

Chlorination of Some Bridge-Substituted Acenaphthenes and Related Compounds

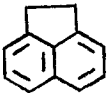
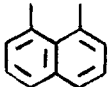
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The increase in reactivity of acenaphthene (I) towards electrophiles has been attributed to internal strain,¹⁾ reduced steric hindrance,²⁾ or electron release from the strained ethylene bridge.³⁾ The discussions seem as yet to be far from being settled. We would like to report here an interesting finding which seems to ascribe a part of activation of I to a second-order hyperconjugation.

We have treated I, perinaphthene (II), and 1,8-dimethylnaphthalene (III) with molecular chlorine in a mixture of carbon tetrachloride and acetic acid (3 : 1, *v/v*) at 15.0°C, and the reaction was kinetically followed by measuring the rate of disappearance of chlorine. The second-order rate constant (k_2) together with *ortho* : *para* ratios of the monochloro compounds are given in Table I. Steric crowding at the most reactive sites considerably differs for these three hydrocarbons. Nevertheless, the relative ratios of the *ortho* and *para* isomers were found to be almost identical. The result is inconsistent with an idea that the greater reactivity of I is due to the more favorable steric environment for the access of electrophile towards the 5-position.²⁾

Table I. Kinetic Data and *Ortho-para* Isomer Ratios for Chlorination of Acenaphthene, Perinaphthene, and 1,8-Dimethylnaphthalene (15.0°C; in CCl₄-AcOH (3 : 1, *v/v*))

			
	I	II	III
k_2 (l/mole. sec)	1.21	1.50×10^{-1}	5.66×10^{-2}
Relative rate	8.40	1.00	0.38
Ortho-para ratio	20/80	21/79	23/77

Substituents on C-1 and C-2 atoms are thought to give little effect on the overall strain caused by placing the ordinary C-C bond (1.54 Å) between the 1- and 8-positions of naphthalene nucleus (*ca.* 2 Å). However, chlorine atoms on the bridge (VII and VIII) were found to decrease the reaction rate to an appreciably greater extent than would be expected from the inductive effect. If the activation of I stems from an enhanced electron

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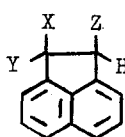
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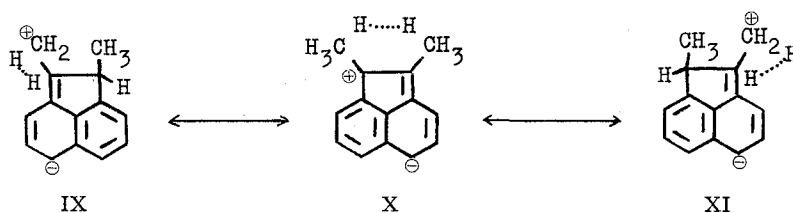
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release from the highly strained C₁-C₂ bond,³⁾ the progressive introduction of methyl groups on C-1 and C-2 atoms would be expected enhance the electron-donating ability of the CH₂-CH₂ bridge, leading to a gradual increase in the reaction rate. However, the bridge-methylated acenaphthenes (IV and VI) were found to react more slowly, conforming to an order demanded by the Baker-Nathan effect (Table II).

Table II. Kinetic Data for Chlorination of Bridge-substituted Acenaphthenes (15.0°C; in CCl₄-AcOH (3 : 1, v/v))

	Compound			k ₂ (1/mole. sec)	Relative rate
	X	Y	Z		
	I	H	H	1.26	1.00
	IV	Me	H	0.98	0.78
	V	Me	Me	0.49	0.39
	VI	Me	Me	0.40	0.32
	VII	Cl	H	5.02 × 10 ⁻²	0.040
	VIII	Cl	H	1.09 × 10 ⁻⁴	0.000087

Noteworthy is a sharp drop of the reaction rate observed when chlorine atoms or the geminal methyl groups were introduced into the CH₂-CH₂ bridge. Marked dependence of the rate on the number of hydrogen atoms on the bridge may be taken as an evidence for the contribution from the carbon-hydrogen hyperconjugation, especially a second-order hyperconjugation effect involving the structures, *ex.* IX to XI.⁴⁾ The geminal methyl groups on the bridge will diminish such structural advantage. Chlorine atoms on C-1 and C-2 atoms would increase a local positive charge on the bridge and make the hyperconjugative contribution (*ex.* type X) more difficult.



Various factors arising from the unique structures are probably responsible for the enhanced reactivity of I, and any single mechanism would hardly be postulated to account for it to satisfaction. Our result provides here an additional contributory factor, not previously considered by other workers.

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