EFFECT OF SUBSTITUENTS ON METHYL AFFINITY OF NAPHTHALENE DERIVATIVES

Sir:

An investigation of the effect of substituents on the rate of addition of methyl radicals to substituted benzenes was carried out in these laboratories a few years ago.[1] The results were in substantial agreement with the findings of Hey and his co-workers,[2,3,4] who studied phenylation of substituted benzenes. Benzene and its derivatives are comparatively unreactive compounds, and this caused some experimental difficulties and introduced some uncertainties in the results. To avoid them a series of more reactive substrates, namely, naphthalene derivatives, was investigated.

The rates of addition of methyl radicals were determined by the method described previously.[5,6] The results are presented in the form k_2/k_1 (Table I) where the subscripts refer to the two reactions

$$CH_3\cdot + \text{solvent} \xrightarrow{k_1} CH_4 + \text{solvent radical} \quad (1)$$

and

$$CH_3\cdot + \text{substrate} \xrightarrow{k_2} CH_3\cdot\text{substrate} \quad (2)$$

Isoöctane was used as a solvent and the reaction was carried out at 65°. Whenever the abstraction of hydrogen atoms by methyl radicals did take place the results were recorded and listed in Table I in the form of k'_3/k_1, k'_3 being the rate constant of abstraction per active hydrogen.

TABLE I

Compound	k_2/k_1	k'_3/k_1	Compound	k_2/k_1
Naphthalene	9.4	..		
1-Methyl-	8.1	0.83	1-Iodo-	18.4
2-Methyl-	13.0	2.05(?)	2-Iodo-	30.1
2,3-Dimethyl-	10.5	1.06	1,4-Dichloro-	20.6
2,6-Dimethyl-	13.9	1.08	1-Methoxy-	8.8
1,5-Dimethyl-	5.8	1.09	2-Methoxy-	7.5
Acenaphthene	4.7	5.15	1-Dimethylamino-	3.5
1-Ethyl-	8.0	4.26	1-Acetonaphthone	20.0
2-Ethyl-	8.9	4.27	2-Acetonaphthone	44.4
1-Fluoro-	10.5	..	1-Naphthonitrile	30.8
2-Fluoro-	13.2	..	2-Naphthonitrile	45.9
1-Chloro-	13.2	..	1-Methyl naphthoate	19.4
2-Chloro-	21.6	..	1-Ethyl naphthoate	22.2
1-Bromo-	8.0(?)	..	2-Methyl naphthoate	40.3
2-Bromo-	21.2	..	1-Naphthylisocyanate	17.1

Several conclusions emerge from the data listed in Table I. Substituents in the α position enhance the addition less than those placed in the β position, 1-methoxynaphthalene being the only exception. This might partially result from the "blocking" of the reactive α position, an effect responsible for the low reactivity of 1,5-dimethylnaphthalene and acenaphthene. The reactivity increases along the series F, Cl, Br, I, 1-bromonaphthalene apparently being an exception. The reaction of these compounds with methyl radicals does not involve abstraction of a halogen atom.

The only substituents decreasing the reactivity are the electron donating ones, namely, methoxy, dimethylamino and ethyl. Methyl group seems to be a border case.

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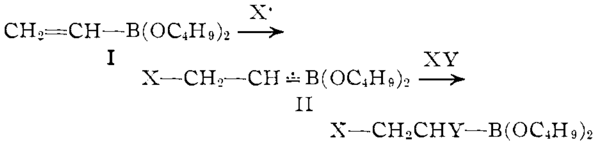
RADICAL CATALYZED ADDITIONS TO DIBUTYL ETHYLENEBORONATE[1]

Sir:

Dibutyl ethyleneboronate (I) reacts with free radicals ($X^\cdot$) to yield a type of intermediate radical (II) that is markedly stabilized by carbon–boron π-bonding, and which reacts further to yield boronic esters (III) containing other functional groups, such as α-halogen, previously inaccessible.



$$\underset{\mathbf{I}}{CH_2{=}CH{-}B(OC_4H_9)_2} \xrightarrow{X^\cdot} \underset{\text{II}}{X{-}CH_2{-}CH \doteq B(OC_4H_9)_2} \xrightarrow{XY} X{-}CH_2CHY{-}B(OC_4H_9)_2$$

IIIa, $X = CCl_3$, $Y = Cl$;
b, $X = CCl_3$, $Y = Br$;
c, $X = n\text{-}C_6H_{13}S$, $Y = H$

The first transfer constant[2] in the reaction of dibutyl ethyleneboronate (I) with carbon tetrachloride is approximately 1×10^{-3}. This low value, which would not be due to polar factors[2] and which is similar to that for styrene[2] (0.6×10^{-3}), indicates that the energies involved for adjacent carbon *p*-orbital overlap with phenyl and with dialkoxyboron groups are similar in magnitude. Stabilization of the radical II is consistent with simple molecular orbital calculations, provided one chooses parameters for the electronegativity and *p*-orbital overlap of boron that are not too low.

Dibutyl ethyleneboronate[3] (I) was prepared by addition of vinylmagnesium chloride[4] in tetrahydrofuran to methyl borate in ether under nitrogen at −60°, acidification with a 2*M* phosphoric–1*M* hydrochloric acid solution, addition of 0.3 g. of phenothiazine to prevent polymerization on contact with air, extraction with 1-butanol, removal of excess water by freezing at −70°, distillation of butanol–water azeotrope and solvents at 20–40 mm., and distillation of the product through a Vigreux column onto 0.02 g. of phenothiazine; yield 134 g. (72%), b.p. 35–40° (0.08 mm.), $n^{24.5}D$ 1.4167. *Anal.*[5] Calcd. for $C_{10}H_{21}BO_2$: C, 65.2; H, 11.5; B, 5.9. Found: C, 65.06; H, 11.66; B, 6.47.

Preparation of the carbon tetrachloride adduct IIIa was best accomplished by slow (40 hr.) addi-

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(1) Presented in part at the Northwest Regional Meeting of the American Chemical Society, June 18, 1959.

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