J. Chem. Soc. (B), 1969

Bromination of Cyclic Olefins. Part I. Critical Dependence of Carbonium Ion Stability on Coplanarity

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The kinetics of bromination of 3-phenylindenes (1), 1,2-dihydro-4-phenylnaphthalenes (2), and 6,7-dihydro-9-phenyl-5H-benzocycloheptenes (3) in methanol at 25° were studied. The rate constants for compounds with various substituents in the phenyl group were correlated in terms of the Hammett equation by use of a for compounds (2) and σ^+ for compounds (3). This difference in the transmission of resonance effects has been interpreted in terms of the geometries of the systems : in compounds (3) the substituted phenyl ring is coplanar with the carbonium ion intermediate, but in compounds (2) the phenyl ring rotates out of this plane. Carbonium ion stability (and therefore the σ value appropriate to a given substituent) is dependent on the amount of $p-\pi$ overlap between the carbonium ion centre and the aryl ring.

ONLY a single aromatic ring may become coplanar at any one time with a di- or tri-arylcarbonium ion (I), because of steric crowding.¹ The necessity of coplanarity for the stabilization of the carbonium ion by a given substituent in Ar, and the variation of stability with the amount of overlap between the π -orbitals of the aryl ring and the vacant p-orbital of the carbonium ion, are controversial points.² In reactions which involve the formation of ions of the type (I), the effects of multiple substituents in Ar¹ and Ar² do not show additivity, *i.e* two similar substituents do not stabilize the carbonium ion by the sum of the effects of the single substituents acting independently.³

We have therefore examined the change in electron demand (measured by the calculated Hammett o value applicable to the substituents) by such carbonium ions when the aryl ring containing the substituent is inclined to the carbonium ion at fixed and known angles; the transition state of the bromination of the cyclic olefins (II) was used as a model. Whether the

C-R C=CH (I) (II)

geometric factor alone is sufficient to account for the observed non-additivity could then be determined.⁴

RESULTS AND DISCUSSION

The rates of bromination of the cyclic olefins (II), where n = 5, 6, or 7 and the substituent X is varied,

³ See, e.g. S. Nishida, J. Org. Chem., 1967, **32**, 2692, 2695, 2697; E. Berliner and M. Q. Malter, *ibid.*, 1968, **33**, 2595.

⁴ Preliminary communication, A. F. Hegarty and J. E. Dubois, *Tetrahedron Letters*, 1968, 4839.



¹ D. Bethell and V. Gold, 'Carbonium Ions,' Academic Press,

London, 1967, p. 128. ² (a) I. I. Schuster, A. K. Colter, and R. J. Kurland, J. Amer. Chem. Soc., 1968, **90**, 4679; A. Singh, L. J. Andrews, and R. M. Keefer, *ibid.*, 1962, **84**, 1179; N. N. Lichtin and M. J. Vignale, *ibid.*, 1957, **79**, 579; (b) N. C. Deno, *Prog. Phys. Org. Chem.*, 1964, 2, 177.

are listed in Table 1. The rate constants were all measured, despite the large differences in reactivities $(1-10^{6} \text{ l. mole}^{-1} \text{ sec.}^{-1})$ under the same conditions [at 25° in methanol containing sodium bromide (0.2M)]. The effect of a given substituent X on the rate of bromin-

TABLE 1

Rate constants for the bromination of the olefins (II) in methanol containing sodium bromide (0.2M), at 25.0°

	k (l. mole ⁻¹ sec. ⁻¹)				
Х	n = 5	6	7		
<i>p</i> -MeO		340,000	60,500		
<i>ф</i> -Ме		64,500	470		
<i>m</i> -Me		29,000	$75 \cdot 2$		
Н	20,800	16,600	41.8		
<i>p</i> -Br		2200	12.5		
<i>m</i> -Br		655			
<i>m</i> -Cl			$2 \cdot 3$		

ation is widely different in compounds (II), depending on whether the substituent occupies a *meta*- or a *para*position. meta-Substituents (X = H, m-Me, m-Cl, or m-Br) have about the same rate accelerating or depressing effect on the two systems studied in detail (II; n = 6 or 7). This is best seen by expressing the constants in terms of the Hammett equation, log $k/k_0 = \rho\sigma$; when n = 6, $\rho = -3.58$ and when n = 7, $\rho = -3.22$. Thus both series have about the same sensitivity to the inductive effect of substituents X, and the same amount of charge is developed in the transition states of both reactions. On the other hand, the rate change brought about by para-substituents is markedly different in the two series. The rate constants for n = 6 are correlated with some precision (*i.e.* without a large change in the calculated ρ) by using ordinary σ values 5 (Figure 1). We conclude that the resonance



