**2'-Methoxy-2,6-dimethyl-9-oxo-7,8-homobenzomorphan (XX).**—To a solution of XVII (306 mg), $CrO_3$ (165 mg) in 1 *N* $H_2SO_4$ (62 ml), was added 10 *N* $H_2SO_4$ (9 ml) at room temperature during 3 hr, and the mixture was allowed to stand for 20 hr. It was basified with $NH_4OH$, extracted with $Et_2O$, dried, and evaporated. The residue was recrystallized from hexane to give XX (165 mg, 52%): mp 118–119°; ir, 1660 $cm^{-1}$; uv (EtOH): 227 mμ (ε 12,000), 278 (12,300).[10] *Anal.* ($C_{16}H_{21}NO_2$) C,H,N. **Methobromide XXIa** was prepared in $Me_2CO$ in a usual manner, mp 211–213°. *Anal.* ($C_{17}H_{24}BrNO_2$) C,H,N. **Methoperchlorate XXIb** was prepared from XXIa by addition of aq $NaClO_4$, mp 217–219° (from MeOH). *Anal.* ($C_{17}H_{24}ClNO_6$) C,H,N.

**1-(3-Dimethylaminopropyl)-7-methoxy-1-methyl-1,2,3,4-tetrahydronaphthalene (XXII)·HCl.**—A mixture of II (10.35 g), KOH (10 g), $NH_2NH_2 \cdot H_2O$ (10 ml), and diethyleneglycol (90 ml) was heated at 175° for 3 hr and worked up in the usual manner to give XXII·HCl (5.4 g, 46%), mp 151–153° (from $Me_2CO$–EtOH–$Et_2O$). *Anal.* ($C_{17}H_{28}ClNO$) C,H,N.

**3,4-Dihydro-4-(3-dimethylaminopropyl)-6-methoxy-4-methyl-1(2*H*)-naphthalenone (XXIII)·HBr.**—XXII (from 5.38 g of the hydrochloride) was oxidized with $CrO_3$ in $H_2SO_4$ in the usual manner.[10] Crude base was converted into the hydrobromide to give 3.29 g (54%): mp 137–141°; analytical sample, mp 142–144° ($Me_2CO$–$Et_2O$); ir, 1652 $cm^{-1}$; uv (EtOH), 227 mμ (ε 14,100), 280 (15,700).[10] *Anal.* ($C_{17}H_{26}BrNO_2$) C,H,N.

**2-Bromo-3,4-dihydro-4-(3-dimethylaminopropyl)-6-methoxy-4-methyl-1(2*H*)-naphthalenone (XXIV)·HBr.**—XXIII·HBr (2.35 g) was brominated in AcOH (30 min, at 55–65°) to give XXIV·HBr (2.41 g, 87.5%) mp 113–116°; analytical sample, mp 115–117° (from $Me_2CO$). *Anal.* ($C_{17}H_{25}Br_2NO_2 \cdot 0.5H_2O$) C,H,N.

**Cyclization of XXIV·HBr.**—To a stirred suspension of XXIV·HBr (2.4 g) in $H_2O$ (8 ml), 5.6% $NH_4OH$ (4 ml) was added with cooling. The mixture was stirred at room temperature for 2 hr and evaporated *in vacuo* to dryness below 40°. The residue was extracted with hot $Me_2CO$ (100 ml in two portions) and filtered from inorganic material. Evaporation of the combined $Me_2CO$ gave a crystalline residue (1.72 g, mp 120–123°),[10] which was dissolved in $H_2O$, basified with $NH_4OH$, extracted with $Et_2O$, dried, and evaporated. Conversion of the residue into the salt gave **4-(3-dimethylaminopropyl)-6-methoxy-4-methyl-1(4*H*)-naphthalenone (XXV)·HBr** (1.67 g, 85%): mp 125–127° (from $Me_2CO$–$Et_2O$); ir, 1643 $cm^{-1}$; uv (EtOH), 237 mμ (ε 15,500), 303 (ε 11,300); nmr ($D_2O$), olefinic protons, τ 3.55 (d, 1, *J* = 10 Hz) and τ 2.88 (d, 1, *J* = 10 Hz). *Anal.* ($C_{17}H_{24}BrNO_2 \cdot 0.5H_2O$) C,H,N. The $H_2O$ layer was evaporated *in vacuo* below 40°, the residue was dissolved in $H_2O$ (1 ml), $NaClO_4$ (140 mg) was added, and the solution was cooled in a refrigerator overnight to give XXIb (10 mg, 0.5%), mp 216–218°. This was identical with the sample previously obtained from XX (mp, ir, and tlc).

