600, 1485 cm^{-1}; UV λ_{max} 221 nm (log ε 4.25), 262 (3.81), 292 (3.52); ^1H NMR ($CDCl_3$) XL-200 δ 1.22 (3 H, s, Me), 1.76–2.94 (6 H, m), 2.18 (3 H, s, COMe), 3.24 (2 H, br s, $ArCH_2$), 3.84 (3 H, s, $ArOCH_3$), 6.66–6.80 (2 H, m, ArH), 7.30 (1 H, m, ArH). Anal. Calcd for $C_{17}H_{20}O_2$:C, 79.65; H, 7.96. Found: C, 79.55; H, 8.05.

2-Acetyl-1,2,3,4,9,10-hexahydrophenanthrene (18a). This was obtained in 85% yield from acid **17a** in the same way as above: bp 180–185 °C (0.1 mm); IR (neat) 2925, 1708, 1488, 1352 cm^{-1}; UV λ_{max} 264 nm (log ε 4.1), 270 (4.10); ^1H NMR (CCl_4) δ 1.25–2.97 (11 H, m), 2.11 (3 H, s, COMe), 6.93–7.10 (4 H, m). Anal. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 85.07; H, 7.98.

1-Acetyl-4-phenylcyclohex-3-ene (30a). This was obtained in 90% yield starting from acid **29a** as low-melting solid: mp 38 °C (light petroleum ether); IR (KBr) 2920, 1705, 1640, 1595 cm^{-1}; UV λ_{max} 246 nm (log ε 4.08); ^1H NMR (CCl_4) δ 2.10 (3 H, s, $COCH_3$), 1.92–2.66 (7 H, m), 6.0 (1 H, m, ArC=CH), 7.0–7.00 (5 H, m, ArH). Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 84.0; H, 8.16.

Preparation of β-Diethoxyethyl Ketones 2a–c, 24a,b, 14a–c, 25, and 31a–d. 2-Methyl-2-(1-oxo-3,3-diethoxypropyl)-1,2,3,4,9,10-hexahydrophenanthrene (2a). A related procedure was adopted.[4] A solution of freshly distilled $Et_2O{\cdot}BF_3$ (1.2 mL, 10 mmol) in 5 mL of CH_2Cl_2 was added dropwise to freshly distilled ethyl orthoformate (1.4 mL, 8 mmol) at −30 °C with stirring under nitrogen. The mixture was then allowed to warm to 0 °C, and stirring was continued at this temperature for 15 min. The resulting mixture was then cooled to −78 °C, and the solution of the ketone **1a** (960 mg, 4 mmol) in 5 mL of CH_2Cl_2 was added, followed by dropwise addition of *N,N*-diisopropyl ethylamine (3.2 mL, 12 mmol), over a period of 10 min. The temperature of the resulting mixture was then allowed to rise up to −10 to −20 °C, and the mixture was stirred at that range of temperature for 2 h. The reaction mixture was then poured rapidly to a saturated sodium bicarbonate solution (50 mL). More CH_2Cl_2 was added

(12) Ghatak, U. R.; Alam, S. K.; Chakraborti, P. C.; Ranu, B. C. *J. Chem. Soc. Perkins Trans. 1* **1976**, 1669.

and stirred vigorously for 20 min. The organic phase was separated and washed with cold, dilute sulfuric acid (2% v/v) followed by another washing with water. The CH_2Cl_2 solution was dried and evaporated to leave **2a** as yellow viscous liquid: 1.12 g (88%); IR (neat) 1700, 1625, 1590 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10 (6 H, t, J = 8 Hz, Me), 1.17 (3 H, s, tertiary Me), 2.76 (2 H, br d, J = 5 Hz, $COCH_2CH(OEt)_2$), 3.43–3.73 (4 H, m, OCH_2Me), 4.86 (1 H, t, J = 5 Hz, $COCH_2CH(OEt)_2$), 7.0 (4 H, m, ArH).

β-Diethoxyethyl 4-Phenylcyclohex-3-enyl Ketone (31a). This was obtained in 100% yield starting from ketone **30a** in the same way as above: IR (neat) 1710, 1600 cm^{-1}; ^1H NMR (CCl_4) δ 1.16 (6 H, t, J = 8 Hz, CH_3), 1.66–2.63 (7 H, m), 2.73 (2 H, d, J = 5 Hz, $COCH_2CH(OEt)_2$), 3.33–3.76 (4 H, m, OCH_2CH_3), 4.83 (1 H, t, J = 5 Hz, $COCH_2CH(OEt)_2$), 6.03 (1 H, m, ArC=CH), 7.06–7.33 (5 H, m, ArH).

