

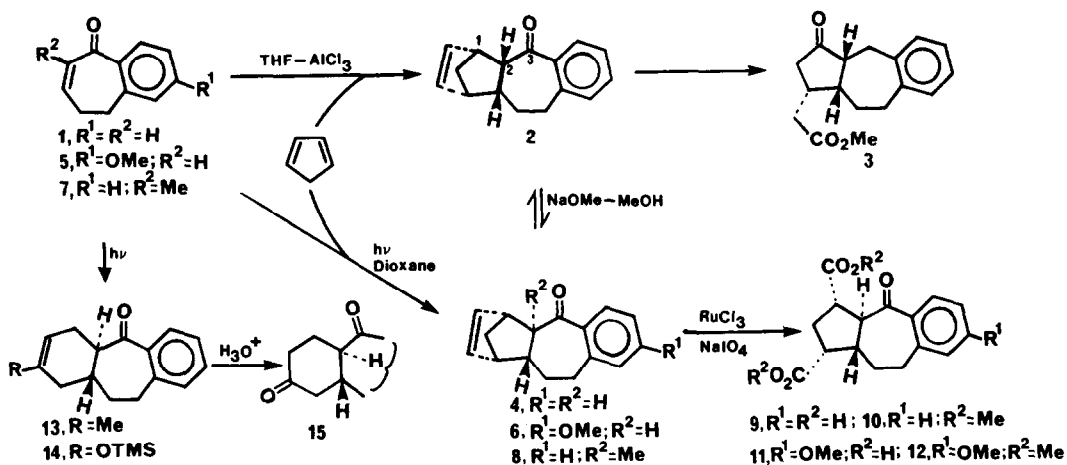
PHOTO-INDUCED DIELS-ALDER REACTION. A NOVEL ROUTE TO TRANS FUSED BENZOBICYCLO-  
 [5.3.0]DECANES AND [5.4.0]UNDECANES

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Abstract: Photoisomerization of cis-benzocycloheptenone to trans benzocycloheptenone and its [4 + 2] cycloaddition with selected dienes is reported for the synthesis of trans fused benzobicyclo[5.3.0]decanes **10**, **12** and benzobicyclo[5.4.0]undecanes **13**, **15**.

Recently we have demonstrated<sup>1</sup> that benzocycloheptenone **1** undergoes aluminum chloride catalyzed Diels-Alder cycloaddition with cyclopentadiene to form **2** which was efficiently transformed to cis-fused benzobicyclo[5.3.0]decane **3**. In connection to our interest in the synthesis of terpenoids, a trans-fused 5/7 ring system was needed. Attempted base promoted epimerization of either **2** or **3** to a practically inseparable mixture of cis and trans-isomers dictates an alternative approach which allows the synthesis of trans isomer exclusively. We now wish to report that benzocycloheptenone, on photo-irradiation, isomerizes<sup>2</sup> to a highly strained cyclic trans enone which undergoes facile [4 + 2] cycloaddition with a variety of dienes leading to a novel stereoselective route to trans fused carbon framework.



Irradiation of a solution of benzocycloheptenone **1** in dioxane in the presence of an

excess of cyclopentadiene for 2 h afforded trans-fused [4 + 2] adduct **4**<sup>3</sup>, m.p. 118°C in 77% yield. The trans-fusion of the ring system in **4** was established from its <sup>1</sup>H NMR analysis. The remarkable feature in <sup>1</sup>H NMR is the absorption of C<sub>2</sub>-H at δ 3.44 as a broad singlet in **4** instead of a doublet of a doublet at δ 3.41 (J = 10.3 and 3 Hz) in the cis adduct **2**. This difference in splitting pattern suggests that C<sub>2</sub>-H is endo in **4** thus exhibiting an endo-exo coupling which is much less<sup>4</sup> compared to an exo-exo coupling as observed for C<sub>2</sub>-H in **2**. Conclusive evidence that **4** indeed has a trans ring fusion is available from the observation that **2**, on treatment with excess sodium methoxide in refluxing methanol, led to a mixture of **2** and **4** in ca. 1:1 ratio. The methoxy analogue **5**, when irradiated similarly, in dioxane in the presence of cyclopentadiene gave the adduct **6**, m.p. 86°C in 65% yield. The enone **7**, a relatively hindered dienophile, after irradiation with cyclopentadiene afforded **8**, m.p. 95°C in 25% yield. The trans ring fusion in the adducts **6** and **8** was established in analogy to **4**.

The adducts **4** and **6** were finally transformed to trans-fused benzobicyclo[5.3.0]decanes by fission of norbornene double bond with ruthenium tetroxide oxidation developed by Sharpless *et al.*<sup>5</sup> Thus, treatment of **4** with catalytic quantity of RuCl<sub>3</sub>·H<sub>2</sub>O in the presence of excess of NaIO<sub>4</sub> in CCl<sub>4</sub>-CH<sub>3</sub>CN-H<sub>2</sub>O for 4 h afforded the dicarboxylic acid **9**, m.p. 185°C (dec) in 71% yield; <sup>1</sup>H NMR of the dimethyl ester **10** (CH<sub>2</sub>N<sub>2</sub>, 95%, m.p. 96°C) δ 3.4(1H,q,J=8Hz), 3.68(3H,s), 3.76(3H,s), 7.21-7.49(3H,m) and 7.78(1H,dd,J=8 & 2Hz). Similarly, **6** gave **11**, m.p. 186°C in 74% yield; <sup>1</sup>H NMR of the dimethyl ester **12** (CH<sub>2</sub>N<sub>2</sub>, 91%, m.p. 78°C) δ 3.35(1H,q,J=8Hz), 3.7(3H,s), 3.76(3H,s), 3.86(3H,s), 6.72(1H,d,J=2Hz), 6.86(1H,dd,J=8 & 2Hz) and 7.70(1H,d,J=8Hz).

To increase the synthetic potentiality of this photoinduced [4 + 2] cycloaddition reaction, two other representative dienes were chosen. **1** with isoprene afforded benzobicyclo[5.4.0]undecane **13**<sup>6</sup> as a viscous liquid in 35% yield. The adduct **14**<sup>6</sup> from **1** and 2-trimethylsilyloxy-1,3-butadiene was directly hydrolyzed (THF-H<sub>2</sub>O-HCl) to **15**, m.p. 91°C (37% from **1**). The structure and trans configuration at the ring fusion in **13** and **15** was determined by IR, <sup>1</sup>H NMR and high resolution mass spectra as well as from their mode of formation. Thus, the smooth photoisomerization of **1** to a trans cyclic enone and its facile cycloaddition provides a promising method of constructing trans fused tricyclic carbon network.

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#### REFERENCES AND NOTES

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6. The dimer of benzocycloheptenone was isolated from this reaction in ca. 15% yield.

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