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THE THERMALLY INDUCED INTRAMOLECULAR CYCLIZATION OF THE TETRACYCLO[3.3.2.$0^{2,4}$.$0^{6,8}$]DEC-9-ENE SYSTEM[1)]

Takashi TODA, Chie-ko TANIGAWA, Akira YAMAE,
and Toshio MUKAI

Department of Chemistry, Faculty of Science, Tohoku University,
Sendai 980

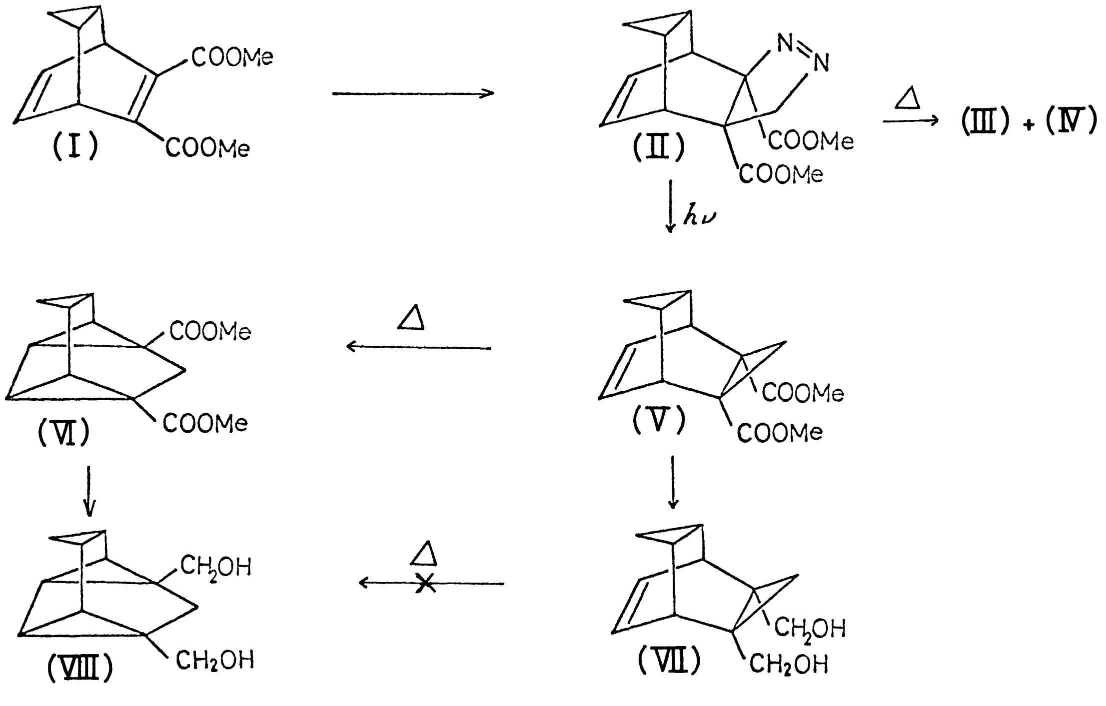
Dimethyl tetracyclo[3.3.2.$0^{2,4}$.$0^{6,8}$]dec-9-ene-2,4-dicarboxylate has been synthesized from cycloheptatriene in three steps, and its thermal and photochemical behaviors have been investigated. It was inert to light, but gave a pentacyclic compound on heating. In the same way, dimethyl tricyclo[3.2.1.$0^{2,4}$]oct-6-ene-2,4-dicarboxylate afforded an analogous tetracyclic compound.

In connection with a new finding on the intramolecular cyclization between a double bond and cyclopropane ring, that is, thermal (2_s+2_s) cyclization,[2)] we have studied the thermal and photochemical behaviors of tetracyclo[3.3.2.$0^{2,4}$.$0^{6,8}$]dec-9-ene derivatives. The valence isomerization of this ring system would be of interest from the view-point of such thermal skeletal transformations, because the system possesses an additional cyclopropane ring and affords a choice of cyclization between the double bond and cyclopropane or direction of the ring formation as well as the substitution-effect observed in the thermal reaction.

Treatment of dimethyl endo-cyclopropylene-$\Delta^{1,4}$-dihydrophthalate (I) [3)] with diazomethane gave a pyrazole derivative (II), mp 66°C, in a quantitative yield. The uv spectrum of II shows absorption maxima at 212 and 323 nm. The nmr spectrum of II exhibits complex multiplets due to protons of the cyclopropane at δ 1.07 and 1.63 ppm. This inequivalency of the anisotropic effect of the pyrazole ring takes place from the exo-side.

