bath for 3.5 hr, poured into ice, and extracted with Et_2O. The extracts were washed and distd to give 20.5 g (63.5%) of an oil: bp 130–133° (1 mm); $n^{25}D$ 1.5548; ir, strong band at 5.85 μ.

2,3-Diethyl-6-methoxyindan-1-one (6).—To 70 g of NaOMe was added with stirring 80 g (0.42 mole) of **5**. With cooling 400 g of EtI was added rapidly and the mixture was stirred for 30 min and then heated on the steam bath for 3 hr. Excess EtI was removed by distn, H_2O added, and the mixture extracted (Et_2O). The solvent was evapd after drying (Na_2SO_4) and the residue was distd: yield 74.5 g (81%); bp 155–160° (1 mm); $n^{25}D$ 1.5393. *Anal.* ($C_{14}H_{18}O_2$) C, H.

Pyridyllithium Reactions. 2-(*p*-Methoxyphenyl)-1-(2-pyridyl)-cyclohexanol.—To an Et_2O soln (400 ml) of BuLi prepared under N_2 at −10° from 4.1 g (0.6 mole) of Li and 41.1 g (0.3 mole) of BuBr was added at −40°, 47.4 g (0.3 mole) of 2-bromopyridine in 200 ml of Et_2O. After 1 hr, a soln of 30.6 g (0.15 mole) of 2-(*p*-methoxyphenyl)cyclohexanone[3b] in 500 ml of Et_2O was added dropwise with stirring and the mixture was allowed to warm to room temp. Stirring was continued for 6 hr. H_2O was cautiously added, the organic layer was sepd and combined with an additional Et_2O extract. The combined Et_2O soln were extracted with 10% HCl and, after preliminary washing (Et_2O), the acid soln was basified (NH_4OH) and extracted ($CHCl_3$). The $CHCl_3$ soln was washed (H_2O) and coned on the steam bath to an oil which was triturated with pet ether (bp 30–60°) and recrystd from hexane: yield 24.7 g (58%); mp 74–75°. The ir spectrum showed a typical OH band at 3 μ. *Anal.* ($C_{18}H_{21}NO_2$) C, H, N.

1-(2-Pyridyl)-2,3-diethyl-6-methoxy-indan-1-ol was prepared by a similar procedure: yield 74%; bp 183–189° (1 mm); $n^{25}D$ 1.5722; strong OH in ir at 3.0 μ. *Anal.* ($C_{19}H_{23}NO_2$) C, H, N.

1-(3-Pyridyl)-2,3-diethyl-6-methoxy-1-indene (8b).—This compound was obtained from 3-bromopyridine by the above procedure in 61% yield: bp 180–185° (1 mm); $n^{25}D$ 1.5923; log $\epsilon_{265\ m\mu}$ 4.05. *Anal.* ($C_{19}H_{21}NO$) C, H, N.

Dehydration Procedure (Mixture 4).—A mixture of 10 g (0.035 mole) of 2-(*p*-methoxyphenyl)-1-(2-pyridyl)cyclohexanol and 40 g of powdered potassium pyrosulfate was placed in a bath at 240° and the temp raised to 240–260° with manual stirring until the fusion was completed and held at this temp for 1 min. The mixture was allowed to cool somewhat and poured into ice, made basic (NH_4OH), and extracted ($CHCl_3$), washed, and distd: bp 172–175° (2.5 mm); yield 5.8 g (63%); $n^{25}D$ 1.6063. *Anal.* ($C_{18}H_{19}NO$) C, H, N.

1-(2-Pyridyl)-2,3-diethyl-6-methoxy-1-indene (8a).—A mixture of the 2-pyridyl carbinol (10 g) and 7 ml of 85% H_3PO_4 was heated under reflux for 6 hr and poured into ice. The solution was made basic (NaOH) and extracted ($CHCl_3$). The solvent was removed and the residue was distd: yield 7 g (76%); bp 173–178° (1 mm); $n^{25}D$ 1.5838; log $\epsilon_{248\ m\mu}$ 4.08. *Anal.* ($C_{19}H_{21}NO$) C, H, N.

***p*-Methoxyphenyl-2-(2-pyridyl)cyclohexane (2).**—A soln of 5.0 g (0.019 mole) of mixture **4** in 250 ml of EtOH was hydrogenated in a Parr hydrogenator in presence of 0.5 g of PtO_2. The reduction required 20–22 hr. The catalyst was filtered and the residue after removal of the solvent was distd: yield 4.3 g (85%); bp 190–192° (3 mm); $n^{25}D$ 1.5766. *Anal.* ($C_{18}H_{21}NO$) C, H, N.

1-(2-Pyridyl)-2,3-diethyl-6-methoxyindane (3).—The indene **8a** (5.5 g, 0.02 mole) in 150 ml of EtOH was reduced for 20 hr in a Parr hydrogenator using Raney Ni catalyst. The catalyst was removed and the product was distd: yield 3.8 g (83%); bp 185–190° (1 mm); $n^{25}D$ 1.5696. *Anal.* ($C_{18}H_{23}NO$) HN, calcd: C, 81.10; found: C, 80.68.

