NOTES.

The Mechanism of Substitution at a Saturated Carbon Atom. By I. Dostrovsky, E. D. Hughes, and C. K. Ingold.

Our recent calculations (*J.*, 1947, 173) on symmetrical, bimolecular, halogen substitutions, $\bar{X} + RX \longrightarrow XR + \bar{X}$, have evoked comment by Evans, Evans, and Polanyi, mainly with respect to the problem of estimating the R . . . X distances in the transition states of such substitutions (*J.*, 1947, 558). Reply is necessary, because the fundamental difference of outlook between these authors and ourselves is not, as their note suggests, that they have paid due regard to the criterion of minimum energy, whilst we have not: it is that their picture of the electron distribution in the transition state is different from ours, and that, correspondingly, they and we have taken account of energy minimisation in different ways.

The transition state can be described in terms of resonance between two structures, $\bar{X}$ R—X and X—R $\bar{X}$, of equal energy with all RX distances identical. The difference of view mentioned relates to the degree of importance attached to this resonance. Ogg and Polanyi suppose it to have only a negligible effect on the charge distribution, energy, and interatomic distances (*Trans. Faraday Soc.*, 1935, **31**, 604). Baughan and Polanyi accept this picture, introduce the further assumption that resistance to compression commences steeply when $\bar{X}$ and R are separated by the covalent radius of carbon plus the ionic radius of halogen, and in this way derive the conclusion that the energy of the symmetrical system is minimised when the atoms of the bond R—X are also separated by just the same distance (*ibid.*, 1941, **37**, 648).

On the contrary, Hughes and Ingold have throughout regarded the resonance as fully effective in *distributing* the ionic charge in the transition state, reducing its energy, and creating a pair of partial covalencies, which will be of order one-half in a symmetrical transition state,

$$(-\tfrac{1}{2}e)\ X\ .\ .\ .\ R\ .\ .\ .\ X\ (-\tfrac{1}{2}e).$$

They based their theory of solvent effects in nucleophilic substitution on this picture of the transition state (*J.*, 1935, 252), as well as the analogous theory of salt effects (*J.*, 1940, 979). It followed that the energy of the transition state would be minimised with CX distances adjusted by the resonance; and we made a first estimate of the distances by using the empirical connexion between bond-length and bond-order—in effect, extrapolating, for the apppropriate bond, to order 0·5 the relation known to apply, alike to CC and CO bonds, between orders 1 and 3. Furthermore, in the development of the calculation, we applied the principles of the transition-state method (cf. Ogg and Polanyi, *loc. cit.*), adapted to our model and procedure, again employing the criterion of minimum energy. The resulting estimate of the distance was not very different from the original one (*e.g.*, 2·25 A., as against 2·31 A., for CBr). Contrary to Evans, Evans, and Polanyi, we should have been surprised if there had been a great difference, in view of the empirical guides adopted.

Two reasons can be given for regarding our model and method as the more correct. The first is that Polanyi's method tends to give unacceptably high transition-state distances, though much has been done to reduce the derived values. We have already disagreed (*J.*, 1947, 176) with the use of gaseous ionic radii, rather than crystal radii, as an approximation for ionic radii in solution. This proceeding deducts 0·20—0·24 A. from the calculated distances, which have been further reduced by rounding (Baughan and Polanyi, *loc. cit.*; A. G. Evans, *Trans. Faraday Soc.*, 1946, **42**, 719; " Reactions of Organic Halides in Solution ", *Mem. Manchester Phil. Soc.*, vol. 87). The CCl distance, for example, has thus been first reduced from 2·58 A. to 2·34 A., and then quoted in the unconventionally approximate form 2·2 A.

The second reason is that the distributed charge model alone is consistent with all that is known concerning solvent and salt effects in nucleophilic substitutions generally. Symmetrical halogen substitutions are only one particular case; but for this case Baughan has admitted that the localised-charge (low resonance) model requires a zero salt-effect, whereas the distributed-charge (high resonance) model demands a negative salt-effect (*Trans. Faraday Soc.*, 1941, **37**, 654). Hughes thereupon cited evidence that a negative salt effect exists (*loc. cit.*). This fact we have now fully confirmed by experiments which will be published later.

Evans, Evans, and Polanyi conclude their note by expressing the opinion that increased steric repulsion from methyl to *tert.*-butyl is alone responsible for the decrease of bimolecular reaction rate in this series of halides, there being no contributory polar effect. This seems to us to neglect the totality of chemical evidence for polar effects in substituent methyl groups, and their influence in bond-making and bond-breaking processes. Correcting a suggestion to the contrary, we would remark that such considerations seem at least as important to us as our calculations, even though the latter yield consistent conclusions. The chemical evidence is too extensive to be discussed here, but we shall refer to it when later presenting a series of new results bearing directly on this question.—University College, Bangor. University College, London. [*Received, September* 11*th*, 1947.]

