

THE METALATION OF TOLUENE BY POTASSIUM AND SODIUM¹

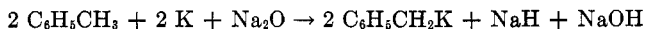
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A previous paper (1) described the metalation of fluorene by potassium hydroxide with the assistance of metallic sodium to remove the water formed simultaneously. An attempt to apply a similar principle to the preparation of benzyl-sodium or -potassium was only slightly successful but led eventually to the discovery that toluene can be metalated smoothly by potassium in the presence of sodium oxide in excellent yield. Calcium and magnesium oxides may also be used.

Several attempts to use sodium metal separately or in conjunction with potassium reveal no comparable activity.

The over-all reaction can be expressed nicely by the equation below in which the sodium oxide serves as an acceptor for the displaced hydrogen, but the



actual steps are probably more complicated than this simple picture shows. Carbonation of the reaction product should produce some formic acid along with the phenylacetic acid, and a qualitative test for the former by means of chromotropic acid (2) was positive.

Sodium or potassium in the presence of potassium hydroxide had only a slight effect upon toluene and little difference existed between the two metals, whereas in the presence of sodium oxide potassium metal was extremely effective and the only metal at all active. Such results emphasize the success which can be achieved with the proper kinds and proportions of solid reagents and are in line with the other successes which have been found with the Alfin reagent (3) where the sodium cation and other ions are essential, with alkoxides in the metalation of *tert*-butylbenzene (4) where some promoted mono- and others di-metalation, with the dimetalation of benzene (5) where the lithium ion of the alkoxide favored *meta* substitution and the potassium ion favored the *para* position, and with the combination needed for the mercuration of benzene (6) and ketone (7) where specific oxides and dehydrating agents were great aids to mercuric nitrate.

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EXPERIMENTS

All reactions were carried out in a 500-ml. creased flask attached to the high-speed stirring apparatus which was operated at 5000 r.p.m. Toluene, 300 ml. was used in all tests. Potassium sand was prepared just prior to each reaction but the sodium sand was prepared

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TABLE I
METALATION OF TOLUENE IN THE PRESENCE OF OXIDES^a

K, g.	Na, g.	Oxide, ^b g.	Temp., °C.	P.A. Acid	
				g.	% ^c
17		S 56	90	49	83
8.5		S 56	90	25	84
8.5 ^d		S 56	90	26	87
4.3	4.3	S 56	90	14	90
0	8.5	S 56	90	0	
0	8.5	S 56	110	0	
0		S 56	90	0	
8.5		S 28	90	21	69
8.5		S 14	90	2	8
8.5		S 56	35	5	17
8.5	[NaX] ^e	S 42	90	10	30
8.5		C 56	90	10	42
8.5		M 56	90	3	11
8.5	NaH + KOH		90	0 ^f	

^a The reaction time was 14 hours unless otherwise noted.

^b S, C and M refer respectively to sodium, calcium, and magnesium oxide.

^c The percentage yield is calculated on the basis of the amount of potassium metal used.

^d The reaction time was 3 hours.

^e NaX refers to a mixture of sodium isopropoxide and sodium oxide, prepared by addition of 0.22 mole of isopropyl alcohol to 56 g. (1.1 moles) of sodium oxide before addition of potassium metal.

^f Small amounts of unidentified acid were formed.

previously and was taken from a large storage bottle as needed. The sodium oxide was very kindly supplied by the du Pont Company. The magnesium and calcium oxides were commercial preparations and were used without additional treatment. A reaction time of 14 hours was needed in the initial experiments with alkali metal and potassium hydroxide and was used for the tests with the oxides. That this time was not required with the latter reagents was shown by the results for the three-hour experiment with sodium oxide and also by the development of the intense brick-red color within 15 minutes, which was indicative of a reaction. At the end of the reaction, all reaction mixtures were forced onto solid carbon dioxide and the phenylacetic acid was recovered by the usual acidification and extraction. The crude recovered acid melted at 72–75°. After one crystallization from water, the melting point was 75.1–77.5°.

TABLE II
REACTION OF POTASSIUM AND SODIUM WITH TOLUENE IN THE PRESENCE OF
POTASSIUM HYDROXIDE AND OTHER MATERIALS

K, g.	Na, g.	KOH, g.	Temp., °C.	P.A. Acid, g.
0.7	9.8	56	90	1
8.5	9.8	56	90	4
17		56	90	0
0	24.5	112	90	3
8.5		0	90	0
8.5	8.5	0	90	1

All results obtained in the presence of the oxides are listed in Table I. Those in the presence of potassium hydroxide are recorded in Table II.

SUMMARY

Sodium oxide, calcium oxide, or magnesium oxide with potassium metal is a new and unique metalating agent which has made possible the metalation of toluene in a yield as high as 90%. Sodium is not effective under these conditions. In the absence of these oxides, metalation by either potassium or sodium occurs to a small extent only.

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