path is provided by a comparison of products from the reduction of *o*-methoxybenzyl alcohol and *o*-methylanisole. Whereas the former undergoes 59% carbon–oxygen cleavage, the latter is reduced to the same extent as anisole.

TABLE V
REDUCTION OF HALOANISOLES WITH LITHIUM ALUMINUM HYDRIDE[a]

Haloanisole, (no.)	Recovered starting materials, %	Product yield, % Anisole	Halophenol	Phenol
o-Iodoanisole (1)	0	40	3	57
o-Bromoanisole (2)	18	58	9	14
p-Iodoanisole (3)	9	91	0	0
p-Bromoanisole (4)	62	35	2	1
Anisole (5)	96	[b]	...	4
o-Methoxybenzyl alcohol (6)	41	...	...	59
o-Methylanisole (7)	96	...	...	4

[a] All reductions were carried out with 1.0 mole of lithium aluminum hydride per mole of substrate for 24 hr in diglyme at 100°. [b] The leaders indicate that the reaction was not studied under these conditions.

The preparative usefulness of the reduction of aromatic halides with lithium aluminum hydride does not equal the analogous aryltin hydride reductions. Although yields from lithium aluminum hydride reductions in diglyme at 100° are equal to or better than those resulting from triphenyltin hydride reductions[15] at 94°, the latter reagent may be used at temperatures as high as 154°. Significantly higher yields from unreactive halides are then obtained. However, the ready availability of lithium aluminum deuteride allows the specific introduction of deuterium into an aromatic nucleus. For example, treatment of *p*-iodotoluene with lithium aluminum deuteride in diglyme at 100° for 24 hr gave *p*-deuteriotoluene in near quantitative yield. Treatment of 8-bromo-1-naphthylcarbinol with lithium aluminum deuteride in tetrahydrofuran also gave quantitative yields of 8-deuterio-1-naphthylcarbinol.

(15) D. H. Lorenz, P. Shapiro, A. Stern, and E. I. Becker, *J. Org. Chem.*, **28**, 2332 (1963).

Experimental Section

Materials.—Commercially available aromatic halides were used without purification. The preparation of 8-bromo-1-substituted naphthalenes from 8-bromo-1-iodonaphthalene was carried out according to established procedures.[16] Ether, tetrahydrofuran, and diglyme were dried by distillation from lithium aluminum hydride just prior to use. Diglyme was distilled at reduced pressure.[17]

Procedure.—The following general procedure was used for the reductions. Lithium aluminum hydride, 0.36 g (10 mmoles), was added to 25 ml of dry solvent in a 50-ml single-necked, round-bottomed flask that was fitted with a condenser and drying tube. The aromatic halide (10 mmoles) was added to the hydride slurry and the resulting mixture was refluxed or heated at constant temperature for 24 hr. After reaction, the unreacted hydride was quenched by careful dropwise addition of water. Next, 30 ml of 10% sulfuric acid was added followed by extraction with three 75-ml portions of ether. The ether extract was washed with 25 ml of saturated sodium bicarbonate solution and four 50-ml portions of water, dried over anhydrous magnesium sulfate, and evaporated.

Product Analysis.—Reaction product mixtures were analyzed for reduced aromatic hydrocarbon and aromatic halide by nuclear magnetic resonance or vapor phase chromatography. Aromatic halides with proton-containing functional groups were analyzed by vapor phase chromatography on an Aerograph A-90-P. All peaks were identified by comparison of retention times with known standards. In a number of instances product mixtures were analyzed by both techniques and the results were in agreement. The reported per cent yields are accurate to ±5%.

Acknowledgment.—We thank the National Science Foundation for financial support (GP-3343).

(16) L. F. Fieser and A. M. Seligman, *J. Am. Chem. Soc.*, **61**, 136 (1939).
(17) For a report of an explosive decomposition of lithium aluminum hydride from diglyme distillation at atmospheric pressure, see R. H. Watson, *Chem. Ind.* (London), 665 (1964).

