

POTASSIUM DERIVATIVES OF ALKYL BENZENES

G. GAU

*Institut de Pétrochimie et de Synthèse Organique Industrielle, Rue H. Poincaré,
13013 Marseille (France)*

(Received April 24th, 1976)

Summary

Phenylpotassium was directly prepared from chlorobenzene and finely divided potassium, and was used to metalate toluene, *o*-, *m*- and *p*-xylenes, ethylbenzene and cumene. The relative acidities of these hydrocarbons were obtained from the equilibria between their potassium salts in presence of *N*-permethylated tertiary polyamines.

Introduction

Phenylsodium is usually prepared by the halogen-metal exchange reaction [1,2] from chlorobenzene and fine dispersions of sodium. The most reactive sodium dispersions are obtained by ultrasonic irradiation with a magnetostrictive ultrasonic transducer [3,4] and this presents obvious advantages over other methods (sodium reduction of diphenylmercury or of phenylmethylether, reaction of phenyllithium with sodium alkoxides, etc.). Gilman et al. [5] prepared phenyl- (and benzyl-) potassium in 82% yield by adding chlorobenzene to potassium sand suspended in toluene. We now report the reaction of chlorobenzene with fine potassium dispersions obtained by ultrasonic irradiation and show that this technique makes the direct preparation of phenylpotassium relatively easy.

The main goal of this study was to determine whether the relative acidity scale of the alkylarenes as obtained by equilibration of their alkali salts in competitive metalation experiments [4] is sensitive to the counterion (sodium or potassium) and to the nature of the chelating Lewis base. We have previously shown [4] that the equilibrium constants of the sodium salts give a good Brønsted plot against the kinetic scale of acidity deduced from hydrogen isotope exchange by Streitwieser et al [6,7]. A recent report [8] on the competitive metalation of alkylbenzenes by metallic cesium in THF notes the high relative acidities of *o*-xylene, ethylbenzene and cumene obtained in this system. The chelating bases used in our studies were the *N*-permethylated tertiary polyamines (I).

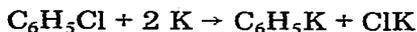


$x = 1$: N, N, N', N' , Tetramethylethylenediamine (TMED); $x = 2$: N, N, N', N'', N'', N'' , Pentamethyldiethylenetriamine (PMDT); $x = 3$: $N, N, N', N'', N''', N''', N'''$, Hexamethyltriethylenetetramine (HMTT). It has been shown that the number of coordination sites has a dramatic effect on the rate constant of the hydrogen-metal exchange reaction [9], but does not appear to have a large effect on the equilibrium constants of the methylbenzenes [4]. We have compared the equilibrium constants obtained with the organosodium and the organopotassium compounds in association with tertiary polyamines having different numbers of coordination sites. A reinvestigation of the role of the polyamine on the equilibria of the lithium salts is underway and will be described later.

Results

(1) Phenylpotassium preparation

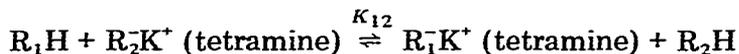
The molten potassium is dispersed by the method of Pratt and Helsby [3] (see Experimental section). In this method the potassium particles must fall by gravity towards the disintegrator, sealing the bottom of the flask. Methylcyclohexane is practically the only hydrocarbon dispersing medium which can be used on the laboratory scale (lower specific gravity than potassium, boiling point higher than the melting point of the metal). Grey blue dispersions of very fine particles are obtained which after cooling to 20°C are treated with chlorobenzene:



The yield (based on $\text{C}_6\text{H}_5\text{Cl}$) is practically quantitative and in all cases higher than 98% as determined by methylation of the product with dimethylsulfate and GLC analysis. No coupling products due to the Wurtz-Fittig reaction could be detected.

(2) Potassium-Hydrogen exchange reaction

The acidity of benzene is sufficiently low that the phenylpotassium releases all of its potassium to the alkylbenzenes. The reaction of the solid particles, made of a mixture of phenylpotassium, potassium chloride and excess potassium metal, with the alkylbenzene is fairly slow but can be accelerated if the reaction is carried out at high temperatures or in the presence of a tertiary amine. Although phenylpotassium cannot be dissolved in the hydrocarbons even after chelation with the polyamines, the potassium compounds of the alkylbenzenes chelated with the tetramine (HMTT) are soluble and after centrifugation a highly coloured solution free of potassium metal and potassium chloride can be obtained. This prompted us to investigate the potassium-hydrogen exchange reaction (sometime called the transmetalation reaction):



in this homogeneous system in the hope that our results would be free of the complications observed when solid organoalkali compounds are used [10].

As an illustrative example let us consider the *m*-xylene/*p*-xylene transmetalation. The phenylpotassium is chelated with a stoichiometric amount of tetramine (HMTT) and after it has reacted with an excess of *p*-xylene (R_2H) the suspension is centrifuged. The *p*-xylylpotassium (R_2K) solution is recovered and allowed to react with *m*-xylene (R_1H) for less than one minute at 25°C. The solution is then quenched with dimethylsulfate.

