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REACTIONS OF AROMATIC RADICAL ANIONS V. EVIDENCE FOR ANION INTERMEDIACY IN THE REACTION OF ALKYL CHLORIDES, BROMIDES AND IODIDES WITH SODIUM NAPHTHALENE.

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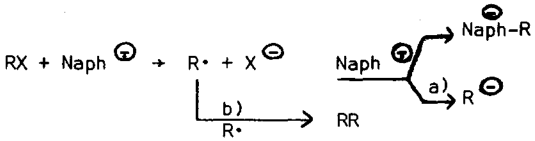
An effective trapping agent has been devised for the anion intermediate formed from the reaction of alkyl halides with sodium naphthalene I. Our results present evidence for an anion intermediate in the reaction of iodides as well as bromides and chlorides.

Whereas there is evidence for the intermediacy of an anion in the reaction of chlorides and bromides, experiments designed to demonstrate standard behavior of the alkyl sodiums have been unsuccessful (1,2). Proving the existence of this intermediate is crucial to the understanding of the reaction as depicted in the general scheme (1-6) below.



(1)

Alkyl chlorides and bromides were thought to react largely by path (a), whereas iodides by path (b). The anion (R^-), a sodium alkyl, is not stable in ether solvents, tetrahydrofuran (THF) and dimethoxyethane (DME), and is rapidly converted to the hydrocarbon by proton abstraction from the solvent.

A suitable trapping agent must be stable to I and to the alkyl halide, must react rapidly with the anion, and must give a product that is both stable to the reaction conditions and readily amenable to quantitative analysis. We have found all of these requirements to be fulfilled adequately by anhydrous magnesium bormide. The halogen-metal interchange proceeds both rapidly and irreversibly giving rise to the stable Grignard reagent which is converted to the deuterated hydrocarbon by quenching in deuterium oxide.

n-Hexyl chloride, bromide and iodide were reacted with I both with and without anhydrous magnesium bromide in tetrahydrofuran at ambient temperatures. The resulting solutions were quenched in D_2O and analysed by vapor phase chromatography and infrared spectroscopy. The results are summarized in Table I.

Table I Yields for Reactions of n-Hexyl Halides with I[a]

Halide	$MgBr_2$[b] Present	% Hexane[c] (Total)	% Hexane[d,e] (Deuterated)	% Dodecane[c]
Chloride	-	30	0	3
	+	37	85	4
Bromide	-	37	0	5
	+	36	85	4
Iodide	-	18	0	32
	+	35	80	15

a) Reactions were performed by injecting ca I M I in THF into stirred solutions of ca 0.2 M halide in THF or into ca 0.2 M halide and ca 0.27 M $MgBr_2$ in THF until the deep green color of I persisted.

b) Anhydrous $MgBr_2$ was prepared by dropping $Br(CH_2)_2Br$ into Mg in THF to form a saturated solution. The concentration was determined by titration with EDTA.

c) Analyses were by vpc using internal standards. Yields were ±5% of that reported.

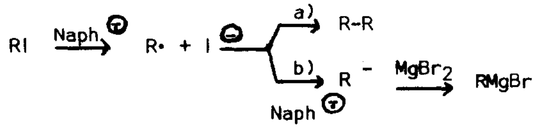
d) Analyses were by infrared spectroscopy absorption at 2180 cm^{-1} using standard solutions of authentic $CH_3(CH_2)_4CH_2D$ prepared from the Grignard reaction. These results were reproduced when $n\text{-}C_4H_9Br$ was reacted with $MgBr_2$ and I and subsequently with acetone to give $CH_3(CH_2)_3C(OH)(CH_3)_2$ whose IR and vpc were identical to that formed from the standard Grignard preparation.

e) Inverse addition of halides and $MgBr_2$ to I gave comparable results.

Inspection of the table reveals four important features. First, anhydrous magnesium bromide is a highly effective trapping agent (∿85% of the recovered hydrocarbon is deuterated). This represents the first successful trapping of the very reactive anion intermediate. Second, the product distribution with n-hexyl chloride and bromide is unaffected by the inclusion of the trapping agent. This would indicate that alkyl chlorides and bromides indeed react through anion intermediates. Third, the yield of deuterated hydrocarbon from the iodide reaction is essentially the same as that from the chloride and bromide, and finally, the product distribution is markedly affected.

