565. *The Transmission of Polar Effects through Aromatic Systems. Part II.*[1] *The Nitration of Benzyl Derivatives.*

By J. R. Knowles and R. O. C. Norman.

The partial rate factors for nitration, by nitric acid in acetic anhydride, of toluene, benzyl methyl ether, chloride, and cyanide, ethyl phenylacetate, and phenylnitromethane have been measured. They are discussed with reference to the original Baker–Nathan theory of hyperconjugation and to more recent theories. It is concluded that time-variable release of electrons from methylene groups bonded to the benzene nucleus is important in determining rates of substitution at that nucleus. It is found also that the ability of a group $-CH_2X$ to release electrons in this way falls off as the electron-attracting capacity of X increases. The relation between the observed rates of nitration and the electron-attracting power of X (measured by Taft's σ_I-parameter) is discussed.

Since the original proposal by Baker and Nathan[2] in 1935 that alkyl groups bonded to unsaturated systems can release electrons by a conjugative mechanism, several theories have been advanced to explain the behaviour of these groups in such environments. Burawoy and Spinner[3] postulated that the Baker–Nathan order of electron-release by alkyl groups results from steric hindrance to bond contraction in electron-deficient transition states. They suggested that in the solvolysis of an alkyl halide $R\cdot CH_2X$ the contraction and stabilisation of the $R-CH_2^+$ bond (in the transition state which precedes the carbonium ion) will be reduced by steric repulsions increasing with the size of R, making methyl more reactive than t-butyl. Price and his co-workers[4] suggested that introduction of a bulky alkyl group *meta* or *para* to the reaction centre in aromatic side-chain reactions would to some extent prevent the solvent dipoles from stabilising the charge on the molecule in the transition state, decreasing the solvation energy and effectively increasing the activation energy. This "bulk" effect explained the hydrolysis rates of *m*- and *p*-alkylbenzoic esters, and the similarity between the relative rates of the bromination in the PhR and $Ph\cdot CH_2R$ series, which are both[5] Me > Et > Pr^i > Bu^t, whereas this order for the $Ph\cdot CH_2R$ series does not follow from the Baker–Nathan postulate. Schubert *et al.*[6] extended Price's ideas, and said that the *inherent* order of

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[1] Part I, *J.*, 1961, 2221.

[2] Baker and Nathan, *J.*, 1935, 1844.

[3] Burawoy and Spinner, *J.*, 1954, 3752.

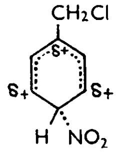
[4] Price and Lincoln, *J. Amer. Chem. Soc.*, 1951, **73**, 5836; Price and Belanger, *ibid.*, 1954, **76**, 2682.

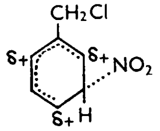
[5] Berliner and Berliner, *J. Amer. Chem. Soc.*, 1949, **71**, 1195.

[6] Schubert, Craven, Minton, and Murphy, *Tetrahedron*, 1959, **5**, 194; Schubert and Sweeney, *J. Org. Chem.*, 1956, **21**, 119.

electron-release from alkyl groups is the inductive one, but that for experiments in polar solvents (where the Baker–Nathan order may obtain) we are seeing, not an inversion of the inherent inductive order, but an indirect effect of steric hindrance to solvation of electron-deficient sites near the alkyl group.

(I)





(II)

Schubert's theory has been of much value in the re-interpretation of many solvolytic reactions and aromatic substitutions where the electronic effects of alkyl groups are important. His theory is relevant to the comparison of the behaviour of one alkyl group with that of another, but it was not clear whether it could take account of the behaviour of an alkyl *residue*, for instance, the methylene group in benzyl compounds.

The known values of the partial rate factors of benzyl chloride in nitration [7] cannot be reconciled with an extension of the theory of Schubert *et al.* to alkyl residues. The *meta*-position of this molecule is deactivated, which indicates that the chloromethyl group is electron-withdrawing relative to hydrogen. Now, in the transition state for electrophilic substitution at the *para*-position, $C_{(1)}$ of the benzene nucleus bears a partial positive charge (cf. I), and so, because of the $-I$ effect of the chloromethyl group, the *para*-position should be more deactivated than the *meta*-position in the transition state for which there is less positive charge on $C_{(1)}$ (II). Moreover, both the theory of Burawoy and Spinner (the $-CH_2X$ group being bulkier than hydrogen), and the theory of Schubert *et al.* (the $-CH_2X$ group restricting solvation more than hydrogen), predict that benzyl compounds will be less reactive at the *ortho*- and *para*-positions than at the *meta*-positions. This is contrary to the facts for benzyl chloride, for which the *meta* : *para* ratio in nitration is about 1 : 3.