The Synthesis of Triptindan

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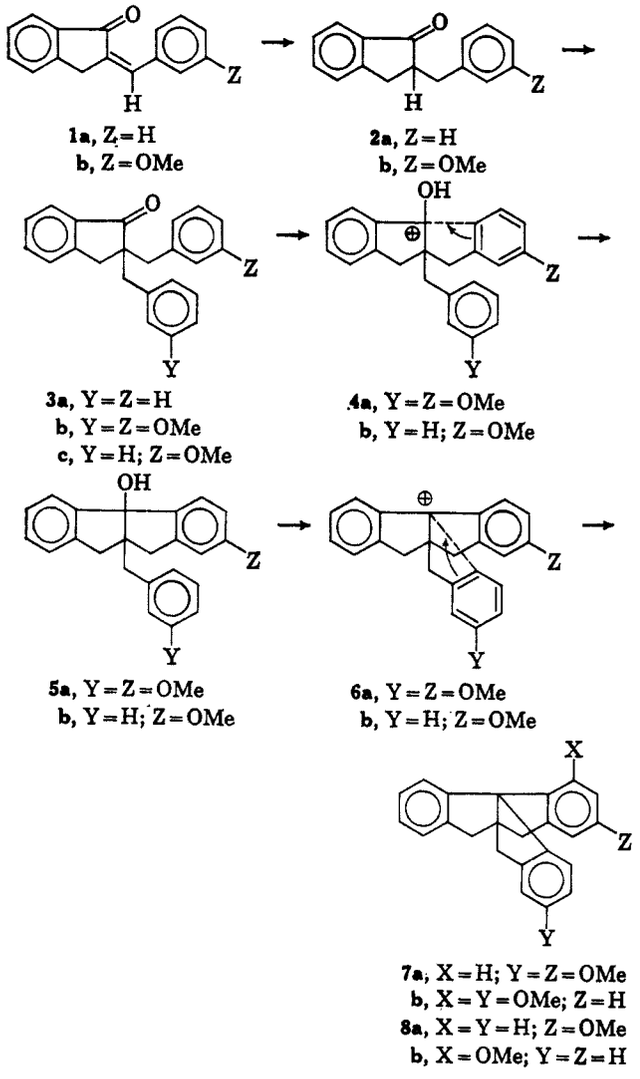
The title compound (**11**),[1] a symmetrical tribenzo derivative of tricyclo[3.3.3.$0^{1,6}$]undecane, has been synthesized by a route involving acid cyclization of a substituted dibenzylindanone. The chemical and spectral properties of compounds related to **11** are described and the spectral properties of **11** are discussed in relation to the possibility of nonbonded π orbital interactions.

As a result of our interest in highly symmetrical compounds,[2-4] particularly in tricyclic systems of the [*n.n.n*.$0^{1,n+2}$] type,[3-7] and because a relatively simple route was available, we undertook the synthesis of **11**, a tribenzo derivative of tricyclo[3.3.3.$0^{1,5}$]undecane. A feature of **11** of particular interest is that its ring system, like that of triptycene,[8] incorporates a substituted triphenylmethane into a rigid arrangement such that some overlap between the isolated π-electron systems may be possible. We hoped that our synthetic scheme might produce triptindans with substituents suitable for assessing such "homoconjugative" interactions.

The synthetic route involves a double acid-catalyzed cyclization of the dibenzylindanone **3** (Chart I). This material should theoretically be obtainable by a double alkylation of 1-indanone with a benzyl halide; however,

(1) P. D. Bartlett, M. J. Ryan, and S. G. Cohen, *J. Am. Chem. Soc.*, **64**, 2649 (1942), foonote 1.
(2) H. O. House, R. W. Magin, and H. W. Thompson, *J. Org. Chem.*, **28**, 2403 (1963).
(3) H. W. Thompson, *Tetrahedron Letters*, 6489 (1966).
(4) H. W. Thompson, *J. Org. Chem.*, **32**, 1222 (1967).
(5) R. L. Cargill and J. W. Crawford, *Tetrahedron Letters*, 169 (1967).
(6) L. F. Fieser and J. T. Dunn, *J. Am. Chem. Soc.*, **58**, 1054 (1936).
(7) J. Altman, D. Becker, D. Ginsburg, and H. J. E. Lowenthal, *Tetrahedron Letters*, 757 (1967).
(8) For a recent brief review of triptycene chemistry, see B. H. Klanderman, "Organic Chemical Bulletin," Vol. 37, No. 1, Research Laboratories of the Eastman Kodak Co., Rochester, N. Y., 1965.

CHART I



in practice, basic reactions of α-unsubstituted cyclopentanones produce high yields of aldol self-condensation products,[9] so that another route to **3a** was necessary. The monoalkylated compound, 2-benzyl-1-indanone (**2a**), is known[10] and is readily available from hydrogenation of the condensation produce (**1a**) of benzaldehyde with 1-indanone.[11]

Since its aldol products are incapable of dehydration, **2a** can be alkylated successfully, and base-catalyzed reaction with benzyl chloride provided 2,2-dibenzyl-1-indanone (**3a**) in 61% yield. However, the desired cyclization of **3a** failed to take place.

The experiences of others[12-15] in acid cyclizations had suggested that reaction temperatures would be necessary which would preclude the use of sulfuric or hydrofluoric acids.[16] Of the remaining reagents, polyphosphoric acid (PPA)[18] seemed most desirable, but **3a** was not soluble in PPA even at elevated temperatures. Heterogeneous PPA reactions gave either unchanged starting material or unidentifiable products, as did attempts at cyclization with aluminum chloride, sodium aluminum chloride,[17] and perchloric acid.[18]

Since our chief problem in the PPA cyclization seemed to be solubility, we attempted the synthesis of **7a**, using as a precursor **3b**, bearing on each benzyl aromatic ring a methoxyl group, which would increase both the nucleophilic reactivity of that ring and the solubility of the compound in polar solvents.

