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SELECTIVE MONO- OR DIMETALATION OF ARENES BY MEANS OF SUPERBASIC REAGENTS

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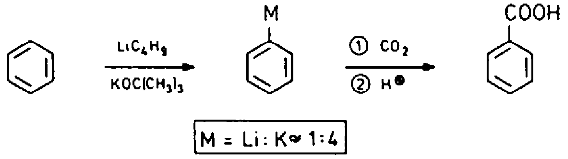
Summary : If employed in tetrahydrofuran, stoichiometric amounts of butyllithium and potassium *tert*-butoxide react with benzene under clean monometalation. In hexane suspension, however, considerable amounts of *meta*- and *para*-disubstituted by-products are obtained (approx. 10%). They become preponderant if a three-fold excess of the metalating agent is used. Naphthalene leads under the same conditions to a mixture of two mono- and ten di-substituted derivatives. - Alkyl groups, as present in *tert*-butylbenzene, retard the metalation at both *m*- and *p*-positions, while trialkylsilyl groups deactivate only *m*-positions. In either case exclusive monosubstitution occurs. - Perdeuterobenzene undergoes metalation and subsequent electrophilic mono- or disubstitution to afford isotope labeled compounds with moderate, though synthetically attractive yields. The kinetic isotope effects and product ratios can be taken as evidence for aggregate formation at the level of both the superbasic metalating reagent and the organometallic intermediates.

The attachment of a "polar" [1] metal to an organic backbone and its subsequent replacement by an electrophile is without doubt the most straightforward and versatile substitution scheme. This approach is particular useful for synthesis if the organometallic intermediate can be generated by hydrogen/metal exchange from a hydrocarbon precursor rather than by halogen/metal exchange from a suitable organic halide. It requires, however, a relatively high CH acidity to bring about such a hydrogen/metal permutation reaction between a hydrocarbon substrate and the classical reagents phenyllithium or butyllithium. They attack rapidly acetylene, fluorene and triphenylmethane, react sluggishly with diphenylmethane [2] and fail completely with toluene [3] and benzene [4] unless additional driving force is provided by heterosubstituents (as present in benzyl methyl ether [5], anisole [6] and fluorobenzene [7]). In particular benzene is a true benchmark since it is much less acidic than any hydrocarbon that gives rise, upon deprotonation, to a resonance stabilized, allyl or benzyl type carbanion.

When activated [8] with *N,N,N',N'*-tetramethylethylenediamine (TMEDA) or other complexing amines, butyllithium becomes powerful enough to effect metalations beyond the CH acidity threshold reached by Gilman and Wittig in their pioneering work. The butyllithium/TMEDA adduct produces in the course of 5 h at 25 °C phenyllithium in 50% yield if stoichiometric amounts of benzene are employed and quantitatively if it is used as a solvent [9, 10]. The reaction times, however, are still relatively long and, though frequently overlooked, the propensity of TMEDA to undergo metalation itself [11] must be considered as a serious drawback. Thus, it marked a breakthrough when in 1966 we found that the equimolar mixture of butyllithium and potassium *tert*-butoxide, which we had designed and successfully tested as a "superbase" [2, 12], brought about the metalation of benzene more rapidly than any other reagent under comparable conditions. Actually, a nearly quantitative yield of benzoic acid was isolated when the "LICKOR" base (LIC = organolithium, KOR = bulky potassium alkoxide) was prepared in benzene as a cosolvent and the mixture was poured on dry-ice after just one minute ! [2]



Previously, much effort had been devoted to systematic studies on the metalation of benzene with alkylsodium [13 - 17] and, more sporadically, also with alkylpotassium reagents [18 - 19] (see Table 1). In view of obvious discrepancies we decided to repeat some part of this older work. At the same time we wanted to reinvestigate our own method having distinct goals in mind : to restrict ourselves to stoichiometric amounts of the substrate, to assess the extent and regioselectivity of dimetalation as a function of the solvent, the temperature and the relative or absolute concentrations and, finally, to extend the scope of applicability to other arenes.

Table 1. Early metalation reactions with benzene as a substrate : yields a) and product composition.