FIGURE 1 Hammett plot of $\log k/k_0$ for the bromination of the olefins (IV) against the σ constants of *para*- (\bigcirc) and *meta*- (\bigcirc) substituents X. A, *p*-MeO; B, *p*-Me; C, *m*-Me; D, H; E, *p*-Br; and F, *m*-Br. Deviations due to resonance contributions are, in all cases, small

contribution in this case (II; n = 6) to the stabilization of the transition state by substituents in the *para*position is small, akin to that of the defining equation for σ constants. In fact the *p*-methoxy-substituted compound does react a little more rapidly than ex-

⁵ D. H. McDaniel and H. C. Brown, J. Org. Chem., 1958, 23, 420.

pected from its σ value (Figure 1); this deviation will be dealt with later.

The rate constants for the bromination of the *para*substituted compound (II) when n = 7 cannot be correlated by the same line as used for the corresponding *meta*-substituents. All react a good deal faster than expected from the magnitude of their σ values (Figure 2). The data for these compounds are far better correlated by using the σ^+ values of Brown and Okamoto,⁶ which have been applied to a wide variety of electrophilic side-chain reactions involving



FIGURE 2 Hammett plot of $\log k/k_0$ for the bromination of the olefins (V) against the σ constants of *para*- (\bigcirc) and *meta*- (\bigcirc) substituents X. A, *p*-MeO; B, *p*-Me; C, *m*-Me; D, H; E, *p*-Br; and F, *m*-Cl. The large deviations shown by *para*-substituents are due to resonance stabilization of intermediate



FIGURE 3 Hammett plot of $\log k/k_0$ for the bromination of the olefins (V) against the σ^+ constants of para- (\bigcirc) and meta- (\bigcirc) substituents X. A, p-MeO; B, p-Me; C, m-Me; D, H; E, p-Br; and F, m-Cl

resonance interaction between the substituent and the reaction centre (Figure 3). However the ρ value obtained by this treatment is more negative (-3.76; cf. -3.22 calculated from data for *meta*-substituents alone), indicating that the resonance contributions of the *para*-substituents are even greater than expected from their σ^+ values. The difference between the two

⁶ H. C. Brown and Y. Okamoto, J. Amer. Chem. Soc., 1958, **80**, 4979.

systems (II; n = 6 and 7) is brought out by considering the change in log k on introduction of a p-methoxygroup (as X). When n = 6, $\Delta \log k = 1.310$ and when n = 7, $\Delta \log k = 3.160$, *i.e.* the methoxy-group increases the rate of bromination of the olefin (II; n = 7) about 60 times more than that of the olefin (II; n = 6). Most of this difference, from the definitions of σ^+ and σ , can be explained in terms of the resonance stabilization of the transition states involved in the formation of the carbonium ions (III) being greater when n = 7 than when n = 6.



This change in the response of bromination to the substituents capable of mesomeric interaction with the reaction centre can be understood in terms of the differences in the geometries of the two systems. When n = 6, the fused aromatic ring is rotated out of the plane of the ethylenic double bond by only a small angle $(ca. 10^{\circ})$. Steric hindrance then prevents the pendant aryl ring from also becoming coplanar with the double bond, as shown by Dreiding models. For an internuclear distance of 2.4 Å (calculated ^{2b} by use of the sum of the Van der Waals radii, 1.2 Å, for hydrogen) to be maintained between the ortho-hydrogens of the aryl rings, these rings must be inclined at an angle greater than 60° to one another. Consequently, the substituted ring in (IV) is rotated out of the plane of the double bond by more than 50° . Much the same situation exists with 1,1-diphenylethylene; here it has been calculated 7 that the two rings are rotated out of the plane of the double bond by a total of 60°, and this has been confirmed by u.v. spectra⁸ and MO calculations.⁹ Since the six-membered diene system in (II; n = 6) is unstrained, these calculations could also apply to this system. Substituents X in the free aryl ring therefore

act on the developing carbonium ion (III) in a situation where the ring is rotated considerably out of the plane of the ion on the assumption that the transition state has the same geometry as the starting olefin. This assumption is not unreasonable, since both have an sp^2 carbon centre.