In a synthesis paralleling our original scheme, *m*-methoxybenzalindanone (**1b**), a known compound,[19] was reduced catalytically[11] to provide 2-(*m*-methoxybenzyl)-1-indanone (**2b**), which was alkylated under basic conditions with *m*-methoxybenzyl chloride.[20] The resulting 2,2-di(*m*-methoxybenzyl)-1-indanone (**3b**) (73% yield) proved to be soluble in PPA and reaction of crude **3b** for 30 min at 100° provided an oily mixture separable by chromatography into two crystalline products.

The larger fraction (43%) gave analytical and spectral data consistent with the expected product, **7a**. This structure is more firmly established for **7a** by its nmr spectrum, which shows, in addition to aromatic hydrogen absorption, two singlets of equal area but of different line width at positions consistent with aromatic methoxyl and benzylic methylene groups. The product obtained in lower yield (22%) is isomeric with **7a**; the exact structure is confirmed by its nmr spectrum, which differs from that of **7a** in the replacement of the isolated methoxyl singlet (6 H, τ 6.4) by a pair of 3 H singlets (τ 6.2 and 6.4). This spectrum is entirely consistent with structure **7b**, produced by one cyclization *para* and one *ortho* to a methoxyl group. This places the *o*-methoxyl in the cavity "behind" the triphenylmethyl portion of the molecule and accounts for the downfield shift[21] of one of the methoxyl singlets relative to the spectrum of **7a**. This assignment is also consistent with the chromatographic behavior of the two compounds, since **7b** is eluted faster in chromatography on Florisil or silica gel. Another cyclization, carried out on purified **3b**, provided **7a** and **7b** in combined yield of 96% and in a ratio (assessed by nmr) of 60:40.

As additional proof of the structures of **7a** and **7b**, we have calculated the ultraviolet spectra of these two substances, using appropriate models, and the agreement with both position and intensity of absorption is good.[3] Of course, the fact of this spectral agreement speaks against any very powerful homoconjugative interactions of the type sought, but we had anticipated from the case of triptycene[8,22] that such interactions might be too subtle for ready detection by simple spectral means.

A third isomer, arising from two *ortho* cyclizations, could theoretically be formed in this reaction. We were unable to detect any of this unfavorable isomer,

(9) E. E. Royals, "Advanced Organic Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1954, p 714.
(10) A. Hassner and N. H. Cromwell, *J. Am. Chem. Soc.*, **80**, 893 (1958).
(11) N. H. Cromwell and R. P. Ayer, *ibid.*, **82**, 133 (1960).
(12) C. K. Bradsher, *Chem. Rev.*, **38**, 447 (1946).
(13) (a) F. D. Popp and W. E. McEwen, *ibid.*, **58**, 321 (1958); (b) F. Uhlig and H. R. Snyder in "Advances in Organic Chemistry: Methods and Results," Vol. 1, R. A. Raphael, E. C. Taylor, and H. Wynberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, pp 35–81.
(14) J. Koo, *J. Am. Chem. Soc.*, **75**, 1891 (1953).
(15) J. F. Collins and H. Smith, *J. Chem. Soc.*, 4308 (1956).
(16) R. A. Barnes and B. D. Beitchman, *J. Am. Chem. Soc.*, **76**, 5430 (1954).
(17) J. F. Norris and A. J. Klemka, *ibid.*, **62**, 1432 (1940).
(18) B. D. Tilak, R. B. Mitra, and C. V. Deshpande, *Tetrahedron Letters*, 3569 (1965).
(19) P. Pfeiffer and E. Milz, *Ber.*, **71B**, 272 (1938).
(20) J. W. Cornforth and R. Robinson, *J. Chem. Soc.*, 684 (1942).
(21) C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).
(22) C. F. Wilcox, Jr., *ibid.*, **33**, 1874 (1960).

but the isolation of any *ortho* cyclized product at all is unusual and therefore of interest. There are literature examples in which compounds containing aromatic rings activated by a *meta* substituent either have been successfully cyclized or have failed to react when the only available position for cyclization was *ortho* to the activating group.[12,13] However, there are few reported instances in which *ortho* cyclized products have been identified from such condensations when a *para* position was available as well.[23]

Having determined that triptindan compounds could be made by this scheme, we wished to synthesize the parent compound, triptindan itself, using a methoxytriptindan as precursor. In order to have as few methoxyl groups to remove as possible, we attempted synthesis of a monomethoxytriptindan and found that 2-benzyl-2-(*m*-methoxybenzyl)-1-indanone (**3c**) could be cyclized using PPA.

