Nitration of Toluene, t-Butylbenzene, and 4-Substituted 1-Phenylbicyclo[2.2.2]octanes with Nitric Acid–Acetic Anhydride. Evidence for a π-Inductive Effect

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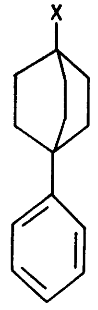
The nitration of toluene, t-butylbenzene, and 1-phenyl-4-X-bicyclo[2.2.2]octanes (X = H, Me, Et, Pr^i, OMe, CO_2Me, Br, Cl, F, CN, or NO_2) in acetic anhydride with fuming nitric acid–acetic anhydride at 25.0 °C has been studied, and the percentages of the mononitro-products formed and values of the partial rate factors (*f*) have been determined. The log *f* values for each position are successfully correlated with σ_I values. The substituent effects on positions in the benzene ring decrease from the *ortho*- to the *para*- to the *meta*-position: this order is compatible with the operation of a π-inductive effect.

DERIVATIVES of saturated alicyclic systems have frequently been used to study the effect of a substituent (X) on a reaction site (Y). For example, investigations of polar and solvent effects have been based on 4-X-1-Y-bicyclo[2.2.2]octanes,[1-7] 4-X-1-Y-cubanes,[8,9] 3-X-1-Y-adamantanes,[10] and *trans*-4-X-1-Y-cyclohexanes.[11]

The 1,4-disubstituted bicyclo[2.2.2]octanes and cubanes are particularly useful because (a) the distance between the substituent and the reaction site is constant, (b) the dipole of a 4-substituent lies on the major axis or ' diagonal ' of the ring system, (c) mesomeric effects involving conjugative unsaturation are absent, (d) the reaction site experiences a steric effect, arising from the bulk of the cyclic system, which is independent of X.

Although electrophilic substitutions, and particularly nitration, of benzene and its derivatives have been much studied,[12-18] we believe that substituent effects in nitration have not been studied by using any of the alicyclic systems mentioned above. In this paper we report an investigation of the nitration of 1-phenyl-4-X-bicyclo[2.2.2]octanes (1) with the intention of investigating the non-conjugative polar effect of substituents on the *ortho*-, *meta*-, and *para*-positions of the benzene ring when the steric effect at each position is constant and independent of the substituent.

The percentages of the nitro-compounds formed on mononitration of toluene, t-butylbenzene, and 1-phenyl-4-X-bicyclo[2.2.2]octanes with fuming nitric acid (*d* 1.5) in acetic anhydride at 25.0 °C are given in Table 1; the results of competitive nitrations are given in Table 2 and the partial rate factors calculated from these results in Table 1. It is difficult to study competitive nitrations by using g.l.c. when the substrates or nitro-products (see below for calculation of results) have very dissimilar retention times and so the relative reactivities of 1-phenyl-4-X-bicyclo[2.2.2]octanes and benzene were determined indirectly by competitive nitrations involving toluene and t-butylbenzene.



(1)

a, X = H
b, X = Me
c, X = Et
d, X = Pr^i
e, X = OMe
f, X = CO_2Me
g, X = Br
h, X = Cl
i, X = F
j, X = CN
k, X = NO_2

The mechanism of aromatic nitration with nitric acid in acetic anhydride has been extensively dis-

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cussed.[12,13,19-22] When the anhydride is in excess over the nitric acid (as in this work) acetyl nitrate and acetic acid are the only components of the solution, whereas with greater concentrations of nitric acid, dinitrogen pentaoxide is also present. In two competitive nitrations (toluene competing with benzene and 1-phenylbicyclo[2.2.2]octane with t-butylbenzene) fuming nitric acid was added to the substrates dissolved in acetic anhydride. In each case the relative rate coefficients were less than when pre-mixed fuming nitric acid–acetic anhydride was used as the nitrating agent (see Table 2) and the lower values of the relative rate coefficients are probably indicative of nitration partly by dinitrogen pentaoxide.[12]

TABLE 1

Nitration of toluene, t-butylbenzene, and 1-phenyl-4-X-bicyclo[2.2.2]octanes in nitric acid–acetic anhydride at 25.0 °C