The fused rings in the olefins (II) when n = 7 are not coplanar. In fact, the fused aromatic ring is largely out of conjugation with the double bond (V). The rotation of this ring out of the plane (calculated as greater than 45°) allows the free aryl ring to become coplanar and conjugated with a double bond while maintaining a minimum internuclear distance of 2.4 Å for the ortho-hydrogens. Thus, substituents X act from positions in which the ring is conjugated with the double bond in (V).

Assuming this picture of the geometry, and noting the differences in the kinetics of bromination of the systems, we can conclude that for maximum stabilization of the carbonium ion (III), the aryl substituents attached directly to the reactive centre must be coplanar with the carbonium ion, *i.e.* there must be maximum overlap between the π -electron system and the vacant p-orbital of the carbonium ion. When the aromatic ring is rotated through ca. 50° [as in the case of (IV)], most of this resonance stabilization is lost. It is possible, therefore, to change the σ constant of a given substituent merely by changing the inclination of the ring to which it is attached, relative to the charged reaction centre. Thus two apparently equivalent positions [say the para-positions in Ar^1 and Ar^2 in (I)] could interact differently with a positive charge merely if the inclinations of the two rings containing the substituents were different. This could be also one of the causes of ' saturation ' of electronic effects observed ¹⁰ in reactions of multiply substituted aryl systems, e.g. the solvolysis of diphenylmethyl chlorides³ and the formation of triarylcarbanions.11

It is predicted that the variation of substituents Y in the fused aromatic ring in the olefins (II) would bring about the opposite effect to that observed for the variation of X, *i.e.* σ^+ would be applicable to the bromination data when n = 6 and σ when n = 7. We have tested this in one instance (n = 6, X = H, and Y =MeO). The rate of bromination of this compound

G. E. Coates and L. E. Sutton, J. Chem. Soc., 1942, 567.

⁸ H. Suzuki, Bull. Chem. Soc. Japan, 1960, 33, 619.

⁹ G. Favini and M. Simonetta, Theor. Chim. Acta, 1963, 1, 294.

J. Hine, ' Physical Organic Chemistry,' McGraw-Hill, 1962,

p. 100. ¹¹ L. D. McKeever and R. W. Taft, J. Amer. Chem. Soc., 1966,

 $(1.67 \times 10^{6} \text{ l. mole}^{-1} \text{ sec.}^{-1})$ is far greater than that of its isomer (n = 6, X = MeO, Y = H); in fact the calculated σ value required (-0.56) to place the data on the correlation in Figure 1 is much closer to the σ^+ than to the σ constant for p-methoxy (although, admittedly, the value is somewhat smaller than expected). A second methoxy-group (II; n = 6, X = Y = MeO) now brings about a relatively small increase in rate $(k = 1.92 \times 10^6 \text{ l. mole}^{-1} \text{ sec.}^{-1})$. This observed nonadditivity of substituent effects can thus be clearly attributed to (at least) two factors. Steric inhibition of resonance ensures that X and Y acting separately do not stabilize the ion (III) to the same extent. With n = 6, the contribution of (IIIb) is negligible; thus, Y acts through both inductive and resonance effects while X only acts inductively. Moreover in the disubstituted compounds (II; n = 6, Y = MeO) much of the charge has been delocalized on to Y, resulting in X interacting with a diminished charge. The ρ value for the variation of X in these compounds (II; n = 6, Y = MeO) would therefore be smaller (less negative) than when Y = H.

Yukawa-Tsuno Equation.---As already mentioned, some residual resonance stabilization of the transition state of the bromination of (IV) remains unaccounted for by the σ values of the *para*-substituents X, while with (V) use of σ^+ values for the *para*-substituents X does not give the same p value as originally calculated from data for the meta-substituted compounds alone. The data in Table 1 were therefore treated more accurately in each case by the Yukawa-Tsuno equation,¹² which was developed to deal with those reactions in which the resonance interactions between the substituent and the reaction centre had some intermediate value, unlike that of the defining reactions for either σ or σ^+ . The equation has the form: *

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

where ρ is calculated from data for well behaved *meta*substituents and is thus free from contributions due to resonance; $\Delta \sigma^+ (= \sigma^+ - \sigma)$ is a constant which measures the resonance contribution of a given substituent; and r is a new parameter introduced as a resonance transmission coefficient, a measure of the degree of resonance involved in a given reaction. Application of this equation (by using the ρ value already calculated

for meta-substituents) gave r values of 0.184 and 1.383for compounds (IV) and (V) respectively [with correlation coefficients of 0.999 (s = 0.009) and 0.998 (s = (0.038)]. The large difference between the r values for the two series confirms that the transmission of resonance from the substituent X is very small in compound (II) when n = 6 (since r is close to zero) \dagger and large when n = 7 (compared with the defining equation, the solvolysis of $\alpha\alpha$ -dimethylbenzyl chlorides,⁶ which has r = 1).

