73%) of **40b**, identical with that obtained by the alternate route (Scheme V), was obtained.

Registry No. 3 (R = CH_3), 4630-82-4; **4** (R = CH_3; R′ = *cis*-$CH_2CH{=}CH(CH_2)_4OTHP$), 75266-82-9; **4** (R = CH_3; R′ = $(CH_2)_7OTHP$), 75266-83-0; **4a** (R = CH_3), 67838-02-2; **4b** (R = CH_3), 75266-84-1; **4c** (R = CH_3), 75266-85-2; **5a**, 67838-03-3; **5b**, 67838-04-4; **5c**, 67838-05-5; **6a**, 75266-86-3; **6b**, 75266-87-4; **6c**, 75266-88-5; **9**, 75266-89-6; **11**, 611-10-9; **13a**, 75266-90-9; *syn*-**14a**, 75330-88-0; *anti*-**14a**, 75330-89-1; *syn*-**14b**, 75266-91-0; *anti*-**14b**, 75330-90-4; *syn*-**14c**, 75266-92-1; *anti*-**14c**, 75330-91-5; **16b**, 75330-92-6; **17a**, 75266-93-2; **17b**, 67838-39-5; **17e**, 67838-46-4; **18a**, 75266-94-3; **19a**, 75266-95-4; **20a**, 75266-96-5; **21b**, 67838-27-1; **21c**, 75266-97-6; **24**, 58101-60-3; **26b**, 75266-98-7; **26c**, 75266-99-8; **28a**, 75267-00-4; **29c** methyl ester, 75267-01-5; **30c**, 75267-02-6; **31**, 32811-76-0; **32**, 67838-07-7; **33b**, 75267-03-7; **35b**, 75267-04-8; **36b**, 75267-05-9; **40a**, 75267-06-0; **40b**, 75267-07-1; **42**, 75267-08-2; **43**, 75267-09-3; **44** (R = *cis*-$CH_2CH{=}CH(CH_2)_3$), 75267-10-6; **44b**, 75267-15-1; **45b** (isomer 1), 75267-11-7; **45b** (isomer 2), 75330-93-7; **46a**, 75267-14-0; **46b**, 75267-16-2; **46b** methyl ester, 75267-12-8; $ICH_2CH{=}CH_2$, 556-56-9; $I(CH_2)_6CH_3$, 4282-40-0; $I(CH_2)_6OTHP$, 65785-44-6; *cis*-$BrCH_2CH{=}CH(CH_2)_4OTHP$, 75267-13-9; $Br(CH_2)_7OTHP$, 10160-25-5; $I(CH_2)_5OAc$, 65921-65-5; $Br(CH_2)_9OAc$, 53596-82-0; 1-heptyl-1-(oxomethyl)cyclohexane, 67838-09-9.

Synthesis and Photochemistry of 17β-Hydroxy-*A*-homo-19-norpregn-5(10)-en-20α-yn-4-one. Synthesis of A,B Spiro Steroids[1,2]

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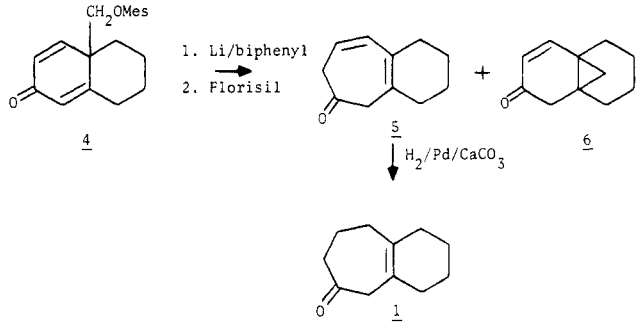
Received January 3, 1979

Bicyclo[5.4.0]undec-1(7)-en-3-one (**1**) and 17β-hydroxy-*A*-homo-19-norpregn-5(10)-en-20α-yn-4-one (**3**) were synthesized in good yield by processes which employed buffered acetolysis of the intermediate mesylates, 10-[(mesyloxy)methyl]-$\Delta^{1(9)}$-octalin (**7**) and 19-(methanesulfonoxy)androst-4-ene-3,17-dione 3-ethylene thioketal (**13**), respectively, for the ring-expansion steps. Photolysis of the β,γ-unsaturated ketones **1** and **3** gave the β,γ-unsaturated spiroketones **2** and **26a** via 1,3 acyl shifts. The structure of **26** was determined by X-ray analysis. These photoisomerizations are reversible, and quenching and sensitization studies showed that these photochemical rearrangements occurred from an excited singlet or short-lived triplet state. The stereochemistry of the photoproduct **26a** is that predicted on the basis of the ground-state conformation of **3**.

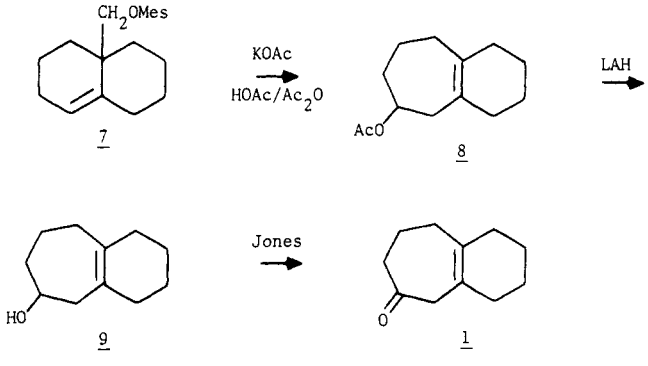
The observation that ground-state molecular conformations can control the mode of reaction for various photochemical reactions has been the topic of recent interest.[3-7] However, it has also been shown that if the lifetime of the excited-state intermediates is sufficiently long, then conformational transformations can sometimes occur, resulting in the formation of different photoproducts.[7,8] Hence it should be possible, knowing the ground-state conformation of a flexible molecule, to predict the stereochemistry of the photoproducts formed, provided no long-lived intermediates are involved.

In order to investigate this question in β,γ-unsaturated ketones, we investigated the photochemistry of the optically active steroid 17β-hydroxy-*A*-homo-19-norpregn-5-(10)-en-20α-yn-4-one (**3**). The A ring of this steroid contains a seven-membered ring incorporating a β,γ-unsaturated ketone whose conformation can be determined from optical rotatory dispersion (ORD).[9] A seven-membered cycloheptene ring is much more rigid than a cyclohexene ring, and Dreiding models indicate the presence of two stable chair conformations.[10] Furthermore, the bicyclo analogue of **3**, namely, bicyclo[5.4.0]undec-1(7)-en-3-one (**1**), has been shown to yield 6-methylenespiro[4.5]decan-