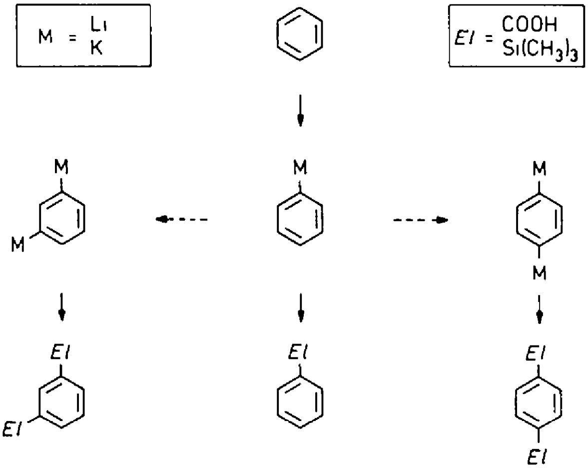
Metal. agent	equiv. of benzene a)	time [min]	metal. temp.	benzoic acid	phenylene diacids	*m/p* ratio	lit ref.
NaC_5H_{11} b)	40	60	25 °C	69%	11%	-	[13]
NaC_5H_{11} c)	8.8	60	25 °C	78%	-	-	[14]
NaC_5H_{11} b,d)	2.7	120	80 °C	37%	4%	80 : 20	[15]
NaC_4H_9 b)	1.2	120	50 °C	27%	-	-	[16]
NaC_5H_{11} b)	0.5	80	75 °C	5%	51%	> 95 : 5	[17]
KC_2H_5 c)	20	$3 \cdot 10^3$	25 °C	33%	14%	-	[18]
KC_4H_9 e)	6.9	$4 \cdot 10^3$	20 °C	60%	5%	60 : 40	[19]
KC_4H_9 e)	7.2	240	65 °C	65%	8%	60 : 40	[19]
KC_5H_{11} e)	7.5	240	65 °C	86%	5%	55 : 45	[19]

a) With respect to the precursor of the organometallic reagent (alkyl chloride or dialkylmercury).
b) Prepared from the corresponding alkyl chloride.
c) Prepared from the corresponding dialkylmercury compound.
d) Contains some 0.1 molar equivalent of sodium pentoxide.
e) Prepared by treatment of butyllithium with potassium or potassium/sodium alloy.

Benzene

In our original study, benzene was used in an 80 fold excess. Shortly afterwards, we had obtained almost identical results with merely a 7 fold excess. While the present work was in progress, reports on the successful metalation of benzene applied in 3 fold excess (treated with butyllithium, potassium *tert*-butoxide and TMEDA in hexane 15 min at -35 °C, 1 h at -25 °C and 30 min at -15 °C; "circa 90%" yield after trapping with dimethyl disulfide [20]) or in equimolar amounts (treated with butyllithium and potassium 2-methyl-2-butanolate in heptane 5 min at 25 °C; 44% toluene and 13% xylenes after trapping with methyl iodide [21]) have appeared.

We have achieved a first improvement by carrying out the metalation in tetrahydrofuran (see Table 2). This solvent is particularly advantageous when resonance stabilized organometallics are to be generated [22] while the metalation at aromatic, olefinic and cyclopropanic positions may be accompanied by extensive side reactions, above all deprotonation of solvent molecules themselves [23]. The yields obtained in tetrahydrofuran are indeed only moderate. This is, however, compensated by the perfect selectivity of the reaction, which cleanly stops at the monometalation level even if an excess of LICKOR is applied (see Table 2, next page).



In hexane suspension inevitably by-products due to dimetalation are formed even if benzene is used in equimolar quantities (see Table 2). With a two- or three-fold excess of metalating agent they become preponderant (up to 55%). No *ortho* isomers have even been identified other than in trace amounts at best. The *meta/para* ratios are somewhat smaller than unity (Table 2).

