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THE REACTION OF n-BUTYLLITHIUM AND POTASSIUM t-AMYLOXIDE WITH BUTENES

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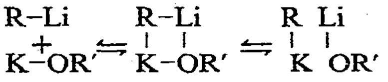
SUMMARY

1-Butene, *cis*/*trans*-2-butene and 2-methylpropene were polymetalated by treatment with the product obtained by combination of n-butyllithium and potassium t-amyloxide. Polymetalation was determined by quenching with deuterium oxide and analysis by gas chromatograph–mass spectrometer combination. The rate of metalation was followed by n-butane evolution. Approximately 20% of *cis*-2-butene exclusively was realized after H_2O quench of the reaction of 1-butene/n-butyllithium/potassium t-amyloxide for 1.0 h at room temperature. A small amount (7%) of a *cis*/*trans*-2-butene mixture was isomerized to 1-butene and the remaining 2-butene was enriched in the *cis*-isomer. The assumption that n-butylpotassium was the active metalating species was confirmed by the dependency on lithium/potassium ratio, relative ease of organometallic decomposition at 70°, rapid reaction with monochlorostyrene at room temperature, and the similarity to organosodium and organopotassium isomerization of olefins.

INTRODUCTION

Organopotassium compounds have been prepared in good yield and relatively pure by treatment of organolithium compounds with potassium t-butoxide[1] or potassium (−)(1*R*)-menthoxide[2]. Potassium t-butoxide by itself is a moderately strong base that will metalate or catalyze reactions with acidic hydrocarbons, such as isocyanoacetates[3], *trans*-1,2,3-triphenylcyclopropane[4], and alkylaromatic compounds[5]. Pentenes and butenes have been isomerized by potassium t-butoxide at 55° in dimethylsulfoxide solution[6].

Hsieh and Wofford[7] employed combinations of potassium t-butoxide and alkyllithiums to prepare homogeneous copolymers of butadiene and styrene. They believed that a dynamic equilibrium existed between carbon–metal bonds and oxygen–metal bonds, the anionic behavior being dependent upon the ratio of lithium and potassium (eqn. 1). Wofford[8] used the mixture as a catalyst with an alkyl-substituted



$$\begin{matrix}\mathrm{R{-}Li}\\ +\\ \mathrm{K{-}OR'}\end{matrix} \rightleftharpoons \begin{matrix}\mathrm{R{-}Li}\\ |\quad\ |\\ \mathrm{K{-}OR'}\end{matrix} \rightleftharpoons \begin{matrix}\mathrm{R\ \ Li}\\ |\quad\ |\\ \mathrm{K\ \ OR'}\end{matrix} \qquad (1)$$

aromatic hydrocarbon to produce low molecular weight polymers. Presumably, the organopotassium formed in the mixture metalated the alkyl-aromatic, which acted as a chain transfer agent.

Propyne reacts with n-butyllithium in hexane to give a polymetalated compound, C_3Li_4[9,10]. Although the reaction is general for terminal acetylenes, the reaction with olefins is limited. In fact, conjugated dienes can be polymerized in an α-olefin medium[11,12] by organolithium initiation. Livshits and Podol'ny[13] have found that a chain-transfer step takes place when conjugated dienes are polymerized with sodium naphthalene in an α-olefin medium. This is probably the result of metalation of the terminal olefin. With this in mind, we undertook the investigation of the reaction of n-butyllithium, a potassium t-alcoholate, and butenes to determine if polymetalation would take place and if this mixture would act as a true organopotassium compound or an alkyllithium activated in the manner as is done by polar compounds such as *N,N,N'N'*-tetramethylethylenediamine and the "glyme"ethers. Potassium t-amyloxide was used in this study because it is hydrocarbon soluble and is readily available.

EXPERIMENTAL

1-Butene and 2-methylpropene were Phillips Petroleum Company Research Grade. 2-Butene was a 45.6/54.4 *cis*/*trans*-Pure grade mixture also from Phillips Petroleum Company. Potassium t-amyloxide (KTA) was obtained from MSA Research Corporation as an 18.4% cyclohexane solution. Commercially available n-butyllithium (BuLi) as a heptane solution was employed. Monochlorostyrene (MCS) was a commercial mixture from Dow Chemical Company of 68.3% 2-chlorostyrene and 31.7% 4-chlorostyrene.

