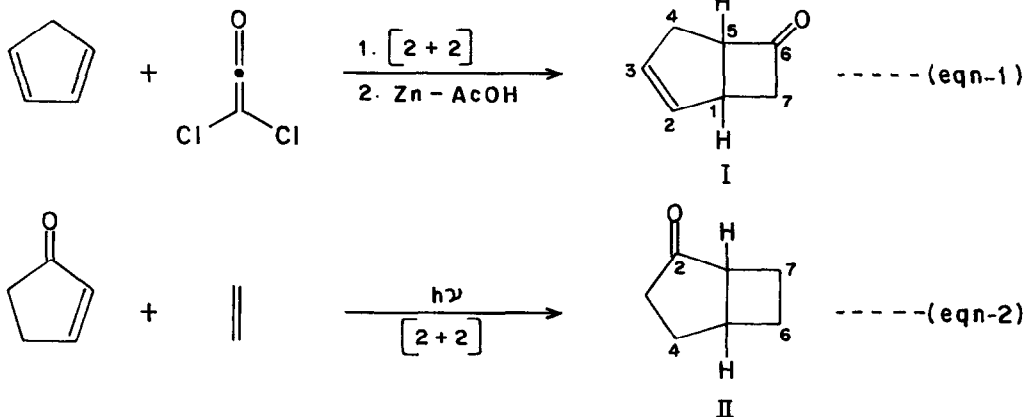


A NEW METHODOLOGY FOR THE SYNTHESIS OF
BICYCLO[3.2.0]HEPTENES FROM CIS-METHYLVINYLCYCLOPROPANES

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SUMMARY: A practical photolytic approach has been developed to furnish synthetically useful bicyclo[3.2.0]heptene derivatives from cis-methylvinylcyclopropanes; such products are not generally accessible by thermal processes owing to the competing retro-ene reaction.

Among bicycloheptanes cis-fused bicyclo[3.2.0]heptane derivatives are becoming increasingly popular as intermediates in a number of synthetic schemes.¹ Mostly, the oxo-derivatives such as I & II have been exploited in the synthesis of a variety of natural products^{2,3} and these are accessible by the methodology depicted in equations (1) and (2) respectively.



In connection with our programme aimed at the synthesis of some biologically active natural products, we needed optically active compounds of the type IV with different functional groups at C-7. In this context, the above mentioned methods appeared somewhat unsatisfactory to generate the required derivatives IV, let alone furnishing optically active products. Therefore, a design of another synthetic methodology to construct IV utilizing vinylcyclopropane-cyclopentene rearrangement⁴ (VCR) was envisaged (Eqn-3).

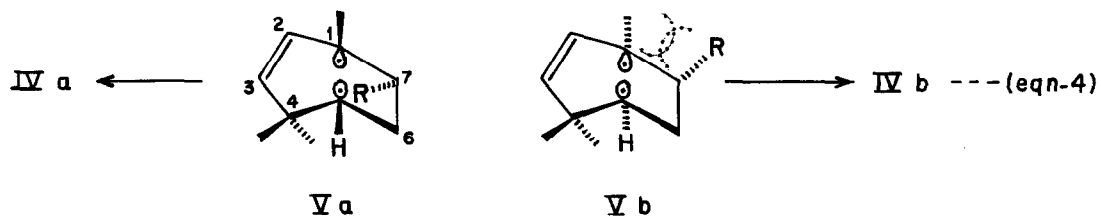
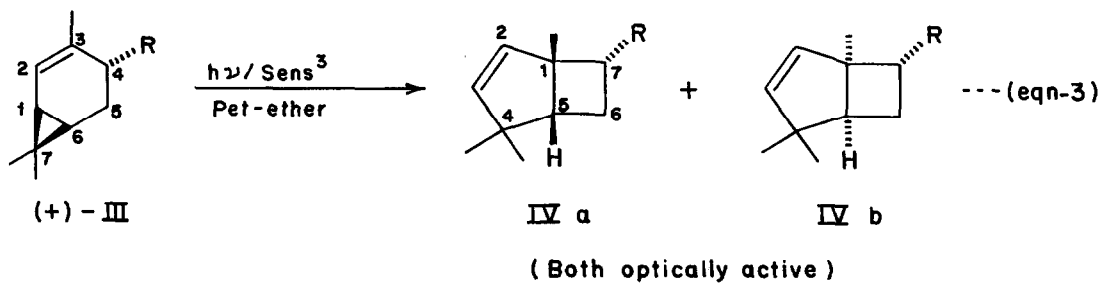