When II was heated above 200°C under nitrogen, a retro Diels-Alder reaction occurred to give cycloheptatriene (III) and dimethyl pyrazole-4,5-dicarboxylate (IV) in 84 and 53% yields respectively. Irradiation of II using a high pressure mercury lamp with a Pyrex filter afforded the desired compound (V), mp 36°C, in a quantitative yield. In the nmr spectrum, signals due to protons of the newly formed cyclopropane ring appear at δ 1.18 and 1.74 ppm as doublets (J=5.8 Hz). Direct heating of V above 200°C for a few hours under nitrogen yielded a new compound (VI), mp 63°C, an isomer of V, in more than 80% yield accompanied by a small amount of dimethyl phthalate. The structure of VI was deduced from its elemental analysis and spectral data, especially from the nmr spectrum; uv, end absorption only; ir in CCl_4, 3075, 3000, 1720, 1600, and 1435 cm^{-1}; nmr, δ, ppm (Hz), 0.25 (1H, d,d, J=4 and 8), 0.75 (1H, m, J=2,4, and 4.5), 1.07 (2H, m, J=ca 0.5, 4.5, and 8), 1.95 (4H, broad, J=ca 0.5), 1.97 (1H, d, J=14), 3.15 (1H, d, J=14), and 3.65 (6H, s). Thus, the structure of VI is shown to be dimethyl pentacyclo$[3.3.2.0^{2,10}.0^{4,9}.0^{6,8}]$-dec-2,4-dicarboxylate.

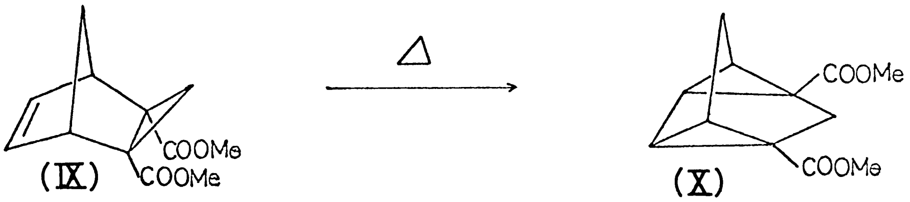
The reduction of V and VI by lithium aluminum hydride gave the corresponding glycols (VII), mp 119°C, and (VIII), mp 110.5°C, respectively. To clarify the substituent-effect for the thermal skeletal transformation, the thermolysis of VII was carried out under the same conditions as in the case of V. The desired product VIII was not obtained, but instead a mixture of several products was formed. This substituent-effect would support that the cyclization proceeds via a radical stepwise process. That is, the bond between the C_2 and C_4 positions of VI is



thermally ruptured to form a 1,3-biradical which is stabilized by methoxycarbonyl groups, and the radicals are trapped by the double bond rather than the similarly situated exo-cyclopropane ring.

This result is compatible with orbital symmetry considerations which predict that the concerted (2_s+2_s) process is thermally forbidden. Recently it has been reported that diphenyltricyclo$[3.2.1.0^{2,4}]$oct-6-ene[4,5] and 1,6-diphenyltricyclo-$[4.1.0.0^{2,5}]$hept-3-ene[6] undergo the thermally induced (2_s+2_s) cyclization. In these cases two phenyl groups should stabilize a 1,3-biradical formed as an intermediate, which supports the above explanation of our result.

Dimethyl tricyclo$[3.2.1.0^{2,4}]$hept-6-ene-2,4-dicarboxylate (IX), which was synthesized from cyclopentadiene by the analogous procedure showed thermal behavior similar to that of V, that is heating of IX at about 180°C afforded dimethyl tetracyclo$[3.3.0.0^{2,8}.0^{4,6}]$octane-2,4-dicarboxylate (X), mp 84°C, in a good yield.



Although labile to heat, V and VI were very stable to light, irradiation of V and VI using a low pressure mercury lamp and quartz vessel or a high pressure mercury lamp with a Pyrex filter formed no photo-products, only starting materials were recovered. The presence of benzophenone during the irradiation of V and VI led to the same result. The above facts show that there is no interconversion between V and VI on irradiation, although it is known that I[7] and some derivatives of tetracyclo$[3.3.2.0^{2,4}.0^{6,8}]$dec-6-ene[8] are transformed into the corresponding photo-isomers.

Further studies on ring size and the substituents effects in this skeletal transformation are in progress.

References and Footnotes

1) Presented at 25th annual meeting of the Chemical Society of Japan, Tokyo, Oct., 1971 : Organic thermal reactions, XVII. Part XVI : Y. Akasaki and T. Mukai, submitted to Tetrahedron Letters. Satisfactory elemental analyses were obtained for all new compounds. Nmr spectra were measured by using Varian A- and T-60 and HA-100 MHz spectrometer and referred to TMS in carbon tetrachloride solutions, and assignment of all protons were done by double and triple resonance technique.
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