Scheme I



Scheme II



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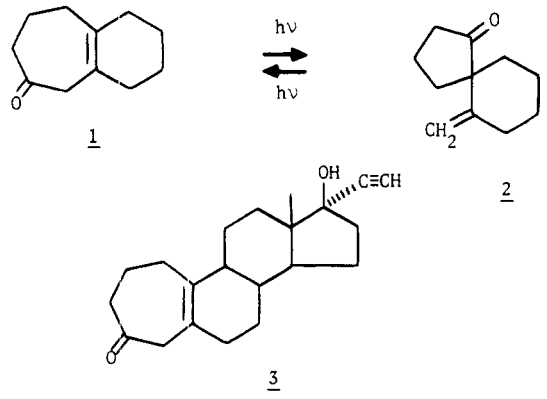
1-one (2) upon direct irradiation.[5a] This 1,3 acyl shift occurs via a singlet or short-lived triplet state and so should be faster than conformational changes.[11]



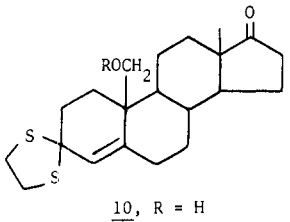
1 2 3

Results

Synthesis of Reactants 1 and 3. The β,γ-unsaturated ketone 1 was synthesized according to the method of Wieland and Anner[12] as outlined in Scheme I. However, the overall yield of 1 from 2-carbethoxycyclohexanone from the nine-step sequence was 2%.[13] Thus a new method was developed, as shown in Scheme II, based on Tadanier's solvolytic process[14] for ring enlargements. By use of Scheme II the overall yield of 1 from 2-carbethoxycyclohexanone in eight steps was 38%, which is a significant improvement over the Wieland and Anner procedure.[12]

The synthesis of the desired 17β-hydroxy-*A*-homo-19-norpregn-5(10)-en-20α-yn-4-one (3) was attempted by using a sequence very similar to that outlined in Scheme II. A 3-monothioketal, 10, of the starting 19-hydroxyandrost-4-en-3,17-dione was prepared in >95% yield.[15] Methanol was found to be the best solvent for this reaction since it avoided the problem of acetate formation when acetic acid was used.[16]

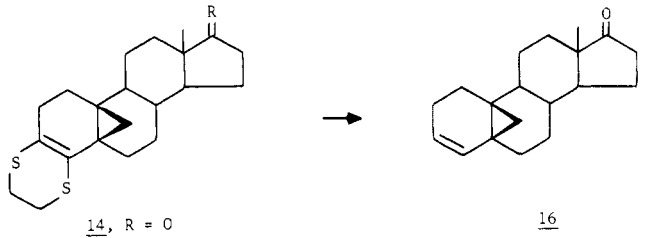
Unfortunately, insurmountable problems were encountered in the next step. Raney nickel desulfurization of the thioketal 10, which had worked in 93% yield[13] for the



10, R = H
11, R = Ac
12, R = THP
13, R = Mes

bicyclic system, gave a mixture of the C-2 and C-3 olefins in very low yield. Attempts to desulfurize 10 by using sodium in ammonia,[17] hydrazine hydrate and potassium hydroxide,[18] or aluminum amalgam[19] led to the formation of what was believed to be the C-2 and C-3 olefins and the saturated steroid. None of the desired C-4 olefin was obtained. To avoid the influence of the 19-hydroxy group, we prepared the 19-acetate 11, and the 19-tetrahydropyranyl derivative 12 from 10. Desulfurization of these molecules also led to complex mixtures. Why the Raney nickel desulfurization reaction should work so well in the synthesis of the bicyclic ketone 1 but not in the case of the steroid analogue 10 cannot be explained at the present time.

To avoid the problems encountered with the desulfurization reaction, the solvolytic rearrangement was attempted first, followed by desulfurization. Solvolysis of the mesylate 13 gave varying results.[20] Use of the mildest acetolysis conditions (KOAc, H_2O, CH_3COCH_3) gave no reaction. By use of buffered acetolysis conditions[14] (KOAc, HOAc, Ac_2O), 13 yielded the dithiane 14 (67%). In the absence of buffer, the acetolysis (HOAc) of 13 gave the acetate 11 (65%), but the dithiane 14 was not converted to 11 under these conditions. Hydrolysis (H_2SO_4, H_2O, CH_3COCH_3) of 13 gave a low yield of the dithiane 14. Desulfurization of 14 with Raney nickel afforded the cyclopropyl olefin 16 (70%).



14, R = O
15, R = α-C≡CH, β-OH
16

These results indicate that only the kinetically formed homoallylic cation 17 is produced.[14,21] In the case of the

17 18

buffered acetolysis conditions, the carbonium ion 17 is trapped by a sulfur migration before the ion has a chance to rearrange to the carbonium ion 18, which is the precursor to the thermodynamic product.[21] Loss of a proton following the sulfur migration affords the dithiane 14. There is also ample precedent that the Δ^4-19-acetoxy steroid 11 is also formed via the homoallylic carbonium ion 17, since Δ^5-19-mesylates have been shown to rearrange under similar conditions via a homoallylic cation.[14,21]

Hydration of the vinyl cyclopropane 16 with aqueous sulfuric acid in acetone afforded the rearranged *A*-homosteroid 19. The structure of 19 was proven by oxidation of 19 with chromium trioxide in pyridine to the 4,17-dione 20, which was identical with the compound synthesized by Wieland and Anner.[12]

To avoid photoepimerization and to investigate potential biological properties, we ethynylated the 17-ketone in 19 using a lithium acetylide–ethylenediamine complex to yield 21. Improved yields were obtained if the 4-hydroxyl group

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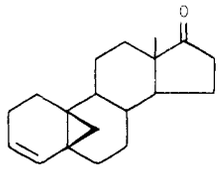
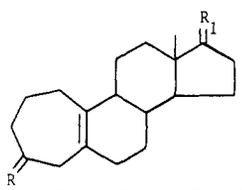
(21) Tadanier, J. *J. Org. Chem.* **1966**, *31*, 2124.



16



19, R = H, OH; R_1 = O

20, R = O; R_1 = O

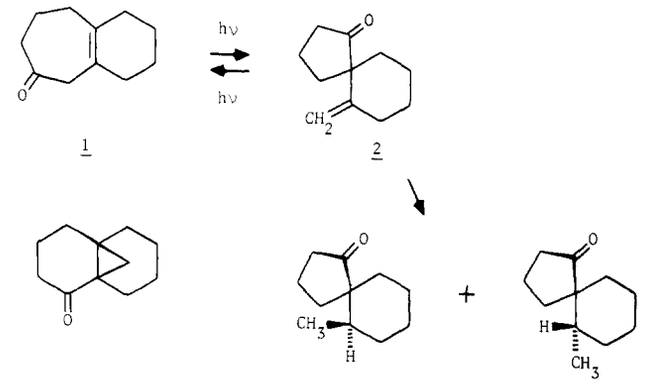
21, R = H, OH; R_1 = α-C≡CH, β-OH

22, R = H, OTHP; R_1 = O

3, R = O; R_1 = α-C≡CH, β-OH

in 19 was first protected as the tetrahydropyranyl ether 22. Sarett oxidation of 21 gave the desired β,γ-unsaturated ketone 3. The overall yield of 3 from 19-hydroxyandrost-4-en-3,17-dione was 4.4%.