Apparently aggregate effects are at the origin of dimetalation and its solvent dependence. But how to rationalize then the absence of *ortho* metalation which should be strongly favored on the basis of proximity ? Obviously the discrimination against *ortho* dimetalates reflects to some extent the tendency to avoid an unfavorable quasi-parallel alignment of two identical dipoles. The expansion of the metal binding σ-orbital which imposes a deformation (as indicated by arrows in formula 1 ; see two pages later) on the π-electron cloud should play an

Table 2. Metalation of benzene as a function of solvent, stoichiometry, reaction time and temperature: yields of gas chromatographically identified products [a)]

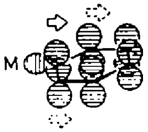
solvent [b)]	LICKOR equiv. [c)]	metal. time and temper.			electrophile *El*-X	mono-substitution	*meta*-di-substitution	*para*-di-substitution
HEX	1.0	1	min	25°C	$(H_3C)_3Si\text{-}Cl$	15%	1%	2%
	1.0	5	min	25°C	$(H_3C)_3Si\text{-}Cl$	30%	1%	4%
	1.0	15	min	25°C	CO_2	65%	3%	7%
	1.0	30	min	25°C	CO_2	61%	3%	9%
	1.0	1	h	25°C	CO_2	65%	6%	9%
	1.0	5	h	25°C	CO_2	52%	8%	11%
	1.0	25	h	25°C	$(H_3C)_3Si\text{-}Cl$	51%	12%	13%
	2.0	1	h	25°C	CO_2	42%	24%	26%
	2.0	25	h	25°C	CO_2	39%	20%	29%
	3.0	1	h	25°C	$(H_3C)_3Si\text{-}Cl$	32%	28%	27%
	3.0	25	h	25°C	$(H_3C)_3Si\text{-}Cl$	31%	25%	28%
THF	1.0	1	min	-75°C	CO_2	2%	0%	0%
	1.0	5	min	-75°C	CO_2	2%	0%	0%
	1.0	30	min	-75°C	CO_2	4%	0%	0%
	1.0	5	h	-75°C	CO_2	13%	0%	0%
	1.0	25	h	-75°C	CO_2	22%	0%	0%
	1.0	1	min	-50°C	$(H_3C)_3Si\text{-}Cl$	24%	0%	0%
	1.0	5	min	-50°C	$(H_3C)_3Si\text{-}Cl$	28%	0%	0%
	1.0	30	min	-50°C	$(H_3C)_3Si\text{-}Cl$	51%	0%	0%
	2.0	30	min	-50°C	$(H_3C)_3Si\text{-}Cl$	60%	0%	0%

a) Silanes were analyzed as such, carboxylic acids after quantitative conversion to the methyl esters by treatment with diazomethane.

b) HEX = hexane, THF = tetrahydrofuran.

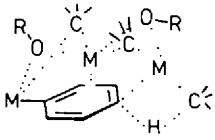
c) LICKOR = butyllithium and potassium *tert*-butoxide.

even more important role [1, 24]. The electron density which accumulates at the *ortho* and, to a lesser extent, *meta* positions diminishes the reactivity of such sites towards bases and nucleophiles.



1

The mixed aggregate which acts as the vehicle for dimetalation has presumably the shape of a distorted cube or octaeder at its ground state [1]. In order to reach the *meta* or *para* position it has to unfold and stretch out linearly, of course. A η^6-donor interaction [25] between the aromatic ring and one of the metal atoms may contribute to the relative stability of such transition states (*e.g.* **2**).



2

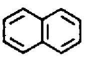
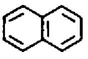
Additional evidence for mixed aggregate formation comes from the progress of hydrogen/metal exchange as a function of time. Neither in hexane suspension nor, although less markedly, in tetrahydrofuran solution, the reaction follows a simple rate law. After an extremely rapid start, it slows down after 25% or 50% of conversion and virtually ceases after 15 min even if substantial amounts of the metalating agent may still be unconsumed. This loss of momentum appears to reflect changes in the homo- and hetero-aggregate composition of the organometallic species being present.