We consider the above results to be strong evidence for anion intermediacy in iodide reduction. Grignard production from alkyl iodide can be rationalized by the following:

A)



(2)

B) $$\mathrm{RI} \xrightarrow{\mathrm{Naph}^{\dot{\ominus}}} \mathrm{R}\cdot + \mathrm{I}^{\ominus} \qquad (3)$$

$$\mathrm{R}\cdot + \mathrm{MgBr_2} \longrightarrow \mathrm{RMgBr} + \mathrm{Br}\cdot \qquad (4)$$

C) $$\mathrm{RI} \xrightarrow{\mathrm{Naph}^{\dot{\ominus}}} \mathrm{R}\cdot + \mathrm{I}^{\ominus} \xrightarrow{\mathrm{Naph}^{\dot{\ominus}}} \mathrm{R}^{\ominus} \qquad (5)$$

$$\mathrm{R}^{\ominus} + \mathrm{MgBr_2} \longrightarrow \mathrm{RMgBr} + \mathrm{Br}^{\ominus} \qquad (6)$$

Previous results would have indicated scheme A where small amounts of Grignard would form from anion in competition with more rapid coupling. This scheme is ruled out unambiguously by the yield data. The trapping agent markedly decreases dimer formation with a concomittant increase in hexane, clearly interfering with the usual pathway.

Scheme B could account for Grignard production, however, we consider this unlikely for the follow reasons. Atom transfer (Equation 4) would have to compete favorably with other potential reactions of the radical. This is unlikely considering that reduction of similar radicals by I is diffusion controlled (6) whereas atom transfer would have a resonable energy of activation (8). In addition, the product distribution from n-hexyl chloride and bromide, where anion intermediacy is clearly demonstrated, is essentially the same as that obtained from n-hexyl iodide. It would be very fortuitous if the selectivity for deuteration were the same for both anion and radical processes.

Accordingly, we favor scheme C where magnesium bromide intercepts the anion in the iodide reduction as in the chloride and bromide reduction. If anions are implicated, however, the high yield of dimer formed in the absence of the trapping agent must be accounted for, as well as the strong evidence that radical intermediates are involved in dimer formation (3). A mechanism that would account for the seeming disparities is given in Equations 7-10 where brackets indicate a caged-radical pair.

$$\mathrm{RI} + \mathrm{Naph}^{\dot{\ominus}} \longrightarrow \mathrm{R}\cdot + \mathrm{Naph} \qquad (7)$$

$$\mathrm{R}\cdot + \mathrm{Naph}^{\dot{\ominus}} \longrightarrow \mathrm{R}^{\ominus} + \mathrm{Naph} \qquad (8)$$

$$\mathrm{R}^{\ominus} + \mathrm{RI} \longrightarrow [\mathrm{R}\cdot + \mathrm{R}\cdot + \mathrm{I}^{\ominus}] \qquad (9)$$

$$[\mathrm{R}\cdot + \mathrm{R}\cdot + \mathrm{I}^{\ominus}] \longrightarrow \mathrm{R{-}R} + \mathrm{I}^{\ominus} \qquad (10)$$

The high yield of dimer products in iodide reduction as well as the intermediacy of radicals are a result of electron transfer (Equation 9) from the anion to the alkyl iodide and subsequent radical collapse (Equation 10). Electron transfer from anion to alkyl iodides would be considerably more rapid than to chlorides and bromides.

Evidence for electron transfer from anions to produce radicals derives from independent experimental observations. Lawler and Ward (9) and Lepley (10) found nuclear polarization in products from reactions of organolithium with alkyl halides. Russell (11) identified radicals produced from the reaction of organolithium and alkyl halides by ESR spectroscopy. Garst concludes from studies of α, w-diiodoalkanes with I that dimers have alkyl sodium precursors (7).

Although dimer formation occurs for the most part from radicals derived from anions, there is evidence that a small amount is produced from direct coupling of initially formed radicals (Eq. Ib). While dimer formation is suppressed considerably by the trapping agent or by evaporation experiments, it is not completely eliminated.

Demonstration that $MgBr_2$ is an effective trapping agent in reactions of alkyl halides with I to give Grignard products suggests an alternative synthesis of Grignard reagents under mild and facile conditions. These implications are being investigated currently.

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