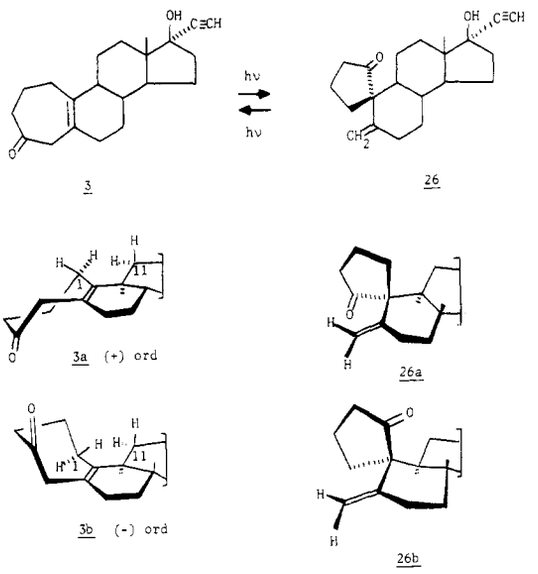
Photochemistry of 1 and 3. Irradiation of 1 in benzene gave 6-methylenespiro[4.5]decan-1-one (2) in 25% yield. The structure of 2 was confirmed by catalytic reduction



1 2 25 23 24

of the exocyclic methylene group in 2 to yield the two isomeric methyl ketones 23 and 24 and by comparison of 24 (IR, NMR, and mass spectra) with material synthesized independently.[22] The photoisomerization of 1 to 2 proceeds via a singlet or short-lived triplet state, since the reaction could not be quenched with 2,5-dimethylhexa-2,4-diene or cyclohexa-1,3-diene, and photosensitization experiments with acetophenone, benzophenone, and acetone led to the disappearance of starting material without the formation of 2 or the conjugated cyclopropyl ketone 25. This photoisomerization is reversible, and a photochemical equilibrium between 1 and 2 (2:3) was reached after irradiation for 5 h. The ratio of 1 to 2 in this equilibrium could be changed by irradiation with monochromatic light near the UV maxima of 1 (292 nm) and 2 (303 nm). The photochemical equilibrium ratio of 1 to 2 at 290 nm was 1:4 and at 325 nm was 3:2, respectively.

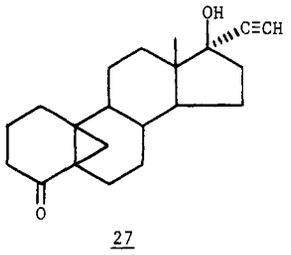
Irradiation of 3 in benzene afforded the spiroketone 26 in 36% yield, and a total of 57% of the reactant 3 was recovered. The IR and NMR spectra and elemental analysis of 26 supported the structure shown. The stereochemistry of 26 was assigned from an X-ray analysis and is shown in Figure 1.[23] The photoisomerization of 3 to 26a proceeds via a singlet or short-lived triplet state, since the reaction could not be quenched with piperylene or naphthalene, and photosensitization experiments with acetone and acetophenone led to the disappearance of



3 26 3a (+) ord 26a 3b (-) ord 26b

Figure 1. Photolysis of 17β-hydroxy-A-homo-19-norpregn-5-(10)-en-20α-yn-4-one (3).

starting material without the formation of 26 or the conjugated cyclopropyl ketone 27.[24] This photoisomerization



27

is reversible, and a photochemical equilibrium between 3 and 26 (1:1) was reached after irradiation for 4 h. Complete conversion of 3 to 26 may be accomplished by recycling the recovered reactant 3. In benzene, 3 is more insoluble than 26, so the reactant 3 can be crystallized directly from the crude photolysis mixture. Thus it is possible to convert all of the material into the desired isomer.

Discussion

The most favorable conformation for cycloheptenes is a chair.[10] Experimentally the barrier height for cycloheptene chair interconversions is ~5.0 kcal/mol,[25] and that for a series of substituted benzocycloheptenes is 10–14 kcal/mol.[26] Hence it is possible for the β,γ-unsaturated ketone in the A ring of steroid 3 to adopt the most stable of the two possible chair conformations (Figure 1). The conformation **3a** has the carbonyl pointing down (α) and that of **3b** point up (β) above the plane of the steroid molecule. Since the circular dichroism (CD) spectrum of 3 shows a positive Cotton effect ($\Delta\epsilon_{298}$ = 1.49), then **3a** is the more stable conformation.[9] This assumes the Cotton effects for the two conformations are approximately equal but opposite in sign. Dreiding models confirm that this is a reasonable assumption.[9]

If ground-state conformation controls the photoisomerization of 3, by analogy with the photoisomerization of 1 to 2, then **3a** should be photoisomerized via a 1,3 acyl

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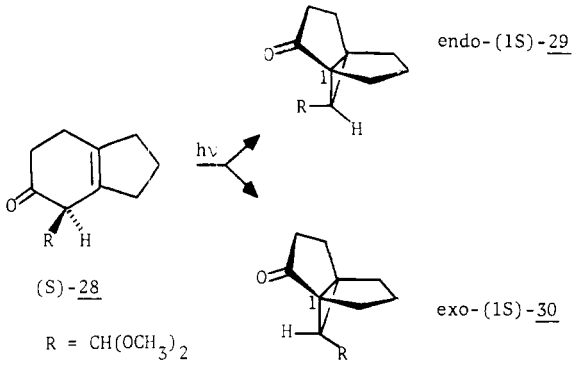
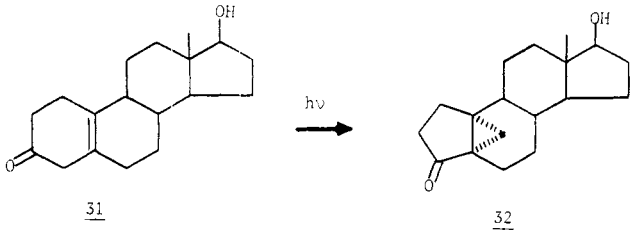
shift to yield **26a**, one of the two C-10 epimers of **26**. Similarly, photoisomerization of **3b** should afford **26b** (see Figure 1). An X-ray analysis[23] on the single photoisomerization product formed confirmed that the structure and stereochemistry at C-10 is that of **26a**. Thus it appears that the ground-state conformation of **3**, namely, **3a**, does control the stereochemistry of the photoisomerization product **26a**. This property may also hold true for other 1,3 acyl shift photoisomerizations of β,γ-unsaturated ketones provided no steric hindrance is involved.

Schaffner has also suggested that this ground-state control may also be extended to the oxadi-π-methane rearrangement exhibited by the triplet excited state of many β,γ-unsaturated ketones. Triplet sensitization of the β,γ-unsaturated ketone (−)-(*S*)-**28** using acetone solution furnished the cyclopropyl ketones **29** and **30**.[27] The ground-state conformational equilibrium of **28** in a polar medium favors the half-chair or boat forms with the dimethoxymethyl substituent in the (pseudo-) equatorial position.[27] The rearrangement to (−)-(1*S*)-**29** and (−)-(1*S*)-**30** requires the same conformation of triplet **28**.



