

Communications

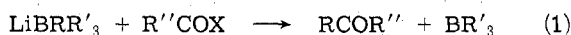
An Intermolecular Alkyl-Transfer Reaction of Tetraorganoborate Anions with Acyl Halides. A Novel Method for Moderating the Carbanion Reactivity

Summary: Lithium tetraorganoborate complexes, readily formed by the reaction of organolithiums with organoboranes, react smoothly with acyl halides to produce the corresponding ketones in high yields without concomitant formation of carbinols, thereby providing a novel method for moderating the carbanion reactivity.

Sir: We wish to report an *intermolecular* alkyl-transfer reaction of tetraorganoborate complexes, which provides a novel method for moderating the carbanion reactivity.

Trigonal organoboron compounds, i.e., organoboranes, function as electrophiles in a variety of reactions¹ but seldom as nucleophiles. Thus organoboranes are usually inert toward typical organic electrophiles, such as alkyl halides, carbonyl derivatives,² and epoxides, under ionic reaction conditions. One way of converting an organoborane into a nucleophilic species would be to form the corresponding borate anion or "ate" complex.³ Surprisingly, relatively little is known as to the *intermolecular* alkyl-transfer ability of the borate anions,^{3,4} although the highly nucleophilic nature of the hydridic hydrogens of borate anions has been amply demonstrated.⁵

We have found that lithium tetraorganoborates, such as lithium tetra-*n*-butylborate (1), react smoothly at 25° with acyl halides, such as benzoyl chloride and valeryl chloride, to form the corresponding ketones (eq 1). To our knowl-



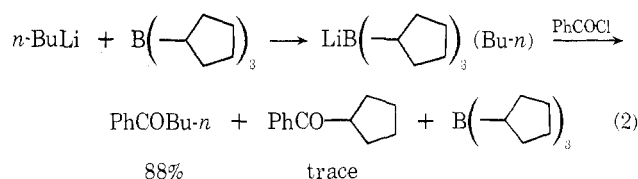
R and R' = alkyl; R'' = alkyl or aryl; X = Cl or Br

edge, such a clean-cut *intermolecular* alkyl-transfer reaction of tetraorganoborate anions under mild reaction conditions has not been reported. Since lithium tetra-*n*-butylborate does not react at any noticeable rate under the same reaction conditions with methyl iodide, benzyl chloride,^{4a} ethyl benzoate, and cyclohexenone,⁶ the reaction shown by

eq 1 provides a potentially highly "chemospecific"⁷ route to "mixed" ketones.⁸

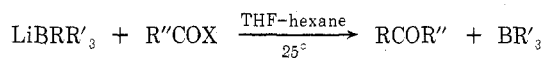
Significantly, the reaction is not complicated by the formation of the corresponding carbinols. The reaction of Grignard reagents or organolithiums with acyl halides usually produces predominantly the carbinols,⁹ and trialkylboranes do not react with the acyl halides under comparable conditions. It is, therefore, unlikely that the reaction involves the predissociation of 2 into the alkylolithium and the trialkylborane. We tentatively conclude that the borate complex 2 is the actual reacting species. The relative reactivities of benzoyl halides are in the order PhCOBr > PhCOCl >> PhCOF, suggesting that the ionization of acyl halides is probably not significant.

There are a few salient features which are worth noting. First, in the reaction of "mixed" tetraalkylborate complexes containing primary and secondary alkyl groups, the primary group is transferred nearly exclusively regardless of statistical factors (eq 2). This is true even when the pri-