The concentrations of the four hydrocarbons R_1H , R_2CH_3 , R_1CH_3 , R_2H (*m*-xylene, *p*-ethyltoluene, *m*-ethyltoluene, *p*-xylene) are determined by GLC and the equilibrium constant calculated from the formula:

$$K_{12} = \frac{[R_1CH_3][R_2H]}{[R_2CH_3][R_1H]}$$

The data obtained for various R_1H/R_2H combinations are given in Table 1. The equilibrium constants for the homogeneous sodium hydrogen exchange [4] in presence of a diamine (*N,N,N',N'* tetramethyl 1-2-diaminocyclohexane) are also listed in Table 1 for comparison. Some of the data are from unpublished results, but in all cases the constants for the sodium/diamine system can be calculated from the table of relative equilibrium acidities already published [4]. It will be seen that ethylbenzene and cumene have high relative acidities in the potassium-tetramine system and the acidity of the *o*-xylene is also somewhat high. These results are not very different from Collignon's data [8] on competitive metalation with metallic cesium in THF.

In order to determine if the differences that exist should be attributed to the cation or to the chelating polyamine, several experiments were made with the sodium-tetramine (HMTT) system.

(3) Sodium-hydrogen exchange in presence of a tetramine

Phenylsodium is prepared from ultrasonically dispersed sodium in decahydro-naphthalene and the procedure is similar to that used for the potassium compounds. The transmetalation is again carried out in homogeneous solution at 25°C and dimethylsulfate used for derivatization. The results are shown in Table 1 and high relative acidities of *o*-xylene, ethylbenzene and cumene are again apparent.

TABLE 1
SUMMARY OF EQUILIBRIUM CONSTANTS

R_1H/R_2H	K_{12} (Potassium/ Tetramine)	K_{12} (Sodium/ Tetramine)	K_{12} (Sodium/ Diamine ^a)
Metaxylene/Paraxylene	14	12	11
Paraxylene/Ethylbenzene	0.4	1.6	7.7
Orthoxylene/Metaxylene	1.8	2.6	1.3
Paraxylene/Cumene	3	2	180
Toluene/Cumene	40		1600
Toluene/ <i>para</i> -Xylene	16		8.9
Toluene/ <i>meta</i> -Xylene	1.2		0.8
Toluene/Mesitylene	1.4		0.8

^a From [4] and unpublished results.

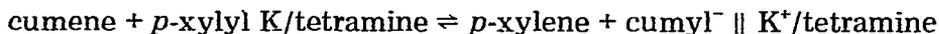
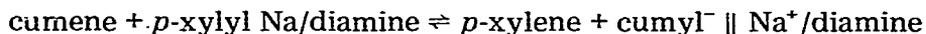
Discussion

This preparation of phenylpotassium from finely dispersed potassium is convenient on the laboratory scale since it does not require the use of high speed stirring equipment. It is appropriate for the preparation of small quantities, and this is an advantage in view of the fire hazards associated with manipulation of molten potassium.

Inspection of Table 1 reveals the main feature of these new systems (potassium/tetramine and sodium/tetramine) is the enhancement of the acidities of cumene and ethylbenzene. The relative acidities of toluene, *p*-xylene and *m*-xylene are also somewhat different from those previously obtained with the system sodium-diamine; it seems that the acidity scale for these three hydrocarbons is somewhat wider when potassium is used. Because of the limited number of hydrocarbons investigated this comparison cannot be pursued further.

The high acidity of cumene and ethylbenzene could of course be attributed to the insolubility of their sodium or potassium chelates, which would be difficult to detect if it were due to gel or colloidal suspension formation.

Another explanation, based on the structure of the ion-pairs, has the advantage of explaining qualitatively the data obtained in hydrogen isotope exchange [6, 11,12], in NMR [13] and in metalation [8] studies. Fraenkel et al [13] have shown that cumylpotassium exists as a loose or solvent separated ion pair as a consequence of steric effects due to the methyl groups. Many tertiary benzyl-lithium or -potassium compounds behave in essentially the same way if they are chelated to polyamines. If we consider the two reactions:



it can be assumed that the cumyl salts in both cases exist as solvent separated ion pairs and the *p*-xylyl salts as tight ions pairs. Due to the smaller size of the sodium cation the *p*-xylyl sodium ion pair is more stable than the *p*-xylylpotassium ion pair; cumene appears to be relatively less acidic in the sodium-diamine system. With the sodium/tetramine system the loss of stability of the xylyl salt

TABLE II
RELATIVE RATES OF HYDROGEN ISOTOPIC EXCHANGE. INFLUENCE OF THE CATALYST

Hydrocarbon	Lithium Cyclohexylamide in Cyclohexylamide [6]	KNH ₂ in NH ₃ [11]	<i>t</i> -BuOK in DMSO [12]
Toluene	1	1	1
<i>ortho</i> -Xylene	0.60	0.97	1.40
<i>meta</i> -Xylene	0.60	0.70	0.51
<i>para</i> -Xylene	0.30	0.23	0.033 (25°C) 0.078 (80°C)
Ethylbenzene	0.11	0.14	0.22
Cumene	0.0079	0.029	0.023
Benzene	0.005–0.01	0.014	10 ⁻⁶ ^a

^a In our metalation runs with the potassium/tetramine system we did not observe any metalation of cumene on the ring which indicates that our relative acidity of benzene is also very low.

could be attributed to partial solvent separation. This argument, developed to explain the metalation selectivity variations could also be applied to the hydrogen isotopic exchange, as will be apparent from Table 2. In this series of isotopic exchange experiments the alkali metal compound of the hydrocarbon is formed in the first step at very low concentrations. There is a large difference between the tight ion pair of the small lithium cation (in cyclohexylamine), the tight ion pair of the large potassium cation (in ammonia) and what may be free ions (in DMSO).