1. *Butane evolution*

The reactions were carried out in dried 20-ml Diels–Alder tubes. The tubes were sealed with perforated bottle caps and self sealing gaskets. The reactants, five ml of cyclohexane, 1.0 mmole 2-methylpropane for an internal standard, 1.0 mmole of olefin, BuLi and KTA, were added by syringe. The reaction was sampled gas phase both before and after KTA addition. The samples were analyzed in a F & M 5754 Research Chromatograph with 13 ft. Perkin–Elmer V columns and ionization detector. The peak areas were calculated by an IBM 1800 GLC data acquisition and reduction system.

2. *Hydrogen evolution*

KTA (12.7 mmoles) and BuLi (12.7 mmoles) were added by syringe to cyclohexane (90 ml) in a 12-oz. soft glass bottle closed with a self-sealing rubber gasket and crown cap. The bottle was agitated in a 70° constant temperature bath. Five-milliliter samples were removed periodically by syringe and transferred to sealed Diels–Alder tubes. Methane (0.25 mmole) was added as an internal standard and the gas phase sampled for hydrogen before and after ethanol hydrolysis. The hydrogen analyses were made with a F&M Scientific 5750 Research Chromatograph with a 10 ft. Linde 13X Molecular Sieve column. Argon was the carrier gas. A parallel experiment was run with only BuLi and cyclohexane as a control.

3. *Reaction with monochlorostyrene* (*MCS*)

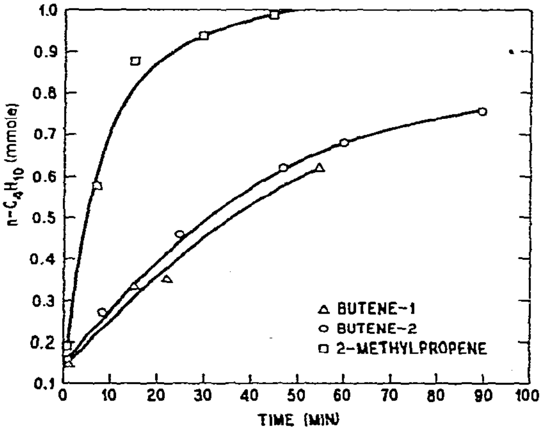
KTA (11.3 mmoles) and BuLi (11.3 mmoles) were added by syringe to appropriate bottles containing 100 ml of cyclohexane and 11.3 mmoles of monochlorostyrene (MCS). The bottles were tumbled in a 70° constant temperature bath. Five-milliliter samples were removed periodically and were hydrolyzed. Normality was determined by titration with HCl.

4. *Deuterium analysis*

The samples were prepared as described in 1 except that they were quenched with 0.5 ml D_2O. The individual components were identified with a combination of a Perkin–Elmer Model F11 gas chromatograph and a Consolidated Electrodynamics Corporation Model 21–130 mass spectrometer (GC-MS). The spectrometer was connected through a nozzle-and-cone type, molecular separator interface system to sample the chromatograph effluent continuously. Mass spectra were recorded for each chromatographic peak as it emerged. The olefin concentrations were calculated from the GC peak areas and the mass spectra were used to calculate the deuterium distributions for each olefin.

RESULTS AND DISCUSSION

The metalation of butenes by the product obtained from the reaction of n-butyllithium (BuLi) and potassium t-amyloxide (KTA) was quite rapid at room temperature in cyclohexane solvent. This was followed by butane evolution from metalation of the olefin by the n-butylmetal. Figure 1 gives the rate of n-butane evolution from the 1/1/1 molar ratio (BuLi/KTA/Butene) reaction. The n-butenes were equally reactive, but 2-methylpropene was much more reactive.



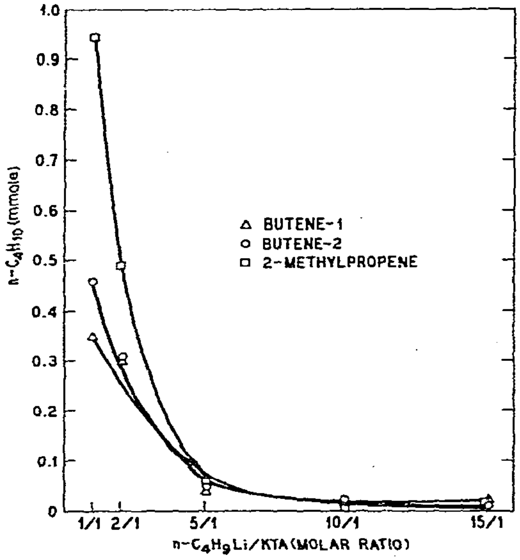


Fig. 1. Butane evolution from equimolar quantities of n-butyllithium, potassium t-amyloxide and butenes at room temperature in cyclohexane.

