

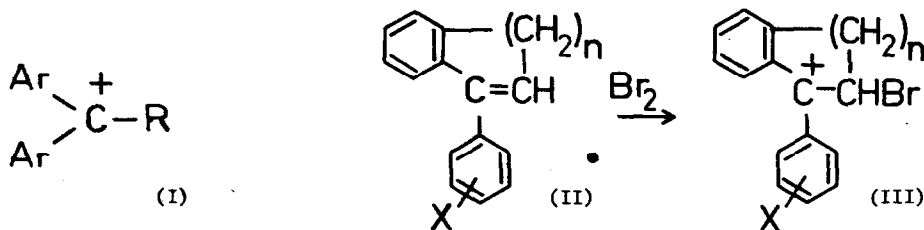
BROMINATION OF CYCLIC OLEFINS - DEPENDENCE OF RESONANCE  
STABILIZATION OF AN ARYLCARBONIUM ION ON CONFORMATION

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The question as to whether or not the aryl rings of a diarylcarbonium ion (I) must approach a coplanar configuration to provide maximum stability has been subject to debate (1). Because of steric interactions, the two aryl rings in (I) cannot lie simultaneously in the same plane and a propeller-like structure of equally twisted rings is thought to be the most stable configuration (2). But the extent to which further twisting of the rings reduces the stability of the carbonium ion is not clear. The results which we have obtained from a study of the bromination of two series of cyclic olefins (II,  $n = 2,3$ ), during which reaction carbonium ion intermediates (III) are formed, are relevant to this problem.



The rate constants for the bromination of compounds (II) with  $n = 2$  and 3 in methanol containing 0.2 M sodium bromide at 25° are listed in Table I. The kinetics of bromination were measured by various electrometric methods which have been previously described (3), and are accurate to within  $\pm 3\%$ . While *m*-substituents affect the rates of bromination for both series of compounds in much the same way (compare  $\log k/k_0$  values in Table I), substituents that can interact by resonance with the forming carbonium ion (e.g. *p*-MeO, *p*-Me, *p*-Br) play a different role dependent on the size of the alkyl group in (II). When  $n = 2$ , the observed rate constants can readily be correlated with ordinary Hammett  $\sigma$  values (4) (Fig. 1a), despite the fact that

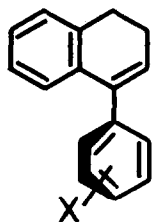
TABLE I. Rate Constants,  $k$  (in  $1.\text{mole}^{-1}\text{sec}^{-1}$ ), for the Bromination of the Ethylenes (II) in Methanol (0.2 M NaBr,  $25^\circ$ ).

Substituent	$k$		$\log k/k_0$	
	$n = 2$	$n = 3$	$n = 2$	$n = 3$
p-MeO	340,000	60,500	1.310	3.160
p-Me	64,500	470	0.588	1.050
m-Me	29,000	75.2	0.241	0.254
H	16,600	41.8	0.000	0.000
p-Br	2,200	12.5	-0.879	-0.524
m-Br	655	-	-1.406	-
m-Cl	-	2.3	-	-1.260

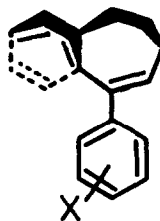
this is an electrophilic side-chain reaction normally correlated with the  $\sigma^+$  values of Brown and Okamoto (5). Conversely, when  $n = 3$  the rate constants are best correlated against  $\sigma^+$ , rather than  $\sigma$  (Fig. 1b).

From the definition of  $\sigma^+$  and  $\sigma$  and by consideration of the types of reactions to which they have been applied (5), we conclude that the amount of resonance interaction between the substituent and the reaction centre is quite different in each case, being close to zero when  $n = 2$  and large when  $n = 3$ . Significantly, the  $\rho$  values for the two series of compounds (calculated using data for *m*-substituted compounds alone, see Fig. 1) are much the same, indicating similar charge densities in the transition states on the carbon to which the substituted aryl ring is attached, in both series.

The results may readily be explained by considering the differences in the geometry of these systems. When  $n = 2$ , the fused aromatic ring is approximately coplanar with the double bond (within  $\pm 10^\circ$ ) (IV). A simple calculation, assuming a minimum internuclear distance of 2.4 Å for the ortho-hydrogens, shows that the free aryl ring must be twisted out of the plane of the double bond by ca.  $60^\circ$  (7). The situation with the cycloheptadiene system (II,  $n = 3$ ), is appreciably different. Here the fused rings are not planar; the ethylenic bond is deconjugated to an appreciable extent (relative to (IV)) with the fused aromatic system. The twisting of this aromatic ring out of the plane then allows the free aryl ring to become planar and conjugated with the ethylenic double bond (V) (8).