New Compounds

1-Dodecylpyridinium Dodecyl Sulfate

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When a mixture of 1-decanol and *N*-bromoacetamide in pyridine is treated with SO_2 under the conditions described for the dehydration of certain steroid alcohols[1] an excellent yield of 1-dodecylpyridinium dodecyl sulfate is obtained. The same compound is obtained when didodecyl sulfate is reacted with pyridine. Evidently this fact had been observed some years ago by Sementsov, *et al.*,[2] but their "S-containing salt of pyridine" had not been characterized.

Experimental Section[3]

A solution of 18.6 g of 1-dodecanol and 27.6 g of *N*-bromoacetamide (NBA) in 160 ml of pyridine was treated with SO_2 at about 25° until all of the NBA had been destroyed. Upon pouring the solution into an ice–water slurry, 20.23 g of 1-dodecylpyridinium dodecyl sulfate, mp 88–90°, precipitated. Recrystallization from EtOAc gave an analytical sample, mp 90–90.5°. Ir and nmr spectra supported the structure. *Anal.* ($C_{29}H_{53}NO_4S$) C, H, N, S.

The sample prepared by dissolving didodecyl sulfate in pyridine, followed by addition to H_2O, had mp 91–92° and spectral properties identical with those of the material prepared by the other route.

(1) See L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 75.

(2) A. Sementsov, R. J. Kiesel, M. E. McGreal, and W. F. Hart, *J. Org. Chem.*, **23**, 2020 (1958).

(3) Melting points are uncorrected. Where analyses are indicated only by the symbols for the elements, analytical results obtained for those elements were within ±0.3% of the theoretical values.

SH Analog of the Estrogen Hexestrol

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The synthetic estrogen *meso*-hexestrol (I) is frequently used in the clinic. A great number of analogous compounds have been prepared.[1] The thiophenol isostere II should at least be useful in making decisions about bonding forces in estrogen–receptor complexes[2] and could be expected to show some interesting biological properties. The synthesis of II by a method similar to one previously described[3] is reported.

Biological Activity.—The thiophenol analog II was

(1) U. V. Solmssen, *Chem. Rev.*, **37**, 481 (1945); J. Grundy, *ibid.*, **57**, 281 (1957).

(2) H. G. Mautner, *Pharm. Rev.*, **19**, 107 (1967).

(3) S. F. Torf and N. V. Khromov-Borisov, *Zh. Obshch. Khim.*, **31**, 2102 (1961). They report II to have mp 155–157°.

tested for uterotrophic[4] and antiuterotrophic[4] activities in the mouse. It was dissolved in olive oil and injected subcutaneously. It displayed no significant activities in 3 daily doses of as much as 300 μg. *In vitro* the thiophenol II showed no competitive binding affinity[4] for estrogen "receptor" sites of the mouse uterus in concentrations 10^3 times the effective concentrations of I.

Experimental Section

meso-**3,4-Hexanebis(phenyl-4-disulfonyl chloride).**—To a solution of 3 g (0.013 mole) of *meso*-3,4-diphenylhexane[5] in 20 ml of dry CCl_4 in a dry atmosphere was added 6 g (0.05 mole) of $ClSO_3H$ and the mixture was stirred for 12 hr at room temperature. The suspension was filtered. The product (8.5 g) was crystallized from $CHCl_3$ after which it melted at 220–226°. *Anal.* ($C_{18}H_{20}Cl_2S_2O_4$), C, H, S.[6]

meso-**3,4-Hexanebis(phenyl-4-thiol) (II).**—The crude disulfonyl chloride was reduced according to a literature procedure.[7] $SnCl_2 \cdot 2H_2O$ (10 g) and 50 ml of HAc was saturated with anhydrous HCl. The solution was maintained at 80°, 6.5 g (0.015 mole) of the sulfonyl chloride was added and the solution was stirred for 1 hr. The solution was cooled, poured into 30 ml of concentrated HCl, and filtered. The filtrate was extracted (Et_2O), dried, and crystallized several times from C_6H_6. The product was sublimed at 170° (0.01 mm); yield 1 g (25%), mp 147–150°.[3] *Anal.* ($C_{18}H_{22}S_2$) C, H, S.[8] Absorption bands (or peaks) of spectra (nmr, ir) were as expected.

Acknowledgments.—Nmr spectra were kindly recorded by Dr. S. O. Almquist at the Department of Chemistry, College of Agriculture, Uppsala. This work was supported by the Swedish Cancer Society.

(4) L. Terenius, *Mol. Pharmacol.*, **4**, 301 (1968).
(5) S. Wawzonek, *J. Amer. Chem. Soc.*, **68**, 1157 (1946).
(6) C: calcd, 49.7; found, 49.1; S: calcd, 14.8; found, 15.6.
(7) C. S. Marvell and P. D. Caesar, *J. Amer. Chem. Soc.*, **73**, 1097 (1951).
(8) The analyses were within ±0.4% of theoretical values. Melting points are uncorrected.

