

A CONVENIENT ROUTE TO TROPONIDS<sup>1</sup>

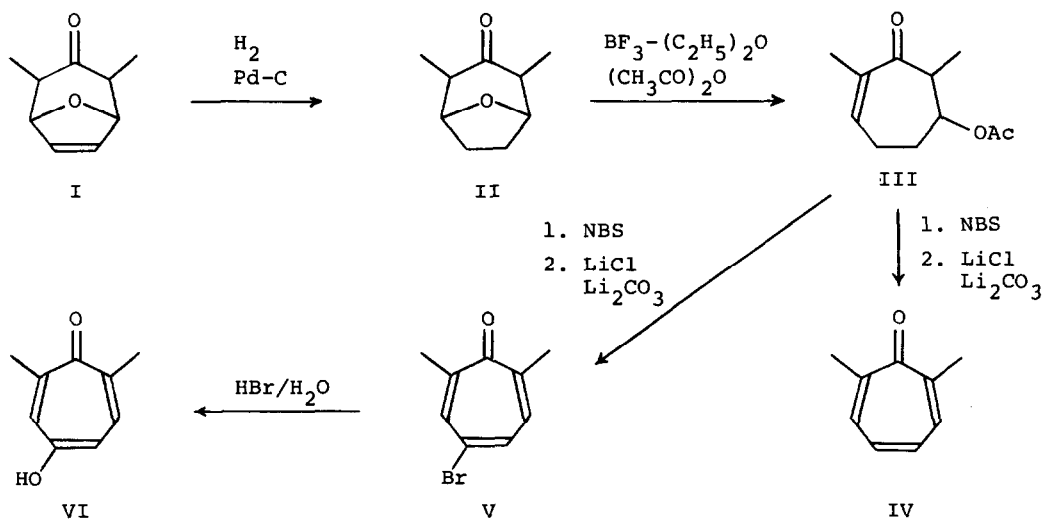
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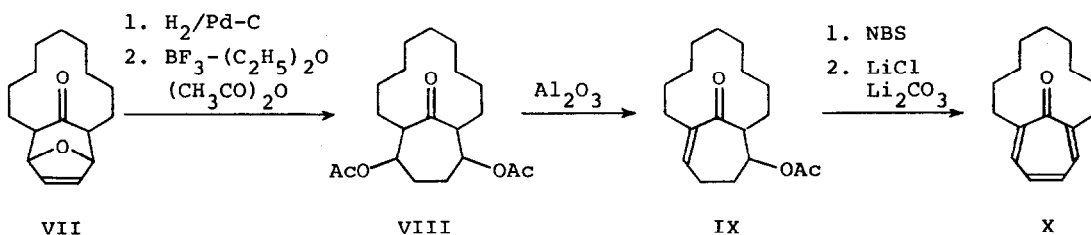
In the preceding communication, we described an efficient coupling reaction of  $\alpha, \alpha'$ -dibromo ketones and furan. We demonstrate here that the adducts can readily be converted to troponoid compounds.

Hydrogenation of the bicyclic adduct I<sup>1,2</sup> over 5% Pd-C in ethanol gave the corresponding saturated ketone II in virtually quantitative yield. Exposure of II to acetic anhydride containing 0.5 equiv of BF<sub>3</sub> etherate at 35° for 48 hr produced the enone acetate III in 50% yield [ir (CCl<sub>4</sub>) 1736 and 1235 (acetate), and 1676 cm<sup>-1</sup> (enone); uv (C<sub>2</sub>H<sub>5</sub>OH) 240 nm (log  $\epsilon$  3.85)].<sup>2,3</sup> Bromination of III with 1.3 equiv of *N*-bromosuccinimide (NBS) in CCl<sub>4</sub> containing a trace amount of benzoyl peroxide (80°, 15 min) and debromination of the resulting bromide with a mixture of LiCl (10 equiv) and Li<sub>2</sub>CO<sub>3</sub> (2 equiv) in dimethylformamide (DMF) (140°, 1.5 hr) gave 2,7-dimethyltropone (IV) in 86% yield, which was identified



by comparison with an authentic sample.<sup>4,5</sup> Bromination of III with 2.5 equiv of NBS and subsequent dehydrohalogenation with LiCl (10 equiv) and Li<sub>2</sub>CO<sub>3</sub> (2 equiv) in DMF (140°, 2 hr) yielded the bromo tropone V<sup>4</sup> in 60% yield, which can easily be hydrolyzed to the  $\gamma$ -tropolone VI.<sup>4</sup>

The 2,7-bridged tropone X was prepared employing an analogous synthetic sequence. Catalytic hydrogenation of the unsaturated keto ether VII (trans isomer)<sup>1</sup> over 5% Pd—C in ethanol, followed by cleavage of ether linkage with BF<sub>3</sub> etherate (0.5 equiv) in acetic anhydride (80°, 15 hr) afforded the diacetate VIII<sup>2</sup> in 55% overall yield. Treatment of VIII with basic alumina (large excess) in benzene at 80° for 4 hr gave the enone acetate IX<sup>2</sup> in 45% yield. Conversion to the troponophane X, mp 61—64°, was achieved by bromination with NBS in CCl<sub>4</sub> (1.3 equiv, 80°, 15 min) followed by treatment with LiCl (10 equiv) and Li<sub>2</sub>CO<sub>3</sub> (2 equiv) in DMF (140°, 2 hr) in 40% yield. The identity was established by comparison with an authentic specimen.<sup>6</sup>



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#### REFERENCES

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3. All new compounds gave correct elemental analyses and/or molecular peak in mass spectra.
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5. The bicyclic adduct I is labile to acidic condition. Attempted ether cleavage with BF<sub>3</sub> etherate resulted in the formation of 2-(2-furyl)-pentan-3-one.
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