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(17) The S.R.C. are acknowledged for financial support (to J.E. and T.W.M.).

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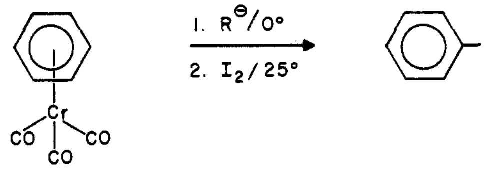
Reactions of Carbanions with π-Benzenechromium Tricarbonyl. Nucleophilic Aromatic Substitution for Hydride

Sir:

Coordination of a chromium tricarbonyl unit to an aromatic ring via π-bonding increases the reactivity of the ring toward attack by nucleophiles.[1-5] We have been interested in using the chromium tricarbonyl unit as an easily attached and removed activating group for nucleophilic aromatic substitution by carbanions.[6,7] Preliminary studies indicated that the substitution of tertiary carbanions for halide proceeded efficiently with π-halobenzenechromium tricarbonyl,[6] and minor products were observed in certain cases from formal substitution for hydride.[7,8] We now report conditions under which this side reaction becomes very efficient and promises a novel approach to coupling of carbon units with aromatic rings.

The method involves reaction of carbanions with π-benzenechromium tricarbonyl (**1**) to generate an intermediate



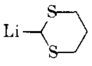
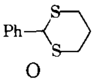
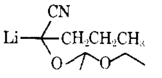
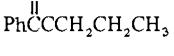
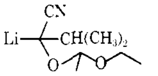
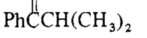
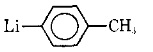
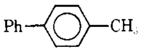
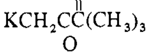
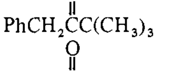
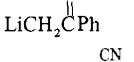
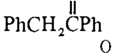
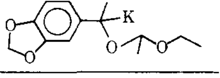
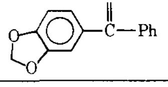
1

eq. 1

which can be converted to the free alkylbenzene by reaction with iodine (eq 1). Table I displays the results with a variety of carbanions. Certain of the carbanions were prepared by proton abstraction with lithium diisopropylamide (entries 1, 2, 4, 5, 8, 10–12, 16), potassium hexamethyldisilylazane (entry 9), potassium hydride (entries 15, 17), or *n*-butyllithium (entry 3), while others arose from reaction of the corresponding organic halide with the metal (Li or Mg; entries 7, 13, 14). *tert*-Butyllithium was obtained commercially. A solution of complex **1**[9] in tetrahydrofuran (THF) is added to the anion (1 mol equiv) in THF at −78°. The mixture is allowed to warm to higher temperature to allow interaction of the anion with the complex, and then excess iodine is added at −78°, as a solution in THF, followed by warming to 25°. The resulting chromium(III) salts are removed by aqueous washing, and the alkyl-arene is isolated from the organic solution. Most of the examples reported in Table I involve ca. 2 mmol scale; the following procedure at 25 mmol scale exemplifies potential preparative applications.

Lithium diisopropylamide[10] was generated from *n*-butyllithium (12.8 ml of a 1.95 *M* solution in hexane, 25.2 mmol) and diisopropylamine (3.84 ml, 27.5 mmol) in 50 ml of THF by mixing the reagents at −78° under argon and allowing the mixture to stir at 0° for 15 min. The pale yel-

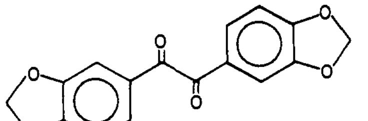
Table I. Coupling of Carbanions with π-Benzenechromium Tricarbonyl