Compounds Related to Insect Juvenile Hormone. V. Derivatives of Citronellol and Citronellylamine

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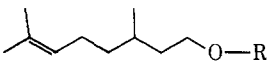
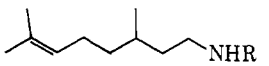
A number of investigators have reported that certain compounds having insect juvenile hormone activity are also inhibitors of embryonic development in some species of insects.[1] Also, the "dihydrochloride" of methyl farnesate has been found to be a very effective sterilant for female *Pyrrhocoris apterus* (L.).[2] In addition, Masner and coworkers described the phenomenon of sexually spread insect sterility that occurred when they used compounds with known juvenile hormone activity.[3]

Among the compounds best known for their chemosterilant activity are tepa [tris(1-aziridinyl)phosphine oxide][4] and hempa (hexamethylphosphoric triamide).[4,5] We therefore prepared a number of derivatives of citronellol (3,7-dimethyl-6-octenol) and citronellylamine (3,7-dimethyl-6-octenylamine), several of which bear a structural resemblance to these sterilants, for testing as potential sterilants and juvenilizers. The test compounds are listed in Table I.

Table I

R	Bp, °C(mm)	Yield, %	Formula
A. Compounds Derived from Citronellol (3,7-Dimethylethyl-6-octen-1-ol)			
			
—P(O)[N(CH$_3$)$_2$]$_2$	128–133(0.15)	63	$C_{14}H_{31}N_2O_2P$
—P(O)(N△)$_2$	142–150(0.10)	53	$C_{14}H_{27}N_2O_2P$
—C(O)N(CH$_3$)$_2$	83–89(0.05)	90	$C_{13}H_{25}NO_2$
—C(O)CN△	84–93(0.05)	86	$C_{13}H_{23}NO_2$
B. Compounds Derived from Citronellylamine (3,7-Dimethyl-6-octenylamine)			
			
—CO$_2$C$_2$H$_5$	102–103(0.10)	87	$C_{13}H_{25}NO_2$
CONH(CH$_2$)$_6$NHC(O)	138–139[a]	97	$C_{28}H_{54}N_4O_2$
—P(O)[N(CH$_3$)$_2$]$_2$	165–180(0.10)[b]	27[b]	$C_{14}H_{32}N_3OP$
—P(O)(N△)$_2$	165–180(0.10)[b]	24[b]	$C_{14}H_{28}N_3OP$[c]
C. Miscellaneous			
R'CO$_2$C$_2$H$_5$[d]	107–111(0.12)	72	$C_{13}H_{23}NO_2$
R''CO$_2$C$_2$H$_5$[e]	123–130°(0.03)	84[f]	$C_{13}H_{25}NO_3$

[a] Melting point following recrystn from EtOH. [b] Decomposes on distn. [c] Combustion analyses were poor, but the nmr spectrum (see Experimental Section) was entirely consistent. [d] Commercial citral was converted into its oxime and reduced with LAH to a mixture of cis and trans amines. R' therefore is (3,7-dimethyl-2,6-octadienyl)amino. [e] R'' is (6,7-epoxy-3,7-dimethyloctyl)amino. [f] Yield of the epoxidation step.

Only *P,P*-bis(1-aziridinyl)-*N*-(3,7-dimethyl-6-octenyl)phosphinic amide showed chemosterilant activity against house flies, *Musca domestica* L. The carbamates and their epoxides were the only compounds to show juvenile hormone activity against *Tenebrio molitor* L.[6,7]

Experimental Section

The chem anal. were performed by Galbraith Associates, Inc., Knoxville, Tenn. Nmr spectra were obtained with a Varian Model T-60 instrument, and ir spectra were recorded as films or mulls with a Perkin-Elmer 137 ir spectrophotometer. Where analyses are indicated only by symbols of the elements, analytical results obtained for those elements were within ±0.4% of the theoretical values (see Table I).

Citronellol Derivatives.—Citronellol was converted into its chloroformate by treatment with 1 equiv each of $COCl_2$ and Et_3N. An ethereal soln of $COCl_2$ was added dropwise to a well-stirred soln of the alcohol and amine in Et_2O while the mixture was held at 20–30°. The mixture was allowed to stand at room temp for 1.5 hr and filtered by suction (Et_2O rinse). The filtrate

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(2) P. Masner, K. Sláma, and V. Landa, *J. Embryol. Exp. Morphol.*, **20**, 25 (1968).
(3) P. Masner, K. Sláma, and V. Landa, *Nature (London)*, **219**, 395(1968).
(4) G. C. LaBrecque, *J. Econ. Entomol.*, **54**, 684 (1961).
(5) S. C. Chang, P. H. Terry, and A. B. Borkovec, *Science*, **144**, 57 (1964).
(6) W. S. Bowers, and M. J. Thompson, *ibid.*, **142**, 1469 (1963).
(7) Mention of a pesticide or a proprietary product in this paper does not constitute a recommendation or endorsement of this product by the U. S. Department of Agriculture.