

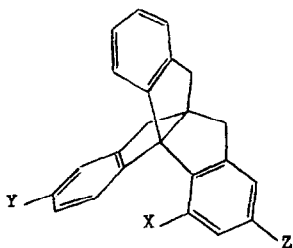
SYNTHESIS OF A TRICYCLO[3.3.3.0<sup>1,5</sup>]UNDECANE SYSTEM

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Because of our interest in symmetrical tricyclic systems of the type [n.n.n.0<sup>1, n+2</sup>] [1] and because a relatively simple route presented itself, we undertook the synthesis of I, a tribenzo derivative of tricyclo[3.3.3.0]-undecane, and wish to report our results.



Ia: X = Y = Z = H  
Ib: X = H, Y = Z = OCH<sub>3</sub>  
Ic: X = Y = OCH<sub>3</sub>, Z = H

The route chosen for synthesis was the double acid-catalyzed cyclization of the dibenzylindanone IV, which could be easily prepared by alkylation of the monobenzylindanone III. This route, involving preparation of III by catalytic hydrogenation of the Claisen-Schmidt condensation product, II, of benzaldehyde with 1-indanone [2], was necessary because indanone, in common with a variety of other  $\alpha$ -unsubstituted cyclopentanones, gives large amounts of self-condensation products when direct base-catalyzed alkylation is attempted.

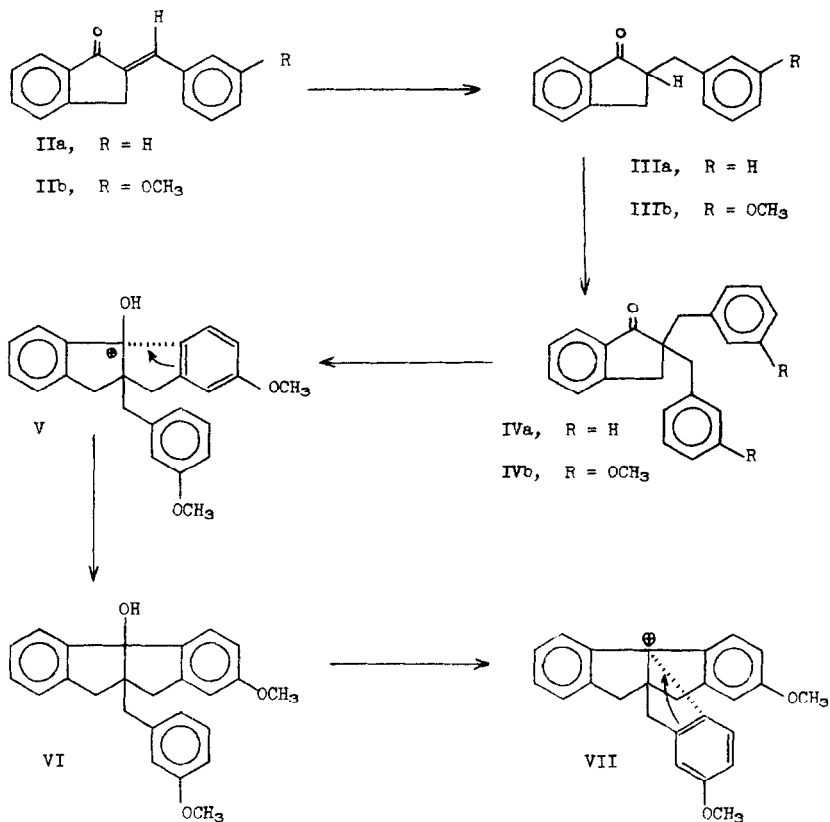
The known 2-benzyl-1-indanone IIIa [3] was converted in 61% yield by base-catalyzed alkylation to 2,2-dibenzyl-1-indanone, IVa, (m.p. 119-119.5°;  $\lambda_{\text{max}}^{\text{EtOH}}$  251 m $\mu$  [ $\epsilon$  12,000], 299 m $\mu$  [ $\epsilon$  2400];  $\nu_{\text{max}}^{\text{CCl}_4}$  1710 cm.<sup>-1</sup>; NMR: 14H complex 2.2-3.0  $\tau$  with sharp peak at 2.90 $\tau$ , pair of 2H doublets at 6.74 and 7.20  $\tau$  [J=13 cps], 2H singlet 6.94  $\tau$ ; Anal. Calcd. for C<sub>23</sub>H<sub>20</sub>O: C, 88.43; H, 6.45; mol. wt., 312. Found: C, 88.19; H, 6.47; mol. wt., 312 [mass spectrum].