It has been noted previously ¹⁴ that r does not seem directly related to ρ ; some reactions with quite small ρ values are better correlated with σ^+ rather than σ . However the reactions compared were often unrelated and studied under diverse conditions. The present confirmation of this idea-the study provides amount of charge developed in the transition state of the bromination of the two series (II; n = 6 and 7) is much the same (as measured by the magnitudes of the ρ values) whereas the difference between the r values is, in fact, greater than]

An estimate of the differences in planarity of the free aryl rings in (IV) and (V) can be made by use of the kinetic data as follows. The energy of conjugation, E_{i} between two aryl systems, one of which has been rotated through an angle θ , has been estimated ¹⁵ as:

$$E = E_0 \cos^2 \theta$$

This relationship, although criticised,¹⁶ has received wide support and some experimental proof.¹⁷ If the free aryl ring in (V) is now assumed to be fully conjugated with the double bond, and the resonance transmission coefficients, r, are used as a measure of E and E_0 (=0.184 and 1.383), then an angle of 68° is calculated for the deviation of the aryl ring from the planarity with the double bond in (IV). This is, in spite of the obvious approximations involved, about the same as the value $(>50^\circ)$ calculated earlier for the differences in the inclinations of the free aryl rings in (V) and (IV).

The data available are too limited to separate rigorously the field (\mathcal{F}) and resonance (\mathcal{R}) effects by the method of Lupton and Swain,^{18a} replacing σ in the Hammett equation by $f\mathcal{F} + r\mathcal{R}$. Nevertheless the same general result obtained from the Yukawa-Tsuno equation may be inferred. Thus the value of r_{ρ} (r being a resonance weighting factor in σ) is much greater (-8.58) for *para*-substituents in the bromination of

^{*} Yukawa and Tsuno have recently modified 13 the original equation, using σ^0 (which, it is claimed, is entirely free of resonance contributions) in place of σ ; this change may readily be made with our calculations, but it does not alter the results; in fact, it is difficult to choose between the two treatments.

[†] A stable conformation with the free aryl ring orthogonal to the double bond is not favoured since the ortho-hydrogens of the adjacent ring would be buried in the π -cloud of this ring. The small r value observed probably thus genuinely indicates some residual resonance, rather than being due to inaccuracy in the σ values used.

¹² Y. Yukawa and Y. Tsuno, Bull. Chem. Soc. Japan, 1959 32, 965, 971.

¹³ Y. Yukawa and Y. Tsuno, J. Chem. Soc. Japan, 1965, 86, 875.

¹⁴ C. D. Ritchie and W. F. Sager, Prog. Phys. Org. Chem., 1964, 2, 323.

¹⁵ B. M. Wepster in 'Progress in Stereochemistry,' ed. W. Klyne, and P.B.D. de la Mare, vol. 2, Butterworths, London, 1958, pp. 102, 122; E. A. Braude in ' Determination of Organic Structures by Physical Methods,' ed. E. A. Braude and F. C. Nachod, Academic Press, New York, 1955, p. 172.
¹⁶ N. L. Allinger and E. S. Jones, J. Org. Chem., 1965, 30,

^{2165.}

¹⁷ (a) R. Huisgen, G. Seidl, and I. Wimmer, Annalen, 1964, 677, 21; (b) P. B. D. de la Mare, E. A. Johnson, and J. S. Lomas, J. Chem. Soc., 1964, 5317; M. J. Kamlet, J. C. Hoffsommer, R. R. Minesinger, and H. G. Adolph, J. Org. Chem., 1968, 33, 3070.

 ¹⁸ (a) C. G. Swain and E. C. Lupton, J. Amer. Chem. Soc.,
1968, 90, 4328; (b) R. Huisgen, Angew. Chem., 1957, 69, 341;
E. A. Braude and F. Sondheimer, J. Chem. Soc., 1955, 3754.