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(10) This was found to be mostly XXV·HBr.

# Preparation of Substituted Naphthylcyclohexane Derivatives and Related Compounds[1]

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The synthesis of various naphthylcyclohexenone derivatives is reported. Methylation of 3-(6-methoxy-2-naphthyl)-2-cyclohexen-1-one (**2**) by various procedures allowed us to prepare the monomethyl (**5c**), dimethyl (5d), trimethyl (**6a**), and tetramethyl (**6b**) derivatives, the structure of which derives from their physical properties. Reduction of the tetrahydrodimethoxyphenylnaphthalene **8c** afforded a mixture of the α,β- and β,γ-unsaturated ketones (**11a**, **11b**). The new substances were submitted for a variety of bioassays. Compounds **4b**, **6a**, **8a**, **9b**, and **11b** were inactive when tested for oral estrogenic and oral antifertility activity.

Interest in seco-steroids generated by the potent antifertility activity of 2-methyl-3-ethyl-4-phenylcyclohex-4-ene carboxylic acid[2] lead us to prepare a series of phenylated cyclohexenones. Condensation reactions between aryl β-dialkylamino ketones and acetoacetic ester or similar compounds possessing an active $CH_2$ constitutes a convenient route for the synthesis of arylcyclohexen-1-one derivatives.[3] This method has been employed to prepare new compounds in the phenylcyclohexenone,[3] naphthylcyclohexenone,[4] and phenylnaphthalenic[5] series. In this work we wish to report the synthesis of new related tricyclic keto derivatives as well as some of their methylated analogs.

Condensation between 2-(β-dimethylaminopropionyl)-6-methoxynaphthalene·HCl (**1b**), readily obtained[4] from 6-methoxy-2-acetyl-naphthalene (**1a**)[6,7] and acetoacetic ester in a basic medium, afforded 3-(6-methoxy-2-naphthyl)-2-cyclohexen-1-one (**2**)[4] as the major compound. Another substance formed during the reaction corresponded to $C_{31}H_{28}O_4$, as evidenced by the mass spectrum molecular ion ($M^+$ 462), and the elemental analysis. Structure **3** is proposed for this compound on the basis of its nmr spectrum which showed 12 aromatic protons and only one olefinic H, besides 2 aromatic methyl ether groupings (see Experimental Section).

Catalytic hydrogenation[4] of **2** provided the substituted cyclohexanone **4a**, along with some of the corresponding alcohol (**4b**). LAH reduction of **4a** yielded a

(1) Contribution No. 370 from Syntex Institute of Organic Chemistry; for Contribution No. 369, see: I. T. Harrison, B. Lewis, P. Nelson, W. Rooks, A. Roszkowski, A. Tomolonis, and J. H. Fried, *J. Med. Chem.*, **13**, 203 (1970).

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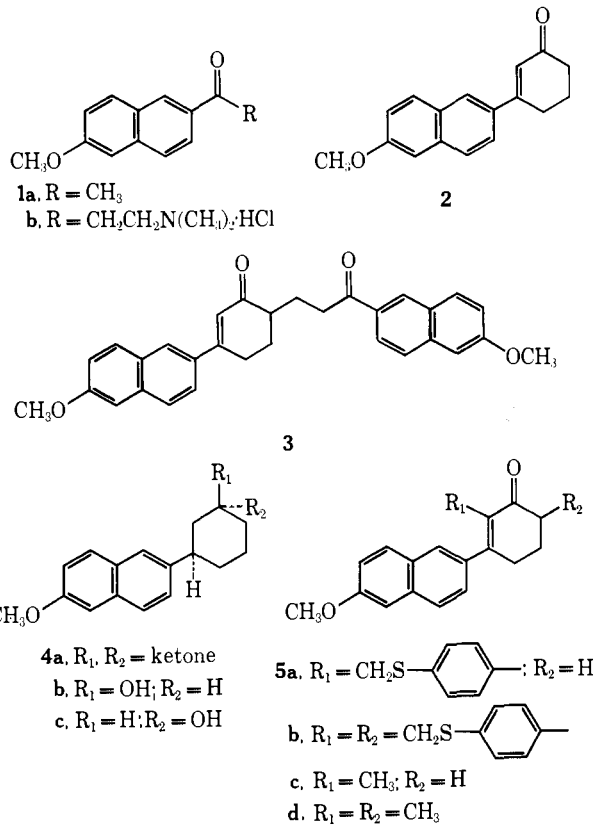