Compound or substituent X	σ_I[24]	Isomer distributions (%)			Partial rate factors f, $\log f$, $\Delta\log f$ [e]									$k_{comp}/k_{C_6H_6}$	$(1 + \log k_X/k_H$
					ortho			*meta*			*para*				
		ortho	*meta*	*para*	f_o	$\log f_o$	$\Delta\log f_o$	f_m	$\log f_m$	$\Delta\log f_m$	f_p	$\log f_p$	$\Delta\log f_p$		
CH_3Ph		63.0 *c*	2.3 *b*	34.7 *b*	50.3	1.701		1.84	0.264		55.4	1.743		26.6	
Bu^{t}Ph		10.6 *b*	10.7 *b*	78.7 *b*	4.57	0.660		4.62	0.664		67.9	1.832		14.4	
H	0.0	13.8 *b*	8.7 *c*	77.5 *c*	10.9	1.039	0.000	6.87	0.837	0.000	123	2.090	0.000	26.5	1.0
Me	−0.05	14.5 *a*	8.9 *a*	76.6 *b*	11.5	1.062	0.023	7.02	0.846	0.009	122	2.085	−0.005	26.5	1.0
Et	−0.05	16.4 *b*	8.8 *c*	74.8 *b*	13.0	1.115	0.076	7.01	0.846	0.009	119	2.074	−0.016	26.5	1.0
Pr^i	−0.06	14.4 *b*	8.6 *b*	77.0 *b*	11.4	1.058	0.019	6.85	0.836	−0.001	122	2.087	−0.003	26.5	1.0
OMe	0.25	11.9 *b*	10.1 *b*	78.0 *c*	4.84	0.685	−0.354	4.12	0.615	−0.222	63.5	1.803	−0.287	13.6	0.7100
CO_2Me	0.30	12.4 *c*	10.1 *c*	77.5 *c*	4.91	0.691	−0.348	4.01	0.603	−0.234	61.5	1.789	−0.301	13.2	0.6990
Br	0.45	10.5 *b*	10.7 *b*	78.8 *b*	2.46	0.391	−0.648	2.52	0.402	−0.435	37.1	1.569	−0.521	7.84	0.4719
Cl	0.47	11.9 *a*	11.2 *b*	76.9 *b*	2.92	0.465	−0.574	2.76	0.441	−0.396	37.8	1.578	−0.512	8.19	0.4914
F	0.52	12.0 *b*	10.7 *b*	77.3 *c*	3.16	0.499	−0.540	2.82	0.450	−0.387	40.6	1.608	−0.482	8.75	0.5197
CN	0.56	11.4 *b*	11.0 *b*	77.6 *b*	2.02	0.306	−0.733	1.96	0.291	−0.546	27.6	1.441	−0.649	5.92	0.3500
NO_2	0.63	11.8 *b*	11.1 *c*	77.1 *d*	1.81	0.257	−0.782	1.69	0.227	−0.610	23.5	1.372	−0.718	5.08	0.2837

[a] ±0.1%. [b] ±0.2%. [c] ±0.3%. [d] ±0.4%. [e] $\Delta\log f = \log f_X - \log f_H$.

TABLE 2

Competitive nitrations of toluene, t-butylbenzene, and 1-phenyl-4-X-bicyclo[2.2.2]octanes in nitric acid-acetic anhydride at 25.0 °C

	Substrate 1	Substrate 2	k_1/k_2
1	CH_3Ph	PhH	26.6 ± 0.8 [h] (7.5 ± 0.5) [f,h]
2	CH_3Ph	Bu^{t}Ph	1.85 ± 0.10 [h]
3	(1a)	Bu^{t}Ph	1.84 ± 0.15 [h] (1.55 ± 0.13) [f,h]
4	(1a)	(1b)	1.00 [e,g]
5	(1a)	(1c)	1.00 [e,g,h]
6	(1a)	(1d)	1.00 [e,h]
7	(1a)	(1e)	1.95 ± 0.10 [h]
8	(1a)	(1f)	2.00 ± 0.10 [h]
9	(1a)	(1g)	3.37 ± 0.15 [g,h]
10	(1a)	(1h)	3.12 ± 0.15 [a,g,h] 3.34 [b]
11	(1a)	(1i)	3.02 [d]
12	(1a)	(1j)	4.47 ± 0.20 [g,h]
13	(1a)	(1k)	5.15 ± 0.15 [a,g] 5.25 [c]
14	(1h)	(1g)	1.01 ± 0.10 [g,h]
15	(1i)	(1g)	1.12 ± 0.10 [g]
16	(1g)	(1k)	1.56 ± 0.10 [g]

[a] Direct determination. [b] Calculated from cases 9 and 14. [c] Calculated from cases 9 and 16. [d] Calculated from cases 9 and 15. [e] Within experimental error. [f] On adding fuming HNO_3 as nitrating agent. [g] Calculated by using equation (2). [h] Calculated by using equation (3).

