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π Donor and π Acceptor Substituent Effects in the Thermal Rearrangement of 9-Substituted cis-Bicyclo[6.1.0]nona-2,4,6-trienes[1]

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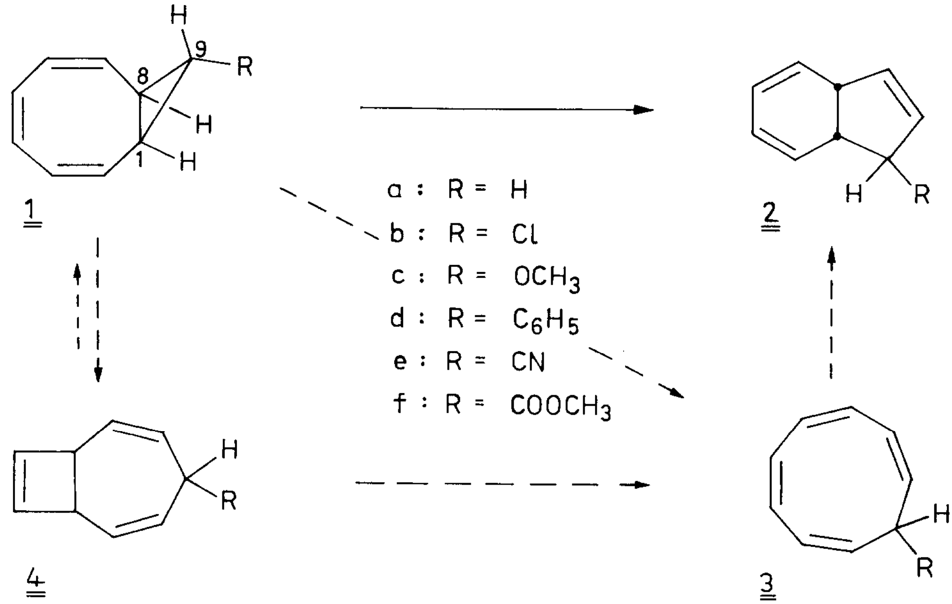
cis-Bicyclo[6.1.0]nona-2,4,6-triene[2] (**1a**) rearranges at 90° to cis-8,9-dihydroindene (**2a**) and trans-8,9-dihydroindene in a 9:1 ratio[2]. The anti-9-substituted cis-bicyclo[6.1.0]nona-2,4,6-trienes **1b**[3], **1c**[4], **1d**[5], **1e**[6] and **1f**[8], which can attain a "folded" conformation[9], also rearrange to cis-8,9-dihydroindenes **2b** - **2f** preferentially, the cis ring junction being revealed by the coupling constant of the 8,9-bridgehead hydrogens.[2,3,8,10]



One can, therefore, assume the same mechanistic scheme for the thermal reorganization of 1a - f to 2a - f and compare the rate of the substituted derivatives with the rate of the parent compound. According to R.Hoffmann[11] and H.Günther[12], π donors should weaken and π acceptors should strengthen the C^1-C^8 bond, which is broken in this process.

We followed the rearrangement kinetically by measuring the rate of disappearance of absorption in the nmr due to H^1, H^8 and H^9 of 1a - f. The results are shown in Table 1.

R	$k_{80^o}\cdot 10^7$ (sec^{-1})	$\Delta G^{\ddagger}_{80^o}$ (kcal/mole)	$\Delta H^{\ddagger f}$ (kcal/mole)	$\Delta S^{\ddagger f}$ (e.u.)
$Cl^{a,c}$	4400	26.0	25.0	-2.3
$OCH_3{}^a$	3200	26.3	24.6	-5.2
$H^{a,d}$	412	27.9	26.1	-5.1
$C_6H_5{}^b$	75.8	29.1	27.6	-4.2
$CN^{b,e}$	5.17	31.0	32.3	3.8
$CO_2CH_3{}^b$	3.72	31.2	32.4	3.3

Table 1: Kinetics of the Isomerization of 1a - f to 2a - f.

a solvent CCl_4; b solvent C_6H_5CN; c cf.ref. 3c; d A.G.Anastassiou and R.C.Griffith, Chem.Comm. 1971, 1301, obtained $\Delta H^{\ddagger}$ = 26 kcal/mole and $\Delta S^{\ddagger}$ = -5 e.u.; e cf.ref. 7; f experimental error: $\Delta H^{\ddagger}$ = ±1.2 kcal/mole; $\Delta S^{\ddagger}$ = ±3.2 e.u.

The substituent effect is significant: $\Delta\Delta G^{\ddagger}$ is 5.2 kcal/mole! As predicted,[11,12] with π donors (Cl, OCH_3) in position 9 of 1, the opening of the 1 - 8 cyclopropane bond is facilitated, and $\Delta G^{\ddagger}$ of the rearrangement is smaller than in 1a*

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* P.v.R.Schleyer and K.Kunde (private communication, March 16, 1973) have measured the rearrangement of anti-9-fluoro-cis-bicyclo[6.1.0]nonatriene. This is the compound with the largest rate of rearrangement: $k_{80^o} = 3.63 \cdot 10^{-3}\ sec^{-1}$, $\Delta G^{\ddagger}_{80^o}$ = 24.8 kcal/mole, $\Delta H^{\ddagger}$ = 24.1 kcal/mole, $\Delta S^{\ddagger}$ = -1.8 e.u.

On the other hand, typical π acceptor substituents (CN, CO_2CH_3), which strengthen the 1 - 8 bonds, raise $\Delta G^{\ddagger}$ substantially. The effect of π acceptors in systems of this kind is conjectured to be greater than that of π donors[13]. The phenyl group apparently functions as an acceptor, which is also the case in the cycloheptatriene - norcaradiene equilibrium[11,14].

Unfortunately, it is impossible to determine whether the observed effect is essentially a ground state or a ground state and transition state effect. all-cis-cyclononatetraenes 3 are likely intermediates in the rearrangement 1 → 2 since 1a rearranges virtually instantaneously at 90° to 2a[15]. But there is no definite information whether 3 is formed directly from 1, or whether 1 first rearranges in a Cope rearrangement to cis-bicyclo[5.2.0]nona-2,5,8-trienes 4, and then isomerizes to 3.

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6. 1e, mp. 91-92°, has been synthesized from the ester 1f by conventional methods; nmr (60 MHz, $CDCl_3$) $H^{1,8}$ (τ = 7.87, 2 H-d, J = 5.5 Hz); H^9 (τ = 8.97, 1 H-t, J = 5.5 Hz). D.Martens, Diplomarbeit Universität München 1971; cf.ref. 7.
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