We therefore surveyed the nitration of benzyl systems quantitatively, in an attempt to elucidate the electronic characteristics of the methylene residue. Nitration was chosen because some information was already available about the nitration of benzyl compounds, because of the convenient rates of reaction, and because of the stability and relative ease of isolation of the nitrobenzyl isomers. The partial rate factors in nitration for a representative series of benzyl systems have now been determined, and are set out in Table 1.

TABLE 1. *Partial rate factors in nitration* (*acetyl nitrate at* 25°).

Compound	*ortho*	*meta*	*para*	Compound	*ortho*	*meta*	*para*
PhMe	42·4	1·89	62·6	Ph·CH$_2$Cl	0·716	0·296	2·24
Ph·CH$_2$·CO$_2$Et	6·29	1·52	7·55	Ph·CH$_2$·CN	0·252	0·208	1·15
Ph·CH$_2$·OMe	9·97	1·32	16·3	Ph·CH$_2$·NO$_2$	0·0822	0·200	0·167

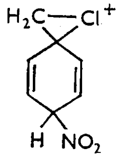
In some cases our results differ from those obtained by previous workers. Only for benzyl chloride,[7] ethyl phenylacetate,[7] and phenylnitromethane [8] had quantitative studies of nitration previously been made, product analyses being by " classical " chemical methods. We checked the overall reactivities in nitration of benzyl chloride and ethyl phenylacetate by competitive experiments between them and between (i) ethyl phenylacetate and t-butylbenzene, (ii) t-butylbenzene and toluene, and (iii) toluene and benzene. From these comparisons, overall reactivities with respect to benzene were calculated. Our value of 25·2 for the overall reactivity of toluene in nitration at 25° falls between the two known values of 27 and 23 for this reaction at 0° and 30° respectively.[9] The overall reactivity of ethyl phenylacetate obtained by us (3·86) agrees tolerably with that obtained

[7] Ingold and Shaw, *J.*, 1949, 575.

[8] Baker, *J.*, 1929, 2257.

[9] Ingold, Lapworth, Rothstein, and Ward, *J.*, 1931, 1959.

by Ingold and Shaw[7] (3·66), but we found a higher value (0·711) for benzyl chloride than they did (0·302). Baker[8] determined approximate isomer ratios for the nitration of phenylnitromethane: we have obtained accurate values, using infrared spectrophotometry for analysis of the isomer mixture. Generally, we have more confidence in our results since our analytical methods are more direct physical techniques.



(III)

The partial rate factors for nitration of benzyl chloride confirm the *ortho-para*-orientation reported previously. This could be explained in terms of a neighbouring-group effect, involving participation of chlorine in a three-membered ring, structures such as (III) being contributors to the transition state in an electrophilic substitution. This type of interaction has been well established for allylic systems.[10,11] The criterion for *ortho-para*-activation in a benzyl system would then be the existence in the side-chain of an atom with unshared electrons in a sterically favourable position for neighbouring-group interaction. We tested this hypothesis in three ways.

First, in benzyl cyanide, the only atom with unshared electrons is nitrogen, but since the CN group is linear this unshared pair can never be in a favourable position for interaction with $C_{(1)}$ of the benzene nucleus. The isomer ratios obtained in the nitration of benzyl cyanide were not very different (*ortho*: 24·4; *meta*: 20·1; *para*: 55·5%) from those of benzyl chloride (*ortho*: 33·6; *meta*: 13·9; *para*: 52·5%). The differences are easily accounted for by the larger inductive effect of the CN group than of Cl (Taft's σ^*-values[12] being CN 1·30 and Cl 1·05). The isomer ratios would not have been so similar if structure (III) had been important in substitution of benzyl chloride and impossible in that of benzyl cyanide.

The second test involved nitration of benzyl methyl ether. This, like benzyl chloride, has an atom with unshared electrons favourably placed for interaction with $C_{(1)}$ of the benzene nucleus. Further, oxygen is known to participate better in neighbouring-group interactions than chlorine.[11] If, for *ortho*- and *para*-substitution, neighbouring-group structures were important, then for substitution at these positions there should be a larger negative entropy of activation than for substitution at the *meta*-position, where such interactions are irrelevant. The difference between the entropies of activation at the *meta*- and *para*-positions of this compound was obtained from measurements of the isomer distributions in nitration at three temperatures.[13] The value of $\Delta\Delta S^{\ddagger}_{(p-m)} \approx 0{\cdot}45$ e.u. was obtained. Noble and Wheland,[14] after a comparable investigation of the activation entropies in the nitration of ethyl benzoate, point out that differences in activation entropies of this order (*i.e.*, $<0{\cdot}5$ e.u.) cannot be considered significant because of the necessary extrapolation. Thus these measurements provided no confirmation of a neighbouring-group effect.

