

THE PHOTOCYCLOADDITION OF BICYCLO[5.3.0]DEC-1(7)-EN-2-ONE WITH OLEFINS

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The photochemistry of  $\alpha,\beta$ -unsaturated enones has been extensively studied and it has been shown that some cyclic enones, such as 2-cyclopentenone and 2-cyclohexenone, give the  $[2\pi+2\pi]$  photocycloadducts with a variety of olefins and acetylenes in good efficiency,<sup>1)</sup> but 2-cycloheptenone (I) does not give any photocycloadduct with olefins because of the facile isomerization to its trans isomer.<sup>2)</sup> Accordingly, when the unfavorable isomerization of (I) can be severely inhibited, the photocycloaddition of (I) with olefins might be expected to occur. As an appropriate compound for such inhibition, we chose bicyclo[5.3.0]dec-1(7)-en-2-one (II), having a rigid bicyclic system. As shown in Table, the photocycloaddition of the enone (II) with various olefins, such as cyclooctene, cycloheptene, 1,5-cyclooctadiene, 2-butyne, and ethylene, took place smoothly to give the corresponding [5.3.2]propellanes (IIIa,b)-(VII) in good yield.<sup>3a,b)</sup>

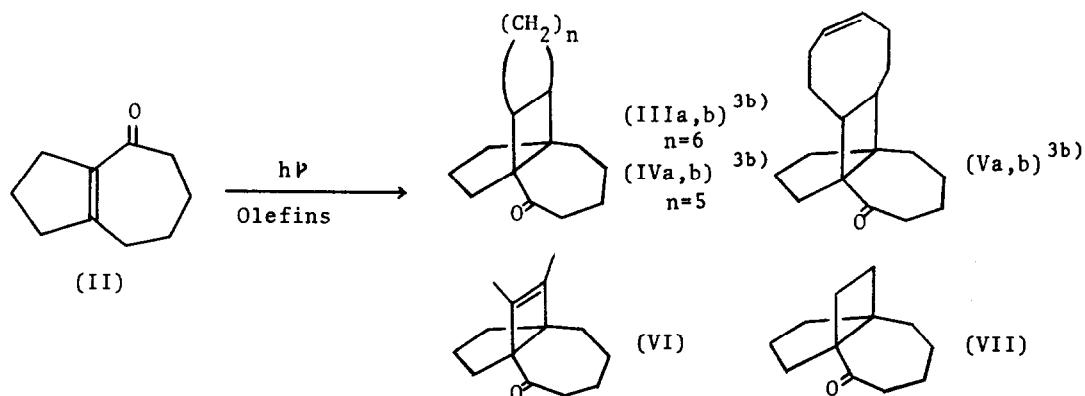


Table Photocycloaddition of Enone (II) with Olefins<sup>a)</sup>

| Olefin                           | Cycloadduct, Yield(%) <sup>e)</sup> | M.p. (°C) | 2,4-dinitrophenylhydrazone<br>M.p. (°C) |
|----------------------------------|-------------------------------------|-----------|---|
| Cyclooctene <sup>b)</sup>        | (IIIa) 48                           | f)        | 169-72                                  |
|                                  | (IIIb) 29                           | f)        | 158-60                                  |
| Cycloheptene <sup>b)</sup>       | (IVa) 40                            | f)        | 124-6                                   |
|                                  | (IVb) 29                            | f)        | 115-6                                   |
| 1,5-Cyclooctadiene <sup>b)</sup> | (Va) 37                             | 64-5      | 123-4                                   |
|                                  | (Vb) 12                             | 106-8     | 140-1                                   |
| 2-Butyne <sup>c)</sup>           | (VI) 71                             | f)        | 125-7                                   |
| Ethylene <sup>d)</sup>           | (VII) 30                            | 44-6      | 139-40                                  |

a) Irradiation was carried out through Pyrex filter using a 500-W high pressure mercury lamp at room temperature and continued until the enone (II) was almost converted (>90%).

b) A neat solution of the enone (II) in 10 molar excess olefin was irradiated.

c) An ethereal solution of (II) (33 mM) and 2-butyne (200 mM) was irradiated.

d) A benzene solution of (II) was saturated with ethylene and irradiated.

e) Products were isolated by vacuum distillation and subsequent glpc purification. The yields were determined by glpc analysis (Poly Ethylene Glycol 20-M).

f) Colorless liquid

Further works on the photocycloaddition of 2-cycloheptenone derivatives, comprised of different bicyclic systems, are in progress and will be reported shortly.

#### REFERENCES

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- 3a) Structural determination was made on the basis of satisfactory elemental analyses and spectrometric data.
- 3b) With the above cyclic olefins, two stereo isomers of respective cycloadducts were always obtained. To clarify the configuration of two stereo isomers, X-ray analysis of the crystalline products (Va) and (Vb) is in progress. Presently, we assume that two trans isomers of four possible ones are more probable candidates because of decrease of large repulsion between rings arising from syn correlation.