The previously prepared 2-(*m*-methoxybenzyl)-1-indanone (**2b**) was alkylated with benzyl chloride to provide **3c** in 87% yield. This material was cyclized with PPA in 96% yield; alternatively, *m*-methoxybenzalindanone (**1b**) could be carried through the reduction, alkylation, and cyclization steps without isolation or purification of the intermediates (66% over-all yield). In both cases the product, purified by chromatography and assessed by nmr, consisted of a mixture of two isomers in the ratio of 7:1. The nmr spectra of the purified components indicate that they are derived, respectively, from *para* and from *ortho* cyclization; analytical and other spectral data are in agreement with this assignment.

This ratio of *para* to *ortho* cyclizations is not compatible in any simple way with the amounts found of the dimethoxytriptindans **7a** and **7b**, where the ratio of *para* to *ortho* cyclizations is 4:1. (Control reactions have established that these ratios are not the result of equilibration or selective destruction of the cyclized products.) If it is assumed that the first cyclization (**4a**) produces *para* and *ortho* cyclized compounds (**5**) in a "normal" ratio of 7:1, the preference for *para* orientation in the second cyclization can then be only about twofold, and we have concluded that *para* cyclization in intermediate **6a** is suppressed by the presence of a substituent at Z. This interpretation is also suggested by examination of models of intermediate **6a**, which show that a substituent at Z could interfere sterically with one at Y, thereby inhibiting the formation of *para,para* product. The corollary that the formation of *ortho,ortho* product is similarly suppressed is difficult to establish on the basis of the evidence, since no such product was found, but it is consistent with that fact.

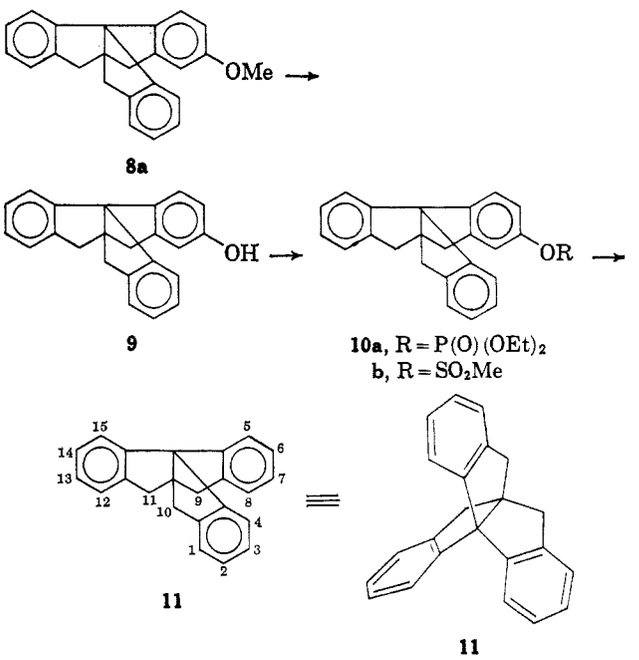
The nature of this interference is of interest since participation in bond formation by methoxyl Y or in charge stabilization by methoxyl Z should tend to restrict the O-methyl groups to the planes of their rings and diminish their steric influences on each other. The principal effect, if steric, may thus be one associated with solvation of the methoxyl oxygens.

2-Methoxytriptindan (**8a**, eluted last) was separable by chromatography from its *ortho* cyclized counterpart and could be converted in good yield into the corresponding phenol[24] (**9**) for removal of the oxygen.

(23) H. O. House and M. Schellenbaum, *J. Org. Chem.*, **28**, 34 (1963).

Of the relatively few methods known for deoxygenation of phenols,[25-31] a number gave discouraging preliminary results with **9**. The procedure of Kenner and Williams,[28,29] however, which involves treatment of a diethyl phosphate or methanesulfonate ester of the phenol with an active metal in ammonia solution, appeared to work well and triptindan was obtained in moderate yields even on a very small scale. The

CHART II



triptindan provided by these reactions can be purified easily by sublimation and chromatography, and crystallizes from hexane as refractory needles or prisms, mp 191.5–192°. (See Chart II.)