Naphthalene

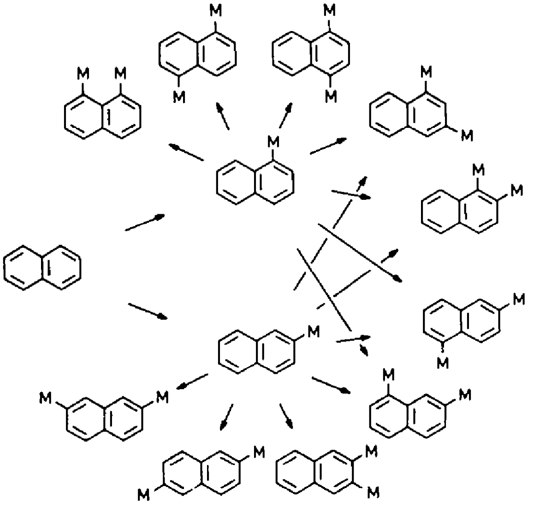
Intraaggregate reactions [1] can well explain the seemingly paradoxical phenomenon of fast dimetalation. Examples are abundant : di(bromomagnesio)acetylene [ethynylene di(magnesium bromide)] [26], 2,5-dilithiofuran [27], 2,5-dilithiothiophene [27], 2,5-disodiothiophene [28], 2,5-dilithio-*N*-methylpyrrole [27], 1,4-dibromo-1,4-dilithio-1,3-butadiene [29], 1,6-dilithio-2,4-hexadiene [30], 1,4-dilithio-2-butene [30], di(1-lithiocyclopropyl)acetylene [31], *o*-, *m*- or *p*-di(sodiomethyl)benzene [32], dilithioisobutene [33], 1,1-dilithio-2-butene [34], 1,1-dilithio-1,2-propadiene [35], dilithiomethane [36], 2,2'-dipotassiophenylacetylene [37], 1-potassio-2-(2'-potassiophenyl)-3-phenyl-1-hexene [38], 2,2'-dilithiobiphenyl [39], 1,8-dilithionaphthalene [40], 1,1'-dilithioferrocene [41] and bis(lithiobenzene)chromium [42] represent just a small choice.

The naphthalene case is particularly intriguing. Gilman *et al.* [43] were the first to succeed in metalating this hydrocarbon. After 36 h treatment with ethereal butyllithium at reflux temperature and quenching with carbon dioxide, they isolated 20% of 1- and 2-naphthoic acid in the ratio of 70 : 30. Using the more powerful reagents pentyl- and octylsodium, Morton *et al.* [44] were able to increase the yield to 26% and 37%, respectively. This time, however, the product mixture, besides small amounts of tricarboxylic acids, contained the naphthoic acids and naphthalenedicarboxylic acids in roughly equal quantities. The latter fraction was claimed to consist essentially of the 1,3-, 1,8- and 2,6-isomers. We wondered whether the superbasic LICKOR reagent would lead to even higher proportions of dimetalation. This was found to be indeed the case. On the other hand, the regioselectivity remained poor (see Table 3).

Table 3. Metalation of naphthalene: total yields of mono- and disubstitution products ("mo" and "di") and isomer distribution as a function of the solvent ("*Sv*" : THF = tetrahydrofuran, HEX = hexane) and the conditions (THF, 1 h -50 °C, or HEX, 25 h 25 °C).

Substrate	*Sv*	∑mo	α : β	∑di	1,4	1,5	1,8	1,2	1,3	1,6	1,7	2,3	2,6	2,7
	THF	23%	52 : 48	<3%	-	-	-	-	-	-	-	-	-	-
	HEX	28%	45 : 55	25%	3%	4 %	5%	<1%	<1%	~3%	~3%	<1%	<1%	3%

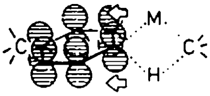
In hexane suspension and with a three-fold excess of LICKOR, 28% and, respectively, 25% of products derived from mono- and dimetalated intermediates were obtained. Furthermore, significant quantities (10 - 15%) of trisubstituted compounds were formed. As gas chromatography revealed, all 10 disubstituted naphthalenes were present, although some of them only at the trace level. The population of the various substitution patterns suggests that metalation occurs more readily at the 1- rather than 2-position, but also that the 1-metallonaphthalene is more prone to a subsequent second metalation than its regioisomer. [45] Consecutive attack at positions 1 and 8, where an electronically unperturbed intraaggregate mechanism can operate, is the most frequent dimetalation event. Nevertheless, the other routes leading to dimetalates prove to be more or less competitive. Apparently the LICKOR base is endowed with too much of reactivity potential in order to exploit fully the assistance offered by intramolecular aggregation as the less powerful organolithium [40] reagents do.



tert-Alkyl Substituted Benzenes

So far only *tert*-butylbenzene has been studied. Despite dozens of attempts, its metalation with pentylsodium [46 - 47] or ethylpotassium [48] gave only low yields (see Table 4). Thus, we were pleased to obtain reasonably good yields of products when we treated *tert*-butylbenzene, 1,3-di(*tert*-butyl)benzene and (1-methylcyclopropyl)benzene with excess LICKOR reagent in hexane (see Table 5).

