[Contribution from the Department of Chemistry, Massachusetts Institute of Technology]

METALATION OF THE *alpha* CARBON OF ALKYLARYL HYDROCARBONS[1], [2]

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A previous paper (1) reported that potassium metal in the presence of sodium oxide was especially effective for the metalation of toluene. The present work shows that this combination, as well as those with other oxides, is even more unique as a specific agent for replacing hydrogen on the *alpha* carbon of alkylaryls. For example, *n*-hexylbenzene becomes 1-phenyl-*n*-hexylpotassium. Cumene yields phenylisopropylpotassium only. By contrast amylsodium attacks cumene almost entirely on the ring (2, 3) and dimetalates extensively (4). Ethylpotassium also substitutes primarily on the ring (5). Sodium and diethylmercury have been recorded (6) as metalating cumene in the *alpha* position, but that combination requires the preparation of another organometallic compound.

Table I records the success with this new reagent upon a variety of hydrocarbons and shows also that several other oxides besides sodium are effective. The hydrocarbons are arranged in the order of decreasing reactivity for a given set of conditions. This order, and the position attacked when two possibilities exist, are what would be predicted from the probable acidities of the various hydrocarbons (7). For example, additional methylene or alkyl groups decreased the yield in monocyclic compounds, the methylnaphthalenes were more reactive than toluene, and the methyl group of *p*-cymene was preferred over the isopropyl group. The agreement may not be perfect in some fine details but is surprisingly good in view of (a) the steric influences which should prevail during adsorption and reaction on a solid surface and (b) the change of medium with each monocyclic compound tested.

The differences between the oxides were observed readily with β-methylnaphthalene because that hydrocarbon was metalated easily. Calcium, strontium, barium, and even cerium oxide allowed the displacement of hydrogen to take place. Barium oxide provided a nice discrimination between toluene and β-methylnaphthalene. Only the latter reacted, even when an equi-molar mixture of the two was tried.

DISCUSSION

The unusual selectivity of this reagent naturally suggests a precise operation akin to other unusual effects caused by the composition of solid reagents of this general type. Several examples exist. In Alfin catalysis (8) a specific ternary

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[2] This paper was, in part, presented at the meeting of the American Chemical Society, in Cincinnati, 1955.

TABLE I

METALATION OF ALKYLARYL HYDROCARBONS BY POTASSIUM IN THE PRESENCE OF CERTAIN OXIDES

Hydrocarbon[a]	Amount[b] Solvent or Mole	Oxide 0.9 Mole of	React. time, Hrs.	RCOOH Yield	
				g.	%[c]
Toluene	S	Na	3	26	87
m-Xylene	S	Na	3	24	71
p-Xylene	S	Na	3	10	31
Ethylbenzene	S	Na	3	10	31
Cumene	S	Na	3	3	11
p-Cymene	S	Na	3	0	0
p-Cymene (P)	S	Na	3	23	58
Cumene (P)	S	Na	3	4	12
Cumene	S	Na	14	14	40
n-Hexylbenzene	S	Na	14	17	38
tert-Butylbenzene	S	Na	14	0	0
α-Methylnaphthalene	0.3	Na	3	23	55
β-Methylnaphthalene	.3	Na	3	22	53
Toluene	.3	Na	3	9	28
Phenylcyclohexane	.3	Na	3	0	0
β-Methylnaphthalene	.6	Ba	3	10	24[d]
Toluene + β-Methylnaphthalene	.6[e]	Ba	3	14	34
Toluene	S	Ba	3	0	0
β-Methylnaphthalene	.3	Sr	3	20	48
β-Methylnaphthalene	.3	Ce	3	6	16
β-Methylnaphthalene	.3	Ca	3	4	10

[a] The arrangement is in the order of decreasing hydrocarbon activity where other factors are constant, or in decreasing oxide activity with one hydrocarbon. "P" means purified by a pre-run. [b] "S" refers to the use of the hydrocarbon as the solvent. In all other experiments the medium was heptane. [c] Referred to potassium metal. [d] The yield is low because the hydrocarbon had not been recrystallized. [e] Each hydrocarbon was 0.3 mole. The gummy appearance of the product mentioned in the preceding experiment was absent in this case.

combination of sodium salts favored polymerization and minimized branching and cross-linking so that the molecular weights of soluble polybutadiene were vastly greater than could be attained by the use of any other reagent. In the dimetalation of benzene by amylsodium (9), lithium alkoxides favored the *meta* position and the potassium ion favored the *para* position. In the metalation of *tert*-butylbenzene, one type of alkoxide favored dimetalation while others favored monosubstitution (10).