Because of its symmetry, triptindan gives simple infrared and nmr spectra, the latter displaying a sharp singlet at τ 7.0 for all the benzylic hydrogens and a complex multiplet for the aromatic hydrogens extending from τ 2.3 to 3.0. This complex includes a nearly symmetrical multiplet at lowest field (τ 2.5) with one-fourth of the aromatic proton area, and presumably represents the three "cavity" hydrogens at positions 4, 5, and 15. These are expected to appear at lower field than the other aromatic hydrogens because each cavity proton lies in a zone of greater negative shielding due to the adjacent rings than do any of the other protons.[21]

Triptindan's ultraviolet spectral properties are of especial interest from the point of view of nonbonded electronic interactions, since overlap of π orbitals at carbon atoms not adjacently bonded would mean exchange of electrons between such orbitals and might be

(24) W. E. Bachman, S. Kushner, and A. C. Stevenson, *J. Am. Chem. Soc.*, **64**, 974 (1942).
(25) A. Schönberg and F. L. Warren, *J. Chem. Soc.*, 1840 (1939).
(26) G. W. Kenner and M. A. Murray, *ibid.*, S178 (1949).
(27) H. Dannenberg and T. Köhler, *Ber.*, **97**, 140 (1964).
(28) G. W. Kenner and N. R. Williams, *J. Chem. Soc.*, 522 (1955).
(29) S. W. Pelletier and D. M. Locke, *J. Org. Chem.*, **23**, 131 (1958).
(30) M. S. Newman and H. A. Karnes, *ibid.*, **31**, 3980 (1966).
(31) (a) M. T. Bogert and J. R. Tuttle, *J. Am. Chem. Soc.*, **38**, 1361 (1916); (b) J. P. Schaefer and J. Higgins, *J. Org. Chem.*, **32**, 1607 (1967).

expected to result in a bathochromic shift relative to models such as *o*-xylene, indan, or tetralin.[32,33]

We have measured the ultraviolet spectrum of triptindan and have found it essentially superimposable on that of indan or tetralin. In this, triptindan differs from triptycene, whose maxima are shifted 3–5 mμ to longer wavelength than in *o*-xylene or tetralin, although the intensities of the maxima are approximately normal. This shift has been attributed to a homoconjugative type of interaction[34] and more recently merely to interaction of weak transition dipoles.[22]

On the basis of the present evidence we therefore conclude that either there is far less homoconjugative orbital overlap in triptindan than in triptycene, or that the dipole interaction which accounts for triptycene's shifts is inoperative in triptindan.

We are presently considering the theoretical implications of the spectral properties of triptindan and studies of substituted triptindans are planned or in progress.

Experimental Section[35]

2,2-Dibenzyl-1-indanone (3a).—A solution was prepared of 888 mg (4.0 mmoles) of 2-benzyl-1-indanone (**2a**) in 10 ml of a 1:1 (by volume) mixture of dry dimethylformamide and dry dimethoxyethane. This was added with stirring over a 10-min period to a suspension of 10 ml of the above solvent and the sodium hydride (washed free of oil) from 175 mg (4.0 mmoles) of 56% sodium hydride dispersion. The mixture was stirred and heated at 60° for *ca.* 10 min, during which time gas was evolved. Benzyl chloride (0.460 ml, 4.0 mmoles) in 15 ml of the above solvent was added to the cooled solution and the mixture heated at reflux for 3 hr under nitrogen. Isolation by addition of water, extraction with ether, and chromatography of the concentrated extracts on alumina yielded 768 mg (61%) of crude crystalline dibenzyl ketone, mp 117–119.5°, which melted at 119–119.5° after recrystallization from hexane: $\nu_{max}^{CCl_4}$ 1710 cm^{-1}; λ_{max}^{EtOH} 248.5 mμ (ε 11,400), 297 mμ (ε 2930); nmr (CCl_4) 14 H complex at τ 2.2–3.0 with a sharp peak at 2.9, pair of 2 H doublets at 6.8 and 7.2 (J = 13 cps), 2 H singlet at 6.95.

Anal. Calcd for $C_{23}H_{20}O$: C, 88.43; H, 6.45; mol wt, 312. Found: C, 88.19; H, 6.47; mol wt 312 (mass spectrum).

2-(*m*-Methoxybenzyl)-1-indanone (2b).—A suspension of 750 mg (3.0 mmoles) of 2-(*m*-methoxybenzal)-1-indanone (**1b**) in 30 ml of ethyl acetate was hydrogenated with magnetic stirring over 60 mg of 5% palladium on carbon in a low-pressure hydrogenation apparatus. A total of 81 ml (*ca.* 3.2 mmoles) of hydrogen was absorbed at 25° over a period of 2 hr and the resultant solution, freed of catalyst by filtration, was concentrated under reduced pressure and the residue distilled in a short-path still at *ca.* 160° (0.05 mm) to give 739 mg (98.5%) of colorless liquid: $n^{25}D$ 1.5955; $\nu_{max}^{CCl_4}$ 1710 cm^{-1}; λ_{max}^{EtOH} 245.5 mμ (ε 14,300), 281.5 (4060), 292.5 (2800); nmr (CCl_4) 8 H complex at τ 2.2–3.6, 3 H singlet at 6.3, 5 H complex at 6.5–7.7.

Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39; mol wt, 252. Found: C, 80.33; H, 6.29; mol wt, 252 (mass spectrum).

2,2-Di(*m*-methoxybenzyl)-1-indanone (3b).—The procedure used to obtain **3a** was followed, utilizing 252 mg (1.0 mmole) of 2-(*m*-methoxybenzyl)-1-indanone (**2b**), the sodium hydride from 70 mg (1.6 mmoles) of 56% dispersion, 0.153 ml (1.1 mmoles) of *m*-methoxybenzyl chloride, and a total of 7 ml of the solvent mixture. The product was isolated as described for **3a**, distilled in a short-path still to give 315 mg of volatile material, purified by chromatography on 15 g of alumina (elution with ether–pentane mixtures), and finally redistilled at *ca.* 200° (0.02 mm) to yield 273 mg (73%) of extremely viscous oil: $n^{25}D$ 1.6054; $\nu_{max}^{CCl_4}$ 1710 cm^{-1}; λ_{max}^{EtOH} 248 mμ (ε 11,800), 274.5 (4870), 281 (5120); nmr (CCl_4) 12 H complex at τ 2.3–3.6, 6 H singlet at 6.3, pair of 2 H doublets at 6.85 and 7.25 (J = 13 cps), 2 H singlet at 6.95.

Anal. Calcd for $C_{25}H_{24}O_2$: C, 80.62; H, 6.50; mol wt, 372. Found: C, 80.33; H, 6.29; mol wt, 372 (mass spectrum).

2,7-Dimethoxytriptindan (7a) and 2,5-Dimethoxytriptindan (7b).—The crude product (1.14 g, 3.0 mmoles) derived from alkylation of 1.2 g of **2b** under the conditions described was mixed with 26 g of polyphosphoric acid (3 g of phosphorous pentoxide per 2 ml of 85% phosphoric acid) and heated with occasional swirling in a boiling water bath for 30 min. During this time the clear yellowish solution became cloudy and a floating oil separated. The mixture was worked up by addition of water, extraction with ether, and concentration of the dried extracts. Repeated chromatography on columns of alumina and Florisil (elution with ether–pentane or ether–hexane mixtures) and fractional crystallizations allowed the separation of 243.5 mg (22.5%) of 2,5-dimethoxytriptindan (**7b**), mp 143–144°, whose infrared spectrum (CCl_4) has no absorptions attributable to hydroxyl or carbonyl functions: λ_{max}^{EtOH} 231 mμ (ε 20,600), 268 (3440), 273.5 (4480), 279 (4170), 287 (2240); nmr (CCl_4) 10 H complex at τ 2.1–3.5, 3 H singlets at 6.2 and at 6.4 (each 1.5 cps wide at half-height), 6 H singlet at 7.0 (3.5 cps wide at half-height).

Anal. Calcd for $C_{25}H_{22}O_2$: C, 84.72; H, 6.26; mol wt, 354. Found: C, 84.44; H, 6.06; mol wt, 354 (mass spectrum).

A total of 467 mg (43%) was obtained of the component eluted last on chromatography, 2,7-dimethoxytriptindan (**7a**). This compound, mp 144.5–147°, has an infrared spectrum (CCl_4) which resembles that of **7b** except for differences in the fingerprint region; λ_{max}^{EtOH} 235 mμ (ε 22,400), 268 (4100), 274 (5560), 280 (5320), 288.5 (4390); nmr (CCl_4) 10 H complex at τ 2.5–3.5, 6 H singlet at 6.4 (1.5 cps wide at half-height), 6 H singlet at 7.0 (3.5 cps wide at half-height).

Anal. Calcd for $C_{25}H_{22}O_2$: C, 84.72; H, 6.26; mol wt, 354. Found: C, 85.05; H, 5.91; mol wt, 354 (mass spectrum).

Purified and distilled 2,2-di(*m*-methoxybenzyl)-1-indanone (314.5 mg, 0.845 mmole) was treated with 6.5 g of polyphosphoric acid (2 g of phosphorous pentoxide per 1 ml of 85% phosphoric acid) by heating as previously described for 1 hr. The mixture was worked up as described previously and the dimethoxytriptindan fractions, weighing 288 mg (96%), were combined and freed of solvent *in vacuo*. Comparison of the areas under the methoxyl peaks in the nmr spectrum indicated 39–41% **7b** and 59–61% **7a**.

Synthetic mixtures of **7a** and **b** in ratios of 80:20 and 27:73 were subjected to the polyphosphoric acid reaction conditions, recovered, analyzed by nmr, and found to be substantially unchanged.