Preparation of Bridged Dienones 3a–c, 15a–c, 26a,b, 27, and 32a–d. 2α-Methyl-1,2,3,9,10,10a-hexahydro-2β,10aβ-(11-oxopropeno)phenanthrene (3a) by Reaction of β-Diethoxyethyl Ketones 2a with $HClO_4$. To a stirred cooled (0 °C) solution of ketone **2a** (400 mg, 1.14 mmol) in 5 mL of benzene was added 70% aqueous $HClO_4$ (0.3 mL) under N_2. The reaction mixture was stirred at 0 °C for 2 h followed by 1 h at room temperature and then poured into 5% aqueous Na_2CO_3 solution (50 mL) and extracted with Et_2O (4 × 25 mL). The Et_2O solution was washed with brine and dried (Na_2SO_4). Evaporation of solvent left a gummy mass that on chromatography over neutral alumina (8 g) [benzene–petroleum ether (1:9)] afforded a solid (248 mg, 87%) identical with the sample of **3a** mentioned earlier.[1]

7-Methoxy-1,2,3,9a-tetrahydro-2β,9aβ-(10-oxopropeno)-fluorene (27). (A) The reaction of ketone **25** (200 mg, 0.58 mmol) with $HClO_4$ (0.25 mL) in the same way as above followed by chromatography [benzene–petroleum ether (1:1)] gave **27**: 80 mg (55%); mp 151 °C; IR (KBr) 2920, 1665, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.43–2.97 (7 H, m), 3.80 (3 H, s, $ArOCH_3$), 5.77 (1 H, t, J = 4 Hz, ArC=CH), 5.85 (1 H, d, J = 9 Hz, α-keto CH), 6.71–7.37 (4 H, m, ArH, with β-keto CH). Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 80.87; H, 6.46.

(B) The reaction of methyl ketone **20** (300 mg, 1.24 mmol) with $HC(OMe)_3$ (7 mL) in the presence of $HClO_4$ (0.8 mL) under the identical condition as above followed by chromatography gave the intermediate methoxy ketone **28** (X = Me): (148 mg (42%); mp 175–176 °C; IR (KBr) 1702, 1612 cm^{-1}; UV λ_{max} 262 nm (log ϵ 4.40), 302 (3.40); ^1H NMR ($CDCl_3$) δ 1.60–2.93 (9 H, m), 3.15 (3 H, s, OMe), 3.30–3.53 (1 H, m, oxyCH), 3.78 (3 H, s, $ArOCH_3$), 5.93 (1 H, t, J = 4 Hz, ArC=CH), 6.56–6.73 (2 H, m), 7.20–7.33 (1 H, m). Anal. Calcd for $C_{18}H_{20}O_0$: C, 76.03; H, 7.09. Found: C, 75.76; H, 7.11. This methoxy ketone, **28** (X = Me) (100 Mg, 0.35 mmol), was refluxed with 50 mL of benzene in the presence of *p*-TsOH, washed with water, and evaporated to leave a solid residue **27** 78 mg (88%).

6-Phenylbicyclo[3.3.1]nona-3,6-dien-2-one (32a). The reaction of ketone **31a** (325 mg, 1.07 mmol) with $HClO_4$ (0.25 mL) under the same condition as above followed by chromatography [benzene–petroleum ether (1:9)] gave **32a**: 125 mg (60%); bp 120 °C (0.05 mm); IR (neat) 2930, 1665, 1595, 1500 cm^{-1}; UV λ_{max} 237 nm (log ϵ 4.25); ^1H NMR (CCl_4) δ 1.83–3.46 (6 H, m), 5.83 (1 H, d, J = 6 Hz, α-keto CH), 5.9 (1 H, t, J = 5 Hz, ArC=CH), 7.1–7.4 (5 H, m, ArH), 7.2 (1 H, d, J = 6 Hz, β-keto CH). Anal. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.96; H, 6.45.

Preparation of the Bridged Enones 4a–c, 16a–c, 33c, and 33d. 2α-Methyl-1,2,3,9,10,10a-hexahydro-2β,10aβ-(11-oxopropano)phenanthrene 4a. (A) By Reaction of β-Diethoxyethyl Ketone 2a with $CH(OEt)_3$ and $HClO_4$. To a stirred cooled (−5 °C) solution of ketone **2a** (400 mg, 1.14 mmol) in 5 mL of benzene containing freshly distilled HC $(OEt)_3$ (7 mL) was added 70% aqueous $HClO_4$ (0.4 mL) under N_2. After being stirred at 0 °C for 2 h followed by 2 h at room temperature, the reaction mixture was worked up in the usual way. Chromatography of the gummy residue over neutral alumina (8 g) and elution with benzene–petroleum ether (1:3) gave after crystallization from light petroleum ether **4a** [305 mg (89%)] identical with the sample mentioned earlier.[1]

(B) By Reduction of Dienone 3a. The dienone **3a** (100 mg, 0.4 mmol) was hydrogenated in dry piperidine (3 mL) in the presence of 10% Pd–C (20 mg) at room temperature and atmospheric pressure for 2 h. The catalyst was then filtered off, and the solution was diluted with ice-cold 2 M HCl (25 mL) and extracted with Et_2O (3 × 20 mL). The Et_2O extract was washed with brine and dried (Na_2SO_4). Evaporation of Et_2O followed by crystallization from light petroleum ether gave **4a**, 91 mg (91%).