In Table 3 the values of k(toluene)/k(benzene) and k(t-butylbenzene)/k(benzene), the percentages of nitro-isomers for the nitration of toluene and t-butylbenzene, and their partial rate factors are compared with values from other investigations. The present work confirms that f_m and f_p values for t-butylbenzene are greater than those for toluene and therefore the σ-inductive effect and/or the field effect operates, possibly in conjunction with carbon–carbon and carbon–hydrogen hyperconjugation.[23]

The correlation of the relative rate coefficients of nitration of 1-phenyl-4-X-bicyclo[2.2.2]octanes with the σ_I values [24] for the substituents can be tested in several ways (see Table 4). The logarithm of the total rate coefficient of each substrate relative to the unsubstituted compound (X = H) can be correlated with σ_I values (item 1) or the log f values for each position can be correlated separately with σ_I (items 2—4). These correlations have been repeated omitting the values for the ethyl and isopropyl substituents to determine whether or not inclusion of the data for three alkyl substituents biases the correlation unduly. The correlations are always satisfactory and almost equally successful showing that the electronic effects which operate are inductive in nature, although the halogen substituents are exceptional in causing an increase in reactivity with an increase in σ_I value. The alkyl substituents do not appear to act as electron donors except, possibly, to the *ortho*-position. However, the magnitude of the effects is small and it has been noted that a methyl group does not always act as an electron donor.[3]

The similar success of the correlations in items 2—4 suggests that changing the substituent does not alter the steric environment at the *ortho*-, *meta*-, or *para*-positions. The values of the slopes in these correlations will be discussed later.

Exner and his co-workers have in recent years studied

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[24] O. Exner in 'Advances in Linear Free Energy Relationships,' eds. N. B. Chapman and J. Shorter, Plenum, 1972, Table 1.4, p. 37.

substituent effects in benzene derivatives quantitatively.[25-29] They considered substituents and reaction centres which do not carry a lone pair of electrons at the α-position and found that the electronic effect of the substituent is transmitted more effectively to the *para*- than to the *meta*-position as indicated by a value of λ greater than unity in equation (1) [27] where the *k* values

$$(\log k_p - \log k^\circ) = \lambda(\log k_m - \log k^\circ) \qquad (1)$$

represent rate or equilibrium constants. From dissociation constants of benzoic acids,[25,27-29] from reactions of these acids with diazodiphenylmethane,[25,26] and from the solvolysis of t-cumyl chlorides,[25] the values of λ lie within the range 1.13—1.17.

TABLE 3

Nitration of toluene and of t-butylbenzene in acetic anhydride

	$k_X/k_{benzene}$	*o* (%)	*m* (%)	*p* (%)	f_o	f_m	f_p
X = Toluene							
$AcONO_2$–Ac_2O; 25 °C [a]	26.6	63.0	2.3	34.7	50.3	1.84	55.4
$AcONO_2$–Ac_2O: 30 °C [b]	23	58.4	4.4	37.2	40	3.0	51
$AcONO_2$–Ac_2O; 0 °C [b]	27	58.1	3.7	38.2	47	3.0	62
$AcONO_2$–Ac_2O; 25 °C [c]	23	63.3	2.8	33.9	46.5	2.1	48.5
$AcONO_2$; 0 °C [d]	27	61.4	1.6	37.0	49.7	1.3	60.0
$AcONO_2$; 25 °C [e]	25.2	56.1	2.5	41.4	42.4	1.89	62.6
X = t-Butylbenzene							
$AcONO_2$–Ac_2O; 25 °C [a]	14.4	10.6	10.7	78.7	4.57	4.62	67.9
$AcONO_2$–Ac_2O; 25 °C [c]	11.5	10.3	10.3	79.4	3.8	3.8	57.7
$AcONO_2$; 0 °C [d]	15.1	10.0	6.8	83.2	4.5	3.0	75.5

[a] This work. [b] C. K. Ingold, A. Lapworth, E. Rothstein, and D. Ward, *J. Chem. Soc.*, 1931, 1959. [c] L. M. Stock, *J. Org. Chem.*, 1961, **26**, 4120. [d] J. R. Knowles, R. O. C. Norman, and G. K. Radda, *J. Chem. Soc.*, 1960, 4885. [e] J. R. Knowles and R. O. C. Norman, *J. Chem. Soc.*, 1961, 2938.

TABLE 4

Least-squares analyses of data in Table 1

Analysis no.	No. of data sets	*y*	*x*	Slope (error)	Intercept (error)	Correlation coefficient
1	11	$(1 + \log k_X/k_H)$	σ_I	−1.02(0.05)	0.964(0.018)	0.990
2	11	$\log f_o$	σ_I	−1.20(0.06)	1.018(0.023)	0.988
3	11	$\log f_m$	σ_I	−0.85(0.05)	0.815(0.019)	0.985
4	11	$\log f_p$	σ_I	−1.01(0.05)	2.050(0.019)	0.989
5	11	$\Delta \log f_o$	$\Delta \log f_m$	1.40(0.05)	0.01(0.02)	0.993
6	11	$\Delta \log f_o$	$\Delta \log f_p$	1.18(0.04)	0.03(0.02)	0.994
7	11	$\Delta \log f_p$	$\Delta \log f_m$	1.18(0.02)	−0.02(0.01)	0.999