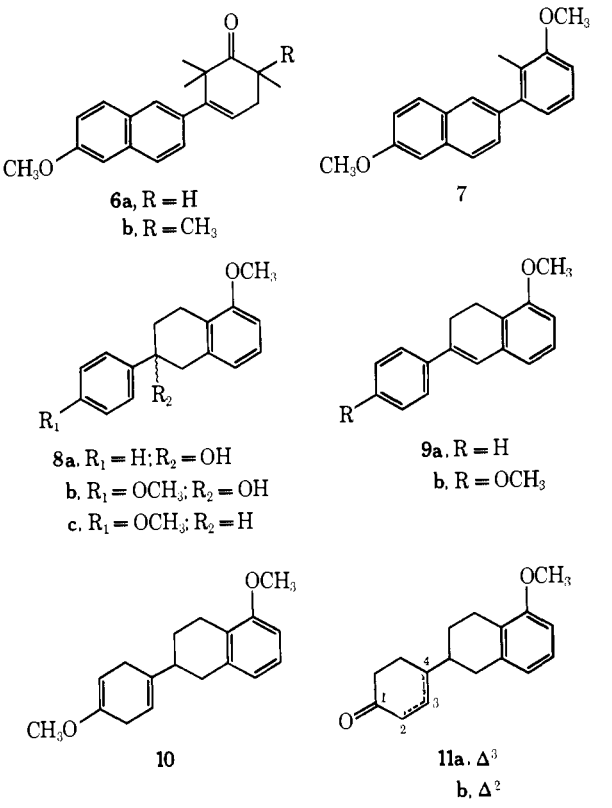


mixture of isomeric alcohols (**4b**, **4c**), which were separated by tlc. The equatorial (**4b**) and axial (**4c**) configuration of the OH group was assigned on the basis of the resonance of the proton on the C bearing the OH (see Experimental Section).

When the substituted cyclohexenone **2** was allowed to react with *p*-toluenethiol and formaldehyde in triethanolamine,[8] a mixture of mono- (**5a**) and bis- (**5b**) alkylated compound was formed. Chromatographic separation afforded the pure noncrystalline **5a** and **5b**, which were treated separately with Raney Ni to provide the monomethylcyclohexanone **5c** and dimethylcyclohexanone **5d**, respectively.

Direct methylation of ketone **2** with an excess of MeI in presence of *t*-BuOK[9] gave a mixture of 4 compounds, besides some recovered starting material. Tlc separation yielded the monomethyl (**5c**), dimethyl (**5d**), trimethyl (**6a**), and tetramethyl (**6b**) derivatives, whose structures result from examination of their nmr, ir, and uv properties (see Experimental Section).

When the monomethyl ketone **5c** was treated with MeI under similar conditions, several compounds were formed of which only two could be isolated in low yield. The main substance was the tetramethyl ketone **6b** (10%). The other compound, which did not show any C=O absorption in the ir, exhibited a very intense uv absorption at 234 nm, and its nmr presented two MeO groups and one aromatic Me. Structure **7** was assigned to this substance on the basis of these properties, as well as its mass spectrum ($M^+$ 278) and elemental analysis (see Experimental Section). In order to account for this structure, dehydrogenation must have occurred after C- and O-alkylation of **5c**.

The 7,8-dihydro-1-methoxyl-6-phenylnaphthalenes (**9a**, **9b**) were prepared by known procedure[5] *via* the carbinols (**8a**, **8b**), which could be isolated (see Experimental Section). Catalytic hydrogenation of **9b** afforded the tetrahydrodimethoxyphenylnaphthalene **8c**. Birch reduction of **8c** under controlled conditions, followed by mild acid treatment of the methyl enol ether **10**, gave the β,γ-unsaturated ketone **11a**, readily isomerized to the conjugated ketone **11b**.