The third test depended on the fact that a chlorine isotope effect should be observed in the nitration of benzyl chloride if there were a neighbouring-group interaction. If we assume complete formation of the Cl–$C_{(1)}$ bond at the transition state [see (III)], and neglect $C_{(\alpha)}$–Cl stretching and the strain in the three-membered ring, a maximum theoretical isotope effect can be calculated. The ${}^{35}k/{}^{37}k$ rate ratio (calculated on the basis of the difference in zero point energies[15]) is 1·047, and this, for 90% reaction of benzyl chloride (85% of which results in the formation of the *ortho*- and *para*-isomers), corresponds to a maximum possible isotopic enrichment in the unchanged material of about 13%. If this value is high by about a factor of ten (because of the simplifications made in its derivation)

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[10] de la Mare and Pritchard, *J.*, 1954, 3910; de la Mare and Salama, *J.*, 1956, 3337; de la Mare and Ballinger, *J.*, 1957, 1481; de la Mare, Naylor, and Williams, *Chem. and Ind.*, 1959, 1020.

[11] de la Mare and Pritchard, *J.*, 1954, 3990.

[12] Taft, in " Steric Effects in Organic Chemistry," ed. Newman, John Wiley and Sons, Inc., New York, 1956, p. 595.

[13] Kent and Norman, *J.*, 1959, 1724.

[14] Noble and Wheland, *J. Amer. Chem. Soc.*, 1958, **80**, 5397.

[15] Cf. Bell, " The Proton in Chemistry," Methuen and Co., London, 1959, p. 184.

an isotope effect should still be measurable by the mass-spectrometric method employed, by which the $^{35}Cl : ^{37}Cl$ ratio was determined within $\pm 0{\cdot}14\%$. Samples of benzyl chloride remaining after 70%, 80%, and 90% nitration showed no detectable difference in this ratio when compared with an unchanged sample.

From these three pieces of evidence it is concluded that neighbouring-group effects, if they occur, are kinetically insignificant (at least in nitration).

The pattern of the partial rate factors obtained (see Table 1) depends basically on the inductive effect of the group CH_2X. We see gradations in the behaviour of these compounds as the $-I$ effect increases, from compounds ($Ph{\cdot}CH_2X$) in which both *meta*- and *para*-positions are activated (X = H, OMe, CO_2Et) to compounds in which the *meta*-position is deactivated but the *para*-position activated (X = Cl, CN), to a compound in which both the *meta*- and the *para*-position are deactivated (X = NO_2). One important feature is that both benzyl chloride and benzyl cyanide are deactivated at the *meta*-position but activated at the *para*-position. The deactivation of the *meta*-positions in these compounds indicates that the groups CH_2Cl and $CH_2{\cdot}CN$ are electron-withdrawing with respect to hydrogen. Yet the activation of the *ortho*- and *para*-positions cannot be explained by the $-I$ effect. Nor can the theories of Burawoy and Spinner and of Schubert *et al.* account for this activation; indeed, they predict the reverse, as is pointed out above.

We have therefore to invoke some polarisability effect for the CH_2Cl and $CH_2{\cdot}CN$ groups, and this, since it must involve time-variable electron-release from a methylene group, is what is understood as hyperconjugation.

On the basis of these arguments, the rate of substitution at the *meta*-position of a benzyl compound should be governed by the inductive effect of the CH_2X group. It has been found that the Hammett relation is obeyed for the substitution of many aromatic compounds at the *meta*-position.[16] Since few of the σ-values of the CH_2X groups are known, a direct Hammett plot (of the logarithm of the *meta*-partial rate factor against σ_m of the CH_2X group) cannot be realised. However, if there is a linear relation between Taft's σ_I-values for X,[17] and the σ_m-values for the CH_2X group, a linear graph of the Hammett type should be obtained. The results from this procedure are not very well fitted by a straight line, but the trend of decreasing f_m (where f_m is the *meta*-partial rate factor) with increasing inductive electron-withdrawal, is clear (Table 1). σ_I-Values derived by Taft [17] from different reaction series vary from 0·60 to 0·68, and from 0·50 to 0·58, for the NO_2 and the CN group respectively. Variations in σ_I of this order vitiate a more detailed analysis of our results in terms of Hammett constants. Another reason for the poor correlation is that the amount of *meta*-isomer obtained from the benzyl compounds is relatively small (usually less than 20%), and, since the range of *meta*-reactivities is only about one power of ten, $\log_{10} f_m$ is very sensitive to small errors in the isomer distribution.

For *para*-substitution in benzyl systems, both the inductive effect of the CH_2X group and the time-variable release due to the methylene residue are important. The graph of σ_I (for X in CH_2X) against $\log_{10} f_p$ is a curve (see the Figure) in which $\log_{10} f_p$ falls off increasingly rapidly as σ_I increases. Here the reactivities range over three powers of ten, and $\log_{10} f_p$ is less sensitive to small errors in the percentage of *para*-isomer. Our interpretation of the curve is as follows. Since the curve indicates that $\log_{10} f_p$ decreases more rapidly for a given change in σ_I at high values of σ_I, the contribution of hyperconjugation from the methylene group to the rate of reaction must itself fall off with increasing electron-demand by X. This is reasonable, since as the electron-pull of X in CH_2X increases, there will be a reduced concentration of electrons in the carbon–hydrogen bonds available for time-variable release.