Attempts to cyclize IVa to Ia with a variety of acid systems were, however, unsuccessful due probably to the lack of activating groups on the benzyl aromatic rings [4] and the low reactivity of aromatic ketones in this type of cyclization [5], a situation, aggravated by the compound's insolubility in polyphosphoric acid, necessitating destructively drastic reaction conditions. Accordingly the analogous route to Ib by cyclization of the appropriately activated dibenzylindanone IVb was undertaken.

Reaction of *m*-methoxybenzaldehyde [6] with 1-indanone in ethanolic potassium hydroxide [2] produced the known *m*-methoxybenzalindanone IIb [7] as needles, m.p. 138-140°, from ethanol in greater than 80% yield. Catalytic hydrogenation of IIb in ethyl acetate over 5% palladium-on-carbon [3] gave, in 98.5% distilled yield, the *m*-methoxybenzylindanone IIIb as a viscous and colorless fluid, b.p. ca. 160° [0.05mm.], whose spectral and analytical data were consistent with the expected structure:  $\lambda_{\text{max}}^{\text{EtOH}}$  248 m $\mu$  [ $\epsilon$  13,500], 283 m $\mu$  [ $\epsilon$  3800];  $\nu_{\text{max}}^{\text{CCl}_4}$  1710 cm.<sup>-1</sup>; NMR: 8H complex 2.1-3.5 $\tau$ , 3H singlet 6.23 $\tau$ , 5H complex 6.4-7.6  $\tau$ ;  $n_D^{25}$  1.5955; Anal. Calcd. for C<sub>17</sub>H<sub>16</sub>O<sub>2</sub>: C, 80.93; H, 6.39; mol. wt., 252. Found: C, 80.61; H, 6.44; mol. wt., 252 [mass spectrum].

Alkylation of this ketone with 1.1 equivalents of *m*-methoxybenzyl chloride [8], employing excess sodium hydride [9] in equal parts of dimethoxyethane and dimethylformamide at reflux temperature, gave the anticipated product IVb in 73% yield after chromatography and distillation at ca. 200° [0.02mm.]. This compound was isolated as an extremely viscous liquid

possessing the following properties:  $\lambda_{\text{max}}^{\text{EtOH}}$  250  $m\mu$  [  $\epsilon$  13,000 ], 283  $m\mu$  [  $\epsilon$  5500 ];  $\nu_{\text{max}}^{\text{CCl}_4}$  1710  $\text{cm}^{-1}$ ; NMR: 12H complex 2.3-3.6  $\tau$ , 6H singlet 6.32 $\tau$ , pair of 2H doublets 6.79 and 7.25 $\tau$  [  $J=13$  cps ], 2H singlet 6.96 $\tau$ ;  $n_D^{25}$  1.6054; Anal. Calcd. for  $\text{C}_{25}\text{H}_{24}\text{O}_3$ : C, 80.62; H, 6.50; mol. wt., 372. Found: C, 81.47; H, 6.46; mol. wt., 372 [mass spectrum].



