

## Detritiation of Monosubstituted 1-Tritionaphthalenes

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WE have measured the rates of detritiation of some monosubstituted 1-tritinationaphthalenes in anhydrous trifluoroacetic acid at 70.0°. The results, which provide, we believe, the first quantitative information about effects of substituents on the rate of electrophilic substitution in the naphthalene system, are shown in the Table as values of  $k_{rel}$ , the rates relative to that for 1-tritinationaphthalene (for which  $k_1 = 110 \times 10^{-7}$  sec.<sup>-1</sup>).

The main features are: (a) Contrary to behaviour in the benzene system,<sup>1</sup> a 2-fluoro-substituent activates the 1-position, and the chloro- and bromo-substituents do not deactivate more from the 2- than the 4-position. (b) The methyl group

the methoxyl group must interact with the solvent.<sup>4</sup> (Contrast the situation in 4'-substituted 4-tritiationbiphenyls.<sup>4</sup>) (d) Tautomeric effects can operate from the 5-position, as shown by the influence of the 5-methoxyl group and by the fact that the 5-fluoro- deactivates less than the 5-chloro-substituent. Such effects also operate from the 7-position, and the 7- is several times more reactive than the 5-chloro-compound. (e) The 6- and 8-chloro-compounds are surprisingly reactive. (f) A 4-phenyl substituent activates much less than in the benzene system (for which  $f_p^{Ph} = 163$ ),<sup>5</sup> no doubt because it cannot become coplanar with the naphthalene rings.

Subst.	$k_{rel}$	Subst.	$k_{rel}$	Subst.	$k_{rel}$
H	1.00	4-Br	0.135	2-Me <sup>a</sup>	290 ± 20
2-F	1.71	5-F	0.043	3-Me	2.75
2-Cl	0.264	5-Cl	0.0283	4-Me <sup>a</sup>	75 ± 20
2-Br	0.165	5-Br	0.0252	5-Me	2.18
3-Cl	0.0023	6-Cl	0.0315	2-MeO	1 × 10 <sup>6b</sup>
4-F	4.58	7-Cl	0.138	4-MeO	6 × 10 <sup>5b</sup>
4-Cl	0.265	8-Cl	0.045	5-MeO	3.87
				4-Ph	15.9

<sup>a</sup>Rate constant obtained by extrapolation from lower temperatures.

<sup>b</sup>Approximate value at -10.8°.

activates more from the 2- than the 4-position, and activates more from the 2- but less from the 4- and 3-position than in benzene (for which,<sup>2,3</sup>  $f_p^{Me} = 450$ ;  $f_o^{Me} = 220$ ;  $f_m^{Me} = 6.1$ ). (c) The methoxyl group activates more from the 2- than the 4-position. It activates more from the 5-position than does the methyl group even though

Combination of these results with the partial rate factors for the 1- and 2-positions of naphthalene<sup>6</sup> enables prediction to be made of the points of predominant further substitution in monosubstituted naphthalenes (*cf.* ref. 3).

(Received, March 22nd, 1965.)

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<sup>3</sup> K. C. C. Bancroft, R. W. Bott, and C. Eaborn, *J. Chem. Soc.*, 1964, 4806.

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<sup>5</sup> R. Baker, R. W. Bott, and C. Eaborn, *J. Chem. Soc.*, 1963, 2136.

<sup>6</sup> R. Taylor and C. Eaborn, *J. Chem. Soc.*, 1961, 1012.