In conclusion we note that our results for the potassium/tetramine system show some accordance with the relative rates of isotopic exchange with potassium *t*-butoxide in dimethylsulfoxide.

Experimental

Potassium dispersions; phenylpotassium preparation

A titanium rod of 40 mm diameter is fitted to an ultrasonic transducer (Soni-masse 150 T manufactured by Ultrasons Annemasse, France) of a resonant frequency of 20 KHz and dissipating 150 watts of ultrasonic power. By means of a Viton O Ring Seal, the top of the rod seals the bottom of the Pyrex cylindrical flask containing the dispersing medium (methylcyclohexane) and the potassium. The flask is heated with a heating tape, the temperature being maintained between the melting point of potassium (62–63°C) and the boiling point of methylcyclohexane (101°C). The apparatus is swept continuously with nitrogen. After one hour irradiation a grey blue dispersion is formed; this is siphoned into a reaction flask contained in a cold bath, so that the liquid particles are rapidly frozen.

In a typical experiment, 9 g of potassium are dispersed in 250 ml of methylcyclohexane. A few drops of oleic acid are added to increase the efficiency of the dispersion. Chlorobenzene (10 ml) diluted in 25 ml of methylcyclohexane is slowly added (30 min) to the frozen potassium dispersions, the temperature being maintained at 20–25°C. The phenylpotassium suspension may be stored for months in an inert atmosphere at –10°C.

Illustration example: m-xylene/p-xylene. Transmetalation reaction

The homogenized phenylpotassium dispersion (14 ml) containing 0.005 mol C_6H_5K and 0.005 mol KCl, plus some unreacted potassium metal is introduced into the reactor maintained at 25°C and swept with nitrogen; *p*-xylene (5 ml, 0.04 mol), *m*-xylene (5 ml, 0.04 mol) are added followed by 1.2 ml (0.005 mol) of *N,N,N',N'',N''',N''''*, hexamethyltriethylenetetramine (HMTT). After 30 min a 2 ml sample of the suspension is withdrawn with a syringe and injected into a solution of dimethylsulfate (0.005 mol) in 5 ml benzene. After treatment with an excess of dilute hydrochloric acid the hydrocarbon layer is analyzed by GLC, on a 17' by 1/8" column, with a stationary phase of bentone 34 and dinonyl phthalate. The contents of the reaction flask are then transferred to a centrifugation tube purged with nitrogen. After centrifugation at 4000 rpm. the highly colored solution is analyzed as above.

The concentrations of *p*-ethyltoluene and *m*-ethyltoluene were identical in the two experiments.

A run was made to verify that equilibrium had been obtained. First *p*-xylene was metalated and after 30 min the solution was analyzed and then *m*-xylene was added. Within a very short time (less than one minute) the same compositions as in the previous run were obtained.

References

- 1 I. Fatt and M. Tashima, *Alkali Metal Dispersions*, Van Nostrand, New York 1961.
- 2 J.F. Nobis and L.F. Moormeier, *Ind. Eng. Chem.*, 46 (1954).
- 3 M.W.T. Pratt and R. Helsby, *Nature*, 184 (1959) 1694.
- 4 G. Gau and S. Marques, *J. Amer. Chem. Soc.*, 98 (1976) 1538.
- 5 H. Gilman, H.A. Pacewitz and O. Baine, *J. Amer. Chem. Soc.*, 62 (1940) 1514.
- 6 A. Streitwieser Jr., and J.H. Hammons, *Prog. Phys. Org. Chem.*, 3 (1965) 41.
- 7 A. Streitwieser Jr., M.R. Granger, F. Mares and R.A. Wolf, *J. Amer. Chem. Soc.*, 95 (1973) 4257.
- 8 N. Collignon, *J. Organometal. Chem.*, 96 (1975) 139.
- 9 G. Gau, *Bull. Soc. Chim. Fr.*, (1972) 1942.
- 10 A.A. Morton, *Solid Organonoalkali Metal Reagents*, Gordon and Breach, New York 1964.
- 11 A.I. Shatenshtein, *Adv. Phys. Org. Chem.*, 1 (1963) 161.
- 12 J.E. Hofman, R.J. Muller and A. Schriesheim, *J. Amer. Chem. Soc.*, 85 (1963) 3000, 3002.
- 13 G. Fraenkel, J.G. Russel and Y.H. Chen, *J. Amer. Chem. Soc.*, 95 (1973) 3208.