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PHOTOCHEMISTRY OF TRANS-5-CYCLODECENONE:
A TRANSANNULAR PATERNO-BUCHI REACTION

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Several examples of oxetane formation *via* an intramolecular Paterno-Buchi Reaction have been reported.[1,2] We now report an example of a transannular Paterno-Buchi Reaction involving a medium-ring unsaturated ketone.

A 0.6% solution of *trans*-5-cyclodecenone (I)[3] in benzene was irradiated in Vycor tube for 50 hrs. with a 254 mμ source (Rayonet Model RPR 208 Reactor). The yellow oil remaining after removal of the solvent was distilled (short path at 1.8 mm., bath temperature 45-55°) to give a 55% yield of a colourless liquid; ir (CCl_4) 935, 913, 890, 871 $cm.^{-1}$; nmr (CCl_4) τ 4.08 (1H, m). The same product was obtained when cyclohexane was used as the irradiation solvent.

Spectral data suggested the photoproduct was an oxetane and the following transformations established the structure as 11-oxatricyclo[$5.3.1.0^{1,6}$]undecane (II). Reductive cleavage of (II) with lithium aluminum hydride in 1,2-dimethoxyethane heated under reflux for 40 hrs. afforded *trans*-9-decalol (III) (32%) identical with an authentic sample.[4] Injection of (II) onto a Carbowax 20M glc column at 150° resulted in the detection of only 7% (II) plus three rearrangement products: (i) 4-(1-cyclohexen-1-yl)butanal (IV) (61%), identical with a sample prepared by diisobutylaluminum hydride reduction[5] of 4-(1-cyclohexen-1-yl)butanoic acid;[6] (ii) the octalol (V) (14%), identical with the major component isolated from lithium aluminum hydride treatment of a mixture of the two 1-acetoxy-Δ^4-octalins;[7] and (iii) an unidentified component (18%), possessing a trisubstituted double bond and a secondary alcohol. The formation of (IV) and (V) is analogous to a reported[2] acid-catalyzed rearrangement of a tetracyclic oxetane. The transformations described herein are all consistent with the structure, including relative stereochemistry, proposed for oxetane (II).

Irradiation of cis-5-cyclodecenone[3] in either benzene or cyclohexane using the conditions described above, resulted in complete isomerization within 10 hrs. to the trans-isomer (I), which then was converted to oxetane (II). The photochemical behaviour of other medium-ring 5-cycloalkenones is presently under investigation.

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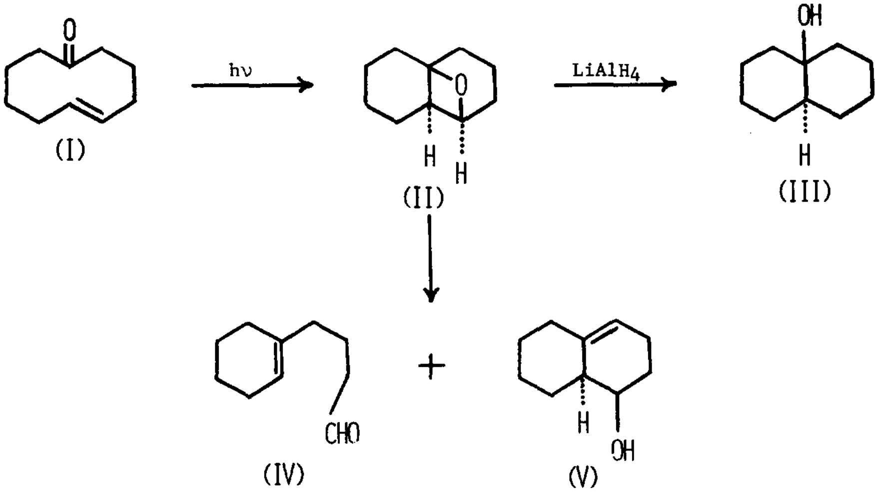

(I) (II) (III) (IV) (V)

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