Novel and Regioselective Aromatic Double Substitution Involving Borate Anions and a Regio- and Stereo-selective Route to Dihydroaromatic Derivatives

By Ei-ichi Negishi* and Ronald E. Merrill

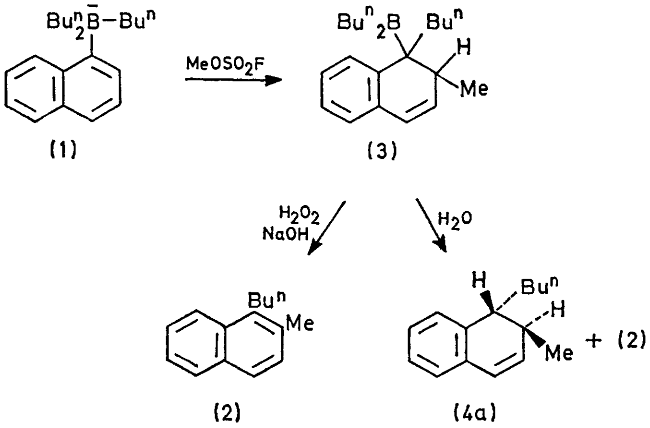
(*Department of Chemistry, Syracuse University, Syracuse, New York* 13210)

Summary An aromatic substitution of aryltrialkylborate anions with methyl fluorosulphonate, which permits the preparation of *ortho*-dialkyl-substituted aromatic compounds as well as the corresponding dihydroaromatic derivatives, is described.

We report here a novel aromatic substitution involving arylborate anions, which permits the introduction of two different alkyl substituents on one aromatic ring in one step in a highly regioselective (*orthc–ipso*) manner. A minor modification in the work-up procedure provides a regio- and stereo-selective route to certain dihydroaromatic derivatives that cannot be obtained by the Birch reduction (Scheme 1.)

Although a number of arylborate anions have been prepared,[1] their potential as intermediates in organic synthesis has not been studied. We have found that the reaction of compound (**1**) with $MeOSO_2F$ (1 mol. equiv.) produces, after oxidation, only one major bicyclic product (**2**) in 70% yield along with several minor products (see Table for other examples). No other bicyclic product was obtained in more than 7% yield. The reaction appears to represent the first successful trapping of a carbocationoid intermediate in aromatic substitution with a carbanionoid reagent.[2]

The nearly exclusive attack at the *ortho* position (*ortho*: *para* = 96 : 4) by $MeOSO_2F$ is noteworthy. We tentatively interpret the result in terms of the electrostatic interaction of the borate anion with either $MeOSO_2F$ or the methyl cation (ion-pair formation). Also noteworthy is the low yield (5%) of 1-methylnaphthalene, in contrast to the known reaction of Ph_4B^- with HCl.[3]



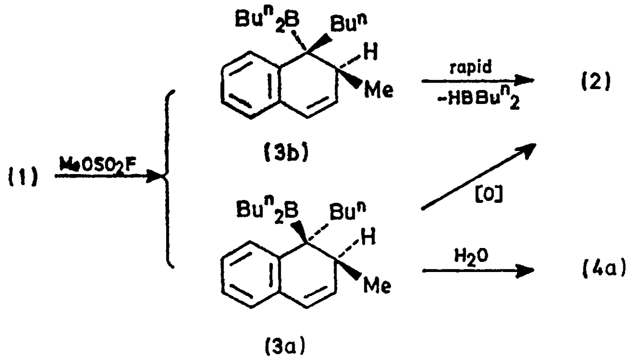
Scheme 1

TABLE

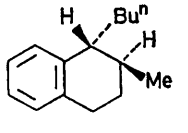
LiBR$_3$Ar Ar	 R	Work up[a]	Yield (%) of alkylated aromatic product[b] Di *ortho*	 *para*	 Mono *ipso*	 Non	Yield (%) dihydro- product
Ph	Bu^n	A	52	2	6	4	c
,,	,,	B	38	2	9	4	c
1-Naphthyl	Et	B	63	3	7	12	Tr.
,,	,,	C	13	Tr.	3	12	42^{d,e}
,,	Bu^n	B	70	3	5	7	Tr.
,,	,,	C	22	Tr.	5	9	56^{d,e}
9-Phenanthyl	,,	A	75	—	11	13	Tr.
2-Methyl-1-naphthyl	,,	C	—	Tr.	35	3	28^d

[a] A: Trimethylamine *N*-oxide (3 equiv.; 20 h reflux) then H_2O, and 85% H_3PO_4–H_2O; B: 30% H_2O_2 then 3N-NaOH (2 h, reflux); C: 3N-NaOH (30 min; 25°) then 30% H_2O_2 (2 h, reflux). [b] Tr. = trace. [c] Not determined. [d] New products gave satisfactory analytical and spectral data. [e] *trans*:*cis* 98:2.

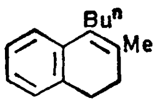
If the formation of the naphthalene (**2**) involves the intermediacy of (**3**), its protonolysis should produce the dihydronaphthalene (**4**). Indeed, treatment of the mixture obtained by the reaction of (**1**) with $MeOSO_2F$ with aqueous NaOH produced (**2**) and (**4**) {δ ($CDCl_3$; Me_4Si) 0·75—1·05 [m, 6H, with a doublet centred at δ 0·94 (J 7 Hz, 3H)], 1·15—1·7 (m, 6H), 5·89 (dd, J 10 and 8 Hz, 1H), 6·35 (d, J 10 Hz, 1H) and 6·9—7·2 (m, 4H)} in 22 and 56% yield, respectively. G.l.c. examination of the reaction mixture, before protonolysis, showed the presence of (**2**) in 22% yield, but (**4**) was not present. The reaction is stereoselective as well as regioselective, yielding nearly exclusively ($\gg$ 98:2) one isomer of (**4**) (g.l.c.). We suggest the reaction proceeds as in Scheme 2. The reaction presumably produces an approximately 70:30 mixture of (**3a**) and (**3b**). In view of the exclusively *cis* nature of the hydroboration–dehydroboration reaction,[4] the *cis*-isomer (**3b**) is expected to dehydroborate spontaneously and rapidly to form (**2**), whereas the *trans*-isomer (**3a**) presumably persists. The protonolysis of (**3a**) should proceed with retention of configuration to produce (**4a**). The *trans*-geometry of (**4a**) was established by its conversion into (**5**) by hydroboration (BH_3 in tetrahydrofuran then oct-1-ene) followed by protonolysis (aq. NaOH); the compound obtained was identical with the major product of the reduction of (**6**) with K–liq. NH_3. The *cis*-isomer of (**5**) prepared by hydroboration–hydrolysis of (**6**) exhibited a slightly longer g.l.c. retention time than (**5**).



SCHEME 2



(5)



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[1] See, for example (a) G. Wittig, *Quart. Rev.*, 1966, **20**, 191; (b) W. Tochtermann, *Angew. Chem. Internat. Edn.*, 1966, **5**, 351.
[2] G. A. Olah, 'Friedel-Crafts and Related Reactions,' vol. II, Part 1, Interscience, New York, 1964.
[3] J. N. Cooper and R. E. Powell, *J. Amer. Chem. Soc.*, 1963, **85**, 1590.
[4] H. C. Brown, 'Hydroboration,' Benjamin, New York, 1962.