Assuming that the mesomeric effects of the substituents considered by Exner are negligible, the value of λ represents the relative intensity of the inductive effect in the *para*- and *meta*-positions and has been explained [29] in terms of the π-inductive effect, although other workers dispute the existence of such an effect.[1,30] In these simple derivatives of benzene, the transmission of the electronic effect of the substituent could be considered only for *meta*- and *para*-positions because of the difficulty of separating polar from steric effects for the *ortho*-position. However, in 1-phenyl-4-X-bicyclo[2.2.2]-octanes the substituent cannot exert a mesomeric effect and, since changing the substituent does not alter the steric effect experienced at positions in the benzene ring, it is possible to estimate quantitatively the extent of transmission of an inductive effect to *ortho*-, *meta*-, and *para*-positions.

Some of the comparisons that can be made by correlating the Δlog *f* values at one position with those at another, and the results of these correlations, are given in Table 4 and a plot of $\log f_p$ against $\log f_m$ is displayed in the Figure. The lines for each analysis (5—7) have not been forced through the origin but, as shown by the value of the intercept and the error in the intercept, they pass through a point extremely close to the origin. All the lines 5—7 have slopes greater than unity and this indicates that the substituent influences the *ortho*- more than the *para*-, and the *para*- more than the *meta*-position; * the substituent effect is transmitted (a) to the *ortho*- more effectively than to the *para*-position in the ratio λ(*o* : *p*) = 1.18, (b) to the *para*- more effectively than to the *meta*-position in the ratio λ(*p* : *m*) = 1.18, and (c) to the *ortho*- more effectively than to the *meta*-position in the ratio λ(*o* : *m*) = 1.40. An alternative, but essentially similar, approach for determination of the λ values can be made by considering the slopes of the lines correlating log *f* values with σ_I (see Table 4). The slope of each line is a measure of the susceptibility of the reaction at the position being considered to the influence of substituents and therefore λ(*o* : *m*) could be expressed

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* The same conclusion can be reached by considering the variation of the *o* : *p*-, the *m* : *p*-, and the *o* : *m*-ratios with increasing electron withdrawal in the 1-phenyl-4-X-bicyclo[2.2.2]-octanes. The ratios decrease, increase, and decrease respectively indicating that the substituents affect the *ortho*- more than the *para*-, and the *para*- more than the *meta*-position.

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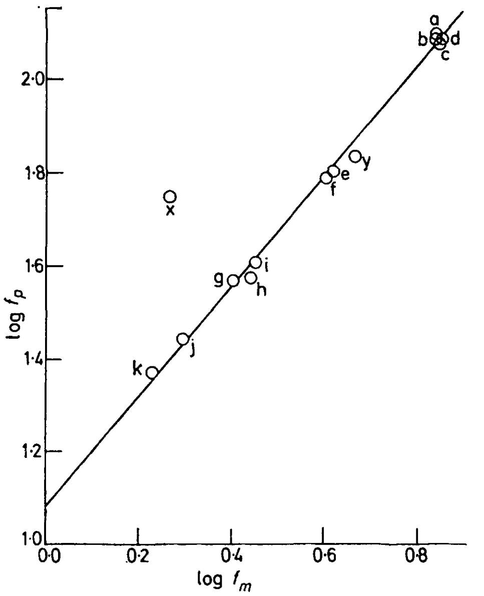
as the ratio of the slopes for case 2 and 3. In this way we find $\lambda(o:m) = 1.41$, $\lambda(o:p) = 1.19$, and $\lambda(p:m) = 1.19$. The $\lambda(p:m)$ value of 1.18—1.19 agrees quite well with Exner's λ values mentioned above (which range from 1.13 to 1.17) and with his most recently quoted value of 1.13 ± 0.03.

Taken separately the $\lambda(o:m)$ or $\lambda(o:p)$ values could be explained on the basis of σ-inductive or field effects. However, the former value is greater [as a consequence of $\lambda(p:m)$ being greater than unity] and any rationalisation of the two values requires the operation of an effect which transmits part of the substituent effect at the *ortho*-position more effectively to the *para*- than to the *meta*-position.