Some experiments by Burton and Ingold [18] can also be best interpreted on this

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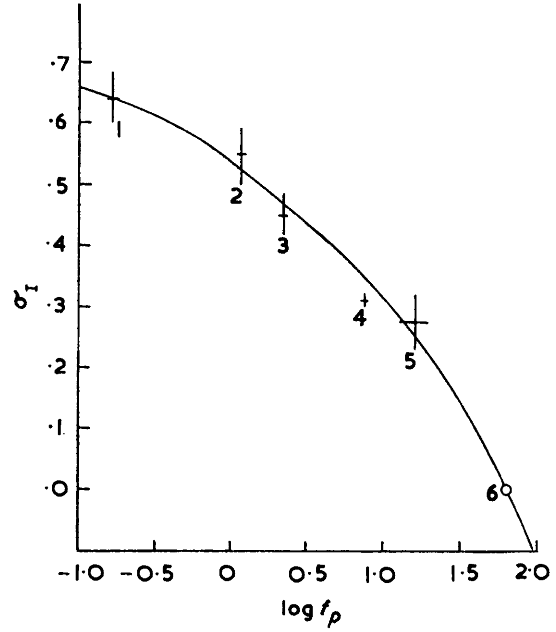
[16] Roberts, Sanford, Sixma, Cerfontain, and Zagt, *J. Amer. Chem. Soc.*, 1954, **76**, 4525.

[17] Taft, *J. Phys. Chem.*, 1960, **64**, 1805.

[18] Burton and Ingold, *J.*, 1929, 2022.

view, but it is opposite to a contention by Baker *et al.*[19] that hyperconjugative release *increases* when the electron-releasing system is attached to an electron-attracting group. The experiments of Baker *et al.* involved addition of bromine to various allylic compounds, and they obtained an order F > Cl > Br > CN for the reactivity of X in $X{\cdot}CH_2{\cdot}CH{=}CH_2$. It is very probable that, as is well established in other allylic systems, the order of reactivities which Baker *et al.* found is due, not to a decrease in hyperconjugative release, but to neighbouring-group effects. The degree of participation in neighbouring-group interactions is exactly in the order they found.



Plot of log f_p *for* $Ph{\cdot}CH_2X$ *against* σ_I *for* X. X = : 1, NO_2; 2, CN; 3, Cl; 4, CO_2Et; 5, OMe; 6, H.

It is difficult, with the available data, to make any more specific or quantitative deductions about the electronic factors important in benzyl systems owing to the inaccuracy and variability of σ-values and the relatively small range of reactivities in benzyl compounds.

EXPERIMENTAL

Materials.—Ethyl phenylacetate, benzyl methyl ether, benzyl chloride, benzyl cyanide, t-butylbenzene, toluene, benzene, acetic anhydride, and bromoform were commercial materials, purified by distillation. "AnalaR" concentrated sulphuric acid and "AnalaR" fuming nitric acid (*d* 1·5) were used, a small quantity of urea being added to the latter before all nitrations. Phenylnitromethane was prepared by the method of Black and Babers [20] and was stored at −40° (m. p. −6° to −7°).

Analytical Methods.—Isomer ratios were determined by gas chromatography or infrared spectroscopy. For the gas chromatography, column conditions were those in which the three isomers were completely resolved. Standard mixtures of pure isomers were injected to confirm the proportionality between peak area and weight of isomer. The peak areas were calculated from the triangles formed by tangents to the Gaussian curve and the interpolated base-line. The isomers were extracted from the nitration mixture with ether four times. Standard mixtures of isomers were subjected to this procedure to check that no isomer was preferentially lost in the extraction.

For the infrared analyses, the region 9—13 μ was used, the experimental isomer concentrations being calculated from the spectra of near-replica synthetic mixtures of isomers, or

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[19] Baker, Brieux, and Saunders, *J.*, 1956, 404.