Absorption would appear to be a prerequisite for these reactions. If some activation and orientation are granted as logical consequences of this step, a simple explanation can be offered for the present case. Any alkylaryl hydrocarbon would be expected to be made more acidic because of attachment to a cation by adsorption or coordination (10) somewhat after the manner that acidity in adjacent alkyl groups is increased by attachment of a positively charged substituent on the ring. Only a slight increase in acidity might be needed. Toluene, for instance, is nearly acidic enough without activation to permit replacement of hydrogen by alkali metal (11). An increase accompanied by a proper orientation or placement so that potassium metal is near the *alpha* carbon atom and the hydrogen being ejected is near the oxide would be all that is needed broadly to explain the effect. The possibility that potassium metal and the oxide in contact with the hydrocarbon may undergo some interchange or have an easier electron release is deemed less important but is not denied.

The process is unusually exact in its requirements. That metallic sodium lacked the power to displace hydrogen, even in β-methylnaphthalene at 120°, testifies to the great specificity of the metal. That a variety of oxides but only one metal was useful shows the relative importance of the latter. That sodium oxide affects only the reaction with potassium and does not alter the position where amylsodium metalates cumene, indicates unusual selectivity. The failure of the oxide to affect the reaction of amylsodium may be explained on the basis of a recent interpretation (10, 12). The cation of amylsodium serves as a point for adsorption and also as a source of atomic sodium. Therefore hydrogen displacement can occur at or near the point of initial attachment and next to amyl. Sodium oxide could scarcely displace amyl from such an ideal spot for accepting hydrogen.

The order of hydrocarbon activity and the preferential reaction at the methyl instead of the isopropyl group in *p*-cymene dispose of the chief argument of Bryce-Smith (5, 13) for anionic predominance in metalation by organoalkali metal reagents. Because the order was toluene > ethylbenzene > cumene for metalation by ethylpotassium, but was the reverse for abstraction of hydrogen by a free radical, he reasoned that the former could not be by a radical mechanism and that an alternative anionic process had to be correct. He overlooked, however, the activity of sodium as a radical which ejects hydrogen. Metalation by amylsodium and other organoalkali metal reagents can be assumed (10, 12) to occur by dissociation of the salt with its adsorbed hydrocarbon into two radicals, followed by a displacement of hydrogen in the hydrocarbon by atomic sodium and acceptance of that hydrogen by the alkyl radical. Both the metal radical and the alkyl radical participate in the reaction to the maximum permitted by steric or other factors, but the tendency of atomic sodium to lose an electron and to form a new salt contributes heavily to the rate. The results recorded in the present paper are in beautiful accord with this new concept. Metallic potassium does, indeed, displace hydrogen from the *alpha* position of toluene, ethylbenzene, and cumene in the same order as does either amylsodium (3) or ethylpotassium (5). The oxide serves as a hydrogen acceptor just as does an alkyl radical in the organoalkali metal reagents. The similarity between the metal and the organosodium reagent is even more marked in the ease of *p*-cymene where potassium metal-sodium oxide and amylsodium (3) substitute exclusively on the methyl group and not at the less acidic tertiary position of the isopropyl group. Hence the assumption of biradical activity (8, 9) for the organoalkali metal salts with hydrogen displacement by atomic alkali metal is entirely reasonable. All of Bryce-Smith's results (5, 13) are in complete accord with the suggestion that organoalkali metal reagents are sources of radicals and that the radical from the cation acts dynamically by displacement of hydrogen and that the organic radical terminates rather than initiates the reaction.

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EXPERIMENTS

Metalation conditions. High-speed stirring (5000 r.p.m.), a nitrogen atmosphere, and other conditions were approximately the same as described for the previous work (1). Either the hydrocarbon being metalated or heptane was used as the medium. The reaction temperature of 90° was above the melting point of potassium metal and insured good dispersal of the metal through the reaction mixture. Actually in heptane alone, with no possibility of metalation, the potassium was so intimately dispersed that no separation into a metallic phase was discernible to the eye when the mixture was cooled.

