341. *The Homolytic Methylation of Naphthalene.*

By J. A. Kent and R. O. C. Norman.

The reaction of naphthalene with the free methyl radical has been investigated, di-*tert.*-butyl peroxide being used as the source of methyl radicals. The ratio of the amounts of the two methylnaphthalenes formed has been determined at various temperatures, from which the differences in activation energies and entropies for reactions at the α- and the β-positions of the naphthalene nucleus have been calculated. An analysis of the importance of the steric hindrance to α-substitution and of the difference in polarisability of the α- and the β-positions has been made in the light of these results.

It has been predicted by molecular-orbital theory[1] that naphthalene should be more reactive in the α-position than in the β-position towards free radicals. This prediction has been confirmed for the phenylation of naphthalene by the free phenyl radical, the α-position proving to be about four times as reactive as the β-position.[2,3] A more detailed treatment of this problem necessitates two refinements: first, an evaluation of the difference in electronic polarisability in the α- and the β-position, for comparison with theoretical quantities such as the difference in atom-localisation energies: secondly, an evaluation of the steric hindrance to substitution at the α-position by the *peri*-hydrogen atom.

With these objects, the α/β ratio of methylnaphthalenes formed by the attack of the free methyl radical on naphthalene has been measured over a range of temperatures, and from the results have been calculated the differences in activation energies, $\Delta H^{\ddagger}$, and in activation entropies, $\Delta S^{\ddagger}$, between reactions at the α- and the β-position. The methyl radicals were generated by the decomposition of di-*tert.*-butyl peroxide at the temperatures at which the reaction was being investigated.

EXPERIMENTAL

Reaction of Methyl Radicals with Naphthalene.—Di-*tert.*-butyl peroxide (5 g.) was added to a solution of naphthalene (5 g.) in chlorobenzene (100 ml.). The solution was heated on a water-bath at 98° for 3 weeks (about twice the half-life of the peroxide at this temperature), *tert.*-butyl alcohol and acetone being removed (through a short fractionating column) as formed, in order to keep the temperature constant. The remaining volatile materials and chlorobenzene were removed by fractional distillation and the residue was examined by gas chromatography.

In later experiments, at different temperatures, di-*tert.*-butyl peroxide (5 g.) and naphthalene (5 g.) in the appropriate solvent (100 ml.) were refluxed together for approximately five times the half-life of the peroxide at this temperature. The solvents used were chlorobenzene, bromobenzene, and *o*-dichlorobenzene. The procedure employed was that described above for the reaction at 98°.

The reaction at 156° was repeated with 7·5, 2·5, 1·0, and 0·5 g. of di-*tert.*-butyl peroxide severally. The methylnaphthalenes produced were analysed by gas chromatography as described below: the ratio of α- to β-methylnaphthalene remained constant, within experimental error, throughout this set of experiments (see Table 2).

Gas Chromatography.—The column (497 cm. × 4·5 mm.) was packed with 24·8% apiezon L coated on firebrick and operated at 179° with a carrying stream of hydrogen (70 ml./min.), a slightly increased inlet pressure (25 lbs./in.^{2}) and atmospheric pressure at the outlet. A hydrogen-flame detector was employed, coupled to a Honeywell Brown recorder which gave a linear response. Under these conditions the peaks due to α- and β-methylnaphthalene were completely resolved, their retention times being 53½ and 45 min. respectively. The column yielded 3750 theoretical plates.

[1] " Progress in Organic Chemistry," ed. by J. W. Cook, Butterworths, London, 1953, Vol. II, p. 23; Wheland, *J. Amer. Chem. Soc.*, 1942, **64**, 900.

[2] Huisgen and Grashey, *Annalen*, 1957, **607**, 46.

[3] Marshall and Waters, *J.*, 1959, 381.

The injection of standard mixtures of α- and β-methylnaphthalene showed that the ratio of the peak areas was proportional to the ratio of quantities of the two materials, the areas being measured by constructing triangles made up of tangents to the Gaussian curves and the intercepts on the base-line. 0·5—0·6 ml. of the reaction mixture was injected, this quantity containing enough α-methylnaphthalene to give almost full-scale deflection on the recorder (*ca.* 0·03 ml.). A large peak due to unchanged naphthalene (approximately 90% of the reaction mixture) was recorded first, followed by β- and then α-methylnaphthalene. The experiment in *o*-dichlorobenzene yielded a fourth peak of retention time consistent with its being for a methylated *o*-dichlorobenzene.

Comparison of the ratio of materials in standard mixtures with the ratio of areas of the chromatographic peaks showed that the analysis was accurate to 3%.

The results of methylation experiments carried out at 98—179° are recorded in Table 1. Table 2 records the α/β ratios obtained at a constant temperature with different concentrations of peroxide.