[20] Black and Babers, *Org. Synth.*, 1943, Coll. Vol. II, p. 512.

by determining the extinction coefficients of each pure isomer at three different wavelengths and calculating the experimental isomer concentrations by solving the three simultaneous equations obtained. The method of calculation was checked by determining the concentration of synthetic mixtures containing known proportions of isomers. Carbon disulphide is not a good enough solvent for nitrobenzyl isomers; nitromethane absorbs increasingly between 11 and 13 μ; however, bromoform does not absorb seriously in the 9—13 μ region (only having a weak band at 870 cm.$^{-1}$) and dissolves at least 80 mg./ml. of the isomers. The purity of the bromoform is critical, since carbonyl bromide has a strong absorption band in the 750—800 cm.$^{-1}$ region. Bromoform was therefore redistilled (b. p. 40°/18 mm.) before each set of determinations. Depending on the extinction coefficients of the isomers concerned, 1 mm. or 0·1 mm. cells were used. Even with the 1 mm. cells, the weak absorption band of bromoform at 870 cm.$^{-1}$ was completely cancelled, the spectrometer retaining its response in this region. Conditions were always chosen to give peaks of between 30% and 70% absorption. The products were freed from unchanged starting material by distillation. The extraction procedure was in each case checked by means of synthetic mixtures. Spectroscopic determinations were made on a Perkin–Elmer self-recording infrared spectrophotometer, model 21A.

Overall reactivities were determined by competitive nitrations, the mixtures being analysed by gas chromatography. For most of the compounds, the relative decreases in the amounts of the reactants after the nitration were measured. To obtain the absolute differences in amount of material before and after nitration an internal standard was used. This was a compound entirely resistant to nitration under the conditions used * with a retention time different enough from those of the reacting compounds to give complete resolution. The ratios of the peak heights of each of the two compounds compared with that of the internal standard were obtained for the mixtures before and after nitration. In every case, changes in the ratios of peak heights were found to correspond to changes in the ratios of amounts of material to within 2%. Thus decreases in the values of (peak height of compound): (peak height of internal standard) were directly proportional to decreases in compound concentration. For all nitrations, a mixture of the two competing reactants and the internal standard was divided into two parts, which were placed in the thermostat bath. To one was added the nitrating mixture (nitric acid in acetic anhydride), and, to the other, acetic anhydride alone. After a suitable time, water was added to each part and the organic material extracted four times with ether. These mixtures were then injected alternately on to the gas-chromatographic column, and decreases in amount of each reactant determined. Between 60 and 100 injections of " pre "- and " post "-nitration mixtures from at least four competitive experiments were made in each comparison.

There are two limitations to this method of determining the overall reactivity. Reactivities cannot differ by a factor of more than about five, since the decreases in peak heights are too disparate for accurate determination of each; and compounds of widely differing boiling points ($>100°$) cannot be compared, since the retention times and peak shapes differ too much for easy or accurate analysis. The experimental ratio R, in which the compounds have undergone reaction, is equal to k_x/k_y, the true rate ratio, only in the limit of small amounts of reaction. At large amounts of reaction, the competing compounds will no longer be present in their initial ratio x_0/y_0. However, Ingold and Smith [22] deduced that, even for reasonable amounts of reaction, $k_x/k_y = \log (x/x_0)/\log (y/y_0)$, where x_0 and y_0 are the initial concentrations, and x and y are the final concentrations. This relation was used to calculate k_x/k_y in the present experiments.

The overall reactivity of toluene with respect to benzene was determined by *product* analysis, rather than by analysis of the amounts of starting material before and after nitration. Here again, the experimental ratio P, of formed products, is only equal to k_x/k_y in the limit of small amounts of reaction. The simplest procedure (which was adopted here) for obtaining k_x/k_y from product analysis is to nitrate 1 : 1 molar mixtures of reactants so that the total degree of nitration varies, say, from 5% to 50%. The value of P is plotted against the degree of nitration (which is known from the amount of acetyl nitrate added), and the line obtained extrapolated to zero reaction. This is the limit where $P = k_x/k_y$ and gives the latter ratio. Overall reactivities obtained in the various competitive reactions are set out in Table 2.

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* It has already been shown that the straight-chain hydrocarbons (decane, undecane, and dodecane) do not react under the conditions used here.[21]

[21] Knowles, Norman, and Radda, *J.*, 1960, 4885.

[22] Ingold and Smith, *J.*, 1938, 905.

Nitration of Ethyl Phenylacetate.—Pure samples of the three nitro-isomers were obtained by esterification of the corresponding acids,[23] by the Fischer–Speier method. Ethyl *o*-nitrophenylacetate had m. p. 65·5° (lit.,[24] 69°); ethyl *m*-nitrophenylacetate, m. p. 11—13°, b. p. 110°/0·1 mm. (Found: C, 57·05; H, 5·2; N, 7·15. Calc. for $C_{10}H_{11}NO_4$: C, 57·4; H, 5·3; N, 6·7%); ethyl *p*-nitrophenylacetate, m. p. 63·5—64° (lit.,[25] 64—66°).