Similarly the conformation of the A ring in the closely analogous steroid 17β-hydroxyestra-5(10)-en-3-one **31** has C-1, C-10, C-5, C-4, and C-3 coplanar with C-2 in the α configuration.[28] Since it is known that the oxadi-π-methane rearrangement proceeds via initial C-3 to C-5 bonding,[27] which in **31** should occur on the β face of the molecule, α-cleavage (C-3 to C-4) must then afford the observed α-cyclopropyl compound **32**.[24] This result further supports the generality of ground-state control of the oxadi-π-methane rearrangement.



31 32

Attempts to relate the sign of the chiroptical effect to the molecular geometry of β,γ-unsaturated ketones found in spiro photoproducts such as **26a** has led to problems.[29] Recently a new symmetry rule was developed.[30] However, if it is applied to **26a**, it predicts the wrong stereochemistry at C-10.

The original correlations were done on relatively flat molecules with specific orientations between the carbonyl and olefin.[9] However, if we use the original octant rule and consider the olefin as a "super substituent", then the structure of these spiro β,γ-unsaturated ketones can be related to the sign of their CD spectra.

The positive CD of **26a** ($\Delta\epsilon_{302}$ = 4.72) would initially appear to contradict the octant rule since the olefin is in a negative quadrant. However, inspection of a Dreiding model indicates that the exocyclic methylene is on the plane between the front and back octants and therefore makes very little contribution to the CD. Thus, in **26a** the positive chiroptical effect is due to the steroid nucleus.

Experimental Section

Melting points were determined with a Thomas-Hoover melting point apparatus and are uncorrected. IR spectra were recorded with a Perkin-Elmer Infracord Model 137 spectrometer fitted with sodium chloride prisms. Ultraviolet spectra were determined in methanol with a Cary 14 recording spectrometer. NMR spectra were obtained with Varian A-60A and XL-100 spectrometers in chloroform-*d* unless another solvent was indicated. The mass spectra were measured on an AEI MS-9 mass spectrometer at an ionizing energy of 70 eV. Optical rotatory dispersion curves were measured on a Cary Model 60 recording spectropolarimeter. Microanalyses were performed by Micro-Analysis, Inc. Vapor-phase chromatography was done by using an Aerograph Model 90 P-3 with a 4 ft × 0.25 in. column which was packed with 20% Carbowax 20M on 60–80-mesh Chromosorb WAW-DMCS (column A) and with a 6 ft × 0.25 in. column which was packed with 15% SE-30 on 60–80-mesh Chromosorb WAW-DMCS (column B).

10-[(Mesyloxy)methyl]-$\Delta^{1(9)}$-octal-2-one.[21] To an ice-cold solution of 41.1 g (0.83 mol) of 10-(hydroxymethyl)-$\Delta^{1(9)}$-octal-2-one-2-dioxolane,[31] 27.8 g (0.274 mol) of triethylamine, and 800 mL of dichloromethane was added slowly 23.2 g (0.201 mol) of methanesulfonyl chloride. The ice bath was removed, and the reaction mixture was stirred overnight at room temperature. The reaction mixture was then washed with water, dilute HCl, and water until neutral. The dichloromethane solution was vacuum evaporated.

The oily mesylate was dissolved in a solution of 150 mL of methanol and 100 mL of 10% aqueous hydrochloric acid, and this mixture was refluxed for 15 min. The product was extracted with dichloromethane. The dichloromethane layer was washed with dilute Na_2CO_3 solution and water until neutral, dried (Na_2SO_4), and concentrated. The semicrystalline residue was recrystallized from 3:1 ethyl acetate–hexane to yield 37.5 g (80%) of 10-[(mesyloxy)methyl]-$\Delta^{1(9)}$-octal-2-one as clear prisms: mp 96.5–97.5 °C; UV max (EtOH) 234 nm (ϵ 15 460); IR (KBr) 3020 (CH=C), 1678 (conj C=O), 1350 and 1170 cm^{-1} ($COSO_2C$); NMR ($CDCl_3$) δ 5.91 (s, 1), 4.34 (s, 2, CH_2OMes), 3.04 (s. 3, CH_3SO_2); mass spectrum (70 eV), *m/e* (relative intensity) 260 (3), 259 (12), 258 (55, M^+), 175 (18), 174 (74), 163 (17), 162 (64), 160 (20), 148 (60), 147 (17), 135 (55), 132 (54), 133 (20), 122 (100), 121 (17), 120 (25), 109 (47), 108 (26), 107 (70), 95 (95), 93 (50), 71 (29), 69 (26), 57 (45), 55 (45).

Anal. Calcd for $C_{12}H_{18}SO_4$: C, 55.79; H, 7.02; S, 12.41. Found: C, 55.74; H, 6.94; S, 12.17.

10-[(Mesyloxy)methyl]-$\Delta^{1(9),3}$-octal-2-one (4).[21] A solution of 3.3 g (0.013 mol) of 10-[(mesyloxy)methyl]-$\Delta^{1(9)}$-octal-2-one, 3.0 g (0.013 mol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, and 50 mL of dry dioxane was refluxed under a stream of nitrogen for 3 h. The reaction mixture was air cooled, concentrated, and chromatographed on 300 g of alumina (activity I, 30.0 × 3.7 cm column). Elution with hexane and 3:1 hexane–ethyl acetate gave an oil which crystallized at −70 °C. The product was recrystallized from 3:1 ethyl acetate–hexane to yield 2.02 g (61%) of 10-[(mesyloxy)methyl]-$\Delta^{1(9),3}$-octal-2-one (**4**) as clear prisms: mp 76–78 °C; UV max (EtOH) 236 nm (ϵ 14 100); IR (KBr) 3015 (CH—C), 1663 (conj C=O), 1350 and 1170 cm^{-1} ($COSO_2C$); NMR ($CDCl_3$)

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δ 6.84 (d, 1, J = 10 Hz, 4-H), 6.45 (d, 1, J = 2 Hz, 3-H), 6.28 (s, 1, 1-H), 4.42 (s, 2, CH_2OMes), 2.97 (s, 3, CH_3SO_2); mass spectrum (70 eV), m/e (relative intensity) 258 (2), 257 (3), 256 (18, M^+), 232 (15), 173 (11), 172 (45), 161 (50), 160 (100), 158 (13), 146 (11), 134 (25), 133 (20), 131 (21), 129 (13), 124 (16), 107 (54), 97 (48), 95 (20), 81 (21), 67 (15), 57 (24), 55 (23).

Anal. Calcd for $C_{12}H_{16}SO_4$: C, 56.23; H, 6.29; S, 12.51. Found: C, 56.53; H, 6.31; S, 12.74.