Entry	Carbanion	Product	Yield (%)[a]
1	$LiC(CH_3)_2CN$	$PhC(CH_3)_2CN$	94
2	$LiCH_2CN$	$PhCH_2CN$	68
3			93
4		 $PhC(=O)CH_2CH_2CH_3$	90[b]
5		 $PhC(=O)CH(CH_3)_2$	88[b]
6	$LiC(CH_3)_3$	$PhC(CH_3)_3$	97[c]
7			71
8	$LiC(CH_3)_2CO_2$-*t*-Bu	$PhC(CH_3)_2CO_2$-*t*-Bu	~10
9	$KC(CH_3)_2CO_2$-*t*-Bu	$PhC(CH_3)_2CO_2$-*t*-Bu	88
10	$LiC(CH_3)_2CO_2$-*t*-Bu	$PhC(CH_3)_2CO_2$-*t*-Bu	91[d]
11	$LiCH_2CO_2$-*t*-Bu	$PhCH_2CO_2$-*t*-Bu	87[d]
12	$LiCH(CH_3)CO_2$-*t*-Bu	$PhCH(CH_3)CO_2$-*t*-Bu	88[d]
13	$BrMgCH_2CH{=}CH_2$	$PhCH_2CH{=}CH_2$	<5
14	$ClMgC(CH_3)_3$	$PhC(CH_3)_3$	<5
15	 $KCH_2C(=O)C(CH_3)_3$	 $PhCH_2C(=O)C(CH_3)_3$	~20[e]
16	 $LiCH_2C(=O)Ph$	 $PhCH_2C(=O)Ph$	<5
17			<5[b,d]

[a] The yields are based on isolated material unless otherwise noted. The products were identified by comparison of spectral data and melting point (if solid) with published data or with data collected on a sample prepared by established procedures. [b] The final product was obtained by sequential acid and base hydrolysis according to the method of G. Stork and L. Maldonado, *J. Amer. Chem. Soc.*, 93, 5286 (1971). [c] This yield was determined by quantitative GLPC using an internal standard after careful concentration of the ether extract from the isolation procedure. [d] The medium is 1 : 1 THF : HMPA. [e] The medium is 1 : 5 THF : HMPA.

low solution was cooled to −78°, and isobutyronitrile (2.20 ml, 25 mmol) was added dropwise over a period of 5 min. The mixture was warmed at 0° for 15 min, cooled to −78°, and a solution of π-benzenechromium tricarbonyl (**1**) in 25 ml of THF was added dropwise over 5 min. The yellow solution was warmed at 0° for 30 min, cooled to −78°, and a solution of iodine (25 g, 98 mmol of I_2) in 75 ml of THF was added dropwise over 15 min. After the resulting mixture had been stirred at 24° for 3 hr (CO evolution), it was partitioned between ether (200 ml) and 5% aqueous sodium bisulfite solution (100 ml). The ether layer was washed successively with water and aqueous salt solution, dried over anhydrous magnesium sulfate, and concentrated to leave a yellow liquid. Flash distillation at 25° (0.001 Torr) afforded 3.562 g (98% yield) of a colorless liquid with spectral properties identical with phenylisobutyronitrile.[11]

Several generalizations are clear from Table I. Very reactive organolithium reagents (entries 1-7) give efficient phenylation under mild conditions in THF. Organomagnesium halides (entries 13, 14) and lithium enolates of ketones and esters (entries 8, 16) do not give significant yields of phenylation products under these conditions. However, ester enolates undergo phenylation much more efficiently if a polar, aprotic solvent is added to the medium (entries 10-12) or if the potassium cation is used (entry 9). In contrast to phenylation using π-(chlorobenzene)chromium tricarbonyl,[6] secondary and primary ester enolates participate in the reaction just as well as tertiary ester enolates (entries 11, 12). Ketone enolates, even with potassium as the counterion and using high concentrations of hexamethylphosphoric triamide (HMPA), fail to give preparatively useful amounts of α-phenyl ketones (e.g., entry 15). The more stabilized cyanohydrinacetal anion of entry 17 also fails to undergo phenylation, even using the potassium counterion (from potassium hydride-THF) and HMPA. In this case the anion presumably is not interacting with the π-benzenechromium tricarbonyl (**1**); the observed product, the α-diketone **2**,[12] is obtained in 92% yield after iodine oxidation in the presence or absence of **1**.