TABLE 1. *Variation of* α : β *ratio of methylnaphthalenes with temperature.*

Solvent	PhCl	PhCl	PhBr	*o*-$C_6H_4Cl_2$
Temp.	98°	132°	156°	179°
No. of expts.	4	3	3	6
Mean α : β ratio	5·3	3·8	2·9	2·7

TABLE 2. *Variation of* α : β *ratio of methylnaphthalenes with peroxide concentration.*

Peroxide (g.)	7·5	5·0	2·5	1·0	0·5
Wt. ratio of peroxide : naphthalene	1·5	1·0	0·5	0·2	0·1
No. of expts.	2	3	2	2	2
α : β ratios	3·0, 2·9	2·8, 2·9, 2·9	3·1, 3·0	3·0, 2·9	2·9, 2·9
Mean α : β ratio	2·95	2·90	3·05	2·95	2·90

DISCUSSION

One possible source of error in using the ratio of α- to β-methylnaphthalene as a measure of the relative reactivity of the α- and the β-position of naphthalene was that the two methylnaphthalenes might themselves react with methyl radicals, either in the aromatic nucleus or in the side chain, and to unequal extents. An experiment in which a mixture of α- and β-methylnaphthalenes was attacked by methyl radicals showed that the α-compound was the more reactive, so that further reaction on these products was a real source of error. However, experiments in which decreasing quantities of di-*tert.*-butyl peroxide were employed to react with naphthalene showed that the α : β ratio did not change, within experimental error, with the amount of reaction on naphthalene. Evidently the amount of reaction on naphthalene was always so small that further reaction of the two main products was negligible.

The possibility that the change in the α : β ratio reflects a change in the selectivity of the methyl radical in different solvents rather than, or in addition to, relative changes in rate due to activation energy and entropy differences has also to be considered. Thus, Russell has found that the effective reactivity of a chlorine atom is altered considerably by change of solvent, there appearing to be some type of complex formation between chlorine atoms and aromatic solvents.[4] Such an effect did not seem to be operative here, since the largest variation in the α : β ratio occurred when the aromatic solvent in two cases was kept constant (chlorobenzene) and only the temperature was varied. Furthermore, the changes in α : β ratio were large compared with the corresponding changes for phenylation of naphthalene with different solvents.[2] It is probable that any alteration in the reactivity of the methyl radical in these experiments was small; certainly the much smaller effect of complex formation on the phenyl radical [2] than on the chlorine atom [4] is consistent with this. It may be that such complex formation is important only when the accepting atom or radical is one of high electronegativity.

[4] Russell, *J. Amer. Chem. Soc.*, 1957, **79**, 2977.

A treatment based on transition-state theory shows that:

$$\ln (k_{\alpha}/k_{\beta}) = \Delta S^{\ddagger}(\alpha - \beta)/\boldsymbol{R} - \Delta H^{\ddagger}(\alpha - \beta)/\boldsymbol{R}T$$

where k_{α}, k_{β} are the velocity constants for methylation at the α- and β-position. The ratio of the quantities of α- and β-methyl derivatives are, in this case, a measure of the relative rate constants, and so $k_{\alpha}/k_{\beta} = \alpha/\beta$. Therefore from the plot of ln (α/β) against the reciprocal of the absolute temperature, the gradient gives $\Delta H^{\ddagger}$ and the intercept on the ln (α/β) axis gives $\Delta S^{\ddagger}$. The values obtained from the linear graph were: $\Delta H^{\ddagger}(\alpha - \beta) = -3{\cdot}4$ kcal./mole; $\Delta S^{\ddagger}(\alpha - \beta) = -5{\cdot}6$ e.u. The difference in activation energies, $\Delta H^{\ddagger}(\alpha - \beta)$, depends on both the difference in polarisability of the α- and the β-position and the non-bonding steric interaction between the *peri*-hydrogen atom and the α-methyl group.

It is not possible cleanly to separate these two quantities, but an estimate has been made [5] of the non-bonding steric interaction in α-methylnaphthalene itself of 1·6 kcal./mole. Scale models suggest that the interaction will be somewhat less in the transition state concerned in the present investigation, so that 1·6 kcal./mole provides an upper limit for this interaction. This value, coupled with the experimental value for $\Delta H^{\ddagger}$, indicates a difference in π-electron-excitation energies of the α- and the β-position of about —5 kcal./mole.

A model frequently used for the transition state in an aromatic substitution is one in which the aromatic carbon atom under attack has become bonded to the reagent and has changed its hybridisation from sp^2 to sp^3, being removed from conjugation with the remainder of the aromatic system. For the difference in π-electron-excitation energies between the α- and the β-position in naphthalene in the attainment of such a transition state a theoretical value of 0·31β has been obtained, where β is the resonance integral.[1] β has the approximate value of —20 kcal./mole for aromatic hydrocarbons such as naphthalene,[6] whence the theoretical difference in excitation energies of the α- and the β-position is approximately —6 kcal./mole. Our experimental upper-limit value, —5 kcal./mole, is significantly less than this, and may indicate that the transition state in the methylation is one in which the aromatic carbon atom undergoing attack is not fully bonded with the methyl radical and is still partially conjugated with the rest of the aromatic system. This reasoning accords with that of Dewar *et al.* who proposed similar models for the transition states in aromatic nitration [7] and chlorination,[8] and suggested that the structure of the transition state depends on the nature of the reagent.[8]

It is difficult to draw positive conclusions from the difference in activation entropies for reaction at the α- and the β-position, for $\Delta S^{\ddagger}$ has often been found to be a function of $\Delta H^{\ddagger}$. Nevertheless the difference is in accord with the possibility that, in addition to the non-bonding strain, there is restriction to rotation of the methyl group in the transition state for methylation at the α-position.

THE DYSON PERRINS LABORATORY, OXFORD. [*Received, October 23rd*, 1958.]

---

[5] Packer, Vaughan, and Wong, *J. Amer. Chem. Soc.*, 1958, **80**, 905.
[6] Wheland, *J. Amer. Chem. Soc.*, 1941, **63**, 2025.
[7] Dewar, Mole, and Warford, *J.*, 1956, 3581.
[8] Dewar and Mole, *J.*, 1957, 342.