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DI-Π-METHANE REARRANGEMENT OF ARTEMISIA TRIENE (1)

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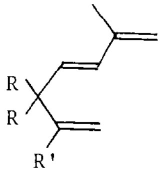
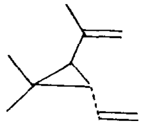
Contrary to a number of the examples of di-π-methane rearrangement in the photolyses of 1,4-diene systems (2,3), there seems no definite report of the same rearrangement in that of 1,3,6-heptatrienes (4), but only photosensitized *cis-trans* isomerizations of several 1,3,6-heptatrienes including 2,6-dimethyl (I), 5-methyl, and unsubstituted analogues have been known (5). We wish to report a facile di-π-methane rearrangement of artemisia triene II (2,5,5-trimethyl-1,3,6-heptatriene)(6) in both sensitized and non-sensitized solution photolyses.



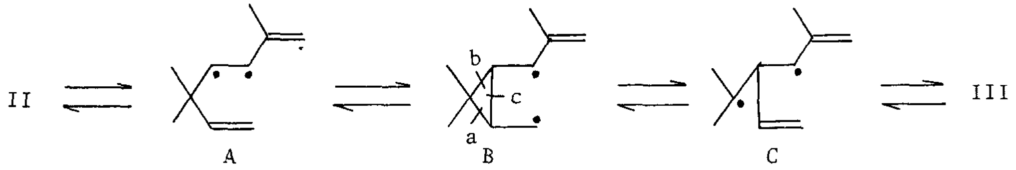
I ; R= H, R'= Me
II; R= Me, R'= H



III

Sensitized (β-acetonaphthone) irradiation of a 0.5% benzene solution of II under a nitrogen atmosphere at room temperature for 48 hr with a 100 W high pressure mercury lamp through a pyrex filter gave a single monomeric product III isolated as an oil by flask to flask distillation at 60-70^{o}/25 mm. The structure was characterized as *trans*-1-isopropenyl-2-vinyl-3,3-dimethylcyclopropane on the basis of the following spectral data: m/e 136(M^{+}); ν_{max}(neat) 3080, 1645, 990 and 910 (vinyl), 1635 and 895 (end-methylene) cm^{-1}; τ(CCl_4) 4.42, 5.00 and 5.10 (each 1H, ABX pattern m), 5.23 and 5.38 (each 1H, m), 8.26 (3H, s), 8.60 (1H, d,d, J=7 and 5 Hz), 8.88 (1H, d, J=5 Hz, overlapped with a methyl signal at τ8.89), 8.89 and 9.02 (each 3H, s). The presence of the signals at τ 8.62 and 8.88, and the coupling constant of 5 Hz between C_1-H and C_2-H are good indicatives of a *trans*-divinyl cyclopropane moiety in III. No trace of a *cis*-isomer of III was detectable on glpc and nmr analyses. Non-sensitized photolysis of a 0.5% *n*-hexane solution of II for 50 hr under similar conditions yielded also approximately 35% yield of III as a single monomeric product.

The above results suggest that the di-π-methane rearrangement of II to III proceeds via a triplet excitation, and the intersystem crossing of the lowest singlet state to the triplet may be predominant over the transformation of the singlet to a cyclobutene derivative (7), contrary to the observations in other acyclic 1,4-dienes by Zimmerman (2,8,9). The different behavior of II from I is apparently ascribable to the presence of a C_5-gem-dimethyl group, which might favor *a*-fission of B, a diradical intermediate produced from an initially excited triplet diradical A, to give C rather than *b*-fission because of a better minimumization of the electron density. Recyclization of C can give rise to III, the more stable *trans* isomer selectively. However, if C is not stabilized by absence of C_5-substituent, the rearrangement may not proceed, and photolysis results in only *cis-trans* isomerization via c-fission of B as in the case of I (5).



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