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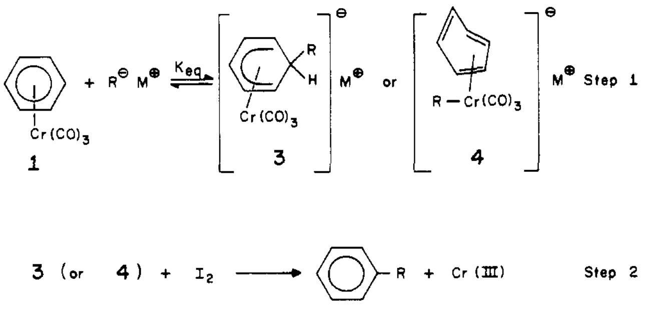
The nature of the intermediate and the steps in the iodine oxidation procedure are not yet clear, but two reasonable alternatives (**3** and **4**) for the structure of the intermediate are suggested in Scheme I. Intermediate **3** results from carbanion attack at the π-arene ligand, a process with abundant precedent in the chemistry of ionic π-arenemetal complexes.[3-5] Intermediate **4** represents initial attack at chromium and is more easily reconciled with the apparent reversibility of the first step.[13]

Scheme I



The failure of the more stable anions (ketone enolates, aryl substituted cyanohydrin-acetal anions) to give efficient phenylation presumably arises from a low equilibrium constant, K_{eq}, for step 1. Similarly, using HMPA solvent or potassium counterions in phenylation of ester enolates may have the effect of raising K_{eq} and thus providing a high concentration of the intermediate (**3** or **4**) prior to quenching with iodine. Studies are underway to elucidate the structure and reactivity of the proposed intermediate.

References and Notes

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(10) Prepared according to the procedure used by H. Wynberg, *Tetrahedron Lett.*, 3001 (1971).
(11) An authentic sample of phenylisobutyronitrile was prepared by methylation of phenylacetonitrile using excess methyl iodide and sodium amide.
(12) The α-diketone exhibited ir, ^{1}H NMR, and mass spectral data consistent with the structure.
(13) Unpublished work by H. T. Hall, M. Yoshifuji, and J. Belasco in these laboratories.
(14) Fellow of the Alfred P. Sloan Foundation and recipient of a Camille and Henry Dreyfus Teacher-Scholar Grant.

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Computational Evidence for a Stable Intermediate in the Rearrangement of 1,2-$C_2B_4H_6$ to 1,6-$C_2B_4H_6$

Sir:

Few reaction pathways in rearrangements[1] of boron compounds are mechanistically well understood. The isomerization of 1,2-$C_2B_4H_6$ to 1,6-$C_2B_4H_6$ is a polyhedral rearrangement for which the cooperative twist dsd (diamond-square-diamond)[1a] mechanism has been suggested. This interconversion proceeds measurably[2] at 250°, but a CNDO/2 study[3] failed to find an energetically accessible pathway. We report here a PRDDO[4] study of this interconversion (see Figure 1) and of the analogous degenerate rearrangement of $B_6H_6^{2-}$ which utilizes and serves to introduce a new approach for computing reaction pathways.[5] A principal result is a subtle but energetically significant modification of the dsd mechanism which implicates a third stable geometry on the $C_2B_4H_6$ energy surface as an intermediate in the interconversion. A second focus is the effect—and predictability—of carbon substitution on the energetics of the parent $B_6H_6^{2-}$ rearrangement. Based on past experience,[4b] we expect the results presented here to be of essentially ab initio minimum-basis-set quality.

The reaction pathways approach we have developed and employ here will be fully described in a forthcoming paper;[5] for reasons of space, we give here only a brief introduction. First, we construct an initial *linear synchronous transit*