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(II) when n = 7 than when n = 6 (-4.49); the total amount of charge at the centre (as measured by the f and r values for the *meta*-substituted compounds) is almost identical in both series.

Effect of Ring Size.—The absolute difference in the rate constants for bromination between the olefins with 6- and 7-membered fused rings (II; X = Y = H, n = 6 and 7) is very large (ca. 400). The difference between (II; n = 5) and (II; n = 6) is, however, much smaller (Table 1). A similar sharp change has been noted in the u.v. extinction coefficients of the cyclic ketones ^{17a,18b} (VI) and in the solvolysis of the chlorides ¹⁹ (VII) when n is changed from 6 to 7, relative to the change that takes place when n is varied from 5 to 6 or from 7 to 8. This has been attributed to a loss



in coplanarity of the ring system when n = 7. Baddeley and his co-workers ²⁰ have identified another factor in the solvolysis of the chlorides (VII) which contributes to the diminution of the rate constant when n = 7, namely, steric hindrance to solvation by the puckered alkyl ring. Methyl substituents in the alkyl bridge in (VII) *reduced* the rate of solvolysis, although the configuration of the chlorides (as judged by the spectra of the corresponding ketones) remained the same as in the unsubstituted compounds. The similarity in the relative magnitudes of the rate constants for the bromination of the olefins (II) and the solvolysis of the chlorides (VII) when n is varied (Table 2), in spite of the different

TABLE 2

Variation in relative rates of reaction with ring size

$$n = 7$$
 6 5
Olefins (II; X = Y = H) + Br₂ $k_{rel} = 1$ 400 500
Chlorides (VII) + EtOH $k_{rel} = 1$ 45 170

reactions and solvents involved, indicates that changes in solvation might also have a considerable influence on the order observed for the bromination reaction (rather than, say, changes in steric effects on the entry of bromine). Also in the olefins (II) when n = 5 or 6 the alkyl bridge (which acts as an *ortho*-methyl group) is so placed that it can interact mesomerically with the charged centre. However when n = 7, the group can no longer mesomerically stabilize the transition state. This second factor would also lead to an increase in the rate of bromination of the olefins (II) when n = 5 or 6 relative to n = 7.*

The rates of reaction of the open chain analogues of (II) and (VII) also show similarities. Thus, 1-phenylethyl chloride reacts at about the same rate in ethanolysis as the cyclic chloride (VII) when n = 7, whereas the rates of bromination of 1,1-diphenylpropene (VIII; $R^1 = Me, R^2 = H$) (99·4 l. mole⁻¹ sec.⁻¹) and 1-phenyl-1-(o-tolyl)ethylene (VIII; $R^1 = H, R^2 = Me$) (130 l. mole⁻¹ sec.⁻¹) are much closer to that of (II) when n = 7 than when n = 5 or 6. It therefore appears that the more rapid rate of bromination of (II) when n = 5or 6 is due rather to spatial enhancement of solvation and resonance stabilization in this case than to any unusual retardation when n = 7.

EXPERIMENTAL

Substrates.-5-Phenylvaleric acid (44 g.) was added to polyphosphoric acid (1230 g.) and the mixture was heated at 110° for 2 hr. It was left to cool overnight, then poured into cold water (1 l.) and extracted with benzene (4 imes50 ml.). The extracts were washed with 10% sodium hydroxide (2 \times 50 ml.), dried (Na₂SO₄) and evaporated. The resulting oil was distilled to give (25·2 g.) benzocyclo-heptanone, b.p. 148°/20 mm., $n_{\rm p}^{20}$ 1·5650 (lit.,²¹ b.p. 142°/9 mm., $n_{\rm p}^{20}$ 1·5653); dinitrophenylhydrazone, m.p. 208-210° (from methanol-water) (lit.,²² 210°). The cyclic olefins were all prepared in the same general manner from benzocycloheptanone; the following is a typical example. Benzocycloheptanone (5 g.) in dry benzene (60 ml.) was added to p-bromophenylmagnesium bromide (9.06 g.). The ether was distilled off and the benzene solution was refluxed for 2 hr. The adduct was decomposed with 6N-hydrochloric acid (50 ml.) and extracted with ether $(2 \times 50 \text{ ml.})$. Evaporation of the washed and dried extracts gave an oil which on distillation with a few crystals of iodine gave 6,7-dihydro-9-phenyl-5H-benzocycloheptene (5.8 g.), b.p. $182^{\circ}/15$ mm., \bar{n}_{D}^{20} 1.6232 (lit.,²¹ b.p. 174— 178°/8 mm., $n_{\rm p}^{20}$ 1.6232). The oil slowly solidified; m.p. 40° [from light petroleum (b.p. $35-60^{\circ}$)] (lit.,²² 40°). The analytical and physical data for the other cyclic olefins prepared by this route are listed in Table 3. If complete dehydration did not occur during distillation, the alcohololefin mixture (except in the case of the methoxy-substituted compound, where this treatment caused decomposition) was heated at 50° in sulphuric acid-methanol (1:1) for 1 hr. On cooling, the pure olefin precipitated or was recovered by extraction with ether.

