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# RING-FLAPPING AND VALENCE ISOMERIZATION OF BICYCLO[6.2.1]UNDECA-2,4,6,9-TETRAENE[1]

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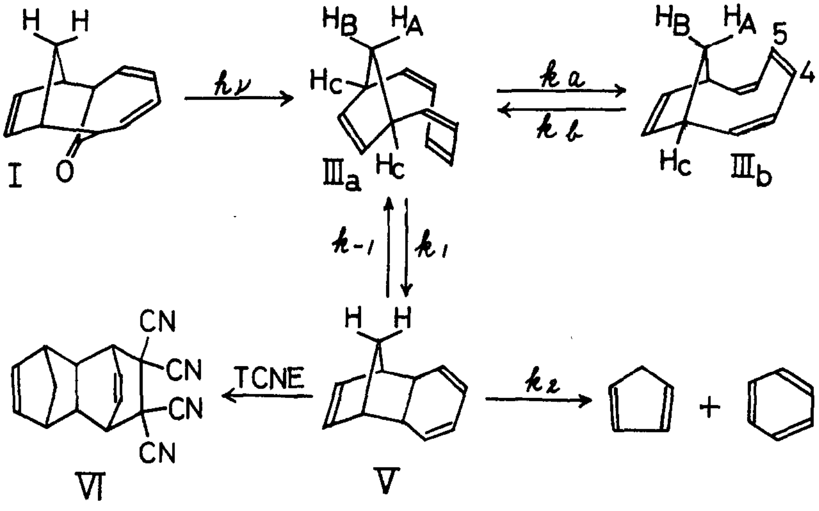
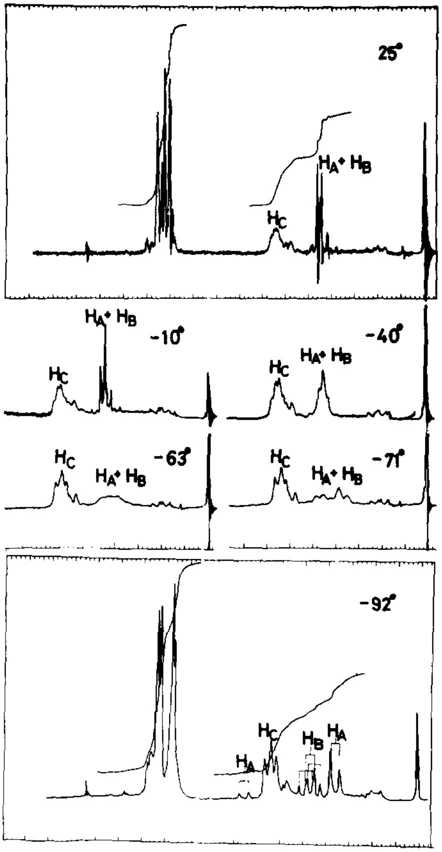
Recently we have reported that the (6+4) π-type adducts (I) and (II) of tropone with cyclopentadiene and cyclohexadiene (2), on irradiation, underwent decarbonylations leading to the $C_{11}H_{12}$ (III) and $C_{12}H_{14}$ (IV) hydrocarbons (3). The thermal and photochemical behavior of these hydrocarbons, especially of III, would be interesting in comparison with that of other methano-bridged cyclic polyenes such as bicyclo[4.2.1]nona-2,4,7-triene and bicyclo[4.4.1]undeca-2,4,7,9-tetraene (4). In connection with chemistry of the $C_{11}H_{12}$ hydrocarbons (5), studies on III would also be attractive. We wish to report preliminary evidence concerning the ring flapping of III, i.e., the thermal stability of two conformers (IIIa) and (IIIb) and valence isomerization between III and tricyclo[$6.2.1.0^{2,7}$]undeca-3,5,9-triene (V)(6,7).