2-Benzyl-2-(*m*-methoxybenzyl)-1-indanone (3c).—2-(*m*-Methoxybenzyl)-1-indanone (412 mg, 1.63 mmoles) dissolved in 8.0 ml of dry dimethoxyethane was treated with the sodium hydride (washed with hexane) from 165 mg (3.44 mmoles) of 56% hydride–oil dispersion by stirring at room temperature for 25 min, during which time gas was evolved. (This solvent alone appears to be preferable to the previously used solvent mixture in that fewer by-products are formed.) Benzyl chloride (0.205 ml, 1.80 mmoles) was added and the mixture was refluxed under nitrogen for 3 hr. The solvent was removed under reduced pressure and the residue extracted with ether and water. Concentration of the dried ethereal portion and chromatography on 25 g of alumina (elution with ether–pentane mixtures) provided purified material, which was distilled at *ca.* 180° (0.04 mm) in a short-path still to give 488 mg (87%) of extremely viscous liquid: $n^{25}D$ 1.6086; $\nu_{max}^{CCl_4}$ 1710 cm^{-1}; λ_{max}^{EtOH} 248.5 mμ (ε 11,600), 281 (3160); nmr (CCl_4) 13 H complex at τ 2.3–3.7 with a sharp peak at 3.0, 3 H singlet at 6.4, pair of 2 H doublets at 6.85 and 7.25 (J = 13 cps), 2 H singlet at 6.95.

Anal. Calcd for $C_{24}H_{22}O_2$: C, 84.18; H, 6.48. Found: C, 84.39; H, 6.66.

2-Methoxytriptindan (8a) and 4-Methoxytriptindan (8b). Method A.—A solution of 493 mg (1.44 mmoles) of **3c** in 10 g of polyphosphoric acid (2 g of phosphorus pentoxide per 1 ml of 85% phosphoric acid) was heated with occasional swirling for 1 hr in a boiling water bath. The mixture was diluted with water

(32) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951.

(33) "Organic Electronic Spectral Data," Vol. I–IV, Interscience Publishers, Inc., New York, N. Y.

(34) P. D. Bartlett and E. S. Lewis, *J. Am. Chem. Soc.*, **72**, 1005 (1950).

(35) Melting points were determined with a Mel-Temp apparatus and are uncorrected; infrared spectra were taken using a Beckman IR-10 spectrometer; ultraviolet spectra were determined with a Cary Model 14 spectrophotometer; nmr spectra were taken using a Varian A-60 spectrometer (CH_2Cl_2 or TMS internal standard); mass spectra were obtained from either a CEC Model 21-103C or an AEI Model MS-9 mass spectrometer; microanalyses were performed by Micro-Tech Laboratories, Skokie, Ill.

and extracted with ether and the dried extracts were concentrated. The resulting colorless oil was completely soluble in pentane and was chromatographed on 20 g of alumina (elution with ether–pentane). The crystalline fractions obtained by chromatography totalled 450 mg (96.5%) and were recombined for nmr analysis, which showed 87–88% one isomer and 12–13% a second (methoxyl peaks).

Method B.—In an alternative procedure, 500 mg (2.0 mmoles), of 2-(*m*-methoxybenzal)-1-indanone (**1b**) in 10 ml of dry dimethoxyethane was hydrogenated at room temperature in a low pressure apparatus over 50 mg of 5% palladium on carbon, as previously described. When reduction was complete the sodium hydride from 192 mg (4.5 mmoles) of 56% hydride–oil dispersion was added directly to the hydrogenation mixture without removal of catalyst. This mixture was stirred for 25 min at room temperature, benzyl chloride (0.250 ml, 2.2 mmoles) was added, and the mixture was stirred at room temperature for 20 min and then heated at reflux for 70 min. Removal of the solvent under reduced pressure provided a residue which was treated with 14 g of polyphosphoric acid (as prepared previously) at 100° as described for method A. The previous aqueous work-up, extraction, and chromatography procedure served to separate crystalline 2-methoxy- and 4-methoxytriptindan, totalling 428 mg (66% from **1b**). The combined crystalline fractions, as assessed by nmr, contained **8a** and **b** in the same ratio as previously found.

Synthetic mixtures of **8a** and **b** in ratios of 93:7 and 45:55 were subjected to the polyphosphoric acid reaction conditions, recovered, analyzed by nmr, and found to be substantially unchanged.

When separated from the mixture by chromatography (eluted last from alumina with ether–pentane) and by fractional crystallization, 2-methoxytriptindan (**8a**) was obtained as needles, mp 124.5–125.5°, from hexane and showed no infrared absorption (CCl_4) attributable to hydroxyl or carbonyl groups; λ_{max}^{EtOH} 261.5 mμ (ε 2280), 267.5 (3860), 274 (4810), 281 s (2500), 288.5 (2200); nmr (CCl_4) 11 H complex at τ 2.5–3.5, 3 H singlet at 6.4 (1.5 cps wide at half-height), 6 H singlet at 7.0 (3.3 cps wide at half-height).