3-Aryl-1,2-dihydronaphthalenes (II; n = 6).—These were prepared from the commercially available tetralone (or 6-methoxytetralone) and the appropriate Grignard reagents from substituted bromobenzenes by the general ²⁰ G. Baddeley, J. W. Rasburn, and R. Rose, J. Chem. Soc.,

1958, 3168. ²¹ W. Treibs and H. Klinkhammer, *Chem. Ber.*, 1950, **83**, 367.

²² H. Cristol, Y. Delhoste, and M. Mousseron, Bull. Soc. chim. France, 1959, 1238.

^{*} The ratio of the rate constants, $k_{n=6}$: $k_{n=7}$, can, however, be varied merely by changing the substituent X, *e.g.*, the ratio is only 6 for the bromination of olefins (II; Y = H, X = p-MeO).

¹⁹ G. Baddeley and J. Chadwick, *J. Chem. Soc.*, 1951, 368; R. Huisgen, I. Ugi, and E. Mergenthaler, *Annalen*, 1954, **586**, 1.

Analytical and physical data for 9-aryl-6,7-dihydro-5H-benzocycloheptenes (II; n = 7, Y = H)

	B.p. (mm.)	Found (%)				Required (%)			
х	or m.p.	С	н	Hal.	Formula	С	н	Hal.	
p-MeO	61°	85.8	7.35		$C_{18}H_{18}O$	86·4	$7 \cdot 2$		
p-Me	67	92.25	7.8		$C_{18}H_{18}$	92.3	7.7		
m-Me	154 (1.5)	91.4	8∙4		$C_{18}H_{18}$	92.3	7.7		
Н	40	92.75	$7 \cdot 2$		$C_{17}H_{16}$	92.7	$7 \cdot 3$		
p-Br	85	67.9	$5 \cdot 2$	26.6	C ₁₇ H ₁₅ Br	68.2	5.1	26.7	
m-Cl	156 (1.5)	79.8	$5 \cdot 4$	14.4	C ₁₇ H ₁₅ Cl	80.2	5.05	13.9	

TABLE 4

Analytical and physical data for the 3-aryl-1,2-dihydronaphthalenes (II; n = 6)

		B.p. (mm.)	For	ind (%)		Requ	ired	(%)	
х	Y	or m.p.	С	н	Br	Formula	С	\mathbf{H}	Br	
p-MeO	Н	61.5°	$85 \cdot 6$	$7 \cdot 1$		C17H16O	86.4	6.8		
p-Me	н	178 (8)	92.7	$7 \cdot 2$		$C_{17}H_{16}$	92.7	$7 \cdot 3$		
m-Me	н	174 (7)	92.7	$7 \cdot 4$		$C_{17}H_{16}$	92.7	$7 \cdot 2$		
н	н	162 (6)	93.6	6.8		$C_{16}H_{14}$	93.3	6.8		
p-Br	н	210(6)	$66 \cdot 8$	$5 \cdot 2$	27.0	$C_{16}H_{13}Br$	67.0	4 ∙6	28.0	
m-Br	н	205(7)	67.5	$4 \cdot 5$	27.7	$C_{16}H_{13}Br$	67.0	4 ·6	28.0	
H	MeO	73	85.5	7.1		$C_{17}H_{16}O$	86.4	6.8		
p-MeO	MeO	101	80.8	$6 \cdot 9$		$C_{18}H_{18}O_2$	81.2	6.7		

methods already described. Their analytical and physical data are listed in Table 4. 3-Phenylindene (II; X = Y = H, n = 5), b.p. 158°/7 mm. (Found: C, 93.45; H, 6.6. C₁₅H₁₂ requires C, 93.7; H, 6.3%), was similarly prepared from equimolar quantities of indan-1-one and phenylmagnesium bromide.