**Biological Results.**—Compounds **1a** and **1b** were tested for antiinflammatory activity utilizing carrageenin-induced inflammation of the paw of female rats[10] and were found to be inactive (<0.1 × phenylbutazone). These two compounds were also tested for oral analgetic activity using phenylquinone-induced writhing in male mice by the method of Hendershot and Forsaith.[11] Compound **1a** elicited weak activity (approx 0.07 × aspirin), whereas **1b** appeared to be toxic at the dose used (200 mg/kg).

Compound **2** was inactive when tested subcutaneously[12] ( <0.2 × progesterone) and orally[13] (<0.1 × norethindrone) for antiestrogenic activity in female mice.

The following compounds were found to be inactive when tested for oral estrogenic activity[14] in female mice using estrone (E) as the reference standard: **4b** (<0.0-005 × E), **6a** (<0.3 × E), **8a**, and **9b** (<0.005 × E), and **11b** (<0.02 × E).

None of the compounds which were tested for oral

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TABLE I

| No. | Mp, °C | Yield, % | $\lambda_{max}$, nm | Log $\epsilon$ | $\nu_{max}$, $cm^{-1}$ | Nmr, ppm | Formula | Analyses |
|---|---|---|---|---|---|---|---|---|
| 1a | 107–109 | | 242 | 4.56 | 1675 | 2.63 (—CO—$CH_3$) | $C_{13}H_{12}O_2$ | C,H,O |
| | | | 258 | 4.44 | 1620 | 3.89 (—$OCH_3$) | | |
| | | | 310 | 4.13 | 1600 | 7.00–8.55 (6-aromatic H) | | |
| 2 | 146–147 | 46 | 224 | 4.32 | 1665 | 3.90 (—$OCH_3$) | | |
| | | | 256 | 4.04 | 1630 | 6.54 (olefinic-H) | | |
| | | | 276 | 4.12 | 1595 | 7.00–8.50 (6-aromatic H) | | |
| | | | 332 | 4.14 | | | | |
| 3 | 198–199 | 12 | 222–224 | 4.68 | 1680[c] | 3.95 (2x $OCH_3$) | $C_{21}H_{28}O_4$ | C,H,O[a] |
| | | | 242 | 4.71 | 1645 | 6.59 (olefinic-H) | | |
| | | | 253–254 | 4.73 | 1635 | 7.00–8.60 (12-aromatic H) | | |
| | | | 259–260 | 4.71 | 1600 | | | |
| | | | 318–320 | 4.53 | | | | |
| 4a | 126–127 | 55 | 230 | 4.91 | 1705 | 3.83 (—O—$CH_3$) | | |
| | | | 262 | 3.76 | 1635 | 7.00–7.80 (6-aromatic H) | | |
| | | | 270 | 3.74 | 1610 | | | |
| | | | 318 | 3.21 | | | | |
| | | | 332 | 3.30 | | | | |
| 4b | 135–136 | 84 | 230 | 4.96 | 3320 | 1.97 (s, —OH) | | |
| | | | 252 | 3.64 | 1610 | 2.40–2.90 (m, Ar—CH ax.) | | |
| | | | 260–261 | 3.73 | | 3.43–4.00 (m, CH—OH ax.) | | |
| | | | 270 | 3.72 | | 3.85 (s, —$OCH_3$) | | |
| | | | 318 | 3.21 | | 7.00–7.80 (m, 6-aromatic H) | | |
| | | | 332 | 3.30 | | | | |
| 4c | 132–133 | 12 | 230 | 4.95 | 3300 | 1.75 (—OH) | $C_{17}H_{20}O_2$ | C,H,O[a] |
| | | | 252 | 3.64 | 1610 | 2.82–3.47 (Ar-CH ax.) | | |
| | | | 261 | 3.73 | | 3.84 (—$OCH_3$) | | |
| | | | 270 | 3.71 | | 4.21 (CH-OH eq.) | | |