Anal. Calcd for $C_{24}H_{20}O$: C, 88.85; H, 6.21. Found: C, 89.01; H, 6.25.

4-Methoxytriptindan (**8b**) was recrystallized from heptane, providing prismatic platelets, mp 191.5–192.5°, with an infrared spectrum (CCl_4) very similar to that of **8a** except in the fingerprint region; λ_{max}^{EtOH} 261 mμ (ε 1950), 267 (3220), 273.5 (3970), 278.5 (1900); nmr (CCl_4) 11 H complex at 2.0–3.5, 3 H singlet at 6.2 (1.5 cps wide at half-height), 6 H singlet at 7.0 (2.5 cps wide at half-height).

Anal. Calcd for $C_{24}H_{20}O$: 88.85; H, 6.21. Found: C, 88.99; H, 6.05.

2-Triptindanol (**9**).—2-Methoxytriptindan (127.5 mg, 0.410 mmole) in 2.5 ml of acetic acid was treated with 0.75 ml (6.75 mmoles) of 48% hydrobromic acid by refluxing under nitrogen for 2 hr. The product was isolated by neutralization of the mixture with potassium hydroxide, extraction with ether and concentration of the dried ethereal portions. Crystallization of the residue from cyclohexane provided 91 mg (75%) of crude crystalline 2-triptindanol. Recrystallization from the same solvent gave colorless needles: mp 111–112°; $\nu_{max}^{CCl_4}$ 3620, 3330 cm^{-1}; λ_{max}^{EtOH} 261.5 mμ (ε 2230), 267.5 (3740), 274 (4660), 283 (2450), 288.5 s (2200); nmr (CCl_4) 9 H complex at τ 2.4–3.1, 2 H double peak at 3.4–3.7, 1 H broad singlet at 5.5, 4 H singlet at 7.0, 2 H singlet at 7.1.

Anal. Calcd for $C_{23}H_{18}O$: C, 89.00; H, 5.85. Found: C, 88.72; H, 6.03.

Triptindan (**11**). **Procedure A.**—2-Triptindanol (125 mg, 0.403 mmole) in 1.5 ml of carbon tetrachloride was treated with 0.070 ml (0.55 mmole) of diethyl hydrogen phosphite and 0.085 ml (0.61 mmole) of freshly distilled triethylamine, then enclosed and allowed to stand at room temperature for 22 hr. Volatile material was removed under reduced pressure and the residue, in ether, was washed with water, dried, and freed from solvent *in vacuo*. The resulting oil was taken up in 5 ml of dry tetrahydrofuran, *ca.* 15 ml of anhydrous ammonia was added, and the solution was stirred at reflux while *ca.* 20 mg (0.87 mg-atom) of sodium was added in small pieces to an end point indicated by a persistent blue color. Ammonia and solvent were allowed to evaporate overnight, the residue was extracted with water and ether, and the organic portion was dried and concentrated. The crystalline residue was purified by chromatography on *ca.* 8 g of alumina, using ether–hexane mixtures as eluent, to provide 69.5 mg (58%) of triptindan (**11**).

Procedure B.—2-Triptindanol (125 mg, 0.403 mmole) in 2.5 ml of dry pyridine was refluxed under nitrogen for 1 hr with freshly distilled methanesulfonyl chloride (0.050 ml, 0.645 mmole). Volatile material was removed under reduced pressure and the residue, in ether, was washed with water, dried, and freed of solvent *in vacuo*. The resulting material, mp *ca.* 110° (not characterized), was dissolved in 5 ml of dry tetrahydrofuran. Anhydrous ammonia (*ca.* 15 ml) was added and the solution stirred at reflux while *ca.* 24 mg (1.04 mg-atom) of sodium was added as described in procedure A. The product was isolated and purified as described in procedure A, yielding 42.5 mg (36%) of triptindan.

Triptindan (**11**) can be sublimed at *ca.* 170° (1 mm) and crystallizes from hexane as needles and platelets, mp 191.5–192°. The infrared spectrum of **11** (CCl_4) shows no absorptions due to hydroxyl or carbonyl functions and is simple even in the fingerprint region. Triptindan's ultraviolet spectrum (EtOH) has the following absorptions: 254 s mμ (ε 1250), 261 (2380), 267 (4070), 273.5 (4780). (For the nmr spectrum, see the Discussion section.)

Anal. Calcd for $C_{23}H_{18}$: C, 93.84; H, 6.16. Found: C, 93.68; H, 6.16.

Registry No.—**2b**, 13578-99-9; **3a**, 13578-98-8; **3b**, 13579-03-8; **3c**, 15315-24-9; **7a**, 13859-36-4; **7b**, 15244-23-2; **8a**, 15350-43-3; **8b**, 15350-44-4; **9**, 15350-45-5; **11**, 14838-97-2.

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