Bicyclo[5.4.0]undeca-1(7),5-dien-3-one (5).[21] A mixture of 28.4 g (0.183 mol) of biphenyl, 1.42 g (0.204 mol) of lithium ribbon, and 300 mL of dry tetrahydrofuran was stirred under a stream of argon for 2 h. The deep blue solution was then cooled to −70 °C, and 16.0 g (0.0625 mol) of 4 was added with a little tetrahydrofuran. After 2.25 h the reaction was stopped with the addition of 300 mL of saturated ammonium chloride solution. The product was extracted with toluene. The toluene solution was dried ($MgSO_4$), concentrated, and placed on a 400-g Florisil (40.0 × 5.0 cm) column. The column was washed with 400 mL of toluene and left overnight for 16 h. Elution with toluene and 99:1 toluene–ethyl acetate gave 2.18 g (22%) of 5 as a pale yellow oil: bp 65 °C (0.4 mm); UV max (EtOH) 298 nm (ε 2180), 237 (4810); IR (neat) 3010 (CH=CH), 1710 (C=O), 1660 (tetrasubstituted olefin), 1605 cm^{-1} (cis olefin); NMR δ 6.4–5.5 (m, 2, C**H**=C**H**), 3.02 (t, 4, J = 1.5 Hz, C=CC**H**$_2$COC**H**$_2$CH=CH).

Later fractions gave 3.42 g (34%) of **tricyclo[4.4.1.0^{1,6}]undec-4-en-3-one (6)** as a pale yellow oil: IR (neat) 3020 and 3050 (CH=CH), 1672 (conj C=O), 1610 cm^{-1} (cis olefin); NMR δ 7.21 (d, 1, J = 10 Hz, COCH=C**H**), 5.68 (d, 1, J = 10 Hz, COC**H**=CH), 2.64 (AB, 2, $\Delta\nu_{AB}$ = 20.4 Hz, J_{AB} = 18.5 Hz, $COCH_2\overline{CCCH_2}$), 1.18 (d, 1, J = 4 Hz) and 0.47 (d, 1, J = 4 Hz, $\overline{CCCH_2}$).

Bicyclo[5.4.0]undec-1(7)-en-3-one (1).[21] A solution of 2.18 g (0.0134 mol) of bicyclo[5.4.0]undeca-1(7),5-dien-3-one (5) and 350 mg of 5% palladium on calcium carbonate in 250 mL of absolute ethanol was hydrogenated at atmospheric pressure for 19 h. The reaction consumed 1.55 equiv of hydrogen. The ethanol solution was filtered, concentrated, and distilled, yielding 0.691 g (31%) of 1 as a clear oil: bp 60–64 °C (0.4 mm); UV max (EtOH) 293 nm (ε 212); IR (neat) 2920, 2855, 1708 (C=O), 1668 (C=C), 1445 cm^{-1}; NMR ($CDCl_3$) δ 3.14 (s, 2, C=CC**H**$_2$CO); mass spectrum, m/e (relative intensity) 164 (50, M^+), 149 (25), 146 (12), 135 (34), 121 (52), 109 (68), 108 (69), 107 (55), 94 (63), 93 (89), 91 (96), 79 (100), 77 (77).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 79.65; H, 10.12.

10-[(Mesyloxy)methyl]-Δ$^{1(9)}$-octalin (7). To an ice-cold solution of 3.05 g (0.0181 mol) of 10-(hydroxymethyl)-Δ$^{1(9)}$-octalin,[32] 2.78 g (0.0273 mol) of triethylamine, and 130 mL of dichloromethane was added slowly 2.30 g (0.0199 mol) of methanesulfonyl chloride. After 10 min the ice bath was removed, and the reaction mixture was stirred for 15 min at room temperature. The reaction mixture was then washed with 130 mL of water, dilute HCl, dilute Na_2CO_3 solution, and brine until neutral. The dichloromethane solution was dried (Na_2SO_4) and concentrated to yield 3.99 g (90%) of 7 as a yellow oil. Further attempts to purify the sample were unsuccessful because of decomposition of the mesylate: IR (neat) 3020 (CH=C), 1350 and 1170 cm^{-1} ($COSO_2C$).

3-Acetoxybicyclo[5.4.0]undec-1(7)-ene (8).[15] A solution of 3.25 g (0.0133 mol) of 7 and 270 mL of buffered (K_2CO_3, Ac_2O) acetic acid was kept at 100 °C for 3 h. After cooling to room temperature, the reaction mixture was separated with 400 mL of ether and 200 mL of water. The aqueous layer was extracted twice with 100 mL of ether. The combined ether extracts were washed with water, dilute Na_2CO_3 solution, and water until neutral. The ether layer was dried (Na_2SO_4) and concentrated, yielding 2.36 g (85%) of crude yellow oil. Distillation gave 8 as a clear oil: bp 81–86 °C (0.5 mm); IR (neat) 1732 (ester C=O), 1240 cm^{-1} (CO); NMR δ 1.97 (s, CH_3CO); mass spectrum, m/e (relative intensity) 208 (3, M^+), 149 (21), 148 (100), 135 (15), 133 (39), 120 (33), 119 (26), 107 (15), 106 (21), 105 (45), 93 (19), 92 (27), 91 (64), 79 (38), 43 (61).

Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 75.11; H, 9.61.

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Bicyclo[5.4.0]undec-1(7)-en-3-ol (9). To a suspension of 0.592 g (15.6 mmol) of $LiAlH_4$ in 70 mL of ether was added slowly with stirring 2.3 g (11 mmol) of 8 in 70 mL of ether. This mixture was refluxed for 5 h. The inorganic salts were precipitated with 3 mL of water. The ether solution was filtered, dried (Na_2SO_4), and concentrated to yield 1.72 g (93%) of pale yellow oil. The crude oil (1.5 g) was chromatographed on 50 g of silica gel (activity II, 28.7 × 2.2 cm column). Elution with benzene and 99:1 benzene–ethyl acetate yielded 0.51 g of 9 as an oil: bp 256–259 °C dec; IR (neat) 3350 (assoc OH), 2910, 1443, 1029, 1015 cm^{-1}; NMR δ 3.63 (m, 1, C**H**OH); mass spectrum, m/e (relative intensity) 166 (52, M^+), 164 (22), 162 (16), 148 (76), 133 (82), 131 (27), 122 (28), 120 (74), 119 (66), 109 (38), 107 (51), 106 (59), 105 (83), 95 (47), 93 (85), 92 (64), 91 (100), 81 (63).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.64; H, 10.78.

Bicyclo[5.4.0]undec-1(7)-en-3-one (1). To a solution of 0.217 g (1.3 mmol) of bicyclo[5.4.0]undec-1(7)-en-3-ol (9) in 30 mL of acetone was added 0.8 mL of Jones reagent. The reaction was stirred under a stream of nitrogen for 5 min and then separated by the addition of 120 mL of water and 40 mL of ether. The combined ether extracts (3 × 100 mL) were washed with water until neutral, dried (Na_2SO_4), and concentrated to yield 0.202 g (95%) of 1 as a pale yellow oil. Preparative VPC gave a clear oil: bp 60–65 °C (0.4 mm); UV max (EtOH) 292 nm (ε 250); IR (neat) 2920, 2855, 1708 (C=O), 1668 (C=C), 1445 cm^{-1}; NMR δ 3.14 (s, 2, C=CC**H**$_2$CO); mass spectrum, m/e (relative intensity) 164 (73, M^+), 149 (24), 146 (22), 135 (18), 121 (29), 109 (30), 108 (91), 107 (27), 93 (91), 91 (45), 79 (66), 77 (37).

