THE WURTZ CROSS-COUPPLING REACTION REVISITED

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Abstract

This work was initiated in an attempt to maximize the Wurtz cross-coupling between iodomethane and iodoethane over sodium, yielding propane. Bromoethane and potassium were also studied. The total halide concentrations were varied between 1.0 - 4.0 molar, the mole ratios of iodoethane or bromoethane to iodomethane were varied from 1:1 to 10:1 at room temperature and 0.0 °C in THF, diethyl ether and benzene. The results indicate qualitatively that the organo-halide reactivity is iodomethane > iodoethane > bromoethane, metals are more selective in benzene > diethyl ether > THF and that the system is more selective at lower temperatures. The most important result from this work was that no cross-coupling product, propane, was detected. Theoretical implications of this fact are discussed.

Introduction

The Wurtz reaction, one of the oldest "name reactions" in organic chemistry^{1,2}, involves the coupling of organo-halides over sodium (eq 1).

It has been postulated that organometallics are intermediates in the Wurtz synthesis of alkanes. Spencer and Price³ suggested in 1910 that organolithium compounds were produced as intermediates in the coupling of organo-halides over lithium metal. Gilman and Jones⁴, also proposed organometallics as intermediates, yielding either coupling products or exchange products (eq 2 - 4).

Although, the Wurtz reaction can be used to prepare unsymmetrical hydrocarbons by reacting two alkyl halides with sodium, as illustrated in eq 5,

the yields are generally low due to nearly statistical distribution of RR, R'R', as well as RR'.

We decided, for an undergraduate research project, to systematically study the cross-coupling reaction and attempt to maximize the cross coupling product. In order to keep the system as simple as possible, we chose to study the cross-coupling of iodomethane with iodoethane (eq 6).

Materials and Methods

The iodomethane, iodoethane, bromoethane and potassium were reagent grade Aldrich chemicals. The potassium(Aldrich) and sodium(source unknown) were freshly cut and

weighed before each run. No special precautions were taken to protect the metals from the atmosphere. The THF (Aldrich), diethyl ether (Fisher Scientific) and benzene (Fisher Scientific) were dried over sodium and freshly distilled before each run.

Reactions were carried out in a 50 mL round bottom flask(14/20) fitted with a condenser and attached to a 2 L water displacement tower, fitted with a septum cap for taking gaseous samples. The system was swept several times with helium to remove air from the system in order to have an inert atmosphere and minimize the air peak in the gas chromatogram. At the end of the reaction the system was once again swept with helium to insure all the gaseous products were collected in the tower. The water displacement tower was filled with a saturated NaCl solution and heated to $\sim 80^\circ\text{C}$ in an attempt to minimize hydrocarbon solubility's. The total volume of hydrocarbons and helium collected was ~ 1.5 L. Products of the reactions were analyzed with a Perkin-Elmer Sigma 3B gas chromatograph, equipped with a thermal conductivity detector and a 11 foot BMEA + DES column at 40°C . The volume of solution used was 25 mL and the total ($R_1X + R_2X$) concentration of the halides was varied from 1 to 4 molar. The amount of metal (Na or K) was limited to the quantity needed to react with no more than 20 - 25% of the total halides present. Reactions were studied at 0.0°C and room temperature.

Results

As expected⁵, iodomethane was much more reactive than either iodoethane or bromoethane. What was not expected and is the most significant part of this study, is that the cross-coupling product, propane, was not observed. Iodomethane and iodoethane simply do not cross-couple under the conditions employed in this study. Standard samples of ethane:butane:propane with volume ratios of approximately 20:20:1 were prepared and the propane was readily detectable. Free radical disproportionation products, such as methane and ethene were not detected.

The results from the work employing sodium and THF as the solvent are summarized in Tables I - IV.

Table I. Results of reacting iodomethane and iodoethane, in a 1:1 mole ratio, over sodium at room temperature in THF.

Halide ^a Concen.(M)	ethane ^b butane	propane
0.995	1.04	none
2.01	1.14	none
3.01	1.21	none
3.99	1.54	none

^aTotal molar concentration of iodomethane and iodoethane. ^bGLC peak area ratios.

Table II. Results from increasing the molar ratios of iodoethane to iodomethane in a 1.01 M total halide solution in THF at room temperature, over sodium.

$\frac{\text{C}_2\text{H}_5\text{I}}{\text{CH}_3\text{I}}$ ^a	ethane ^b butane	propane
2.01	4.89	none
10.00	2.12	none

^aMole ratios of halides. ^bGLC peak area ratios.

Table III. Results from lowering the temperature to 0.0 °C and increasing the total halide concentration in THF over sodium with the halide mole ratios of 1:1.

Halide ^a Concen.(M)	ethane ^b butane	propane
1.01	1.24	none
2.00	2.14	none
3.01	3.22	none

^aTotal molar concentration of iodomethane and iodoethane. ^bGLC peak area ratios.**Table IV.** Results from increasing the molar ratios of bromoethane to iodomethane in a 1.04 M total halide solution in THF at room temperature, over sodium.

C ₂ H ₅ Br ^a CH ₃ I	ethane ^b butane	propane
1.04	18.24	none
1.99	9.39	none
10.3	4.89	none

^aMole ratios of halides. ^bGLC peak area ratios.

Other systems were investigated using diethyl ether or benzene in place of THF. Once again as expected⁵, the relative reactivity of the halides is iodomethane > iodoethane > bromoethane and the relative selectivity for the solvents is benzene > diethyl ether > THF. The final three experiments employed potassium in place of sodium and the results of that work indicated that potassium is less selective than is sodium, once again as expected⁵. At no time in this work was the cross-coupling product, propane, detected.

Discussion

The possibility that the more reactive iodomethane couples first and the less reactive iodoethane later is negated in three ways. The reactions are all limited by the quantity of metal used to 25% or less total reaction, the ethane to butane peak area ratios increase with increased total halide concentrations and decrease with an increase in the ratio of iodoethane to iodomethane. It also seems clear that organometallic intermediates (eq 3) are not involved. It is not reasonable to expect that CH₃M would selectively couple with CH₃I and totally unreasonable that C₂H₅M would selectively couple with C₂H₅I.

It seems clear that the coupling that leads to ethane is occurring in a region isolated from the region where coupling leads to butane. A highly speculative possibility is that the coupling is occurring not on the surface of the metal, but below the surface of the metal. Since the methyl group is less sterically hindered, it may be coupling at a lower level (below the surface) than the more sterically hindered ethyl group. We are not necessarily claiming priority for this possibility but are unaware of a precedent.

Regardless of the explanation, this study should be of interest relative to the modern debate between the surface mechanisms of H.L. Walborsky and J.F. Garst⁶. One other area where this work may be pertinent is that in previous work⁵ it was discovered that although lithium and sodium react readily with 2-ethoxyethanol and potassium explosively, upon addition of 0.2 - 1.0 molar halides the evolution of hydrogen completely ceases and the system can be used to study relative organo-halide reactivities.

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