

where this quadratic branching becomes unimportant, suggests that the latter explanation is correct. A 'self-inhibiting' mechanism of the first type may perhaps account for the inhibiting action of methane, which has been described elsewhere<sup>2</sup>.

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<sup>1</sup> Egerton, A., and Warren, D. R., *Proc. Roy. Soc., A*, **204**, 465 (1951).  
<sup>2</sup> Baldwin, R. R., Corney, N. S., and Precious, R. M., *Nature* [**169**, 201 (1952)].

### Effects of Alkyl Groups in Electrophilic Additions and Substitutions

KHARASCH has shown that the addition of hydrogen iodide, and, homolytic processes being suppressed, of other hydrogen halides to propylene and other monoalkylethylenes, involves a practically exclusive terminal uptake of the hydrogen atom<sup>1</sup>. Holleman showed that the nitration of toluene involves a 96-97 per cent *ortho-para*-orientation<sup>2</sup>. It has been found quite generally that alkyl-oriented additions and substitutions are accompanied by large increases of reaction-rate<sup>3</sup>, for example, by a factor of 24.5 for the nitration of toluene as compared with that of benzene. It is a question for discussion whether these strong kinetic effects of alkyl groups are to be credited mainly to hyperconjugation between CH-bonds and the olefinic or aromatic  $\pi$ -system, or to the inductive effect of alkyl groups arising in these cases from an electrical dissymmetry in a  $\sigma$ -CC-bond formed by differently hybridized carbon-atomic orbitals<sup>4</sup>. Evidence on this matter can be obtained by rate-comparisons between the relevant reactions of methyl- and *tert.*-butyl-substituted ethylenes and benzenes. Of these substituents only methyl can provide CH-hyperconjugation. Both groups should have similar positive inductive effects, that of the *tert.*-butyl group being the greater.

Propylene and *tert.*-butylethylene have been compared with respect to rate of addition of hydrogen iodide. The relative rates, determined by the competition method, in solvent methylene chloride at  $-80^\circ$  were 1.00 : 0.88. The circumstance that the rates are so nearly the same, while a weak steric effect might be held responsible for the direction of the difference, shows that hyperconjugation is not an outstanding cause of the strong kinetic effects of alkyl groups in general, and that therefore these effects must be credited largely to the  $\sigma$ -bond dissymmetry which we classify with the inductive effect. Incidentally, the product from *tert.*-butylethylene contained, besides 50 per cent of  $\text{Me}_3\text{C}\cdot\text{CHI}\cdot\text{CH}_3$ , 50 per cent of Wagner-rearranged  $\text{Me}_2\text{C}\cdot\text{CHMe}_2$ . This result is not the first indication of its kind that such additions occur in steps by way of a carbonium ion<sup>5</sup>.

Analogous results have been obtained for the nitration of toluene and *tert.*-butylbenzene. In 90 per cent aqueous acetic acid at  $45^\circ$ , the proportions of the products, determined by infra-red analysis, were as follows :

	<i>Ortho</i> -	<i>Meta</i> -	<i>Para</i> -
Toluene	56.5	3.5	40.0
<i>tert.</i> -Butylbenzene	12.0	8.5	79.5

One sees that the ratios *m./p.* are roughly the same, and that the large differences are in the ratios *o./m.* and *o./p.*. This indicates that the distinction is especially associated with the *o*-position; and the simplest interpretation is that, while the polar effects

of the substituents are not very different, the larger group exerts a selective steric repression of *o*-substitution, as LeFèvre<sup>6</sup> has always maintained\*. This interpretation is confirmed by comparison of rates. The kinetically determined ratio of the first-order nitronium-ion rates in 90 per cent aqueous acetic acid at  $45^\circ$ , nitrous-free nitric acid being in constant excess, is  $\text{Me} : \text{Bu}^t = 1.00 : 0.64$ . From the figures given, it can be computed that the rates of attack on the individual nuclear positions of toluene and *tert.*-butylbenzene, in terms of the rate for one position in benzene as unity, are as follows :



As before, the conclusion is that the most important polar effect of alkyl groups in these electrophilic reactions in an attached  $\pi$ -electron system is their inductive effect, the expected greater importance of which in the *tert.*-butyl group than in the methyl group accords with relations shown by the *m.* and *p.*-rates, which alone are free from the disturbance of steric retardation.

We wish to thank Prof. C. K. Ingold for his interest and help in these investigations.

\* *Added in proof* : In a paper which appeared after this communication was submitted for publication, K. L. Nelson and H. C. Brown (*J. Amer. Chem. Soc.*, **73**, 5605; 1951) have reached a similar conclusion on the basis of their estimates (employing fractional distillation techniques) of the isomeric ratios for the nitration of *tert.*-butylbenzene with  $\text{HNO}_3\text{-H}_2\text{SO}_4$ , as compared with the known ratios for toluene under similar conditions.

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<sup>1</sup> Kharasch, M. S., *et al.*, *J. Amer. Chem. Soc.*, **55**, 2531 (1933), *et seq.*  
<sup>2</sup> Holleman, A. F., Vermeulen, J., and de Mooy, W. J., *Rec. trav. chim.*, **38**, 1 (1914).  
<sup>3</sup> Ingold, C. K., Lapworth, A., Rothstein, E., and Ward, D., *J. Chem. Soc.*, 1959 (1931). Ingold, C. K., and Ingold, E. H., *ibid.*, 2354 (1931). Robertson, P. W., *et al.*, *ibid.*, 1509 (1939), *et seq.*  
<sup>4</sup> Walsh, A. D., *Disc. Farad. Soc.*, **2**, 18 (1947).  
<sup>5</sup> Whitmore, F. C., and Johnston, F., *J. Amer. Chem. Soc.*, **55**, 5020 (1933). Eeke, G. G., Cook, N. C., and Whitmore, F. C., *ibid.*, **72**, 1511 (1950).  
<sup>6</sup> LeFèvre, R. J. W., *J. Chem. Soc.*, 980 (1933), *et seq.*

### Hypotheses relating to the Brain-Mind Problem

MAY I be permitted, at this late date, to comment on Prof. J. C. Eccles's "Hypotheses relating to the Brain-Mind Problem" (*Nature*, July 14, 1951, p. 53), which had previously escaped my notice.

As one of four "subsidiary hypotheses" he proposes : "Only when there is a high level of activity in the cortex (as revealed by the electroencephalogram) is liaison with mind possible. Unconsciousness supervenes instantly the activity is lowered (as, for example, in anoxia, anaesthesia, concussion, sleep)". This would be well enough as a hypothesis if it were not for the phrase "as revealed by the electroencephalogram", which implies that a high level of