Correlation of log f_p with log f_m for nitration of 1-phenyl-4-X-bicyclo[2.2.2]octanes (1a—k) using the data in Table 1. The points for toluene (x) and t-butylbenzene (y) are also shown

In explaining his results Exner [27] considered that a π-inductive effect [31,32] operates in conjunction with a σ-inductive effect and he rejected an electrostatic (field) effect because the dipole of each substituent is at a different distance from and is differently orientated towards the reaction site. In the present work, since the substituents are more distant from the reaction sites and since the dipoles are directed along the major axis of the bicyclo[2.2.2]octane system the difference in orientation of the dipoles with respect to the reaction sites would result in a field effect qualitatively similar to a σ-inductive effect. For this reason we do not reject the operation of a direct field effect [7,9,33] but conclude that a π-inductive effect is simultaneously operating with a σ-inductive and/or a field effect. Indeed there is evidence to suggest that the field effect may be more important than the σ-inductive effect in these systems.[7] Both the σ-inductive and the field effect will decrease from *ortho*- to *meta*- to *para*-position and the π-inductive effect will affect the *para*- more than the *meta*-position; the superimposition of these effects would give the observed order.

Aromatic nitration is mechanistically very different from the side-chain reactions considered by Exner and the value of $\lambda(p:m)$ from this work may only by coincidence be in reasonable agreement with Exner's λ value. We concede that by using the bicyclo[2.2.2]octane system to achieve a constant steric effect at the reaction sites we have attenuated the electronic effects of the substituents and, clearly, it would be of interest to study other aromatic substitutions which yield significant percentages of *ortho*-, *meta*-, and *para*-products and which are more sensitive to substituent effects.

In quantitative studies of substituent effects in benzene derivatives it is usually assumed that the difference in the influence of a substituent on the *para*- and *meta*-position is a measure of the mesomeric effect of the substituent and that its inductive effect is transmitted equally to the two positions. The implications of an effect being transmitted more effectively to the *para*- than to the *meta*-position has been discussed by Exner [27,29] and we shall not elaborate the consequences here.

Recently Ridd and his co-workers [18] have assessed the results of nitration of compounds of the type $Ph[CH_2]_nX^+$ in aqueous sulphuric acid at 25 °C and they have obtained a satisfactory correlation between the partial rate factors and σ_R^0 by taking a value of $\lambda(p:m)$ of 1.17. This value is very close to Exner's values and Ridd and his co-workers suggest that although this agreement may be accidental, the non-conjugative interaction of the substituent deactivates the *para*- more than the *meta*-position.

Ketcham and his co-workers [34] studied the nitration of phenylcyclopropane and isopropylbenzene under various conditions and attributed the former compound's higher $o:p$-ratio partially to less steric hindrance at the *ortho*-position because of the β-carbon atoms of the substituent being held back in a ring system. We find that 1-phenylbicyclo[2.2.2]octane is more reactive than t-butylbenzene at all positions in the benzene ring (see partial rate factors in Table 1) and the bicyclo[2.2.2]octyl substituent is therefore more effectively electron releasing than the t-butyl group.[35]

It is interesting that the log f_p and log f_m values for t-butylbenzene give a point close to the correlation line shown in the Figure, possibly indicating that the t-butyl substituent influences the *para*- more than the *meta*-position in approximately the same ratio as for the 1-phenyl-4-X-bicyclo[2.2.2]octanes. It is impossible to test whether or not the log f values for t-butylbenzene

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fit the correlation lines for reactions at the *ortho*-positions because the steric environment is different for *ortho*-positions in t-butylbenzene from that in 1-phenyl-4-X-bicyclo[2.2.2]octanes. It is possible, however, to use the log f_m and log f_p values for t-butylbenzene and, assuming conformity to the correlation lines for the plots of log f_o against log f_m and of log f_o against log f_p for 1-phenylbicyclo[2.2.2]octanes, to calculate what would be the log f_o value for t-butylbenzene if its *ortho*-position were as hindered as the *ortho*-position in 1-phenyl-4-X-bicyclo[2.2.2]octanes. In this way 'f_o' for t-butylbenzene is predicted to be 5.8 or 6.3 (not unreasonable agreement) and the reduction of these values to the observed value of 4.57 is an indication of the extra steric hindrance at the *ortho*-position in t-butylbenzene.

The log f_m and log f_p values for toluene do not fit the correlation line shown in the Figure because either the f_m value is too small or the f_p value is too large. If the latter is true, this may indicate the operation of an enhanced resonance effect in toluene [36] relative to t-butyl benzene and the 1-phenyl-4-X-bicyclo[2.2.2]octanes.

EXPERIMENTAL

I.r. spectra were recorded by using a Perkin-Elmer 457 spectrophotometer. N.m.r. spectra were recorded at 100 MHz with a JEOL 4H-100 spectrometer, with tetramethylsilane as internal standard and $CDCl_3$ as solvent.

