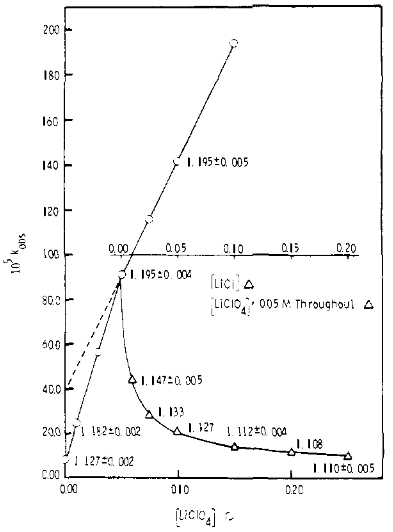

Figure 1. Plot of k *vs.* [LiX] for solvolysis of *p*-methoxybenzal chloride in 85% aqueous dioxane. ○ represents points for $LiClO_4$ in 85% dioxane, while △ represents points for varying LiCl concentration in 85% dioxane containing a constant concentration of $LiClO_4$ [0.05 *M*]. The numbers recorded next to each point refer to the α-D isotope effect determined under those conditions. Analysis of the special salt effect curve using the Winstein equation gives $k^\circ_{ext}/k^\circ = 4.4$ and $b = 26.5$.

characteristic of systems showing the "special" salt effect, although the separation of normal and "special" salt effects is not as pronounced as other cases.[8-11] (The results in 85% dioxane are displayed in Figure 1.) Since perchlorate has been shown to effectively prevent return (by ion pair exchange) of III, it is very interesting to examine the α-D effect as a function of [$LiClO_4$]. As is evident from Figure 1, addition of 0.01 *M* $LiClO_4$ increases the rate of hydrolysis (2.7-fold) and also increases the α-D effect from 1.127 ± 0.002 to 1.182 ± 0.002. This result suggests that most, but not all, return from III has been eliminated. Addition of 0.05 *M* $LiClO_4$ results in an even greater rate enhancement (8.6-fold) and an even larger α-D effect, 1.195 ± 0.004. However, while 0.10 *M* $LiClO_4$ increases the hydrolysis rate even more, there is no further change in the α-D effect, 1.195 ± 0.005. Thus it would appear that all kinetically significant return from III is eliminated by the addition of 0.05 *M* $LiClO_4$ and k_2 now becomes rate limiting.[15,17]

Similar results are obtained in 90% dioxane. Addition of 0.10 *M* $LiClO_4$ increases solvolysis rate (40-fold) and the α-D effect increases from 1.132 ± 0.008 to 1.204 ± 0.004. Interestingly, the same maximum α-D effect (1.199 ± 0.008) is observed for the hydrolysis of the much less reactive benzal chloride in water.

It should be noted here that addition of 0.15 *M* LiCl to 85% dioxane results in only a 13% rate reduction and therefore return from dissociated ions is relatively unimportant in this solvent.[18] However, the α-D effect is reduced slightly (1.114 ± 0.001) showing that some return from IV does occur.

While addition of LiCl to 85% dioxane does not result in substantial rate depression, addition of LiCl to this solvent containing 0.05 *M* $LiClO_4$ results in substantial *induced* depression.[7] Thus, addition of 0.10, 0.15, and 0.20 *M* LiCl to 0.05 *M* $LiClO_4$ (Figure 1) in 85% dioxane results in rate depressions of 5.3-, 6.4-, and 7.6-fold, respectively. The α-D effect in this range is constant and equal to 1.111 ± 0.004 (Figure 1). This then corresponds to the α-D effects expected for rate-limiting attack of solvent on III (k_s^{III}) to produce solvolysis product.

Because further additions of LiCl were not possible for solubility reasons, the limiting rate at high Cl^- could not be obtained. However, the rate in 0.20 *M* LiCl and 0.05 *M* $LiClO_4$ is only 29% greater than the rate observed in 0.15 *M* LiCl alone. Thus, a substantial part of the rate enhancement observed for $LiClO_4$ can be eliminated with additional LiCl.

We are continuing these and related investigations with a view toward establishing the usefulness of this technique in problems of solvolysis mechanisms.

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(17) As was pointed out by a reviewer, it is possible that the rate-limiting step in the presence of perchlorate ion involves formation of perchlorate solvent-separated ion pair from chloride solvent-separated ion pair. This would still give the maximum α-D isotope effect, and we have no information at present which rules out this possibility.

(18) This is to be compared to a 2.7-fold rate reduction observed in 75% dioxane containing 0.15 *M* LiCl. Thus, in this solvent return from dissociated ions is quite important.

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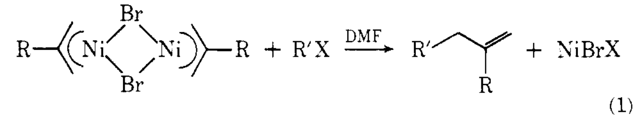
Reaction of π-Allylnickel Bromide Complexes with Organic Halides. Stereochemistry and Mechanism

Sir:

The reaction of π-allylnickel halide complexes with organic halides (eq 1) has been known for several years[1] and



(1)

is finding increased use in organic synthesis.[2] Since this reaction proceeds equally well with alkyl, aryl, and vinyl halides, it is clearly not an S_N2 process. We present herein evidence that this reaction proceeds via a radical chain mechanism.