In tetrahydrofuran the yields were poor, apparently due to loss of the metalating agent by reaction with the solvent. We had to conclude that alkyl substitution significantly retards the deprotonation of arenes. Competition kinetics (for relative rates, see Table 5) have confirmed this view : approximate partial rate factors f_m 0.3 - 0.4 and f_p 0.6 - 0.7 (in hexane) or f_m 0.3 - 0.4 and f_p 0.4 - 0.5 (in tetrahydrofuran) were found. [49] The inaccessibility of the *ortho* positions can, of course, be attributed to steric hindrance. The relative inertness of *meta* and *para* positions, however, must have another origin. Once more [1, 24, 50] we would like to invoke a σ-coupled deformation of the π-electron cloud. If at the transition state of metalation (3) the aromatic sextet wants to recede from the reaction center (as shown by the arrows in 3), the electron-rich alkyl substituent should impede this motion.



3

Attention is drawn to the highly regioselective metalation of 1,3-di-*tert*-butylbenzene. Simple treatment with an ethereal solution of magnesium or lithium bromide [51] cleanly converts the thus formed organometallic species to 1,3-di-*tert*-butylphenylmagnesium bromide [52] or 1,3-di-*tert*-butylphenyllithium [53]. So far these useful reagents had to be prepared by a multi-step procedure.

A Silyl Substituted Benzene

In contrast to *tert*-alkyl, the isologous trialkylsilyl groups can act as electron attractors [54a] and as such may enhance the rate of metalations. In order to probe whether this is also true for arene substrates, tri*isopropyl*silylbenzene was chosen as a model substance since *trimethyl*silylbenzene preferentially undergoes hydrogen/metal exchange at the aliphatic positions, by the way much faster than tetramethylsilane itself [54b]. The metalation of triisopropylsilylbenzene in tetrahydrofuran did indeed proceed quite smoothly giving rise, after carboxylation and neutralization, to regioisomeric carboxylic acids with yields and *m*/*p* ratios of 58% and 28 : 72 in hexane or 24% and 41 : 59 in tetrahydrofuran. Rates of 0.24 and, respectively, 0.29 relative to benzene allowed to calculate site reactivities ("partial rate factors") f_m 0.2 - 0.4 and f_p 1.0 - 1.1.

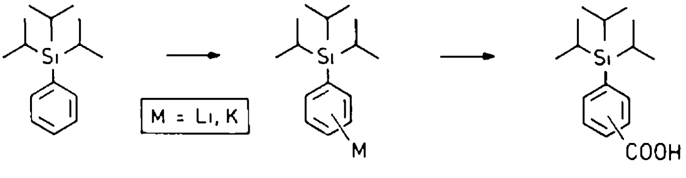


Table 4. Metalation of *tert*-butylbenzene with pentylsodium or ethylpotassium : composition of the product mixture depending on additives, stoichiometry, reaction time and temperature.

M-R [a)]	addit. [b)]	equiv. of substrate	t [h]	T [c)]	mono	*m/p*	di	lit. ref.
NaC_5H_{11}		1.1	4	25 °C	15%	9 : 91 [d)]	1%	[46]
NaC_5H_{11}	$NaO^iC_3H_7$	1.4	4	25 °C	26%	21 : 79	5%	[46]
NaC_5H_{11}	$NaOC_5H_{11}$	1.0	5	20 °C	5%	54 : 46	≤ 1%	[47]
NaC_5H_{11}	KOC_5H_{11}	1.0	5	20 °C	12%	30 : 70	≤ 1%	[47]
NaC_5H_{11}	$NaO^sC_5H_{11}$	1.0	5	20 °C	3%	42 : 58	≤ 1%	[47]
NaC_5H_{11}	$KO^sC_5H_{11}$	1.0	5	20 °C	(64%) [e)]	43 : 57	≤ 1%	[47]
NaC_5H_{11}	$NaO^tC_5H_{11}$	1.0	5	20 °C	16%	50 : 50	≤ 1%	[47]
NaC_5H_{11}	$KO^tC_5H_{11}$	1.0	5	20 °C	34%	50 : 50	≤ 1%	[47]
KC_2H_5	-	6.9	3	85 °C	30%	62 : 38	7%	[48]

a) Pentylsodium was prepared from pentyl chloride using an excess of sodium, ethylpotassium by reacting ethyllithium with elementary potassium.

