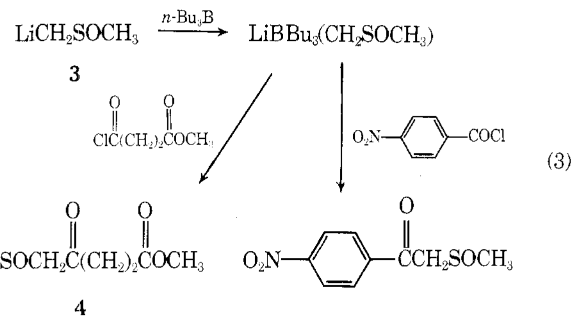
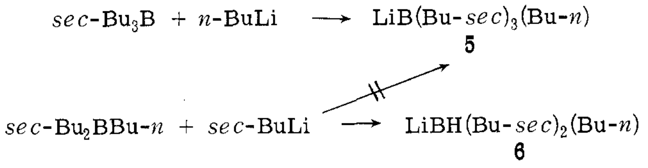


tivity by organoboranes appears a broadly applicable principle as demonstrated by the data in Table I. The data in Table I also indicate that the relative transferability increases in the order secondary alkyl, primary alkyl, and benzyl (or methylsulfinylmethyl), which appears inversely proportional to their basicity.

A few limitations have been observed. First, tetraorganoborate anions containing alkynyl[12] and thioalkoxymethyl[13] groups undergo predominantly *intramolecular* alkyl-transfer reactions with acyl halides. We have found that, although arylborate anions undergo an intramolecular alkyl-transfer reaction with certain alkylating reagents,[14] their reaction with acyl halides involves a clean intermolecular alkyl transfer.[15] Second, although no difficulty exists in the preparation of lithium tri-*sec*-butylmono-*n*-butylborate (**5**) as a thermally stable product (at least for 1 week at 25°) from tri-*sec*-butylborane and *n*-butyllithium, the same borate anion cannot be obtained in high yield by the reaction of di-*sec*-butylmono-*n*-butylborane[16] and *sec*-butyllithium, the major product in this case being the corresponding trialkylborohydride[17] **6** [ir (THF) broad band centered at 2000 cm^{-1}] formed in 80% yield (hydride analysis).[18] Clearly, the difficulty is kinetic rather than thermodynamic.



The following procedure for the preparation of methyl 4-oxooctanoate is representative. All operations are carried out under nitrogen. To a dry 250-ml flask with a septum inlet, a reflux condenser, and a stirring bar were introduced sequentially 10.9 g (50 mmol) of tricyclopentylborane in THF (~50 ml), 20.8 ml (50 mmol) of 2.40 *M* n-butyllithium in hexane (0°, 1 hr), and 7.52 g (50 mmol) of 3-carbomethoxypropionyl chloride (0°, 30 min, then 40–45°, 24 hr). After evaporation of the volatile compounds, distillation provided 6.54 g (76%) of methyl 4-oxooctanoate:[19] bp 57–61° (0.25 mm); $n^{22}\mathrm{D}$ 1.4372; ^{1}H NMR (CCl_4, Me_4Si) δ 0.91 (t, J = 6.5 Hz, 3 H), 1.1–1.8 (m, 4 H), 2.3–2.8 (m, 6 H), 3.63 (s, 3 H) ppm; ir (neat) 1720, 1210, 1160 cm^{-1}. The residue was extracted with petroleum ether. After evaporation, 9.3 g (85%) of tricyclopentylborane was recovered as a crystalline compound.[20]

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, Research Corporation, and Syracuse University for financial support.

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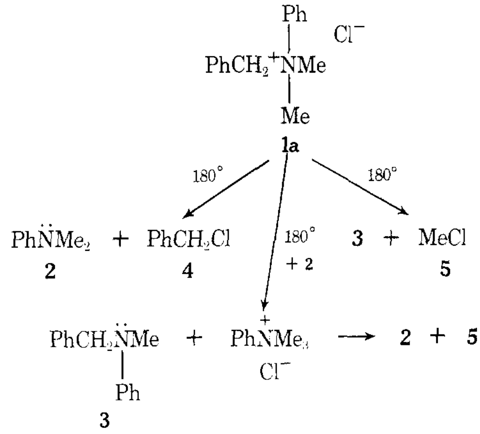
Counterion Effect in the Hofmann–Martius Rearrangement of a Quaternary Anilinium Ion[1]

Summary: Thermolysis of *N*-benzyl-*N,N*-dimethylanilinium iodide (**1b**) gave "monomeric" and cross-alkylated Hofmann–Martius amines with relatively minor amounts of *N,N*-dimethylaniline (**2**). The chloride of the same cation (**1a**) gave only retro-Menschutkin products.