Fig. 2. The effect of BuLi/KTA molar ratio on butane evolution after reaction with butenes for 0.5 h at room temperature in cyclohexane.

This relative reactivity was true at molar ratios of 1/1/1 and 1/0.5/1; however, at higher ratios of BuLi/KTA the butane evolutions became approximately equal, regardless of the ratio (Fig. 2). The butane evolution from the 1/1/1 BuLi/KTA/2-methylpropene reaction after 0.5 h was approximately equal to the amount of KTA added (0.94 mmole n-butane for 1.0 mmole KTA) and from the 1/0.5/1 reaction (0.49 mmole n-butane for 0.5 mmole KTA). The results did not correlate at the lower levels of KTA, possibly because it was difficult to charge such small amounts of the potassium salt. The dependency of n-butane evolution on the amount of KTA charged reinforces the idea that the transmetalation product, n-butylpotassium, is the reactive species.

The heavier metal alkyls, such as n-butylpotassium, are known to decompose rapidly at elevated temperature with the evolution of the olefin and the metal hydride[14]. The metal hydride will give hydrogen upon hydrolysis. This was observed for the reaction product of 1/1 molar ratio BuLi/KTA at 70°. The hydrogen evolved upon hydrolysis is listed in Table 1. n-Butyllithium by itself did not decompose to an appreciable extent under identical conditions.

Combinations of BuLi, KTA and monochlorostyrene (MCS) were heated at 70° and sampled periodically. The sample aliquots were hydrolyzed and the normality determined by acid–base titration (Table 2). MCS had no effect upon the normality of the KTA solution alone, and there was only a slight decrease in normality after reaction of MCS and BuLi, probably because of some halogen–metal interconversion and subsequent coupling of n-butyl chloride and BuLi. However, the normality decreased rapidly when molar equivalents of all three components were brought together, as can be seen by the fact that the normality at mixing, $t = 0$, at room temperature should have been the total of the alkalinities of the previous two reactions (0.25). The remaining alkalinity appears to be approximately that expected if there had been an exchange between BuLi and KTA to give butylpotassium and lithium t-amyloxide, rapid reaction of butylpotassium and MCS to eliminate KCl, and the remaining lithium alcoholate being inert but showing up as alkalinity in the acid–base titration.

Polymetalation of the butenes by the 1/1 BuLi/KTA reaction occurred as shown by quenching the reaction with D_2O and determining the deuterium distribution by the GC–MS combination. The results in Table 3 show that up to three deuteriums were incorporated by quenching the reaction of equimolar amounts of BuLi/KTA/butene after 1.0 h at room temperature.

Isomerized butenes were obtained after H_2O quench of the reaction of butene, BuLi and KTA. Approximately 20% of *cis*-2-butene exclusively was obtained with 1-butene. A small amount of a 2-butene mixture (45.6/54.4 *cis*/*trans*) was isomerized to 1-butene, and the remainder was enriched in the *cis*-isomer over the starting material. This preference for the *cis*-isomer was reported in 1958[15] for isomerization by organosodium compounds. The organosodium catalysis of butene isomerization appears to have required higher reaction temperature (30–195°)[15,16] than is required by the BuLi/KTA reaction product. Isomerization of olefins* is typical of reactive organometallic compounds, such as organosodium[17,18,19] and organopotassium[20], although Broad-

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* The base-catalyzed olefin isomerization reaction has been used recently to compare a wide variety of base-solvent systems, and metal alkylamides in hexamethylphosphoramide were found to be highly reactive[22].

TABLE 1

HYDROGEN EVOLUTION AFTER HYDROLYSIS OF THE REACTION PRODUCT OF EQUIMOLAR n-BUTYLLITHIUM AND POTASSIUM t-AMYLOXIDE AT 70° IN CYCLOHEXANE

Time (min)	*Theoretical hydrogen (%)*	
	BuLi/KTA	*BuLi*
0	1.0	0.8
15	7.1	0.6
30	10.9	0.7
60	22.4	0.7
200	32.0	0.3
308	36.6	0.7
1320	38.3	1.0

TABLE 2

NORMALITY OF HYDROLYZED ALIQUOTS AFTER REACTION OF EQUIMOLAR MONOCHLOROSTYRENE, n-BUTYLLITHIUM AND POTASSIUM t-AMYLOXIDE AT 70° IN CYCLOHEXANE

Time (min)	*Normality of 5-ml aliquots*		
	MCS/BuLi	*MCS/KTA*	*MCS/BuLi/KTA*
0	0.14	0.11	0.16[a]
5			0.14
10	0.12	0.11	0.14
15			0.13
40	0.11	0.11	0.13
55	0.10	0.11	0.13
65	0.09		0.13
120	0.09		

[a] Theoretical normality is 0.25 because it is the sum of the normalities of BuLi and KTA.