(IV)



(V)

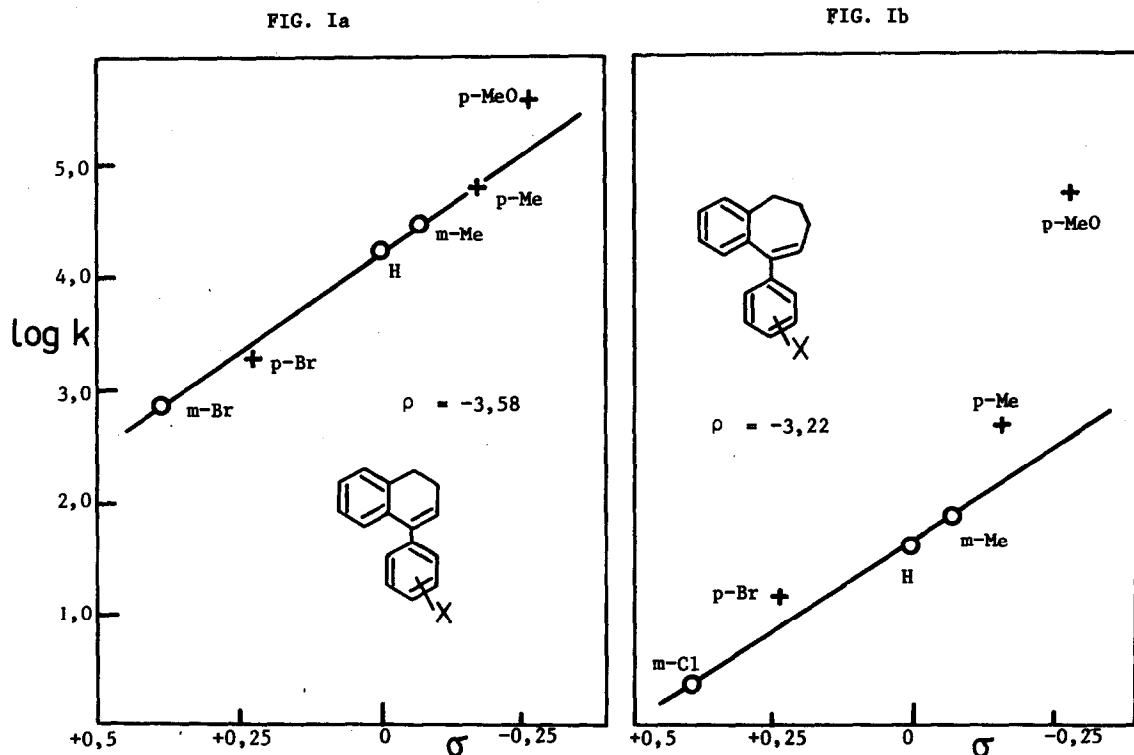


FIGURE 1. Plot of  $\log k$  for the bromination of compounds (II) when (a)  $n = 2$  and (b)  $n = 3$ , against  $\sigma$  values for X = meta- (○) and para-substituents (⊕).

From the observed differences in behaviour of (IV) and (V) in bromination, it can be concluded (assuming that the stereochemistry of the transition state is similar to that of the starting olefin) that the resonance stabilizations, large in the case of (V), small with (IV), of the carbonium ion intermediates (III) are very sensitive to the inclination of the aromatic ring relative to the vacant p-orbital of the carbonium ion. It is likely that such a stereochemical factor is important in determining the observed non-additivity of resonance effects (the so-called "saturation effect") for multiple substitution in aromatic systems (9).

With compounds (V), the  $\sigma^+$  values are not able to fully accommodate all of the observed resonance interaction. Moreover, the point for X = p-MeO lies above the line correlating the m-substituents in (IV) (Fig. 1a). This is not surprising since perfect correlations are expected only when the importance of resonance stabilization in a given reaction is exactly the same as in the defining equation. Using the more general equation of Yukawa and Tsuno (10) :

$$\log k/k_0 = \rho (\sigma + r\Delta\sigma^+)$$

we have calculated  $r = 0.184$  and  $1.383$  (with correlation coefficients of  $0.999$  ( $s = 0.0087$ ) and  $0.998$  ( $s = 0.038$ )) for the bromination of (IV) and (V) respectively. The coefficient  $r$  is a measure of the degree of resonance transmitted by a substituent in the transition state of the reaction. The  $r$  values can be related to the differences in the angles of twist,  $\theta$ , of the substituted aryl ring between the two systems (IV) and (V) as follows :

$$r = r_0 \cos^2 \theta$$

(where  $r$  and  $r_0$  are  $0.184$  and  $1.383$ ), assuming that the same relationship used for the estimation of the variation in the conjugation energy between two aryl systems twisted through an angle  $\theta$  (11), also holds here. This equation gives a  $\theta$  value of  $56^\circ$ , which is close, in spite of the approximations involved, to the value calculated above for the differences in the inclinations ( $0^\circ$  and  $60^\circ$  resp.) of the free aryl rings in (IV) and (V), relative to the ethylenic bond. It is also noted that, as pointed out by Ritchie and Sanger (6a), the magnitude of the  $r$  value does not bear any direct relation to  $\rho$ .

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