The isomer ratio was determined by infrared spectroscopy. Extinction coefficients were calculated for each isomer at 786 $cm.^{-1}$ (mainly *ortho*), 804 $cm.^{-1}$ (mainly *meta*), and 857 $cm.^{-1}$ (mainly *para* and *ortho*). From a synthetic mixture of isomers containing *o*- 44·44, *m*- 11·11, *p*- 44·44% by wt., percentages calculated from the spectrum were *o*- 43·8, *m*- 11·8, *p*- 44·4. A mixture of nitric acid (0·009 mole) in acetic anhydride (0·01 mole) was added dropwise to ethyl phenylacetate (0·01 mole) at 25° during 1 hr. The temperature variation was not more than 0·5°. After 12 hr. the mixture was transferred to a micro-fractional-distillation apparatus, and the system evacuated to 0·075 mm. After acetic anhydride (and any unchanged nitric acid) had distilled over, the temperature was raised slowly to 65°, to rid the mixture of any unchanged ethyl phenylacetate. The flask was cooled, the vacuum released at the flask (so that the incoming air could sweep over any ethyl phenylacetate vapour remaining), and the resulting isomer mixture analysed. To a 1 : 1 : 1 synthetic mixture of isomers were added some ethyl phenylacetate and acetic anhydride. This mixture was subjected to the treatment described above, and it was found that the isomer ratio was the same to within 1% after the distillation as before. Isomer ratios obtained from experimental nitrations were: *ortho* 54·3, *meta* 13·1, *para* 32·6 ± 0·5%.

The overall reactivity of ethyl phenylacetate with respect to benzene was obtained from the

TABLE 2. *Overall reactivities from competitive experiments.*

Competing species		Values of overall reactivity of A relative to B	Mean values	Calc. overall reactivities of A relative to benzene
A	B			
$Ph\cdot CH_2CO_2Et$	$PhBu^t$	0·263 0·254 0·264 0·254	0·26 ($\pm$2%)	3·86
$PhBu^t$	PhMe	0·503 0·713 0·613 0·523 0·700 0·490	0·59 ($\pm$14%)	14·9
$Ph\cdot CH_2Cl$	$Ph\cdot CH_2\cdot CO_2Et$	0·189 0·188 0·184 0·169 0·204 0·170	0·184 ($\pm$5%)	0·711
$Ph\cdot CH_2\cdot OMe$	$Ph\cdot CH_2\cdot CO_2Et$	2·08 1·62 1·85 1·37 1·46 2·08 1·46	1·70 ($\pm$15%)	6·48
$Ph\cdot CH_2\cdot CN$	$Ph\cdot CH_2Cl$	0·506 0·463 0·477 0·497	0·486 ($\pm$3%)	0·345
$Ph\cdot CH_2\cdot NO_2$	$Ph\cdot CH_2Cl$	0·182 0·158 0·160 0·172 0·165 0·188	0·171 ($\pm$6%)	0·122
PhMe	C_6H_6	25·2		25·2

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[23] Norman and Radda, *J.*, in the press.
[24] Reissert and Scherk, *Ber.*, 1898, **31**, 395.
[25] Maxwell, *Ber.*, 1879, **12**, 1767.

following comparisons: (*a*) Ethyl phenylacetate and t-butylbenzene, with dodecane as the internal standard, were allowed to compete for an inadequate amount of acetyl nitrate for 3 hr. Column 1 (Table 3) was used for the anlysis, and the values for the relative reactivity are set out in Table 2.

TABLE 3. *Gas chromatographic columns.*

Columns used were packed with Apiezon " L " grease coated on Embacel (except columns 4 and 6, for which 50—80 mesh firebrick was the support). The bore of all columns was 4·5 mm.

Column no.	1	2	3	4	5	6	7	8	9
w/w % of stationary phase	20	20	20	20	20	30	30	20	10
Carrier gas	H_2	H_2	H_2	H_2	N_2[a]	N_2[a]	N_2[a]	N_2[a]	N_2[a]
Flow rate (ml./min.)	69	67	64	40	34	72	55	24	32
Length of column (cm.)	100	100	100	200	400	50	200	400	100
Inlet pressure[b] of carrier gas (cm.)	61	61	48	49	65	34	46	65	43
Inlet heater temp. (approx.)	250°	250°	200°	250°	200°	130°	240°	240°	270°
Column temp.	178°	140°	154°	150°	145°	93°	156°	180°	148°

[a] Where nitrogen was used as the carrier gas, a hydrogen-inject flame-ionisation detector was used. In all other cases the eluting hydrogen stream was burned directly in such a detector. These detectors, coupled to a Sunvic recorder, gave a linear response. [b] Columns were run with atmospheric pressure at the outlet.

(*b*) t-Butylbenzene and toluene, with undecane as the internal standard. Column 2 (Table 3) was used.

(*c*) Toluene and benzene (for details, see below).