To examine the stereochemistry[3] of this coupling reac-

Scheme I

$$\begin{aligned} &[(\text{allyl})\text{NiBr}] + \text{RX} \longrightarrow \text{RX}\cdot^- + [(\text{allyl})\text{NiBr}]\cdot^+ && \text{(a)} \\ &\text{RX}\cdot^- \longrightarrow \text{R}\cdot + \text{X}^- && \text{(b)} \\ &\text{R}\cdot + [(\text{allyl})\text{NiBr}] \longrightarrow \text{R-allyl} + \text{NiBr}\cdot && \text{(c)} \\ &\text{NiBr}\cdot + \text{RX} \longrightarrow \text{RX}\cdot^- + \text{NiBr}^+ && \text{(d)} \end{aligned}$$

Scheme II

$$\begin{aligned} &\text{R}\cdot + [(\text{allyl})\text{NiBr}] \longrightarrow [\text{R}(\text{allyl})\text{NiBr}]^\cdot \\ &[\text{R}(\text{allyl})\text{NiBr}]^\cdot + \text{RX} \longrightarrow [\text{R}(\text{allyl})\text{NiBrX}] + \text{R}\cdot \\ &[\text{R}(\text{allyl})\text{NiBrX}] \longrightarrow \text{R-allyl} + \text{NiBrX} \end{aligned}$$

tion, π-(2-methoxyallyl)nickel bromide[4] was treated with (*S*)-(+)-2-iodooctane ($[\alpha]^{25}{}_{589}$ +42.2°).[5] The resulting 4-methyl-2-decanone was *completely racemic* by comparison with authentic (*R*)-(+)-4-methyl-2-decanone prepared by an independent method.[6] Racemization occurred in the product-forming step, since (*R*)-(+)-4-methyl-2-decanone ($[\alpha]^{25}{}_{589}$ +1.28°) was not racemized by subjection to the conditions of the reaction and isolation and, when the reaction was run to 30% completion, unreacted (*S*)-(+)-2-iodooctane was recovered without loss of rotation. Furthermore, this reaction was *completely inhibited* by the addition of less than 1 mol % *m*-dinitrobenzene, a potent radical anion scavanger.[7,8]

To test if inhibition by *m*-dinitrobenzene was general π-(2-methallyl)nickel bromide was treated under identical conditions[9] with 2-iodooctane, iodobenzene, β-bromostyrene, and methallyl bromide both in the absence and presence of 1 mol % *m*-dinitrobenzene. With 2-iodooctane, iodobenzene, and β-bromostyrene the uninhibited reactions went essentially to completion, while those containing inhibitor went only to the extent of 5–10% completion. With the highly reactive methallyl bromide, the reaction containing inhibitor went to 50% completion. Thus inhibition of this reaction by very small amounts of radical anion scavanger appears to be general and is strongly suggestive of a radical chain process.

A mechanism consistent with the above observations for the alkyl, aryl, and allyl halides is presented in Scheme I.

One possible chain initiation step (a) involves electron transfer from the nickel complex to the halide to produce the corresponding radical anion.[10] The chain carrying steps (b–c) are similar to those proposed by Kornblum[7a,b] and Russell[7c] for the reaction of nitro carbanions with *p*-nitrobenzyl chloride. Loss of stereochemistry may result from the radical intermediate in steps b and c. Inhibition by *m*-dinitrobenzene can occur by scavenging either $\text{RX}\cdot^-$ or $\text{NiBr}\cdot$. An alternative scheme for steps c, d, and b involves a free radical oxidative addition similar to that proposed by Osborn (Scheme II).[11]

While the reaction of β-bromostyrene with π-allylnickel halide complexes is also strongly inhibited by the presence of small amounts of *m*-dinitrobenzene, the stereochemistry of the double bond is maintained.[4] Thus, while this reaction also appears to be a radical chain reaction, it must differ somewhat in mechanism from the other cases discussed, since free vinyl radicals rapidly lose their stereochemistry.[12]

In contrast to the alkylation of organic halides and tosylates by diorganocuprates, for which a compelling case for an S$_\text{N}$2 mechanism has been made,[13] an electron transfer–radical chain mechanism best accommodates the observations reported above. The role of radical chain processes in other organometallic reactions as well as the use of radical initiators to effect the reaction of organometallic complexes with normally unreactive substrates are under current investigation.[14]

Acknowledgment. Support for this research through grants from the National Institutes of Health (CA 15529-01) and the National Science Foundation (GP-43626) is gratefully acknowledged.

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Signs of Long-Range Carbon–Carbon Coupling Constants. Tri-^{13}C-Labeled Tetrolic Ester

Sir:

With a spin of ½ and with no nonbonding valence electrons, ^{13}C is the nucleus expected to be most like ^{1}H in nmr spin–spin coupling. Indeed, for geometrically equivalent systems, long-range carbon–proton and proton–proton couplings appear to be correlated;[1] the ratio $J_{\text{CH}}/J_{\text{HH}}$ is +0.4 to +0.7.[2] To test the idea that this analogy may be extended to carbon–carbon couplings, one should determine long-range J_{CC} values, including signs, of a system that can be related to a geometrically equivalent carbon–proton system. We wish to report the successful determination of the signs of long-range carbon–carbon couplings of methyl tetrolate (**1**) and to compare these couplings with analogous J_{CH} values of a geometrically equivalent system.

$$\overset{*}{\text{C}}\text{H}_3\text{—}\overset{*}{\text{C}}\equiv\text{C—}\overset{*}{\text{C}}\text{O}_2\text{CH}_3$$

1

Compound **1**, labeled with >90% ^{13}C at each of the positions C-1, C-3, and C-4, was synthesized in a 15-step scheme originating from >90% ^{13}C carbon dioxide.[3] The proton-decoupled carbon nmr spectrum of **1** exhibited a