Examination of the nmr spectrum (60 MHz) of the hydrocarbon III in $CS_2$ at temperatures from 25° to -92° gave the series of spectra shown in the Figure, in which coalescence of pattern occurs at -63°. The most plausible rationalization of the temperature dependence of the signals ascribed to the methylene protons of III is that equilibration is taking place between the two conformers IIIa and IIIb. At room temperature (25°) this equilibration is very rapid but with the aid of decoupling in the 100 MHz nmr spectrum, mean chemical shifts of $H_A$ and $H_B$ are calculated to be at $\tau$ 7.85 and 7.76 or vice versa (8). The sharpening of the spectrum at low temperature (-92°) is ascribed to a decrease in the rate of equilibration. The large doublet ($\tau$ 8.23, $J_{A,B}= 12$, $J_{A,C} \sim 0$ Hz) observed at -92° is assigned to $H_A$ of IIIa, and the smaller doublet ($\tau$ 6.27, $J_{A,B}= 12$, $J_{A,C} \sim 0$ Hz) to $H_A$ of IIIb. Signals due to $H_B$ of IIIa appear as double triplets ($\tau$ 7.70, $J_{A,B}= 12$, $J_{B,C}= 7.5$ Hz), while that of $H_B$ of IIIb is obscure.



Appearance of the $H_A$-signal of IIIb at very low field ($\tau$ 6.27) can be rationalized by the compression effect of the C-4,5 double bond on $H_A$. Such compression effect of the carbon-carbon double bond to the closely located proton has been found in the nmr spectra of cyclopentadiene trimer (9) and the addition product of norbornadiene with tropones (10). This fact may provide strong evidence for the correctness of the conformation assigned to IIIb. The ratio of the $H_A$-signal of IIIb to that of IIIa at -92° corresponds to the equilibrium constant (K) of 0.15, from which value the free energy difference ($\Delta G°$) of 0.68 kcal/mol can be derived. However, the rate from IIIa to IIIb and the activation free energy ( $\Delta F^{\ddagger}$ ) cannot be estimated, because the equilibrium constant (K) is unknown at the coalescence point. If the K is considered to be the same as value at -92°, i.e. K= 0.15, calculation would give a mean life time ( $\tau$ ) of 0.12 sec for the ring flapping of III, and ka= 15.1 $sec^{-1}$ and $\Delta F^{\ddagger}$ = 10.8 Kcal/mol would be obtained (8). The $\Delta F^{\ddagger}$ value is not very different from that for the ring inversion of some cyclooctatrienes (11).

In order to show the existence of the valence isomer (V), the nmr spectrum of III was determined at temperatures from 25° to 70°, in which case no change occurs in the spectrum, except for the appearance of signals due to benzene and cyclopentadiene over 40°. When the rate of the thermolysis of III was determined by nmr spectrscopic measurements from 60° to 70°, good first order kinetics was observed and the following rate constants and activation parameters were obtained : k ($10^5$)= 4.0 at 60°, 7.8 at 65° and 11.0 at 70° ; Ea= 23.1 Kcal/mol; $\Delta H^{\ddagger}$ = 22.4 Kcal/mol and $\Delta S^{\ddagger}$ = -9.3 e.u. (60°). On the other hand, gentle heating (at 70°) of III with tetracyanoethylene in tetrahydrofuran afforded an 1:1 adduct (12), mp 195-196°, in 96 % yield. Of possible structures, VI was assigned for the adduct, although its stereochemistry is uncertain, on the basis of the following spectral data : m/e, no $M^+$, 78 and 66 (base peak) ; nmr (in $CDCl_3$, $\tau$ ), 3.85 (2H, quartet, olefinic), 4.33 (2H, broad singlet, olefinic), 6.45 (2H, multiplet, methine), 7.04 (4H, broad singlet, methine) and 8.53 (2H, AB type of $ABX_2$).

The formation of VI may suggest the existence of an equilibrium between III and V. Such valence isomerization reminds us of that between cycloheptatriene and norcaradiene. However, Tsuji, Teratake and Tanida pointed out that cycloheptatriene underwent Diels-Alder reaction via a transition state of norcaradiene structure (13). In addition, Wilson and Warrener found that 3,6-dimethyl-4,5-diphenyltricyclo[$6.2.1.0^{2,7}$]undeca-3,5,9-triene was stable at -10° but decomposed above 20° ($t_{\frac{1}{2}}$ = 19 min at 33°)(7). These findings may suggest that the rate determining step of the thermolysis of III leading to benzene and cyclopentadiene may be the step from III to V ($k_2 \gg k_{-1}$). Thus the activation parameters obtained above would correspond with those of the valence isomerization of III to V, and it would be concluded that the valence isomer V seems unstable or its equilibrium concentration, if V exists, is very low compared with that of III.

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