

SYNTHESIS OF syn-7,8-BENZOTRICYCLO[4.2.2.0<sup>2,5</sup>]DECA-3,7,9-TRIENE.

A NEW BENZO (CH)<sub>10</sub> HYDROCARBON

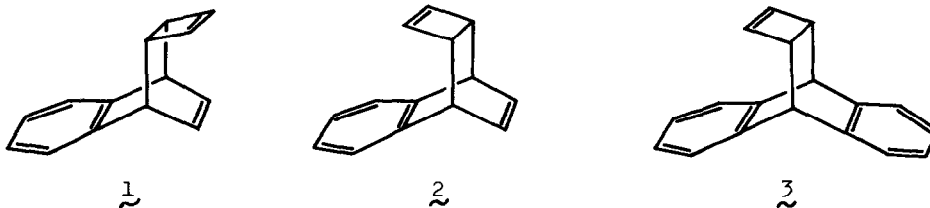
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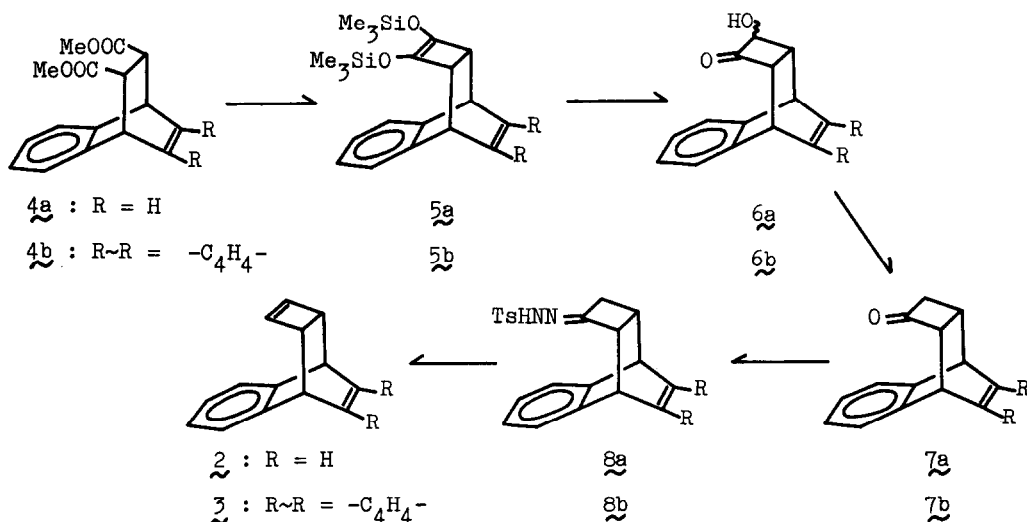
(Received in Japan 25 January 1973; received in UK for publication 27 February 1973)

In the context of the current interest in thermal<sup>1,2)</sup> and photochemical<sup>1,3)</sup> behavior of anti-7,8-benzotricyclo[4.2.2.0<sup>2,5</sup>]deca-3,7,9-triene 1 and in the role of this molecule in the chemistry of the benzo(CH)<sub>10</sub> hydrocarbon series,<sup>4)</sup> we wish to describe the synthesis of a new isomer, syn-7,8-benzotricyclo[4.2.2.0<sup>2,5</sup>]deca-3,7,9-triene 2, and the application of this procedure to the preparation of 7,8:9,10-dibenzotricyclo[4.2.2.0<sup>2,5</sup>]deca-3,7,9-triene 3.<sup>5)</sup>



Starting material for our synthesis of 2, dimethyl syn-5,6-benzobicyclo[2.2.2]oct-2-ene-7,8-dicarboxylate 4a,<sup>6)</sup> preserving the syn-configuration of the two methoxycarbonyl groups respect to the aromatic moiety, is treated with sodium dispersion in refluxing xylene in the presence of trimethylchlorosilane under nitrogen for 6 hr.<sup>7)</sup> Hydrolysis of the bistrimethylsilyl ether of the intermediate enediol 5a by methanol at room temperature gave the acyloin 6a: colorless crystals, mp. 148-9°, ir (KBr), 3530 (OH), 1775 cm<sup>-1</sup>(C=O), nmr (CDCl<sub>3</sub>, 60 MHz), δ 7.17 (m, 4H, aryl), 6.70 (d.t, J=5, 1.5 Hz, 2H, vinyl), 4.26 (m, 3H, benzylic and -CHOH), 3.43 (m, 1H, cyclobutane), 3.00 (m, 1H, cyclobutane) and 1.50 (s, 1H, OH), in 62%

yield. The acyloin 6a, dissolved in toluene, was reduced with amalgamated zinc in 4N hydrochloric acid under refluxing for 1.5 hr to produce the ketone 7a: mp 69-70°, ir (KBr), 1770  $\text{cm}^{-1}$ . The ketone 7a was converted into its p-toluenesulfonylhydrazone 8a, mp. 189-190°, in 81% yield, which, in a typical experiment, was treated with three mole equivalents of n-butyllithium in diglyme at 60° for 3 hr.<sup>8)</sup>