TABLE 1: PHOTOLYSIS OF VINYL-CYCLOPROPANES III

R	Time (hr)	Conversion ^a (%)	Yield ^b (%)	Product distribution (%) ^a	
				IVa	IVb
OCOCH ₃	15	97	91	65	35
CH(OH)CH ₃ (threo)	25	77	80	60	40
COCH ₃ ^c	25	60	90	45	55
OH	23	94	60	30	70
CH(OH)CH ₃ (erythro)	18	86	80	20	80
CH ₂ OCOCH ₃	18	93	75	20	80
COOMe	25	77	60	16	84

^a Determined by GLC (FFAP 5%, 130°, FID)^b Overall isolated yields of distilled products^c Acetone is used as solvent/sensitizer (Ref. 8)

Although VCR is generally amenable under thermal conditions⁴, a review of literature revealed that cis-methylvinylcyclopropanes III undergo preferentially retro-ene reaction⁵ under the conditions. Recently, Hudlicky and Koszyk⁶ have shown that from the cis-methylvinylcyclopropane ie. 6- β -ethenyl-1- β -methyl-bicyclo[3.1.0]hexane-2-one, under flash pyrolytic conditions at higher temperatures ($\sim 600^\circ\text{C}$) especially under PbCO_3 -conditioned Vycor column, mostly VCR products could be obtained. In the absence of such stringent experimental conditions, however, products from both the types of reactions were got in varying proportions. Thus, the problem of achieving reaction selectivity in these types of substrates especially in favour of VCR remains mostly unresolved.

In this communication, we wish to report a method⁷ to furnish exclusively the VCR products; under photosensitized conditions of irradiation, a clean transformation of III into the desired IV could be readily achieved even at ambient temperature (Eqn-3).

In a typical experiment, a solution (1%) of III⁸ in pet. ether ($60-80^\circ$) containing photosensitizer⁹ (toluene, 3 ml/100 ml) taken in an immersion type reactor (230 ml capacity) was irradiated (Vycor filter) with a 200 W high pressure Hanovia lamp (N_2 passed). In each case, the photoproducts comprised two diastereomers IVa & IVb together with some unreacted III (Table-1). The products were separated by preparative GLC and were characterized by their spectral properties (IR, PMR & MS) and by chemical transformations as described by us recently.¹⁰ A highly characteristic $^1\text{H-NMR}$ feature in each case was the sharp singlet displayed by the exo-isomer IVb for its vinylic protons and a double doublet for the corresponding protons of the endo-isomer IVa.

Mechanistically, these transformations can be reasonably assumed to proceed via biradical intermediates¹¹ of the type V (Eqn-4). We believe that the relative steric crowding due to the nonbonded interactions between the substituents at C-7 and the developing angular methyl group at the convex face on one hand and the placement of the C-7 substituents in the hindered concave face on the other, seem to control diastereomeric distribution. The results clearly show that by varying the substituents at C-4 in III, a high degree of diastereoselectivity could be obtained. Moreover, the fact that the substituents at C-7 in the products can be readily interconverted by simple chemical means offers a convenient route to the desired diastereomer.

From a synthetic point of view, the present methodology becomes useful in several ways: i) It selectively affords the VCR products to the total exclusion of retro-ene products¹²; ii) It provides bicyclo[3.2.0]hept-enes IV

bearing a wide variety of substituents at C-7; iii) The reaction has considerable utility; we have already accomplished the synthesis of (\pm)-Grandisol¹³, a pheromone of a male bollweevil, and iv) The diastereoselectivity obtained is of special value in the synthesis of optically active Grandisol and Lineatin¹⁴, a pheromone of Ambrosia beetle which is a serious timber pest in coniferous forests.

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