2α-Methyl-1,2,3,9a-tetrahydro-2β,9aβ-(10-oxopropano)-fluorene (16a). (A) The reaction of ketone **14a** (500 mg, 1.52 mmol) with $CH(OEt)_3$ and $HClO_4$ (0.5 mL) in the same way as above, followed by chromatography (petroleum ether) gave **16a**: 300 mg (83%); mp 110 °C (petroleum ether); IR (KBr) 2925, 1711, 1385 cm^{-1}; UV λ_{max} 254 nm (log ϵ 3.62), 288 (3.34); ^1H NMR ($CDCl_3$) δ 1.13 (3 H, s, CH_3), 1.66–2.80 (10 H, m), 6.06 (1 H, t, J = 4 Hz, ArC=CH), 7.18–7.50 (4 H, m, ArH). Anal. Calcd for $C_{17}H_{28}O$: C, 85.67; H, 7.61. Found: C, 85.63; H, 7.57.

(B) The reaction of ketone **13a** (400 mg, 1.76 mmol) with $CH(OEt)_3$ and $HClO_4$ (0.5 mL) followed by chromatography gave **16a** (352 mg (83%).

(C) Reduction of dienone **15a** (100 mg, 0.42 mmol) in piperidine (3 mL) in the presence of 10% Pd–C (20 mg) gave **16a**, 84 mg (84%).

Preparation of Bicyclo[2.2.2]octanones 22 and 23. 2α-Methyl-7-methoxy-1,2,3,4,4a,9,10,10aα-octahydro-2β,4aβ-(11-oxoethano)phenanthrene (22). The reaction of ketone **1c** (500 mg, 1.85 mmol) in 5 mL of benzene with $HC(OMe)_3$ (7 mL) and 70% $HClO_4$ (1 mL) under identical conditions as above followed by chromatography [benzene–petroleum ether (3:1)] gave **22** [275 mg (55%), identical with the authentic sample.[7]

2α-Methyl-7-methoxy-1,2,3,4,4a,9aα-hexahydro-2β,4aβ-(10-oxoethano)fluorene (23). The reaction of ketone **13c** (200 mg, 0.89 mmol) in 5 mL of benzene with $HC(OMe)_3$ (7 mL) and 70% $HClO_4$ (1 mL) under identical conditions as above followed by chromatography [benzene/petroleum ether (1:1)] gave **23** [94 mg (74%)], identical with the authentic sample.[7]

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Registry No. (±)-**1a**, 94751-79-8; (±)-**1b**, 94751-78-7; (±)-**1c**, 94751-77-6; (±)-**2a**, 99034-27-2; (±)-**2b**, 99034-29-4; (±)-**2c**, 99034-28-3; (±)-**3a**, 99034-39-6; (±)-**3b**, 99034-40-9; (±)-**3c**, 99034-41-0; (±)-**4a**, 99034-52-3; (±)-**4b**, 99034-53-4; (±)-**4c**, 99034-54-5; (±)-**12b**, 81907-95-1; (±)-**13a**, 94751-83-4; (±)-**13b**, 99052-82-1; (±)-**13c**, 94751-82-3; (±)-**14a**, 99034-32-9; (±)-**14b**, 99034-34-1; (±)-**14c**, 99034-33-0; (±)-**15a**, 99034-44-3; (±)-**15b**, 99034-45-4; (±)-**15c**, 99034-46-5; (±)-**16a**, 99034-57-8; (±)-**16b**, 99034-55-6; (±)-**16c**, 99034-56-7; (±)-**17a**, 28114-48-9; (±)-**17b**, 53567-99-0; (±)-**18a**, 99034-20-5; (±)-**18b**, 99034-21-6; (±)-**19**, 28114-47-8; (±)-**20**, 99034-25-0; (±)-**22**, 94840-94-5; (±)-**23**, 94840-95-6; (±)-**24a**, 99034-30-7; (±)-**24b**, 99034-31-8; (±)-**25**, 99052-83-2; (±)-**26a**, 99034-42-1; (±)-**26b**, 99034-43-2; (±)-**27**, 99034-47-6; (±)-**29a**, 61414-85-5; (±)-**29b**, 61414-83-3; (±)-**29c**, 49708-14-7; (±)-**29d**, 61414-84-4; (±)-**30a**, 99034-22-7; (±)-**30b**, 99034-23-8; (±)-**30c**, 99034-24-9; (±)-**30d**, 99034-26-1; (±)-**31a**, 99034-35-2; (±)-**31b**, 99034-36-3; (±)-**31c**, 99034-37-4; (±)-**31d**, 99034-38-5; (±)-**32a**, 99034-48-7; (±)-**32b**, 99034-49-8; (±)-**32c**, 99034-50-1; (±)-**32d**, 99034-51-2; (±)-**33c**, 99034-58-9; (±)-**33d**, 99034-59-0; diethyl ethoxymagnesium malonate, 35227-78-2.

Supplementary Material Available: Detailed preparation and physical data for **18a**, **20**, **30b–d**, **2c**, **2b**, **24a,b**, **14a–c**, **25**, **31b–d**, **3b,c**, **26a,b**, **15a–c**, **32b–d**, **4b**, **4c**, **16b**, **16c**, **33c**, and **33d** (11 pages). Ordering information is given on any current mastered page.