Hydrogenation of 6-Methylenespiro[4.5]decan-1-one (2). A solution of 100 mg of the methylene spiroketone 2 and 15 mg of Adam's catalyst in 25 mL of benzene was hydrogenated at atmospheric pressure for 16.5 h. The benzene was filtered and the reaction mixture evaporated in vacuo. The residue containing syn and anti isomers of **6-methylspiro[4.5]decan-1-one (23** and **24)** was separated by preparative VPC. The syn isomer (**23**) was an oil: 23 mg (23%); bp 225 °C dec; IR (neat) 3021, 2855, 1733 (cyclopentanone C=O), 1444, 1385, 1160, 1148 cm^{-1}; NMR δ 0.86 (d, 3, J = 7 Hz, C**H**$_3$CH); mass spectrum, m/e (relative intensity) 166 (37, M^+), 148 (19), 123 (18), 111 (52), 110 (36), 109 (26), 97 (50), 95 (62), 91 (45), 84 (38), 81 (50), 68 (40), 67 (58), 55 (35), 44 (100). The anti isomer (**24**) was also an oil: 17 mg (17%); bp 225 °C dec; IR (CCl_4) 2925, 2855, 1737 (cyclopentanone C=O), 1455 cm^{-1}; NMR δ 0.69 (d, 3, J = 7 Hz, C**H**$_3$CH); mass spectrum, m/e (relative intensity) 166 (69, M^+), 151 (20), 148 (22), 137 (22), 133 (16), 124 (19), 122 (42), 111 (77), 110 (42), 109 (38), 97 (61), 95 (100), 82 (42), 81 (85), 68 (46), 67 (88), 55 (58), 41 (92).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found for syn isomer: C, 79.55; H, 10.83. Found for anti isomer: C, 79.45; H, 10.85. The IR, NMR, and mass spectra of **30** were identical with the spectra of material synthesized independently.[22]

Ozonolysis of 6-Methylenespiro[4.5]decan-1-one (2). A solution of 30 mg (0.18 mmol) of 6-methylenespiro[4.5]decan-1-one (2), 1 drop of water, and 10 mL of ethyl acetate was stirred at 0 °C for 10 min while ozone was passed through the solution. Then 1.0 mL of water and 0.2 g of zinc dust were added, and the mixture was stirred at room temperature overnight. The ethyl acetate solution was filtered, washed with water until neutral, dried (Na_2SO_4), and concentrated. The product was separated by preparative VPC to yield 10 mg (33%) of **spiro[4.5]decane-1,6-dione** as a clear oil: bp 238–241 °C dec; IR ($CHCl_3$), 1732 (cyclopentanone C=O), 1698 (cyclohexanone C=O); mass spectrum, m/e (relative intensity) 166 (38, M^+), 148 (14), 138 (35), 137 (20), 121 (21), 111 (100), 110 (90), 95 (34), 91 (27), 67 (52), 55 (74), 44 (95), 41 (67).

19-Methanesulfonoxyandrost-4-ene-3,17-dione 3-Ethylene Thioketal (13). To a solution of 4.52 g (11.9 mmol) of 19-hydroxyandrost-4-ene-3,17-dione 3-ethylene thioketal (**10**)[15] in 45 mL of ice-cold pyridine was added 6.66 g (59.4 mmol) of methanesulfonyl chloride. This solution was stirred for 30 min at room temperature and then poured into 300 mL of cold water. The product was extracted with 300 mL of chloroform. The chloroform extract was washed with dilute hydrochloric acid and brine until neutral, dried (Na_2SO_4), and concentrated in vacuo. The residue contained 7.96 g (>100%) of **13** as a semicrystalline solid. All attempts to recrystallize the mesylate were unsuccessful.

Vacuum removal of solvent gave only semicrystalline material: mp 96–105 °C; IR (CCl_4) 1740 (cyclopentanone), 1345 and 1175 cm^{-1} ($COSO_2C$); NMR δ 5.76 (s, 1, C=CH), 4.37 (AB, 2, $\Delta\nu_{AB}$ = 17 Hz, J_{AB} = 10 Hz, H-19), 3.31 (m, 4, thioketal), 2.99 (s, 3, SO_2CH_3), 0.88 (s, 3, H-18).

5β,19-Cycloandrost-3-eno[3,4-*b*]dithian-17-one (14). A solution of 5.43 g (11.9 mmol) of 19-methanesulfonoxyandrost-4-ene-3,17-dione 3-ethylene thioketal (**13**) in 400 mL of buffered acetolysis solution (HOAc, Ac_2O, and KOAc) was heated at 90 °C for 75 min. The solution was diluted with 1 L of brine and extracted with 1 L of ether. The ether extract was washed with saturated sodium carbonate solution and brine until neutral, dried (Na_2SO_4), and concentrated. The oily residue was chromatographed on 100 g of silica gel (activity II, 28.0 × 3.0 cm column) with 1:1 ether–pentane. The product obtained was 2.86 g (67% yield) of **14**. Recrystallization with ethyl acetate–pentane gave colorless crystals: mp 158–160 °C; IR (KBr) 1730 cm^{-1} (cyclopentanone C=O); NMR δ 3.16 (s, 4, thioketal), 0.89 (s, 3, H-18), 0.68 (s, 2, cyclopropylmethylene); mass spectrum, *m/e* 360 (M^+).

Anal. Calcd for $C_{21}H_{28}S_2O$: C, 69.95; H, 7.83; S, 17.78. Found: C, 70.00; H, 7.55; S, 17.75.

17α-Ethynyl-5β,19-cycloandrost-4-eno[3,4-*b*]dithian-17-ol (15). To a solution of 0.500 g (1.39 mmol) of 5β,19-cycloandrost-4-eno[3,4-*b*]dithian-17-one (**14**) in 10 mL of dimethyl sulfoxide was added 0.200 g (2.18 mmol) of lithium acetylide–ethylenediamine complex. This mixture was stirred for 2 h at room temperature and then poured into 200 mL of cold water. The mixture was neutralized with 10% aqueous hydrochloric acid, and the precipitate was filtered off and dried. The product weighed 0.480 g (89% yield). Recrystallization from methanol–water gave **15** as colorless crystals: mp 162–163 °C; IR (CCl_4) 3600 (sharp, OH), 3300 cm^{-1} (acetylene); NMR δ 3.12 (s, 4, thioketal), 2.54 (s, 1, H-21), 0.85 (s, 3, H-18).

Anal. Calcd for $C_{23}H_{30}S_2O$: C, 71.45; H, 7.82; S, 16.59. Found: C, 71.74; H, 7.69; S, 16.62.

5β,19-Cycloandrost-3-en-17-one (16). A mixture of 40.0 g of Raney nickel W-2 and 250 mL of acetone was refluxed for 2 h. To this mixture was added a solution of 4.07 g (11.3 mmol) of 5β,19-cycloandrost-3-eno[3,4-*b*]dithian-17-one (**14**) in 50 mL of acetone. This mixture was refluxed for 20 h, and then 20 g of Raney nickel W-2 was added. After 3 h of reflux the mixture was filtered and concentrated in vacuo. The oily residue was chromatographed on 100 g of silica gel (activity II, 28.0 × 3.0 cm column) with 2:3 ether–pentane. A total of 2.13 g (70%) of **16** was obtained. Recrystallization from methanol–water gave colorless crystals: mp 78–79 °C; IR (CCl_4) 3030 (C=CH), 1740 (cyclopentanone C=O), 1640 cm^{-1} (olefin); NMR δ 5.80 (d, 1, *J* = 10 Hz, H-4), 5.39 (m, 1, H-3), 0.87 (s, 3, H-18), 0.95 (d, 1, *J* = 5.0 Hz), 0.50 (d, 1, *J* = 5.0 Hz, cyclopropylmethylene).