1-Phenyl-1-(o-tolyl)ethylene was prepared by the reaction of equimolar quantities of o-methylacetophenone and phenylmagnesium bromide. The adduct was refluxed for 4 hr. in dry toluene (after removal of the ether) and decomposed in the usual way. Distillation (twice, once over iodine) gave the *ethylene* (65%), b.p. 132—134°/8 mm. (Found: C, 92·5; H, 6·7. $C_{15}H_{14}$ requires C, 92·7; H, 7·2%). 1,1-*Diphenylpropene* was similarly prepared by the reaction of benzophenone with ethylmagnesium iodide and had m.p. 50° (from ethanol) (Found: C, 92·9; H, 7·1. $C_{15}H_{14}$ requires C, 92·7; H, 7·2%).

The olefins were purified, shortly before a kinetic run, by g.l.c. on an SE-30 column (10 ft.) at 180° with an Aerograph A-700 Autoprep. Their purity was verified by use of an SE-30 column (5 ft.) with an Aerograph Hy-FI Model 600-c Chromatograph (min. 99.5% purity in all cases). Although the olefins underwent aerobic oxidation slowly, they could be stored without significant decomposition in sealed ampoules.

²⁴ J. E. Dubois and E. Goetz, *Tetrahedron Letters*, 1965, 303.
²⁵ J. E. Dubois and G. Mouvier, *Compt. rend.*, 1962, **155**, 1104.

Kinetic Measurements.-The rates of bromination of the olefins were measured at $25 \pm 0.1^{\circ}$ in methanol containing sodium bromide (0.2M) by three general methods, all of which have previously been described. Each kinetic experiment was repeated a minimum of five times; the reproducibility of the rate constants was better than $\pm 3\%$. Precision was maintained by calibrating the apparatus from time to time with compounds whose rate of bromination has been well established, *i.e.* cyclohexene ²³ and allyl alcohol.24 The solvent methanol was reagent grade, treated as follows. Bromine (3-4 drops per l.) was added and the mixture was left overnight; the methanol was then fractionated and the middle portion (ca. 50% of total) was retained. The distillate was similarly treated and redistilled; a final distillation from potassium carbonate removed small traces of hydrogen bromide. The methanol thus obtained contained <0.05% water (Karl-Fischer) and did not react significantly with bromine. No correction had to be made for the reaction of the solvent with bromine, since the reaction times were short and the solvent was allowed to stand in contact with bromine (usually for 30 min.) before a kinetic run.

Generally, for those compounds with rate constants in the region 50-10⁵ l. mole⁻¹ sec.⁻¹, the coulometric concentrostat was used. This apparatus, developed by Dubois and his co-workers,²⁵ maintains a constant low bromine concentration (ca. $10^{-6}M$) in the reaction solution. The bromine which reacts with the olefin is replenished by electrolysis of the sodium bromide solution. The integrated electrolysis current is a measure of the bromine (or olefin) consumed at a given time; the constant bromine concentration was estimated at the end of a kinetic run by amperometric titration. Measurements at several initial concentrations of bromine and of the olefin established that the reaction is simple second-order in all cases. Since the bromine concentration is held constant throughout, the reaction becomes pseudo first-order (and thus independent of the initial concentration of olefin). This eliminates any error involved in measuring the small quantity of olefin used or due to the presence of unreactive impurities. For those compounds which reacted more slowly with bromine (k < 50), the potentiometric method of Bell and his coworkers 26 was used; both methods were used for each compound in the region 10-100 l. mole⁻¹ sec.⁻¹. 6,7-Dihydro-9-(p-methoxyphenyl)-5H-benzocycloheptene had a rate constant (3×10^5) near the upper limit for the concentrostatic method. Its rate constant was therefore also measured by an amperometric method,²⁷ as were the rate constants of those compounds which were brominated more rapidly.

[8/1686 Received, November 19th, 1968]

²⁶ R. P. Bell and D. Dolman, J. Chem. Soc. (B), 1968, 500.

²⁷ J. E. Dubois, P. Alcais, and G. Barbier, *J. Electroanalyt. Chem.*, 1964, **8**, 359.

²³ J. E. Dubois, M. Ropars, and P. Fresnet, J. chim. Phys., 1965, **62**, 856.