The Exceptionally Rapid Stereomutation of a Bicyclo[2,1,0]pentane

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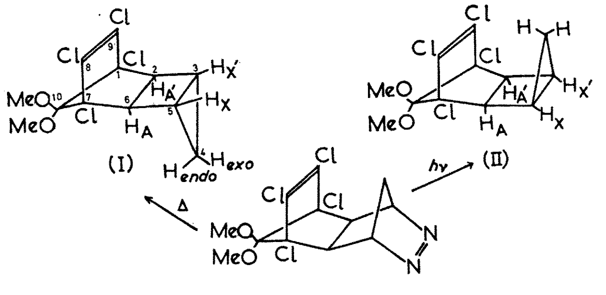
Summary *endo-syn*-1,7,8,9-Tetrachloro-10,10-dimethoxytetracyclo[5,2,1,$0^{2,6}0^{3,5}$]dec-8-ene (II), obtained by photolysis of diazanorbornane derivative (III), isomerises unexpectedly easily into the *endo-anti*-isomer (I).

THE stereochemical consequences of formation of bicyclo[2,1,0]pentanes by thermal deazetation of 2,3-diazanorbornanes[1] and the stereomutation of simple derivatives of the bicyclic system have recently been discussed.[2,3] We report on the formation and properties of the isomeric bicyclo[2,1,0]pentanes (I) and (II) prepared from diazanorbornane (III).

Compound (I), m.p. 83·5—85°, has previously been described as the product of undefined stereochemistry[4] resulting from thermolysis of cyclic azo-compound (III). Whilst our evidence for the formulation of (I) as the *anti*-isomer is incomplete, the observation of methylene-bridge inversion during thermolysis of 2,3-diazanorbornanes,[1] with the thermal stability of (I), strongly supports the structure illustrated. On the other hand, the photolysis of dilute solutions of (III) in carbon tetrachloride (Pyrex filtered mercury arc) gives besides (I) a small yield of the previously unknown type, *stereoisomer* (II) m.p. 83—85°, which is very easily converted into (I) (*vide infra*). The close relationship of (I) and (II) is seen from their i.r. spectra: (I), $\nu_{max.}$ 1610 vs; 1020 ms, *ca.* 3040—3050 w; 6080 w, and 4440 m cm.$^{-1}$ [ClC=CCl; cyclopropane skeletal vib. and C–H stretch; near-i.r C–H stretch overtone and combination bands for a cyclopropane].[5] (II), $\nu_{max.}$ 1598 vs; 1018 m, *ca.* 3040—3050 w; 6140 w, and 4440 m cm.$^{-1}$—correlations as for (I). ^{1}H n.m r. spectral data are also quite consistent with these formulations: (I), τ 6·52 (s), 6·57 (s) $(OMe)_2$; 7·47 (mult.) $(H_AH_{A'})$; 8·46 (mult.) $(H_XH_{X'})$; centred near τ 9·2 (complex) [overlapping sextuplets due to cyclopropane methylene with *endo*-H at higher-field τ 9·24 than *exo*-H (9·16) and coupled to ring junction H_X (J 1·5 Hz.) less strongly than the *exo*-H (J 5 Hz.);[6] $J_{H\text{-}exo\text{-}H\text{-}endo}$ 5 Hz.]. (II), τ 6·5 (s), 6·95 (s) $(OMe)_2$; 6·95 (mult.) $(H_AH_{A'})$; near 8·35 (complex) [overlapping $H_XH_{X'}$ and cyclopropane CH_2, the latter strongly deshielded]. More significantly, the AA′XX′ spin-coupling system for isomer (I) exhibits its low-field multiplet with a narrower separation of the two most prominent lines (2 Hz.) compared to the same pair of lines in the spectrum of (II) (separation 5 Hz.) (due to $J_{AX} + J_{AX'}$ with $J_{AX'}$ negative and positive, respectively). These observations are in agreement with recent correlations for *anti*- and *syn*-isomeric symmetrically substituted cyclobutanes.[7]

An interesting property of *syn*-isomer (II) is its slow conversion during several months ***at room temperature*** into (I). At 40°, (II) has a half-life of *ca.* 10 hr. but only *ca.* 90 min. at 60°. Few examples of stereomutations of cyclopropane rings in bicyco[2,1,0]pentanes have been reported. However, the activation energy for stereomutation of the 2-methylbicyclo[2,1,0]pentanes has been measured (38—39 kcal./mole),[2] from which it is clear that the conversion of (II) into (I) corresponds to an unusually low E_a. The reasons for this are matters for some debate, but increased ground-state ring strain and steric compression in (II) (consistent with the strongly deshielded cyclopropane methylene n.m.r. signals and the higher-frequency i.r. C–H stretching mode), ground-state π–σ electron repulsion in (II), and stabilisation of an intermediate biradical derived by C-3–C-5 bond scission involving participation by the adjacent chlorinated olefin are factors which might be considered. Certain stepwise cycloaddition reactions of bicyclo[2,1,0]pentanes are believed to involve *endo*-attack at the transannular bond, with consequent methylene inversion in the product.[1b] Orbital symmetry conservation precludes resemblance of the energy surface thermally connecting (I) and (II) and that for concerted $\pi + \sigma$ cycloaddition—and therefore a stabilised intermediate resulting from a 'foiled' concerted addition; a favourable interaction of this kind might, however, be involved in the formation of (II) in the photolysis of (III).



(III)

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