Anal. Calcd for $C_{19}H_{26}O$: C, 84.40; H, 9.69. Found: C, 84.16; H, 9.66.

4-Hydroxy-*A*-homo-19-norandrost-5(10)-en-17-one (19). A solution of 1.38 g (5.11 mmol) of 5β,19-cycloandrost-3-en-17-one (**16**), 15 mL of acetone, and 15 mL of 5% aqueous sulfuric acid was refluxed overnight for 19 h. After evaporation of the solvent, the residue was extracted with ether (200 mL). The ether extract was washed with water until neutral, dried (Na_2SO_4), and concentrated. The residue was chromatographed on 60 g of silica gel (activity II, 16.0 × 3.3 cm column) with 1:1 ether–pentane. The first fractions gave 0.204 g of **16**. Later fractions gave 0.963 g (66%) of **19** as a clear oil. All attempts to crystallize the product were unsuccessful: IR (CCl_4) 3450 (br, OH), 1740 cm^{-1} (cyclopentanone); NMR δ 3.62 (m, 1, H-4), 0.86 (s, 3, H-18).

***A*-Homo-19-norandrost-5(10)-ene-4,17-dione (20).** A solution of 50 mg (0.17 mmol) of 4-hydroxy-*A*-homo-19-norandrost-5-(10)-en-17-one (**19**) in 2 mL of pyridine was added to a solution of 80 mg (0.80 mmol) of chromium trioxide in 3 mL of pyridine. After 19 h of being stirred at room temperature, the reaction mixture was diluted with 100 mL of brine. The product was extracted with ether. The ether layer (100 mL) was washed with 10% aqueous hydrochloric acid and brine until neutral, dried (Na_2SO_4), and concentrated. The residue was separated by preparative thin-layer chromatography on 250-μm silica gel plates (10 × 20 cm). Elution with 2:1 ether–pentane gave 30 mg (61%) of **20**. Recrystallization from methanol gave colorless crystals: mp 117–119 °C (lit.[12] mp 118–119.5 °C); IR (CCl_4) 1735 (cyclopentanone C=O), 1710 cm^{-1} (cycloheptanone C=O); NMR δ 3.08 (AB, 2, $\Delta\nu_{AB}$ = 37 Hz, J_{AB} = 13 Hz, H-4a), 0.89 (s, 3, H-18). The IR and NMR spectra were identical with those of authentic material.[12]

***A*-Homo-19-norpregn-5(10)-en-20α-yne-4,17β-diol (21). Method A.**[33] To a solution of 0.82 g (2.8 mmol) of 4-hydroxy-*A*-homo-19-norandrost-5(10)-en-17-one (**19**) in 15 mL of dimethyl sulfoxide was added 1.0 g (11 mmol) of lithium acetylide–ethylenediamine complex. This mixture was stirred for 20 h at room temperature and then poured into 250 mL of cold water. This mixture was neutralized with 10% aqueous hydrochloric acid, and the precipitate was filtered off and dried. The crude product was separated by preparative thin-layer chromatography on 250-μm silica gel plates (10 × 20 cm). Elution with 4:1 ether–pentane gave 0.311 g (35% yield) of **21**. Recrystallization from methanol–water gave colorless needles: mp 78–79 °C; IR ($CHCl_3$) 3600 (sharp, OH), 3450 (br, OH), 3300 cm^{-1} (acetylene); NMR δ 3.64 (m, 1, H-4), 2.51 (s, 1, H-21), 0.87 (s, 3, H-18). No satisfactory analysis was obtained due to solvent incorporation.

21 via Tetrahydropyranyl Ether.[34] **Method B.** A solution of 3.106 g (10.8 mmol) of the hydroxy olefin **19** and 0.2 mL of phosphoryl chloride in 30 mL of 2,3-dihydropyran was stirred at room temperature for 20 min. After dilution with 100 mL of ether, the mixture was washed with saturated aqueous sodium carbonate solution and water until neutral. The ether layer was dried (Na_2SO_4) and concentrated. The residue was chromatographed on 400 g of silica gel (activity III, 36.0 × 4.7 cm) with 1:3 ether–hexane. A total of 2.80 g (73%) of **4-(tetrahydropyran-2-yloxy)-*A*-homo-19-norandrost-5(10)-en-17-one (22)** was obtained. Crystallization with ether–pentane gave colorless needles: mp 153–154 °C; IR ($CHCl_3$) 1735 (cyclopentanone C=O), 1020 cm^{-1} (CO); NMR δ 4.93 (m, 1, OCHO), 4.05 (m, 1, H-4), 3.76 (m, 2, CH_2O).

Anal. Calcd for $C_{24}H_{36}O_3$: C, 77.37; H, 9.74. Found: C, 77.47; H, 9.70.

A solution of 2.3 g (6.2 mmol) of the tetrahydropyranyl ether **22** and 16 g (18 mmol) of lithium acetylide–ethylenediamine complex in 175 mL of dimethyl sulfoxide was stirred for 20 h at room temperature. The mixture was poured into ice–water, neutralized with 10% aqueous hydrochloride acid, and extracted with ether (3 × 150 mL). The ether extract was washed with water until neutral, dried (Na_2SO_4), and concentrated. The crude residue was refluxed with 80 mL of 95% ethanol and 0.5 g of *p*-toluenesulfonic acid monohydrate for 1 h. The product was extracted with ether (3 × 100 mL), neutralized with water, and concentrated to give a brown oil. Filtration of this crude product through a 5-g plug of silica gel (activity II) with ether gave 1.74 g (90%) of the ethynyl diol **21** as a semicrystalline solid: IR and NMR identical with the compound previously prepared.

17β-Hydroxy-*A*-homo-19-norpregn-5(10)-en-20α-yn-4-one (3). A solution of 183 mg (0.583 mmol) of *A*-homo-19-norpregn-5(10)-en-20α-yne-4,17β-diol (**21**) in 5 mL of pyridine was added to a solution of 120 mg (1.20 mmol) of chromium trioxide in 10 mL of pyridine. After 5 h of being stirred at room temperature, the reaction mixture was diluted with 100 mL of brine. The product was extracted with ether. The ether layer (150 mL) was washed with dilute hydrochloric acid and brine until neutral, dried (Na_2SO_4), and concentrated. The residue was chromatographed on 25 g of silica gel (activity II, 23.0 × 1.8 cm column) with 1:1 ether–pentane. The first fractions gave 56 mg (31%) of **3**. Later fractions gave 49 mg (27%) of reactant **21**. Recrystallization of the product from methanol–water gave colorless plates: mp 196–197 °C; UV max (EtOH) 294 nm (ε 231); ORD (MeOH) $[\alpha]_{317}$ +1360, $[\alpha]_{278}$ −566; IR ($CHCl_3$) 3600 (sharp, OH), 3300 (acetylene), 1700 cm^{-1} (cycloheptanone C=O); NMR δ 3.05 (AB, 2, $\Delta\nu_{AB}$ = 33 Hz, J_{AB} = 15 Hz, H-4a), 2.52 (s, 1, H-21), 0.88 (s, 3, H-18).

