Stabilization of Norcaradienes by Electronic Effects

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Summary The synthesis and determination of thermodynamic parameters are described for spiro-norcaradienes (III) substituted in the norcaradiene 6-membered ring.

Various explanations have been advanced for the stability of norcaradiene (I) *versus* its valence isomer cycloheptatriene (II).[1] We report the synthesis, some of the chemical properties, as well as the thermolysis of spiro-norcaradienes (III) which contain different substituents (CF_3, Me) in the norcaradiene 6-membered ring (2- and/or 4-position). With the exception of 2,5,7-triphenylnorcaradiene[2] the substituted spiro-norcaradienes described here are the only examples where the effect of substituents in the norcaradiene ring has been reported.

The spiro-norcaradienes (III) were obtained as previously by photolysis of the corresponding diazo-cyclopentadienes (V) in trifluoromethylbenzene (VIa) or *m*-hexafluorodimethylbenzene (VIb) in the presence of a GW_V-filter ($\lambda > 360$ nm).[3] Chromatography on silica gel gave a mixture of (III) $\rightleftharpoons$ (VI) (Table).

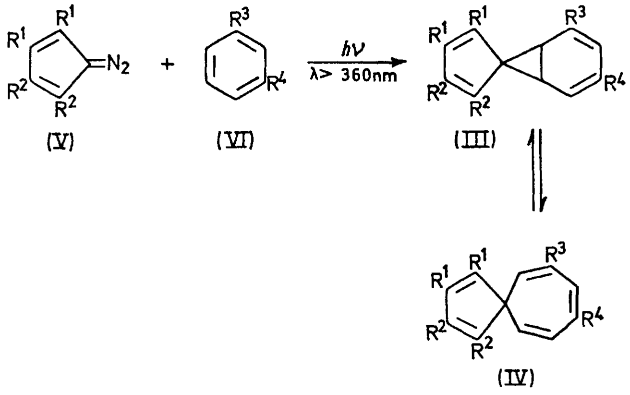
(I) (II)

Table. *Yield of* (III) $\rightleftharpoons$ (IV) *and percentage of* (III) *in the equilibrium mixture*

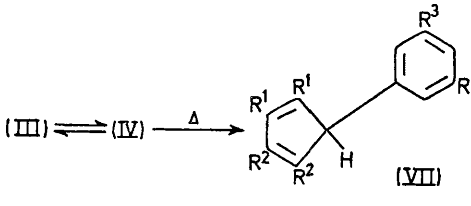
	R^1	R^2	R^3	R^4	Yield (%) of (III) $\rightleftharpoons$ (IV)	% of (III)[a]
a	Cl	Cl	H	H	30[3]	19
b	Cl	Cl	CF_3	H	40	28
c	Cl	Cl	CF_3	CF_3	45	66
d	Ph	*o*-phenylene	H	H	20—25[3]	19
e	Ph	*o*-phenylene	CF	H	35	25

[a] At room temperature.

A variable temperature n.m.r. study demonstrated that in all cases a mixture of the valence isomers (IIIa—e) and (IVa—e) was present. The percentage of isomer (III) at room temperature was calculated from the equation: $\tilde{\nu} = p_A\nu_A + p_B\nu_B$.[4]



Thermolysis of spiro-norcaradienes (IIIa—e) afforded substituted phenylcyclopentadienes (VII). This reaction has been followed by n.m.r. and the free enthalpy of activation $\Delta G^‡$ for (III) $\rightleftharpoons$ (IV) $\rightarrow$ (VII) was calculated.



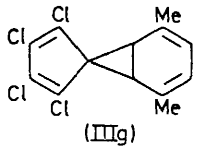
$G^‡$ (kcal mol^{-1}) for the conversion

(III) $\rightleftharpoons$ (IV) $\rightarrow$ (VII)

a, 26·0

b; 27·0

c; 28·5



(IIIg)

Electron donating substituents such as Me destabilise (III) to such an extent that rearrangement into (VII) occurs immediately. Therefore (IIIg) was isolated in the photolysis of (V) in xylene as the sole reaction product. Since the geometrical factors are held constant in (III) the stabilization of (III) at the expense of (IV) clearly can be attributed to the electron transfer to the substituents.

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