The Bromination of 1 : 5-*Dihydroxynaphthalene and its Methyl Ethers.* By Ernst Bergmann.

It is of some interest for the theory of aromatic substitution that 1 : 5-dihydroxynaphthalene, 1-hydroxy-5-methoxynaphthalene, and 1 : 5-dimethoxynaphthalene are substituted differently by halogen and that the direction of the substitution is influenced by the nature of the solvent. According to Carter, Race, and Rowe (*J.*, 1942, 236), 1 : 5-dihydroxynaphthalene is brominated both in glacial acetic acid and in carbon tetrachloride in the 2 : 6-position (m. p. 200°). 1 : 5-Dimethoxynaphthalene brominated in carbon tetrachloride by the same authors gave the 4 : 8-dibromo-derivative, m. p. 187°, whilst we obtained in benzene as solvent the 2 : 6-dibromo-derivative, m. p. 160°, which they prepared by methylation of the 2 : 6-dibromo-1 : 5-dihydroxynaphthalene of m. p. 200°. 1-Hydroxy-5-methoxynaphthalene which, in carbon tetrachloride, is brominated to 2 : 8-dibromo-1-hydroxy-5-methoxynaphthalene, m. p. 130°, gave us in benzene a molecular compound of that derivative with the 2 : 6-dibromo-derivative, m. p. 150°; after methylation, the 2 : 8-dibromo-1 : 5-dimethoxynaphthalene, m. p. 86°, can be separated from the 2 : 6-compound, m. p. 160°; they do not form a molecular compound and exhibit a sufficiently different solubility in alcohol.

It appears, therefore, that the free hydroxyl group directs the substitution by bromine into the ortho-, the methoxy-group into the para-position. In the latter case, however, this is only true for carbon tetrachloride. Benzene as solvent counteracts the effect at least to a certain extent.

When 1 : 5-dimethoxynaphthalene was treated with a large excess (10 mols.) of bromine in glacial acetic acid, a red naphthaquinone was sometimes formed which proved identical with the 2 : 6-dibromo-5-hydroxy-1 : 4-naphthaquinone obtained by Wheeler and Ergle (*J. Amer. Chem. Soc.*, 1930, **52**, 4872) by oxidation of 2 : 6-dibromo-1 : 5-dihydroxynaphthalene.

2 : 6-*Dibromo*-1 : 5-*dimethoxynaphthalene*.—A solution of bromine (1·4 g.) in benzene (5 c.c.) when added gradually to 1 : 5-dimethoxynaphthalene (1·4 g.) in the same solvent (20 c.c.) caused a brisk reaction. After 12 hours, the solvent was distilled off and the residue triturated with, and then recrystallised from, ligroin; m. p. 160°; yield, 20%.

Bromination of 1-*Hydroxy*-5-*methoxynaphthalene in Benzene*.—A solution of bromine (6 c.c.) in benzene (20 c.c.) reacted almost instantaneously with 1-hydroxy-5-methoxynaphthalene (10 g.) in benzene (50 c.c.). After 12 hours, the solution was filtered and evaporated, and the residue recrystallised repeatedly from benzene–ligroin and from methylene chloride; m. p. 102° (Found: C, 39·7; H, 2·4; Br, 48·0; OMe, 9·5; active H, 0·34. Calc. for $C_{11}H_8O_2Br_2$: C, 39·8; H, 2·4; Br, 48·2; OMe, 9·4; active H, 0·30%). That this substance was a molecular compound was shown in the following manner. 5 G. were dissolved in 50 c.c. of water, containing 2 g. of potassium hydroxide, and methylated with 3 c.c. of methyl sulphate. The reaction was completed on the steam-bath (15 minutes), and the oil which had separated induced to crystallise by scratching. Fractional crystallisation from alcohol gave first (at room temperature) 2 : 6-dibromo-1 : 5-dimethoxynaphthalene, m. p. 158°; and after recrystallisation from *iso*butyl alcohol, m. p. 160°, and then (at 0°) 2 : 8-dibromo-1 : 5-dimethoxynaphthalene, m. p. 84°, and after recrystallisation from methanol, m. p. 86°.

2 : 6-*Dibromo*-5-*hydroxy*-1 : 4-*naphthaquinone*.—To a solution of 1 : 5-dimethoxynaphthalene in glacial acetic acid, 10 mols. of bromine were added. After 12 hours at room temperature, the solid product was collected and recrystallised from butyl acetate; dark-red, long needles, m. p. 201° (Found: C, 37·6; H, 1·5. Calc. for $C_{10}H_4O_3Br_2$: C, 37·2; H, 1·2%).—THE DANIEL SIEFF RESEARCH INSTITUTE, REHOVOTH, PALESTINE. [*Received, October 2nd*, 1947.]