Potassium metal (8.5 g. or 0.22 mole), 0.9 mole of metal oxide, and about 300 ml. of liquid were used in all cases. When 0.3 or 0.6 mole of hydrocarbon was used, its addition was after the preparation of the sand. The beginning of a reaction was observed by appearance of a marked color, brick red in the case of toluene (amylsodium with toluene gives a green color), purple with cumene, black with β-methylnaphthalene, brown with *para*-cymene. This color appeared within a few minutes in the case of toluene but in about one-half hour for cumene. The reaction mixture often thickened considerably during the reaction; and more liquid was added.

At the end of the process the contents of the flask were forced onto solid carbon dioxide and the mixture was allowed to stand several hours or overnight. The resulting slush was stirred gently while wet ether was added dropwise to decompose excess potassium, all in an atmosphere of carbon dioxide. Water was added to dissolve the metal salts. The aqueous layer was extracted with ether, and then was acidified. The acids were extracted with ether, and the ether layer was dried over calcium sulfate (Drierite). The solution was filtered, and the ether was evaporated on a steam-bath. The residue was dried in a vacuum desiccator over Drierite.

The crude acid thus obtained usually melted within at least 4° of the correct melting point. In a few cases, such as with the product from *para*-cymene or from β-methylnaph-

TABLE II

PROPERTIES OF THE ACIDS OBTAINED BY CARBONATION OF THE METALATED HYDROCARBONS

Hydrocarbon[a]	Acid	Melting Point[b], °C.		Ref.
		Crude	Rec.	
Toluene	Phenylacetic	75.5–76	76.9	14
m-Xylene	*m*-Toluic	55–61	61	15
p-Xylene	*p*-Toluic	85–92	94	16
Ethylbenzene	1-Phenylpropionic	[88–90	91–92]	17
Cumene	1-Phenylisobutyric	80–80.5	80–81	18
p-Cymene	*p*-Isopropylphenylacetic	49–50	51–52	19
Hexylbenzene	1-Phenylheptanoic	[94.5–95.5][c]		20
α-Methylnaphthalene	α-Naphthylacetic	98–114[d]	131	21
β-Methylnaphthalene	β-Naphthylacetic	141.6	142	22

[a] The compounds are listed in the order of their appearance in Table I. [b] Values enclosed in parentheses are for the amide instead of the acid. [c] The amide, after being recrystallized from water, melted at 95.5–96.5°. The acid was prepared previously but was not characterized. *Anal.* Calc'd for $C_{13}H_{18}O_2$: C, 75.70; H, 8.79. Found: C, 76.07; H, 8.67. [d] The observed melting point of the crude acid was low probably because the technical hydrocarbon contained some of the β-isomer.

thalene in the presence of barium oxide, the acid product was a bit resinous or even gummy, possibly because of a small side reaction or impurity in the starting material. Approximately an equal amount of pentane or toluene plus pentane was added. The mixture was stirred and cooled in a solid carbon dioxide-Cellosolve bath.[3] The crystals thus obtained were recovered by filtration and dried in the desiccator as described. In all such cases the mother liquor was concentrated and again cooled and the process repeated until no more crystals could be obtained.

Hydrocarbons. Toluene was Mallinckrodt's reagent grade, dried over sodium. All other liquid hydrocarbons were the best grade available from Eastman Kodak Company and were used without purification. In the case of *p*-cymene and cumene, a purification was made by a pre-run and reuse of the recovered hydrocarbon. The improvement in yield from *p*-cymene was marked, but from cumene was only trifling. β-Methylnaphthalene was a technical Eastman product, once recrystallized, except that in one experiment marked in the Table, the impure hydrocarbon was used.

Oxides. Sodium oxide was obtained through the courtesy of the Electrochemical Division of the duPont Company. All other oxides were obtained from the stockroom: calcium oxide purchased from Baker Chemical Company, strontium and cerium oxides from Amend Drug and Chemical Company, and barium oxide from Allied Chemical and Dye Company.

Carboxylic acids. A great many of the carboxylic acids and isomers of the acids have been prepared by metalation with amylsodium and other methods. Hence comparisons were readily made. The melting points of the crude or desiccator-dried products are recorded in Table II in order to show the surprising degree to which metalation was restricted to one position only.

SUMMARY

Metalation of alkylaryl hydrocarbons by potassium metal and sodium oxide is a highly selective process which attacks the *alpha* position.

Potassium metal cannot be replaced by sodium but calcium, strontium, barium, and cerium oxides can be substituted for sodium oxide.

In general the ease of metalation parallels the relative acidities which the hydrocarbons or alkyl groups have and this fact suggests that displacement of hydrogen by metal is a primary factor and that the oxide contributes its influence as an acceptor for hydrogen.

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