| | | | 318 | 3.20 | | 6.96–7.78 (6-aromatic H) | | |
| | | | 332 | 3.28 | | | | |
| 5c | 99–100 | 15 | 226 | 4.71 | 1665 | 1.78 (vinylic $CH_3$) | $C_{18}H_{18}O_2$ | C,H,O |
| | | | 270 | 4.31 | 1635 | 3.89 (—$OCH_3$) | | |
| | | | 308–312 | 4.09 | 1605 | 7.10–7.87 (6-aromatic H) | | |
| 5d | 99–100 | 12 | 226 | 4.68 | 1665 | 1.23 (d, $J$ = 7 Hz, $C_6$-$CH_3$) | $C_{19}H_{20}O_2$ | C,H |
| | | | 268–270 | 4.32 | 1630 | 1.77 (t, $J_H$ = 1.5 Hz, vinylic $CH_3$) | | |
| | | | 308 | 4.06 | 1610 | 1.85–2.31 (m, 2H-$C_5$) | | |
| | | | | | | 2.35–2.60 (m, $CH_3$-$C_6$-H) | | |
| | | | | | | 2.61–2.81 (m, 2H-$C_4$) | | |
| | | | | | | 3.92 (—$OCH_3$) | | |
| | | | | | | 7.10–7.81 (6-aromatic H) | | |
| 6a | 82–83 | 1 | 233 | 4.85 | 1710 | 1.13 ($C_2$-$CH_3$ ax.) | $C_{20}H_{22}O_2$ | C,H |
| | | | 263 | 3.77 | 1635 | 1.13, 1.19 (d, $J$ = 6 Hz, $C_6$-$CH_3$) | | |
| | | | 273 | 3.78 | 1610 | 1.32 ($C_2$—$CH_3$ eq.) | | |
| | | | 318 | 3.13 | | 3.91 (—$OCH_3$) | | |
| | | | 331–332 | 3.19 | | 5.68 ($q_1$ $J_1$ = 6 Hz, $J_2$ = 2.5 Hz, vinyl-H) | | |
| | | | | | | 7.10–7.78 (6-aromatic H) | | |
| 6b | 68–69 | 2.4 | 233 | 4.90 | 1680 | 1.15, 1.17 (4x $CH_3$) | $C_{21}H_{24}O_2$ | C,H |
| | | 8 | 261–262 | 3.83 | 1635 | ~2.37 (pair of d, 2H at $C_5$) | | |
| | | | 272 | 3.84 | 1605 | 3.90 (—$OCH_3$) | | |
| | | | 318 | 3.20 | | 5.67 (t, vinyl-*H*) | | |
| | | | 332 | 3.26 | | 7.00–7.90 (6-aromatic H) | | |
| 7 | 102–103 | 7 | 234 | 4.75 | 1635 | 2.16 ($C_2$–$CH_3$) | $C_{15}H_{18}O_2$ | C,H[c] |
| | | | 278 | 4.01 | 1605 | 3.89, 3.94 (2x $OCH_3$) | | |
| | | | 320 | 3.21 | 1580 | 6.80–7.90 (9-aromatic H) | | |
| | | | 334 | 3.24 | | | | |
| 8a | 136–137 | | 271 | 3.10 | 3300 | 2.05 (t, $J$ = 6 Hz, $C_7$) | $C_{17}H_{18}O_2$ | C,H |
| | | | 278 | 3.10 | 1590 | 3.76 (—$OCH_3$) | | |
| | | | | | 1100 | 6.55–7.65 (8-aromatic H) | | |
| 8c | 118–119 | 82 | 224 | 4.35 | 1600 | 2.50–3.20 (5-benzylic H) | $C_{18}H_{20}O_2$ | C,H |
| | | | 278 | 3.51 | 1580 | 3.73 (2x $OCH_3$) | | |
| | | | | | | 6.50–7.26 (7-aromatic H) | | |
| 9a[b] | 82–83 | | 229 | 4.26 | 1570 | 3.82 (—$OCH_3$) | | |
| | | | 306 | 4.34 | 1100 | 6.65–7.70 (H-vinylic + 8-aromatic H) | | |
| 9b[b] | 91–92 | | 312 | 4.44 | 1605 | 2.50–3.20 (m, Ar-$CH_2$-$CH_2$-) | | |
| | | | | | 1580 | 3.82, 3.84 (2x $OCH_3$) | | |
| | | | | | 1100 | 6.65–7.65 (H-vinylic + 7-aromatic H) | | |
| 11a | 113–114 | 5 | 220 (sh) | 3.97 | 1715 | 2.65–3.00 (4-benzylic H) | $C_{17}H_{20}O_2$ | C,H |
| | | | 271 | 3.12 | 1585 | 3.80 (—$OCH_3$) | | |
| | | | 279 | 3.14 | | 5.54 (unresolved t, vinylic H) | | |
| | | | | | | 6.55–7.25 (3-aromatic H) | | |