Materials.—Benzene, toluene, t-butylbenzene, undecane, decane, *m*-dinitrobenzene, 2,4-dinitrotoluene, *o*-, *m*-, and *p*-nitrotoluene, and nitrobenzene were all commercially available and were purified either by fractional distillation or by crystallisation; the m.p.s or b.p.s were identical or similar to literature values and they all gave single peaks on analyses by g.l.c. 1-Phenyl-4-X-bicyclo[2.2.2]octanes (1a—g and j), *o*-, *m*-, and *p*-t-butylnitrobenzene, 1-(*o*-, *m*-, and *p*-nitrophenyl)bicyclo[2.2.2]octane, and 1-(*p*-nitrophenyl)-4-X-bicyclo[2.2.2]octanes (X = Et, Pr^i, OMe, CO_2Me, Br, or CN) were prepared and purified as described in ref. 37.

1-*Chloro*-4-*phenylbicyclo*[2.2.2]*octane* (1h) was prepared from 1-hydroxy-4-phenylbicyclo[2.2.2]octane [37] by treatment with Lucas's reagent ($ZnCl_2$–HCl). Compound (1h) [from light petroleum (b.p. 60—80°)–ethanol (1 : 1)] had m.p. 90—91 °C; $\nu_{max.}$ (KCl) 983, 882, 761, 697, and 538 cm^{-1}; δ 1.87—2.31 (12 H, m) and 7.12—7.32 (5 H, m) (Found: C, 76.4; H, 7.9; Cl, 15.9. $C_{14}H_{17}Cl$ requires C, 76.2; H, 7.7; Cl, 16.1%).

1-Fluoro-4-phenylbicyclo[2.2.2]octane (1i) was prepared from 1-bromo-4-phenylbicyclo[2.2.2]octane [37] by using a modification of the procedure described in ref. 38 for the preparation of 1-fluoroadamantane. Compound (1i) [from light petroleum (b.p. 60—80°)–ethanol (1 : 1)] had m.p. 132—133 °C (lit.,[39] 132—133°); $\nu_{max.}$ (KCl) 1 061, 1 038, 945, 761, 698, and 539 cm^{-1} (Found: C, 82.6; H, 8.2. Calc. for $C_{14}H_{17}F$: C, 82.3; H, 8.4%).

1-*Nitro*-4-*phenylbicyclo*[2.2.2]*octane* (1k) was prepared from 1-amino-4-phenylbicyclo[2.2.2]octane [40] by using a modification of the procedure described in ref. 41 for the preparation of 4-nitro-2,2,4-trimethylpentane. Compound (1k) (46%) (from ethanol) had m.p. 108—109.5 °C; $\nu_{max.}$ (KCl) 1 530, 1 498, 1 369, 804, 764, and 698 cm^{-1}; δ 1.92—2.42 (12 H, m) and 7.12—7.34 (5 H, m) (Found: C, 72.4; H, 7.4; N, 6.2. $C_{14}H_{17}NO_2$ requires C, 72.7; H, 7.4; N, 6.1%).

1-*Iodo*-4-*phenylbicyclo*[2.2.2]*octane* was prepared from 1-hydroxy-4-phenylbicyclo[2.2.2]octane [37] by treatment with hydriodic acid (47%) at 100 °C for 2 h; the product (73%) (from aqueous methanol) had m.p. 126—127 °C; $\nu_{max.}$ (KCl) 1 497, 969, 762, 704, 698, and 538 cm^{-1}; δ 1.85—2.14 (6 H, m), 2.44—2.74 (6 H, m), and 7.12—7.37 (5 H, m) (Found: C, 53.6; H, 5.7. $C_{14}H_{17}I$ requires C, 53.9; H, 5.5%). Nitration of this compound gave a dark solution and variable values from competitive nitrations; the iodine atom is possibly lost by oxidative solvolysis.

The following 1-X-4-*p*-nitrophenylbicyclo[2.2.2]octanes were prepared by the procedure reported in ref. 37 and recrystallised three times from ethanol: 1-*chloro*-4-p-*nitrophenylbicyclo*[2.2.2]*octane* (46%), m.p. 128—130 °C; $\nu_{max.}$ (KCl) 1 594, 1 515, 1 349, 981, and 849 cm^{-1}; δ 1.89—2.33 (12 H, m), 7.43 (2 H, d), and 8.13 (2 H, d) (Found: C, 63.6; H, 6.3; Cl, 13.5; N, 5.2. $C_{14}H_{16}ClNO_2$ requires C, 63.3; H, 6.1; Cl, 13.3; N, 5.3%); 1-*fluoro*-4-p-*nitrophenylbicyclo*[2.2.2]*octane* (37%), m.p. 123—125 °C; $\nu_{max.}$ (KCl) 1 513, 1 349, 1 057, 848, 754, and 695 cm^{-1}; δ 1.94—2.12 (12 H, m), 7.43 (2 H, d), and 8.12 (2 H, d) (Found: C, 67.7; H, 6.5; N, 5.7. $C_{14}H_{16}FNO_2$ requires C, 67.4; H, 6.5; N, 5.6%); 1-*nitro*-4-p-*nitrophenylbicyclo*[2.2.2]*octane* (57%), m.p. 167—169.5 °C; $\nu_{max.}$ (KCl) 1 530, 1 512, 1 455, 1 368, 1 348, 1 327, and 850 cm^{-1}; δ 1.95—2.45 (12 H, m), 7.48 (2 H, d), and 8.18 (2 H, d) (Found: C, 61.2; H, 5.9; N, 10.0. $C_{14}H_{16}N_2O_4$ requires C, 60.9; H, 5.8; N, 10.1%).