Sir: The majority of the studies on the Hofmann–Martius rearrangement of N-substituted anilines dates back to preinstrumental times and, therefore, even in work of excellent quality, some data are necessarily not complete or very accurate, either qualitatively or quantitatively. Mechanistic conclusions also seem in need of a deep revision. Moreover, practically nothing is known about the relative reactivities of quaternary anilinium ions, the migratory aptitudes of different N substituents, and the effect of the counterion.[2] In this context, we wish to report the dramatic effect of the counterion change on the course of the thermolysis of the two halides **1a** (Cl) and **1b** (I) of the *N*-benzyl-*N,N*-dimethylanilinium ion.

When the chloride **1a** was heated at 175–180° without solvent, 90% of the salt reacted in 30 min to give the products arising from the two possible retro-Menschutkin reactions, namely *N,N*-dimethylaniline (**2**) and *N*-benzyl-*N*-methylaniline (**3**), as free bases together with the corresponding alkyl chlorides, benzyl chloride (**4**) and chloromethane (**5**). Amine **3** is in much larger amount than amine **2**, a fact which has a simple explanation in the operation of the Le Chatelier principle.

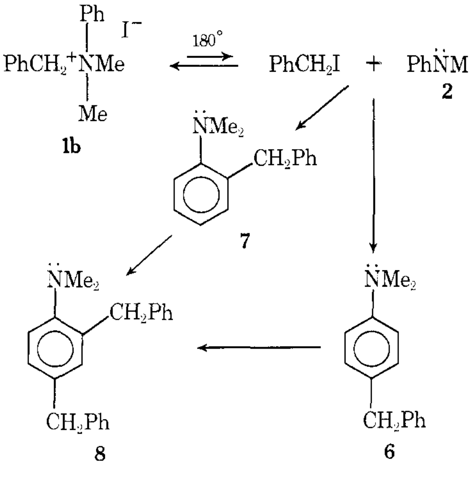
Scheme I



The reaction between **1a** and the *N,N*-dimethylaniline (**2**) being formed in the reaction may be an important source of **3**. In fact, independent experiments showed that *N,N*-dimethylaniline (**2**) reacts with the *N*-benzyl-*N,N*-dimethylanilinium cation to yield **3** at 180°.

The behavior of the iodide **1b** in the same experimental conditions was completely different, giving some amine **2** (~20%), no **3**, but three rearranged products: *p*-benzyl-*N,N*-dimethylaniline (**6**), *o*-benzyl-*N,N*-dimethylaniline (**7**), and *o,p*-dibenzyl-*N,N*-dimethylaniline (**8**). Products **6** and **7** were definitively different from all the Stevens and Sommelet isomers previously identified in the reaction of both **1a** and **1b** with strong bases.[3] The unequivocal identification of the reaction products from the thermolysis of **1b** was reached on the basis of gas chromatographic properties on widely different stationary phases (Carbowax 20M-KOH, silicones, etc.), mass spectrometry (electron impact at 70 and 15 eV), and spectroscopic characteristics (infrared and ^{1}H nuclear magnetic resonance on separated samples). Independent syntheses, which will be reported at a later time, confirmed the identifications.

Scheme II



The ortho/para ratio (~0.35) and the presence of the polyalkylated amine **8** does not suggest the operation of a radical mechanism recently advanced,[4] but rather indicates the possibility of a two-stage process: a predissociation (retro-Menschutkin, a reversible reaction, when no gaseous product is removed from the reacting mixture), followed by direct ring alkylation. Further study of these reactions is in progress.

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The Reaction of Superoxide with Alkyl Halides and Tosylates[1]

Summary: Alcohols are the major end product resulting from the reaction of alkyl halides and tosylates with an *excess* of potassium superoxide in an extraordinarily rapid process in which the carbon–oxygen bond-forming step proceeds with *inversion* of configuration.

Sir: The perspicacious observations of Fridovich and McCord[2] have led to the realization that superoxide is a common by-product produced by virtually all aerobic organisms. Moreover, recent studies suggest that superoxide may be involved in certain biological disorders and defense mechanisms.[3] Despite its apparent importance, much of the basic chemistry of superoxide remains ill-defined.[4] Of singular importance to the understanding of the reactivity of superoxide is a clarification of the ability of $O_2\cdot^-$ to act as either a one-electron reducing agent[6,7] or as a possible nucleophile. We have undertaken to answer this question by examining the reaction of superoxide with a particular class of electrophilic substrates, viz., alkyl halides and tosylates.

In a typical experiment, 1-bromooctane (0.644 g, 3.33 mmol) was added to a vigorously stirred mixture of powdered potassium superoxide[8] (0.710 g, 10.0 mmol) and 18-crown-6 ether[9] (0.264 g, 1.0 mmol) in dry DMSO (20 ml) at 25°.[10] The resulting mixture was allowed to stir for 75 min, then cautiously treated with 10 ml of water saturated with sodium chloride, and finally extracted with three 30-ml portions of petroleum ether. GLC analysis of the combined extracts indicated the presence of 1-octanol (63%), 1-octene (1%), and 1-octanal (12%). Results obtained on similar treatment of other representative substrates are given in Table I.

This sequence seems applicable to the production of alcohols from primary and secondary halides and tosylates; in our hands tertiary halides gave poor yields of alcohols