TABLE I (*Continued*)

| No. | Mp, °C | Yield, % | $\lambda_{max}$, nm | Log $\epsilon$ | $\lambda_{max}$, $cm^{-1}$ | Nmr, ppm | Formula | Analyses |
|---|---|---|---|---|---|---|---|---|
| 11b | 120–121 | 19 | 226 | 4.30 | 1670 | 3.79 (—$OCH_3$) | $C_{17}H_{20}O_2$ | C,H |
| | | | 272 | 3.13 | 1580 | 6.05 (d, $J$ = 10 Hz, H-vinylic $C_2$) | | |
| | | | 279 | 3.15 | | 6.57–7.30 ($C_3$- vinyl-H + 3-aromatic H) | | |

[a] Mass spectrum: 462 ($M^+$). [b] See ref 5. [c] Mass spectrum: 278 ($M^+$).

antifertility activity[15] elicited a positive response. [Mestranol (M) was used as the reference standard.] These included the following: **6b** and **7** (<0.2 × M); **6a** (<0.04 × M); **4b**, **4c**, **8a**, **9a**, **9b**, **8c**, and **11b** (<0.02 × M); and **2** and **4a** (<0.0004 × M).

## Experimental Section[16]

**3-(6-Methoxynaphthyl-2)-2-cyclohexen-1-one** (**2**).—In our hands, the technique described previously[4] afforded 46% of **2** (see Table I). Moreover, 12% of the pentacyclic condensation compd **3** was also isolated. Recrystallization from $CH_2Cl_2$–MeOH gave the anal sample (see Table I).

**3-(6-Methoxynaphthyl-2)-cyclohexanone** (**4a**).—Catalytic hydrogenation of **2**, under the conditions described earlier,[4] gave 55% of cyclohexanone **4a** (see Table I). Furthermore, 17% of alcohol **4b** (see below) was also isolated from the mother liquors.

**Reduction of 4a with LAH.**—To a solution of 1.4 g of **4a** in 50 ml of anhyd THF, 4 g of LAH in 50 ml of THF was added. The reaction mixture was gently refluxed for 1.5 hr, then cooled in an ice bath, and EtOAc was added slowly. After addition of satd aq $Na_2SO_4$ and extraction by the usual procedure, the product was purified by tlc. The equatorial alcohol **4b**[4] (1.1 g, 84%) was first isolated (Table I).

The axial isomer **4c** was recrystd from $Me_2CO$–hexane (see Table I).

**3-(6-Methoxynaphthyl-2)-2-methyl-2-cyclohexen-1-one** (**5c**) **and 3-(6-Methoxynaphthyl-2)-2,6-dimethyl-2-cyclohexen-1-one** (**5d**).—To a solution of 680 mg of *p*-toluenethiol in 6 ml of triethanolamine, 1 g of **2** and 1.4 ml of 40% $CH_2O$ were added. The mixture was refluxed for 20.5 hr under $N_2$. To the cooled solution, $CH_2Cl_2$ was added. Washing with 5% NaOH, 5% HCl, and then $H_2O$ was followed by drying and evaporation of the solvent. Chromatography over 100 g of Florisil gave by elution with $CH_2Cl_2$–hexane (3:7), 290 mg of amorphous **5b**. Further elution with the same solvent furnished 250 mg of **5a**. Treatment of **5a** with Raney Ni in $Me_2CO$, at reflux temp for 6 hr under $N_2$ gave the monomethyl derivative **5c** (see Table I).

Similarly, treatment of **5b** with Raney Ni afforded the dimethyl derivative **5d** (Table I).