TABLE 3

PRODUCT DISTRIBUTION AFTER D_2O QUENCHING OF THE REACTION OF EQUIMOLAR QUANTITIES OF BuLi/KTA/n-BUTENE AT ROOM TEMPERATURE IN CYCLOHEXANE

Reactant	*Product*	*Yield (%)*	*Deuterium distribution (%)*			
			D_0	D_1	D_2	D_3
Butene-1	1-Butene	79.2	87.2	6.3	6.3	0.2
	trans-2-Butene	0				
	cis-2-Butene	20.8	0	35.5	62.5	1.9
Butene-2	1-Butene	7.0	1.4	27.2	69.6	1.8
	trans-2-Butene	37.0	95.5	4.0	0.5	0
	cis-2-Butene	56.0	33.4	20.0	46.2	0.4

dus reported[20] that alkylsodium compounds are more effective in causing isomerization of excess olefin than are alkylpotassium reagents. The olefin isomerization experiments support the idea that an organopotassium was the active species in the reaction.

The distribution of deuterium in the reaction product involving 2-methylpropene is shown in Table 4. There was no evidence of deuterium incorporation in the absence of KTA. The reaction was very rapid when all components were mixed. Approximately ten per cent of the 2-methylpropene was affected immediately, but the extent of metalation did not appear to increase over the next minute. The amount of BuLi consumed was greater than accounted for by deuterated olefin. The reason for this is not known, but it is known that some reaction takes place between the organometallic and KTA other than metal interchange[21]. There was no deuterium detected in the cyclohexane solvent.

TABLE 4

DEUTERIUM DISTRIBUTION AFTER D_2O QUENCHING OF THE REACTION PRODUCT OF BuLi/KTA/2-METHYLPROPENE AT ROOM TEMPERATURE IN CYCLOHEXANE

BuLi/KTA/2-MeC₃ molar ratio	*Time(s)*	*Deuterium distribution (%)*							
		n-Butane		*2-Methylpropene*					
		D_0	D_1	D_0	D_1	D_2	D_3	D_4	D_5
1/0/0	30	0	100	0	0	0	0	0	0
1/0/1	30	0	100	100	0	0	0	0	0
1/1/1	6.5	34.4	65.6	87.2	5.7	7.1	0	0	0
1/1/1	10	30.1	69.4	89.4	5.3	5.3	0	0	0
1/1/1	15	24.6	65.4	85.3	7.3	7.3	0	0	0
1/1/1	30	29.0	71.0	88.7	4.8	6.5	0	0	0
1/1/1	60	29.0	71.0	90.4	4.0	5.6	0	0	0
1/1/1	90	32.0	68.0	88.6	4.7	4.7	0	0	0
1/1/1	3600	97.7	2.3	56.3	3.8	39.9	0	0	0
2/2/1	3600	97.0	3.0	9.0	9.2	80.1	1.7	0	0
3/3/1	3600	83.0	17.0	0	5.7	90.4	3.9	0	0
4/4/1	3600	69.6	30.4	0	9.0	78.6	9.0	3.0	0.4

After 1.0 h (3600 s) at room temperature, almost all the n-butyllithium (98 %) was consumed by metalation as shown by appearance of non-deuterated n-butane. Approximately 44 % of the 2-methylpropene was metalated and accounted for 84 % of n-butyllithium (3.8 % monodeuterated and 39.9 % dideuterated). Fourteen per cent of the n-butyllithium consumed was not accounted for by deuterated product. Increasing the ratio of BuLi/KTA product to olefin increased the polymetalation and decreased the unreacted olefin. There appeared to be a preference for the dideuterated product throughout the series, which might be rationalized as a preference of the olefinic hydrogens for metalation. An attempt was made to locate the position of metalation by converting to higher olefins by quenching with dimethylsulfate, but this was unsuccessful as only trace amounts of higher molecular weight products were produced.

In summary, butenes are easily polymetalated at room temperature by a product obtained by combination of BuLi and KTA. n-Butylpotassium is surmised to be the active metalating species because of the dependency of rate of metalation upon the Li/K ratio and KTA level, the relative ease of organometallic decomposition at 70°, the rapid reaction with MCS at room temperature, and the similarity to organosodium and organopotassium isomerizations of olefins.

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