Nitration of Benzyl Methyl Ether.—*Methyl* 2-*nitrobenzyl ether* was obtained as a yellow liquid by refluxing 2-nitrobenzyl chloride (1 mole) with sodium (1 g.-atom) in methanol for 1 hr. The mixture was poured into water and extracted with ether, and the product was purified by chromatography on alumina. Fractional distillation (b. p. 64°/0·1 mm.) gave a pure product, which produced a single symmetrical peak on gas chromatography (Found: C, 57·7; H, 5·3; N, 8·9. $C_8H_9NO_3$ requires C, 57·5; H, 5·4; N, 8·4%). *Methyl* 3-*nitrobenzyl ether*, prepared by a similar procedure from 3-nitrobenzyl bromide, had b. p. 79°/0·1 mm. (Found: C, 56·7; H, 5·4; N, 8·8%). Methyl 4-nitrobenzyl ether formed yellow crystals, m. p. 26—27° (lit.,[26] 26—27°).

The isomer ratio was determined by gas chromatography. Column 8 (Table 3) was used, the isomers having the following retention times: *ortho* 25½, *meta* 35, *para* 37½-min. Isomer proportions obtained were *ortho* 51·3, *meta* 6·8, *para* 41·9 ± 0·4%.

Benzyl methyl ether was nitrated with a 1 : 1 mixture of nitric and sulphuric acid at 0°, 25°, and 50°, for the determination of the relative activation entropies. Column 8 of Table 3 was used for the analysis, the isomer ratios obtained being, at the above temperatures, *ortho* 27·3, 28·6, 30·9, *meta* 17·4, 18·1, 18·5, and *para* 55·3, 53·3, 50·6% respectively.

The overall reactivity of benzyl methyl ether was determined relative to that of ethyl phenylacetate. Dodecane was the internal standard, and column 4 (Table 3) was used for the analysis.

Nitration of Benzyl Chloride.—Pure samples of the three nitro-isomers were obtained by recrystallising commercial samples from methanol and light petroleum (b. p. 60—80°). 2-Nitrobenzyl chloride had m. p. 49° (lit.,[27] 48—49°); 3-nitrobenzyl chloride, m. p. 45° (lit.,[27] 45—47°); 4-nitrobenzyl chloride, m. p. 72° (lit.,[28] 71°).

The isomer ratio was determined by gas chromatography, column 9 (Table 3) being used. It was not possible to devise a column and conditions which would completely resolve 3- and 4-nitrobenzyl chloride. Resolution was adequate for reasonably reproducible isomer percentages, as follows: *ortho* 33·6, *meta* 13·9, *para* 52·5 ± 0·9%. The retention times of the isomers on the column used were: *ortho* 57½, *meta* 82½, *para* 91 min.

The overall reactivity of benzyl chloride was determined relative to that of ethyl phenylacetate. Dodecane was used as the internal standard and column 3 (Table 3) for the analysis.

Samples of benzyl chloride for the mass-spectrometric analysis were obtained as follows. Benzyl chloride was nitrated at 25° with 2 : 1 sulphuric–nitric acid. After 3 hr. water was added and the organic material extracted three times with ether. The ether extracts were

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[26] Kleucker, *Ber.*, 1922, **55**, 1645.
[27] Gabriel and Bergmann, *Ber.*, 1883, **16**, 2059.
[28] Beilstein and Geitner, *Annalen*, 1866, **139**, 331.

dried and evaporated. Benzyl chloride was obtained at 30°/0·1 mm. in a micro-fractional-distillation apparatus. Amounts of nitro-isomers and unchanged benzyl chloride were weighed to obtain the approximate percentage of nitration. The ^{37}Cl : ^{35}Cl ratio was determined for the following samples: before nitration 0·3206 ± 0·0008, after 70% nitration 0·3208 ± 0·0012, after 80% nitration 0·3208 ± 0·0022, after 90% nitration 0·3207 ± 0·0013. The values obtained do not indicate any change in the isotope ratio greater than experimental error.

Nitration of Benzyl Cyanide.—2-Nitrobenzyl cyanide [29] had m. p. 81·5—82·5° (lit., 82°). 3-Nitrobenzyl cyanide was prepared by refluxing a mixture of 3-nitrobenzyl bromide (1 mol.) in ethanol and potassium cyanide (1 mol.) in the minimum amount of water for 1 hr. After removal of the ethanol by distillation the organic material was extracted with ether and recrystallised from aqueous ethanol as yellow needles, m. p. 58·5—59·5° (lit.,[30] 61°). 4-Nitrobenzyl cyanide had m. p. 116° (from ethanol) (lit.,[31] 114—116°).

The isomer ratio was determined by infrared spectroscopy, the procedure being analogous to that employed for ethyl phenylacetate. Isomer ratios from experimental nitrations were calculated by spectrometric comparison with a synthetic 1 : 1 : 2 mixture of the 2-, 3-, and 4-isomers. The absorption at 786 (*ortho*), 922 (*meta* and *para*), and 831 cm.$^{-1}$ (*para*) was used. Isomer ratios obtained were: *ortho* 24·4, *meta* 20·1, *para* 55·5 ± 0·2%.