After filtration of the resulting lithium p-toluenesulfinate, most of the diglyme was removed under reduced pressure. The silica gel column chromatography of the benzene extract of this residue with pet. ether (bp. 48-65°) affords colorless needles in 40% yield, mp. 43°, whose structure is assigned as the desired 2 on the basis of the following evidences: (i) Mass spectrum of 2 shows a parent peak at  $m/e$  180 ( $\text{C}_{14}\text{H}_{12}^+$ , 100%). (ii) The nmr spectrum (60 MHz,  $\text{CCl}_4$ ) of 2 [Fig. 1a],  $\delta$  7.00(s, 4H, aryl), 6.52 (d.d,  $J=4$ , 3 Hz, 2H, olefinic), 5.82 (s, 2H, cyclobutenyl), 3.65-3.90 (m, 2H, diallylic methine) and 2.70 (m, 2H, methine), exhibits a striking resemblance to that of the anti-isomer 1 [Fig. 1b] except for the chemical shifts of vinyl protons. Thus the cyclobutene formed by the aforementioned reaction can be confidently assigned as the syn-configuration to the benzene ring on the basis of this nmr spectrum in which the cyclobutenyl proton singlet appears 0.23 ppm upfield than that of 1 due to the shielding effect of the proximate benzene ring, whereas the olefinic proton doublet of doublets emerges 0.3 ppm downfield than that of 1 due to the lack of the proximate cyclobutenyl double bond.

This synthetic procedure can be applied to the preparation of 7,8:9,10-dibenzotricyclo[4.2.2.0<sup>2,5</sup>]deca-3,7,9-triene 2 which has already been synthesized by the Diels-Alder reaction of 9,10-dibromoanthracene with cis-3,4-dichlorocyclobutene followed by treatment with lithium-amalgam.<sup>4)</sup> Our preparation of 2 began with readily available 3,4-bistrimethylsiloxy-7,8:9,10-dibenzotricyclo[4.2.2.0<sup>2,5</sup>]deca-3,7,9-triene 5b.<sup>9)</sup> Hydrolysis with ethanol converted the siloxy derivative 5b into the acyloin 6b; mp. 195-197°, ir (KBr), 3550, 3460, 3350, 1775 cm<sup>-1</sup>, which was smoothly reduced in refluxing toluene with amalgamated zinc and 4N hydrochloric acid to give the cyclobutanone 7b; mp. 167-168°, ir (KBr), 1775 cm<sup>-1</sup>, in 83% yield. This was converted to p-toluenesulfonylhydrazone 8b; mp. 228-229°, 78%, which was subjected to the reaction in diglyme with excess n-butyllithium at 120° to give the anticipated cyclobutene 3; mp. 138-139° (lit.<sup>5)</sup> 137°), in 43% yield. The ir and uv spectra of 3 were identical in all respects with those

of the reported values.<sup>5)</sup> In the nmr spectrum (60-MHz, CDCl<sub>3</sub>) of this substance [Fig. 2], the cyclobutenyl protons appear as a singlet at  $\delta$  5.87 denoting the presence of the same structural moiety with 2. The remaining portion of the spectrum consists of a

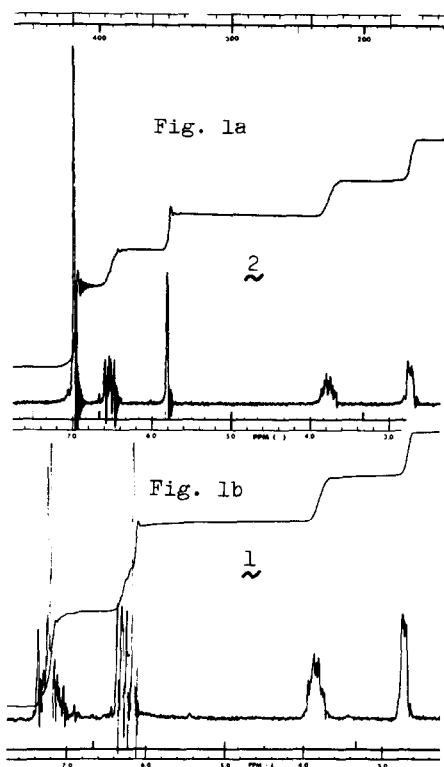


Fig. 1. Nmr spectra of 2 and 1.

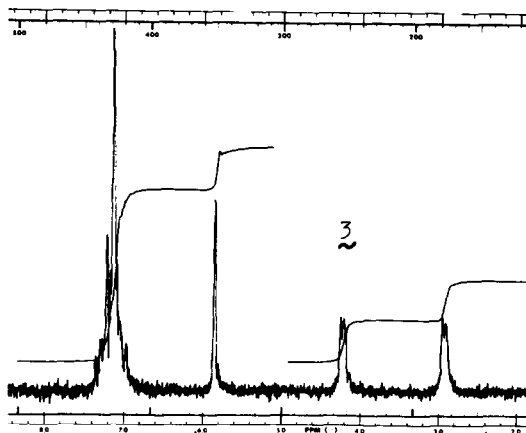


Fig. 2. Nmr spectrum of 3.

multiplet of area 8 at 7.4-6.9 for aryl protons, two 2H multiplets at 4.23 and 2.95 assignable to the dibenzylic methine and allylic methine respectively.

It would appear that the method described in this paper will be especially useful for the construction of the fused cyclobutene. The photochemical and thermal reactions of this new benzo (CH)<sub>10</sub> hydrocarbon<sub>2</sub> are now being undertaken.<sup>10)</sup>

We thank Tokyo Sibaura Electric Co. Ltd. for a gift of trimethylchlorosilane.

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