Anal. Calcd for $C_{12}H_{28}O_2$: C, 80.73; H, 9.03. Found: C, 80.94; H, 8.71.

Photolysis of Bicyclo[5.4.0]undec-1(7)-en-3-one (1). A solution of 1 (202 mg) in benzene (200 mL) was stirred with a

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stream of nitrogen and irradiated with a 450-W Hanovia lamp through a Pyrex filter. The reaction, which was complete in 105 min, was monitored by VPC. The benzene solution was concentrated, and preparative VPC was used to collect 34 mg of 1 and 51 mg (25%) of 6-methylenespiro[4.5]decan-1-one (2) as a clear oil: bp 228–230 °C; UV max (EtOH) 303 nm (ε 68); IR (CCl_4) 3080 (CH_2=C), 1735 (cyclopentanone C=O), 1630 (C=C), 895 cm^{-1} (CH_2=C); NMR δ 4.74 (s, 1), 4.42 (s, 1, exocyclic methylene); mass spectrum, *m/e* (relative intensity) 164 (86, M^+), 150 (16), 149 (75), 146 (76), 135 (56), 131 (69), 121 (72), 120 (43), 109 (100), 108 (81), 107 (80), 94 (100), 91 (61), 79 (80), 67 (78).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.31; H, 9.80.

The other solvents used (pentane, *tert*-butyl alcohol, and methanol) gave similar results in the photolysis in benzene. Longer reaction times led to complete disappearance of 1 and 2 as indicated by VPC. Photolysis using quartz glassware for 4 h resulted in complete destruction of 1. No material could be isolated by preparative VPC. Irradiation of a 25-mL aliquot of 0.061 M 1 (benzene) for 3.5 h in a sealed melting point capillary was done by using a SPEX double monochromator. The 1 to 2 ratio (determined by VPC trace) at 290 nm was 1:4 and at 325 nm was 3:2, respectively.

Quenching Studies with 1. To 0.2-mL aliquots of a solution of 14 mg of 1 in 1 mL of benzene was added 2,5-dimethylhexa-2,4-diene (0.01, 0.10, and 1.0 M solutions). After 22 h of irradiation in degassed 7-mm Pyrex test tubes with a 450-W Hanovia lamp, no change in the rate of the reaction from that of a control solution was observed (rate determined by VPC analyses of product formation).

Sensitization Studies with 1. The same procedure was used as in the quenching studies, except the solutions were prepared so that the sensitizer absorbed over 90% of the light at 313 nm. The following solutions were used: 0.343 M acetophenone, 0.196 M benzophenone, and acetone (neat). VPC analysis after 10 h of irradiation indicated a substantial decrease in the rate of formation of 2 and disappearance of 1 in these solutions.

Photolysis of 6-Methylenespiro[4.5]decan-1-one (2). A solution of 2 mg of 6-methylenespiro[4.5]decan-1-one (2) in 0.1 mL of benzene was irradiated in a degassed 7-mm Pyrex test tube with a 450-W Hanovia lamp. A solution of 2 mg of 1 in 0.1 mL of benzene was irradiated under the same conditions for comparison. After 5 h the VPC trace of the reactions indicated in the photolysis of 2 a ratio of 1 to 2 of 44:57, respectively, and in the photolysis of 1 a ratio of 1 to 2 of 37:63, respectively. Preparative VPC and IR confirmed the formation of 1 in the photolysis of 2.

Irradiation of a 25-mL aliquot of 0.061 M 2 (benzene) in a sealed melting point capillary was done by using a SPEX double monochromator at 325 nm. The 1 to 2 ratio (determined by VPC trace) after 5 h was 3:2, respectively.

Photolysis of 17β-Hydroxy-*A*-homo-19-norpregn-5(10)-en-20α-yn-4-one (3). A solution of 236 mg of 3 in 110 mL of benzene was stirred with a stream of nitrogen and irradiated with a 450-W Hanovia lamp through a Pyrex filter for 3.5 h. The VPC indicated no further change in the reactant–product ratio (1:1) after 3 h. The reaction mixture was concentrated, and the residue was crystallized with dichloromethane–ether to give 90 mg of reactant 3. The mother liquor was separated by preparative thin-layer chromatography on 250-μm silica gel plates (10 × 20 cm). Elution with 4:1 ether–pentane gave 45 mg of 3 (total recovery of 57%) and 85 mg (36%) of **17β-hydroxy-3,19-cyclo-3,4-seco-10β-pregn-20α-yn-4-en-1-one (26).** Recrystallization of 26 with ether–pentane gave colorless needles: mp 167–168 °C; UV (EtOH) 303 nm (ε 53); ORD (MeOH) $[\alpha]_{316}$ +2190, $[\alpha]_{288}$ −1715; IR ($CHCl_3$) 3600 (OH), 3300 (acetylene), 3080 (CH_2=C), 1728 (cyclopentanone C=O), 1633 and 900 cm^{-1} (terminal vinyl); NMR δ 4.73 (s, 1), 4.28 (s, 1, exocyclic methylene), 2.51 (s, 1, H-21), 0.85 (s, 3, H-18).

Anal. Calcd for $C_{21}H_{28}O_2$: C, 80.73; H, 9.03. Found: C, 80.99; H, 8.75.

Photolysis of 3 in methanol gave similar results. Also, photolysis of 3 through quartz with a Vycor filter gave the same reactant–product ratio (1:1) as indicated by VPC.

Quenching Studies with 3. To two separate 0.5-mL aliquots of 0.01 M 3 in benzene were added 2 mg (0.1 M) of piperylene and 2 mg (0.07 M) of naphthalene. These samples were irradiated in degassed 7-mm Pyrex test tubes with a 450-W Hanovia lamp for 18 h. Analysis by VPC of the resulting solutions indicated the same reactant ratio (1:1) as that of the control solution without quencher.

Sensitization Studies with 3. The same procedure was used as in the quenching studies, except the solutions were prepared so that the sensitizer absorbed over 90% of the light at 313 nm. Solutions of 3 in acetone (neat) and acetophenone (0.2 M in benzene) were irradiated as above. The VPC of the resulting solutions indicated no formation of photoproduct but only a rapid decrease in the concentration of reactant 3.

Photolysis of 17β-Hydroxy-3,19-cyclo-3,4-seco-10β-pregn-20α-yn-4-en-1-one (26). A solution of 2 mg of 26 in 0.5 mL of benzene was irradiated in a degassed 7-mm Pyrex test tube with a 450-W Hanovia lamp for 4 h. Analysis of the resulting solution by VPC and thin-layer chromatography indicated the presence of 3 and 26 in a 1:1 ratio.

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