Fuming nitric acid (*d* 1.5) was B.D.H. AnalaR grade. Acetic anhydride (1.5 l) was heated under reflux for 3 h with calcium carbide (100 g) and was then fractionally distilled through a Vigreux column (60 × 2.5 cm). A middle fraction (0.5 l) of b.p. 139.5—140 °C was used.

Apparatus.—G.l.c. analyses were carried out by using a Perkin-Elmer F11 gas–liquid chromatograph [with a flame-ionisation detector and fitted with a glass column (2.0 m × 3 mm i.d.) packed with 20% silicone gum rubber (SE-301) on Chromosorb W (60—80 mesh)], a Leeds and Northrup type W recorder (model S, 0—2.5 mV), and a Honeywell precision integrator and linear amplifier.

Nitrations were carried out at 25.0 ± 0.1 °C in a 5 or 10 ml two-necked flask fitted with a mercury-sealed stirrer and a calcium chloride guard tube. Compounds were weighed (to 10^{-5} g) in the flask used for nitration and the nitrating agent was added to the substrates dissolved in acetic anhydride by using an Agla micrometer syringe.

G.l.c. Standards.—Decane, undecane, *p*-nitrotoluene, or 2,4-dinitrotoluene were used as g.l.c. standards for the competitive nitrations as they were inert towards the reaction mixture.

Nitro-isomer Distributions.—(a) *Nitration with fuming nitric acid–acetic anhydride.* The substrate (1.25×10^{-4} mol) was dissolved in acetic anhydride (0.70 ml) and kept at 25.0 °C. The nitrating agent (80 μl) [prepared by adding fuming nitric acid (0.40 ml, 9.05×10^{-3} mol; *d* 1.5)

[36] Ref. 12 (*a*), p. 165.

[37] N. B. Chapman, S. Sotheeswaran, and K. J. Toyne, *J. Org. Chem.*, 1970, **35**, 917.

[38] R. C. Fort and P. von R. Schleyer, *J. Org. Chem.*, 1965, **30**, 789.

[39] J. Kopecky and J. Smejkal, *Chem. and Ind.*, 1969, 271.

[40] N. B. Chapman and K. J. Toyne, *J.C.S. Chem. Comm.*, 1972, 188.

[41] N. Kornblum and W. J. Jones, *Org. Synth.*, 1963, **43**, 87.

slowly to acetic anhydride (1.39 ml, 1.50 g, 0.014 7 mol) at 25.0 °C] was added slowly during 10—15 min with shaking. After the mixture had been stirred for 3—4 h, water (20 ml) was added and, after 1 h, aqueous 10% sodium carbonate (20 ml) was added. The mixture was shaken with ether (4 × 50 ml) and the ethereal solutions were washed with water (3 × 25 ml) and dried ($MgSO_4$). The ethereal solution was concentrated on a water-bath (45—50 °C) to *ca.* 2 ml and was analysed by g.l.c.

(b) *Nitration with fuming nitric acid.* The substrate (1.25×10^{-3} mol) was dissolved in acetic anhydride (7.00 ml) and was kept at 25.0 °C. Fuming nitric acid (150 μl, 3.393×10^{-3} mol; *d* 1.5) was added dropwise during 15—30 min with shaking. After the mixture had been stirred for 3—4 h it was worked up and analysed as described above.

Standard mixtures of *o*-, *m*-, and *p*-t-butylnitrobenzene and of 1-(*o*-, *m*-, and *p*-nitrophenyl)bicyclo[2.2.2]octane in acetic anhydride were each subjected to the extraction procedure described above and g.l.c. analysis showed that the isomer proportions in the two cases before and after extraction were the same within experimental error (±0.3%).

