

complexes. A full molecular structure determination was carried out on  $\text{Fe}(\text{O}_2\text{C}_{14}\text{H}_8)_3 \cdot \text{O}_2\text{C}_{14}\text{H}_8$  and will be reported separately. A preliminary structure determination carried out on  $\text{Cr}(\text{O}_2\text{C}_{14}\text{H}_8)_3 \cdot \text{C}_6\text{H}_6(\text{OCH}_3)_3$  indicated a geometry similar to those of  $\text{Fe}(\text{O}_2\text{C}_{14}\text{H}_8)_3$  and  $\text{Cr}(\text{O}_2\text{C}_6\text{Cl}_4)_3$ ; so a complete refinement was not carried out. Physical measurements carried out on the 9,10-phenanthrenequinone complexes were on the solvated samples indicated above. Characterization of  $\text{V}(\text{O}_2\text{C}_{14}\text{H}_8)_3$ , which has proven to be quite unstable, remains incomplete.

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- (16) Camille and Henry Dreyfus fellow (1972–1977); A. P. Sloan Foundation Fellow (1976–1978).

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### 1,5-Methano[10]annulene. Synthesis and Characterization of the 3-Methoxy Derivative

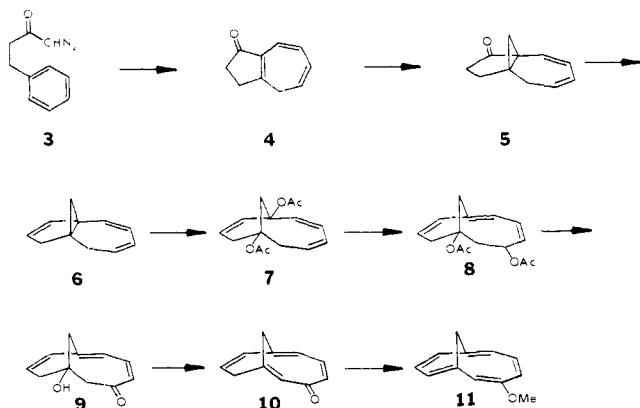
Sir:

Whereas the 10-electron  $\pi$  system of 1,6-methano[10]annulene (**1**) displays aromatic character<sup>1</sup> despite the lack of planarity,<sup>2</sup> a loss of aromaticity resulting from greater distortion of the  $\pi$  system has been predicted<sup>3</sup> for the isomeric 1,5-methano[10]annulene (**2**). Numerous research groups



have heretofore attempted to prepare **2** or derivatives thereof,<sup>4</sup> but only one has succeeded.<sup>5</sup> We describe herein our synthesis of 3-methoxy-1,5-methano[10]annulene and *NMR* evidence which argues against any significant difference in aromatic character between this compound and **1**.

We have previously reported<sup>6</sup> the copper-catalyzed cyclization of diazo ketone **3** to give bicyclic trienone **4**. Subsequently, it was found that selective cyclopropanation of the carbonyl-conjugated olefin in **4** can be conveniently accomplished with dimethylloxosulfonium methylide<sup>7</sup> in  $\text{Me}_2\text{SO}$  (70 °C, 45 min; 67% yield). Thus, all the carbon atoms of **2** can be assembled in their proper arrangement in just two steps from simple starting materials; completion of the synthesis requires



only cleavage of the central C–C bond and functional group manipulations. Conversion of cyclopropyl ketone **5** to triene **6** via the corresponding tosylhydrazone<sup>8</sup> proved unexceptional (66% yield).

Lead tetraacetate in acetic acid (15 °C, 15 min) cleaves the propellane bond<sup>9</sup> in **6** to yield diacetate **7** which suffers subsequent isomerization to the fully conjugated triene diacetate **8** on further heating in acetic acid (75 °C, 6 h, 61% yield from **6**). Other electrophiles likewise open the central bond of propellane **6**.<sup>10</sup>