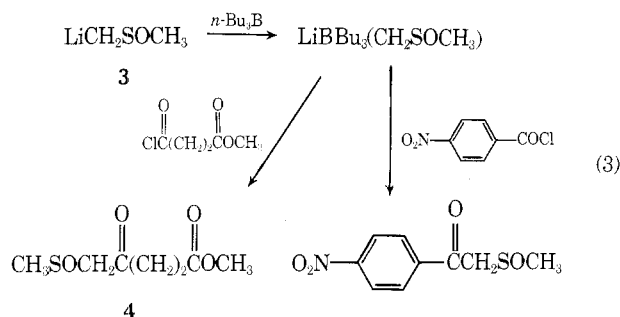
mary group is derived from the trialkylborane moiety (entry 5, Table I). Second, in the reaction shown in eq 2, the organoborane added is recovered quantitatively (>95% by GLC). Thus, the reaction may be viewed as an *organoborane-moderated* reaction of an organolithium with an acyl halide. Such a moderation not only diverts the reaction course (from carbinol formation to ketone formation) but renders the new reaction highly "chemospecific" (eq 3, entries 7, 8, 10, 12, 13). In our hands, the reaction of 3-carbomethoxypropionyl chloride with either 3¹⁰ or the reagent derived from 3 and cuprous chloride or iodide (3/CuX = 1 or 2) did not provide the desired product in any appreciable yield (<5%).¹¹ Third, the moderation of carbanion reac-

Table I
Preparation of Ketones by the Reaction of Lithium Tetraorganoborates with Acyl Halides



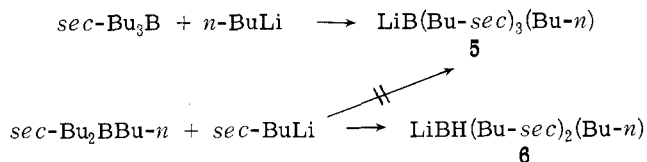
Entry	R	R'	R''	X	Product ^a	Yield, ^b %
1	<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉	Ph	Cl	<i>n</i> -C ₄ H ₉ COPh	80
2	<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉	Ph	Br	<i>n</i> -C ₄ H ₉ COPh	65
3	<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉	Ph	F	<i>n</i> -C ₄ H ₉ COPh	4
4	<i>n</i> -C ₄ H ₉	<i>c</i> -C ₅ H ₉	Ph	Cl	<i>n</i> -C ₄ H ₉ COPh	89
5	<i>n</i> -C ₄ H ₉	<i>c</i>	Ph	Cl	<i>n</i> -C ₄ H ₉ COPh	57
6	<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉	Cl	<i>n</i> -C ₄ H ₉ COC ₄ H ₉ - <i>n</i>	53
7	<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉	CH ₂ =CH(CH ₂) ₈	Cl	<i>n</i> -C ₄ H ₉ CO(CH ₂) ₈ CH=CH ₂	69
8	<i>n</i> -C ₄ H ₉	<i>c</i> -C ₅ H ₉	MeOOC(CH ₂) ₂	Cl	<i>n</i> -C ₄ H ₉ CO(CH ₂) ₂ COOMe	76
9	PhCH ₂	<i>n</i> -C ₄ H ₉	Ph	Cl	PhCH ₂ COPh	88
10	PhCH ₂	<i>n</i> -C ₄ H ₉	<i>p</i> -IPh	Cl	PhCH ₂ COPhI- <i>p</i>	(72) ^d
11	CH ₃ SOCH ₂	<i>n</i> -C ₄ H ₉	Ph	Cl	CH ₃ SOCH ₂ COPh	(51)
12	CH ₃ SOCH ₂	<i>n</i> -C ₄ H ₉	MeOOC(CH ₂) ₂	Cl	CH ₃ SOCH ₂ CO(CH ₂) ₂ COOME	(61)
13	CH ₃ SOCH ₂	<i>n</i> -C ₄ H ₉	<i>p</i> -NO ₂ Ph	Cl	CO ₃ SOCH ₂ COPhNO ₂ - <i>p</i>	(55) ^e

^a All products gave satisfactory ¹H NMR and ir spectra. All new products yielded correct analytical data. ^b By GLC. The numbers in parentheses are isolated yields. ^c BR'₃ = B(C₄H₉-*n*)₂(C₄H₉-*sec*). The borate complex was obtained by the reaction of tri-*n*-butylborane and *sec*-butyllithium. ^d Mp 99–100°. ^e Mp 44–45°.



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 alkynyl¹² and thioalkoxymethyl¹³ 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*-butylborane¹⁶ and *sec*-butyllithium, the major product in this case being the corresponding trialkylborohydride¹⁷ 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-carboxymethoxypropionyl 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*_D²² 1.4372; ¹H NMR (CCl₄, Me₄Si) 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

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Counterion Effect in the Hofmann–Martius Rearrangement of a Quaternary Anilinium Ion¹

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