**Reaction of Ketone 2 with MeI.**—To 3.05 g of K in 105 ml of anhyd *t*-BuOH under $N_2$, 7 g of ketone **2** was added. The mixture was stirred at room temp for 18 hr, under $N_2$. The homogeneous solution was cooled and 2 ml of MeI in 30 ml of *t*-BuOH was added. The reaction mixture was stirred for 1.5 hr, then poured into ice–water, and extracted with $CH_2Cl_2$. The organic layer was washed, dried, and evapd *in vacuo*. The crude material was separated by tlc, in order of decreasing polarity (A–E). Fraction A (2.83 g) was identified as the starting ketone **2**. Fraction B (3.05 g), recrystd from MeOH–$H_2O$ (mp 99–100°), was shown to be identical with the monomethylated derivative **5c** (see above) by usual criteria. Fraction C (160 mg; mp 99–100°) corresponded to the dimethyl ketone **5d** (*vide supra*). Fraction D was recrystd from hexane to give an anal sample (70 mg) of 3-(6-methoxy-2-naphthyl)-2,2,6-trimethyl-3-cyclohexen-1-one (**6a**) (see Table I). Fraction E corresponded to 3-(6-methoxy-2-naphthyl)-2,2,6,6-tetramethyl-3-cyclohexen-1-one (**6b**) (see Table I).

**Treatment of the Monomethyl Ketone 5c with MeI.**—Reaction of 3 g of **5c** with 1.65 g of K in 50 ml of *t*-BuOH, followed by addition of 3.76 ml of MeI in 15 ml of *t*-BuOH was performed as described above. Tlc separation afforded as the most polar substance, the tetramethyl derivative **6b** (266 mg), identical with an authentic sample obtained by the other route (*vide supra*). The less polar material was recrystd from $CH_2Cl_2$–hexane to afford the analytical sample (198 mg) of 3-(6-methoxy-2-naphthyl)-6-methoxytoluene (**7**) (see Table I).

**5,6,7,8-Tetrahydro-1-methoxyphenylnaphthalene-6ξ-ols** (**8a,8b**).—The previously described procedures[5] led to isolation of 1.38 g of carbinol **8a** by reaction of 5 g of 5-methoxytetralone. $HCO_2H$ treatment of **8a** gave the dehydration compd **9a**.[5] Similarly, the noncrystalline carbinol **8b**[5] showed $\lambda_{max}$ 312 nm ($\epsilon$ 27,800); $\nu_{max}$ 3450, 1610, 1590, and 1090 $cm^{-1}$ (in $CHCl_3$). Dehydration with $HCO_2H$ afforded the known **9b**.[5]

**Catalytic Hydrogenation of 9b.**—To the dehydro compound **9b** (2.2 g), dissolved in 20 ml of dioxane, 400 mg of Pd–C (5%) in 10 ml of dioxane was added. The solution was stirred under $H_2$ up to absorption of 1 equiv of $H_2$. After the usual work-up 1.8 g of compd **8c** was obtained (see Table I).

**Birch Reduction of 5,6,7,8-Tetrahydro-1-methoxy-6-methoxyphenylnaphthalene** (**8c**).—To a solution of 86 mg of Li in 50 ml of liquid $NH_3$, 1.5 g of **8c** in 50 ml of dioxane–THF (1:1) was added dropwise, with 1 ml of abs EtOH. The reaction was allowed to continue for 3 hr until disappearance of the blue color. After evaporation of $NH_3$ and extraction with $CH_2Cl_2$, the organic layer was washed, dried, and concentrated *in vacuo*. The crude enol ether **10** (1.5 g) was treated with 2 ml of HCl in 20 ml of MeOH, at reflux temperature for 1 hr. After usual work-up, the crude product, which showed 8 different spots, was separated by tlc. The most polar compound (290 mg) corresponded to the conjugated ketone **11b** (see Table I). A less polar substance (80 mg) which was isolated corresponded to the β,γ-unsaturated ketone **11a**. Recrystallization from $CH_2Cl_2$–MeOH gave an analytical sample of **11a**.

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(15) F. A. Kincl and R. I. Dorfman, *J. Reprod. Fert.*, **10**, 105 (1965).

(16) Melting points are uncorrected and were taken on a Fisher-Johns apparatus. Uv spectra were measured in EtOH on a Beckman DU Model 2400 spectrometer, ir spectra as KBr disks on a Perkin-Elmer Model 21 spectrophotometer. Nmr spectra were recorded on Varian A-60 spectrometer using $CDCl_3$ as solvent. Mass spectra were measured on an Atlas CH-4 spectrometer equipped with TO-4 ion source. Where analyses are indicated only by symbols of the elements, analytical results obtained from those elements are within ± 0.4% of the theoretical value.