Competitive Nitrations.—(a) *Nitration with fuming nitric acid–acetic anhydride.* The competing substrates (1.25×10^{-4} mol of each) and the standard [decane, undecane, *p*-nitrotoluene, and 2,4-dinitrotoluene, or 2,4-dinitrotoluene (0.02 g)] were dissolved in acetic anhydride (0.70 ml) and kept at 25.0 °C. The nitrating agent (as for the isomer distributions; 20—80 μl) was added slowly during 10—15 min. The mixture was stirred for 1.5—3 h and was then worked up as described above.

When the relative rates of nitration were calculated by using equation (2), the solution of substrates and standard in acetic anhydride was halved before nitration. One portion was nitrated with half the volume of nitrating agent and worked up in the usual way and the other portion was worked up without being nitrated. G.l.c. analysis of these two solutions enabled the amount of each substrate remaining after partial nitration to be determined.

(b) *Nitration with fuming nitric acid.* The competing substrates (2.5×10^{-4} mol of each) and the standard [decane, or *p*-nitrotoluene and 2,4-dinitrotoluene (0.02 g)] were dissolved in acetic anhydride (1.40 ml) and kept at 25.0 °C. Fuming nitric acid (5—20 μl, 1.131×10^{-4}—4.524×10^{-4} mol) was added dropwise during 15—30 min with shaking. The reaction mixture was stirred for 1.5—2 h and was then worked up as described above.

Calculation of Results.—A sample made up of weighed amounts of *o*-, *m*-, and *p*-t-butylnitrobenzene and another sample made up of weighed amounts of 1-(*o*-, *m*-, and *p*-nitrophenyl)bicyclo[2.2.2]octane were used to determine the appropriate hydrogen (50—90 ml min^{-1}) and air (300 ml min^{-1}) flow-rates for the g.l.c. detector to give a linear response. It was assumed that the *ortho*-, *meta*-, and *para*-nitro-isomers of the 1-phenyl-4-X-bicyclo[2.2.2]octanes gave a linear response under the above conditions. The validity of this assumption is justified by the agreement of the relative rate coefficient values calculated by using equation (3) (requiring analysis of the nitro-isomers produced) or equation (2) (requiring analysis of the competing substrates before and after partial nitration).

Nitro-isomer distributions were calculated from the peak areas measured by using a Honeywell precision integrator.

The relative rates of nitration were calculated by using equation (2) or (3),[42] where k_1 and k_2 are the rate coefficients for

$$k_1/k_2 = \{\log_{10}(X_1)_0 - \log_{10}(X_1)_T\}/\{\log_{10}(X_2)_0 - \log_{10}(X_2)_T\} \quad (2)$$

$$k_1/k_2 = \{\log_{10}(X_1)_0 - \log_{10}[(X_1)_0 - (N_1)]\}/\{\log_{10}(X_2)_0 - \log_{10}[(X_2)_0 - (N_2)]\} \quad (3)$$

the reactions of the two competing substrates X_1 and X_2 respectively; $(X_1)_0$ and $(X_1)_T$ represent the molar amounts of substrate X_1 initially and finally and (N_1) represents the total molar amount of mononitro-compounds formed from X_1; $(X_2)_0$, $(X_2)_T$, and (N_2) similarly refer to substrate X_2.

For the competitive nitration of benzene and toluene, and of toluene and t-butylbenzene, a standard mixture containing weighed amounts of decane and all four nitro-compounds for the former case, and undecane and all six nitro-compounds for the latter was analysed by using g.l.c. and the relative rate was calculated by using equation (3). [Equation (2) was unsuitable for competitive nitrations involving benzene, toluene, or t-butylbenzene because these volatile substrates were partially lost on concentration of the ether extracts after nitration.] The relative rate coefficient for the competitive nitration of toluene and t-butylbenzene determined as described above was, within experimental error, equal to that calculated by using the weights and peak areas of the *p*-nitro-compounds in the standard mixture assuming that the nitro-isomers have the same relative molar response. Hence for the competitive nitration of t-butylbenzene and 1-phenyl-4-X-bicyclo[2.2.2]octane, and of 1-phenylbicyclo[2.2.2]octane and 1-phenyl-4-X-bicyclo[2.2.2]octanes (X = Et, Pr^i, OMe, CO_2Me, Br, Cl, or CN) a standard mixture containing weighed amounts of the standard (2,4-dinitrotoluene and *p*-nitrotoluene for the former, and 2,4-dinitrotoluene for the latter) and of the *p*-nitro-compounds from both the substrates was analysed by using g.l.c., after a sample from the competitive nitration had been analysed. The relative rates of nitration were then calculated by using equation (3).

Reproducibility of the Results.—At least two determinations of the percentages of nitro-products and of the value for the ratio of rate coefficients were made. For each determination at least four g.l.c. analyses were used and the results were reproducible within the limits indicated in Tables 1 and 2. Calculations of the ratio of rate coefficients by using equation (2) or (3) gave values which agreed within experimental error.

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