Saponification of **8** (KOH, MeOH, 25 °C, 45 min; 97% yield) followed by oxidation of the allylic alcohol ( $\text{MnO}_2$ ,  $\text{CH}_2\text{Cl}_2$ , 25 °C, 3 h; 52% yield) affords  $\beta$ -hydroxy ketone **9** which can be dehydrated via the corresponding mesylate ( $\text{MsCl}$ ,  $\text{Et}_3\text{N}$ ,  $\text{CH}_2\text{Cl}_2$ ; then DBN,  $\text{CHCl}_3$ ) to give the sensitive tetraenone **10** (64% yield from **9**). The infrared spectrum of this homotropone exhibits an amazingly low frequency C=O stretching band ( $1590\text{ cm}^{-1}$ ; cf. tropone,<sup>11</sup>  $1582\text{ cm}^{-1}$ ). The title compound (**11**) is obtained by methylation of the cherry red enolate derived from **10** (LDA, THF, HMPA,  $-78\text{ }^\circ\text{C}$ , 2 min; then *n*-BuLi,<sup>12</sup>  $-78\text{ }^\circ\text{C}$ , 2 min; then excess  $\text{MeOSO}_2\text{F}$  and warm to 0 °C, 15 min; ~50% yield from **10**).

3-Methoxy-1,5-methano[10]annulene<sup>13</sup> (**11**) is bright orange in color;  $\lambda_{\text{max}}^{\text{hexane}}$  490 nm ( $\epsilon$  500), 300 (sh, 5400), 280 (20 300). Its <sup>1</sup>H NMR spectrum ( $\text{CCl}_4$ ) shows signals for seven methine hydrogens ( $\tau$  2.20–3.42 ppm), a methoxy group (6.07), and two nonequivalent bridge hydrogens (10.25 and 10.78,  $J = 10\text{ Hz}$ ). By comparison, the <sup>1</sup>H NMR spectrum of 1,6-methano[10]annulene (**1**) shows a multiplet for eight methine hydrogens ( $\tau$  2.50–3.20 ppm) and a singlet for two equivalent bridge hydrogens (10.50).<sup>1</sup> The remarkable similarity between these two NMR spectra argues against any significant difference in the ability of the two  $\pi$  systems to support an induced diamagnetic ring current. To the extent that this property can be regarded as a measure of aromaticity,<sup>14</sup> the 1,5- and 1,6-methano[10]annulene ring systems thus appear comparable in aromatic character. It remains to be established, however, whether the  $\pi$  system of **2** and its derivatives does in fact deviate more from planarity than that of **1**.

Other properties of the 1,5-methano[10]annulene ring system and synthetic approaches to the parent hydrocarbon (**2**) are currently being explored in our laboratory.

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### References and Notes

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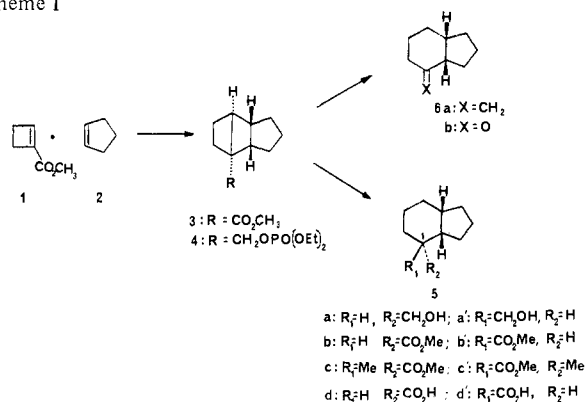
### A Photochemically Mediated [4C + 2C] Annulation. Synthesis of (±)-10-Epijunenol

Sir:

We described in a previous communication<sup>1a</sup> a metathetical route to medium-sized carbocycles and a procedure for differentiated dialkenylation of olefins, methods pertinent to germacranes and elemene syntheses. More recently, our continuing studies on these and related annulation methods<sup>2</sup> have been extended to a further objective of general importance in synthesis design, the controlled synthesis of trans-<sup>3</sup> and cis-fused ring systems. The synthetic salience of a [4C + 2C] route to cis-fused [4.n.0] systems is described herein along with an application of this method to the synthesis of (±)-10-epijunenol (**18**),<sup>4</sup>

As illustrated for the annulation of cyclopentene (Scheme I), a [2 + 2] photocycloaddition<sup>5</sup> is utilized in the present method to effect a latent [4C + 2C] connection under mild thermal conditions (-78 °C to ambient temperature). The second step involving a  $\sigma$ -bond cleavage<sup>6</sup> facilitated by the strain<sup>7</sup> of the bicyclo[2.2.0]hexane subunit is readily performed by addition of the photoadduct (1 mol equiv in diethyl ether containing 5 mol equiv of *tert*-butyl alcohol) to a solution of lithium (10 g-atom equiv) in liquid ammonia (-33 °C). These reducing conditions (A), which provided the alcohols **5a-5a'**<sup>8</sup> in an isolated yield of 87% from photoadduct **3**, can be readily tailored to suit various synthetic objectives. For example, reduction of photoadduct **3** (1 mol equiv in tetrahydrofuran containing 0.8-0.9 mol equiv of aniline) with lithium (2.5 g-atom equiv) in liquid ammonia followed by addition of NH<sub>4</sub>Cl (conditions B) provided esters **5b-5b'**<sup>9</sup> (79%, isolated), while quenching of the ester enolate intermediate with methyl iodide (conditions C) afforded the methylated esters **5c-5c'** (76%, isolated). Alternatively, the commonly occurring methylene-