The overall reactivity was determined relative to that of benzyl chloride with decane as the internal standard. Column 5 (Table 3) was used for the analysis.

Nitration of Phenylnitromethane.—*o*-Nitrophenylnitromethane was prepared by refluxing 2-nitrobenzyl chloride (1 mol.) with sodium iodide (1 mol.) in acetone for 4 hr. The mixture was filtered while hot and the acetone distilled off. The residue of 2-nitrobenzyl iodide recrystallised from ethanol as green plates. It was dissolved in dry ether and treated with a 20% excess of silver nitrite. The mixture was stirred for 6 hr. at room temperature, then refluxed for 4 hr. The excess of silver salt was filtered off after cooling. Evaporation of the ether gave *o*-nitrophenylnitromethane as yellow plates [from ethanol, then light petroleum (b. p. 100—120°)], m. p. 67·5° (lit.,[32] 72°) (Found: C, 46·3; H, 3·25; N, 15·7. Calc. for $C_7H_6N_2O_4$: C, 46·2; H, 3·3; N, 15·4%). *m*-Nitrophenylnitromethane was prepared from a mixture of *m*-nitrobenzyl bromide and a 20% excess of silver nitrite in dry ether, which was stirred for 24 hr. at 0°, then 12 hr. at room temperature. The excess of silver salt was filtered off, and the ether solution concentrated until a solid separated, this product being isolated as above. The off-white needles of *m*-nitrophenylnitromethane had m. p. 95·5° (lit.,[32] 95—96°). *p*-Nitrophenylnitromethane [33] had m. p. 91° (lit.,[32] 90°).

The isomer ratio was determined by infrared spectroscopy by the method described above. Isomer ratios from experimental nitrations were calculated by comparison with synthetic 1 : 2 : 1 mixtures of the *ortho*-, *meta*-, and *para*-isomers. The absorption at 788 (*ortho*), 807 (*meta*), and 856 cm.$^{-1}$ (*para*) was used. Isomer ratios obtained were: *ortho* 22·5, *meta* 54·7; *para* 22·8 ± 0·5%.

The overall reactivity of phenylnitromethane was determined relative to that of benzyl chloride with undecane as the internal standard. A small quantity of dry ether was added to make a homogeneous mixture. Column 6 (Table 3) was used for the analysis.

Nitration of Toluene.—The isomer ratio was determined by gas chromatography of the nitration mixtures obtained from the competitive experiments (see below). Column 7 (Table 3) was used. Ratios obtained were: *ortho* 56·1, *meta* 2·5, *para* 41·4 ± 0·5%.

The overall reactivity of toluene with respect to benzene was measured by product analysis. Five mixtures, each containing 0·01 mole of toluene and 0·01 mole of benzene, were nitrated with acetyl nitrate. To these mixtures severally, 0·001, 0·002, 0·003, 0·006, and 0·01 mole of acetyl nitrate were added dropwise, and the flasks left in the thermostat bath for 48 hr., after which the reaction was virtually complete. From the peak areas of nitrobenzene and *p*-nitrotoluene (all three nitrotoluenes and nitrobenzene resolved under the conditions of column 7), the apparent partial rate factor at the *para*-position of toluene (f_p) was obtained. (This is the peak area of *p*-nitrotoluene divided by one-sixth of the peak area of nitrobenzene.) The values of apparent f_p were plotted against the amount of acetyl nitrate added, and the linear plot

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[29] Rinderneckt, Koechlin, and Niemann, *J. Org. Chem.*, 1953, **18**, 971.
[30] Heller, *Annalen*, 1907, **358**, 349.
[31] Radziszewski, *Ber.*, 1870, **3**, 198.
[32] Holleman, *Rec. Trav. chim.*, 1896, **15**, 367.
[33] Kornblum, Smiley, Blackwood, and Iffland, *J. Amer. Chem. Soc.*, 1955, **77**, 6269.

obtained extrapolated to zero extent of reaction. The gradient of this line was less than one, so slight inaccuracies in the percentage of nitration, or in the values of apparent f_p, did not alter the intercept on the apparent f_p axis very much. The values obtained were:

Nitration (approx. %)	5	10	15	30	50
Apparent f_p (mean; ±2%)	61	58	54	47	38

The intercept at zero nitration is 62·6, which is the real f_p. From the isomer ratio obtained above, this gives an overall reactivity of 25·2 for toluene with respect to benzene in nitration with acetyl nitrate at 25°.

We are most grateful to Mr. H. J. M. Fitches of the Scientific Apparatus Engineering Department of Associated Electrical Industries Limited, for carrying out the mass-spectrometric analyses, and to Mr. A. E. Thompson for assistance with the gas-chromatographic apparatus. One of us (J. R. K.) thanks Merton College for a research scholarship.

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[*Received, December 29th,* 1960.]