Compound IVb dissolved easily in polyphosphoric acid [10] at room temperature and subsequent reaction for 30 min. at 100° [product oils out] followed by the usual aqueous workup, extraction and chromatography, yielded two

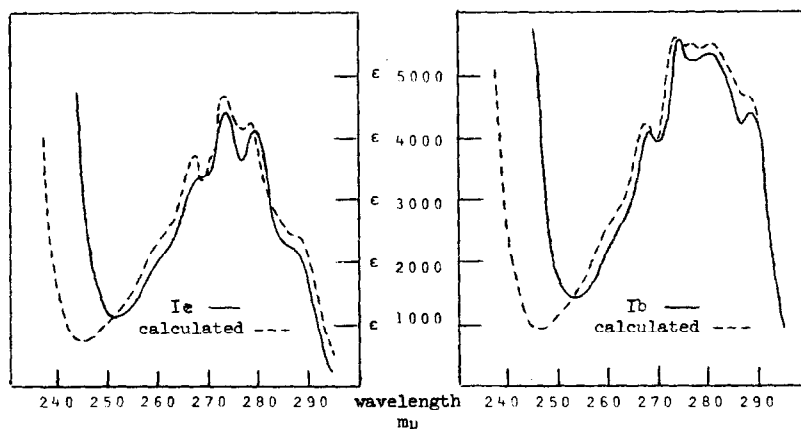
crystalline compounds. The higher-melting compound (147°, needles from pentane), obtained in 45% yield, is eluted last by ether-pentane mixtures from a Florisil column and has the smaller  $R_f$  on thin-layer chromatography [SiO<sub>2</sub>, benzene]. The infrared spectrum of this compound is relatively simple and lacks absorption for either hydroxyl or carbonyl groups. Analytical [Calcd. for C<sub>25</sub>H<sub>22</sub>O<sub>2</sub>: C, 84.72; H, 6.26. Found: C, 84.44; H, 6.06] and mass spectral data [molecular ion peak at m/e 354] are consistent with the expected cyclization product Ib, and the NMR spectrum supports this structure: 10H complex of ca. twelve lines 2.3-3.3τ; sharp 6H singlet 6.22τ with a width of 1.5 cps at half-height; broader 6H singlet 6.86τ, 3.5 cps wide at half-height.

The second crystalline product of the cyclization, which is eluted more rapidly in the chromatographic systems mentioned, was obtained in 23% yield and melts at 144° [prisms from pentane]. Its infrared spectrum, though differing in the fingerprint region, resembles that of Ib above 1500 cm.<sup>-1</sup> and the analysis [Found: C, 85.05; H, 5.91] and the presence of a molecular ion peak at m/e 354 in the mass spectrum suggest that the compound is an isomer of Ib. We have assigned this compound the structure Ic, which can arise by cyclization of intermediate VII at the available position ortho to the methoxyl group. Such an assignment is supported by the chromatographic behavior and by the NMR spectrum of this material, which shows, in addition to complex absorption [ca. 15 lines, 10H] between 2.0 and 3.4τ, two sharp 3H singlets at 5.99 and 6.20τ [1.5 cps wide at half-height] and a broader 6H singlet at 6.65τ [3.5 cps wide at half-height].

The ring system represented by I, which is given the name "triptindane" [11] resembles that of triptycene [12], in that it incorporates a substituted triphenylmethane into an arrangement fixed rigidly in such a way that some overlap between the isolated aromatic pi electron systems may be possible, here presumably at only one carbon atom of each aromatic ring. From this

point of view the ultraviolet spectra of Ib and Ic are of interest.

The theoretical spectra for compounds Ib and Ic may be reasonably calculated from the spectra of indane and methoxy-substituted indanes or tetralins. The basic assumption in such a calculation is that the separated chromophores are independent, hence any appreciable differences between the actual and calculated spectra may be attributed to unusual electronic interactions. As may be seen from Figures 1 and 2, the departures for compounds Ib and Ic from the corresponding calculated spectra are small, suggesting that to a first approximation homoconjugative interactions are slight, as seems to be the case with triptycene [12].



Experiments designed to produce the unsubstituted triptindane Ia and to assess more thoroughly the non-bonded electronic interactions in the triptindane system are planned or in progress.

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