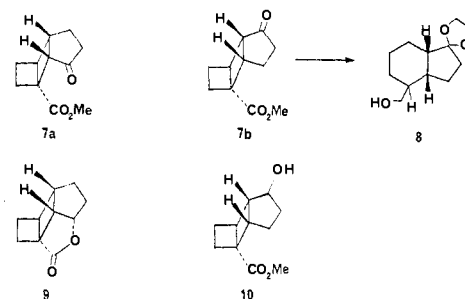
Scheme I



cyclohexane subunit (vide infra) can be elaborated by metal-ammonia reduction of the phosphate ester<sup>10</sup> derived<sup>11</sup> from the photoadduct (e.g., **4** to **6a**).

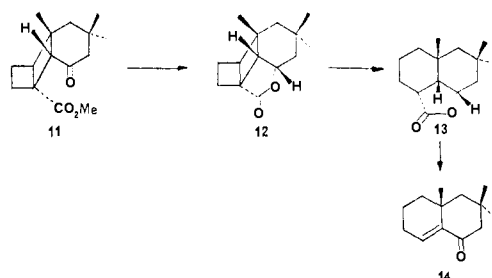
In accordance with a syn mode of photocycloaddition the *ring juncture stereochemistry* developed in this sequence was determined to be exclusively *cis* by the following correlations. Thus, saponification of esters **5b-5b'**, which were demonstrated to be related as C-1 epimers (NaOMe, MeOH) and which share a common ring juncture stereochemistry with **5a-5a'** and **5c-5c'**, gave the corresponding acid mixture from which the known acid **5d** (mp 77 °C, lit.<sup>12</sup> mp 77 °C) was easily isolated. Esterification (CH<sub>2</sub>N<sub>2</sub>) of **5d** afforded **5b**, the major product obtained from the initial cleavage reaction. Finally, acids **5d-5d'** were readily converted<sup>12</sup> to the known *cis*-fused indanone **6b**.<sup>13</sup>

As expected from previous studies,<sup>14</sup> the overall *regioselectivity* of the annulation is governed, in part, by steric and polar effects associated with the photocycloaddition step. While studies on how these effects can be utilized to control orientation are in progress, it is of interest to note at this point that the head-to-tail preference (1:2.5 = **7a:7b**, CH<sub>2</sub>Cl<sub>2</sub>, 50% yield) observed in the photoaddition of cyclopent-2-en-1-one to ester **1** is similar to that found in the related photodimerization of cyclopentenone.<sup>15,16</sup> The head-to-head and head-



to-tail relationship between these adducts was unequivocally established by conversion of the **7a-7b** mixture (1:2 = **7a:7b**) to lactone **9** and ester **10** (1:2 = **9:10**, combined yield 90%);<sup>17</sup> independent transformation of **9** and **10** to adducts **7a** and **7b**, respectively; and comparison of the products obtained from pyrolysis of the original mixture and pure ester **7b**.<sup>8</sup> Finally, ketalization of **7b** followed by reduction (method A) furnished the annelated product **8**<sup>8</sup> (89%, isolated).

In contrast to cyclopentenone, irradiation of isophorone in the presence of ester **1** provided substantially, if not exclusively, adduct **11** (85%, isolated) which was assigned the *cis*-anti-*cis*, head-to-head structure on the basis of its conversion (K-selectride, H<sub>3</sub>O<sup>+</sup>; 76%) to lactone **12**.<sup>1a</sup> Reduction (method



A) of **12** provided a single lactol (mp 127-128 °C) which on oxidation gave lactone **13** (92% overall, isolated). The further conversion<sup>18</sup> of this lactone (**13**) to enone **14** represents a potentially general extension of the annulation to the preparation of octalones.

As demonstrated in the following synthesis of (±)-10-epijunenol, the structural features of the photoadducts and derivatives can be effectively utilized in elaborating stereocenters in the preformed ring. Thus, photoadduct **15** (obtained in 62%