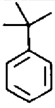
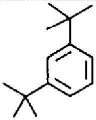
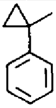
b) Additives : $O^iC_3H_7$ = 2-propanolate, $O^sC_5H_{11}$ = 2-pentanolate, $O^tC_5H_{11}$ = 2-methyl-2-butanolate.

c) Approximate numbers (± 5 °C).

d) In a series of later experiments [47], the *m/p* ratio averaged 20 : 80.

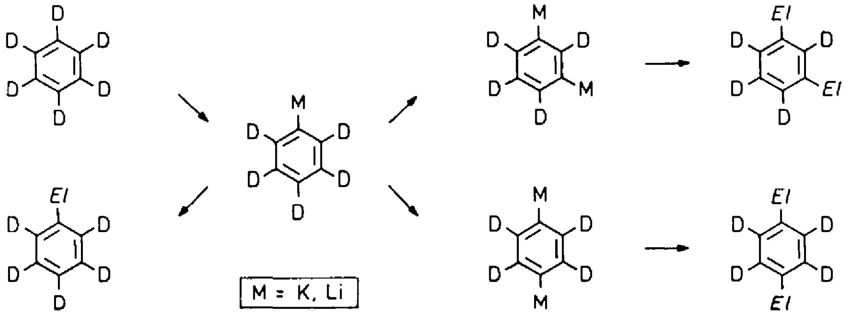
e) We suspect these data to be artefacts since, despite many attempts, we were unable to obtain more than a 25% yield under such conditions.

Table 5. Metalation of *tert*-butylbenzene, 1,3-di(*tert*-butyl)benzene and (1-methylcyclopropyl)benzene with LICKOR in hexane (HEX) or tetrahydrofuran (THF) : yields, regioorientation and relative rates.

hydrocarbon substrate	HEX			THF		
	yield	*m* : *p*	k_{rel}	yield	*m* : *p*	k_{rel}
	53 %	45 : 55	0 23	15 %	55 · 45	0 17
	56%	100 : 0	0.07	0 %	-	-
	52 %	55 : 45	0.22	10 %	70 : 30	0 21

Perdeuterated Benzene

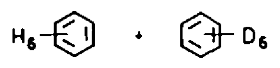
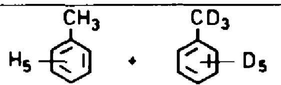
Perdeuterobenzene is relatively inexpensive while derivatives thereof are high-priced specialities if they are commercially available at all. Metalation of perdeuterobenzene was readily accomplished with stoichiometric amounts of the LICKOR reagent in tetrahydrofuran or, better, hexane. Subsequent treatment with carbon dioxide, *N*,*N*-dimethylformamide or fluorodimethoxyborane [52] gave [$^2H_5$]benzoic acid (62%), [$^2H_5$]benzaldehyde (58%) and dimethyl [$^2H_5$]phenylboronate. The latter compound was immediately, without isolation, oxidized with alkaline hydrogen peroxide to afford [$^2H_5$]phenol (47%). With 3 equivalents of LICKOR in hexane, product mixtures were obtained : [$^2H_5$]benzoic acid (36%) and [$^2H_4$]terephthalic acid (12%) after carboxylation, [$^2H_5$]benzaldehyde (33%), [$^2H_4$]isophthaldehyde (12%) and [$^2H_4$]terephthalaldehyde (13%) after formylation and [$^2H_5$]phenol (35%) and [$^2H_4$]hydroquinone (11%) after dimethoxyborylation and oxidation.



The approximate 3 : 1 ratio of mono- *vs.* dimetalation is quite remarkable. Unlabelled benzene gave a 1 : 2 ratio under the same conditions. We have to conclude that deprotonation and aggregate reorganization are competing processes or, in other words, that no aggregate equilibrium is attained while the superbase continues to react. Furthermore, the kinetic isotope effect for the second metalation must be big.

But how big is actually the isotope effect of the first metalation step ? We have determined it by means of competition experiments in both hexane and tetrahydrofuran. For comparison we have measured also the isotope effects of the LICKOR metalation of toluene and, finally, we have included butylpotassium [53] and trimethylsilylmethylpotassium [54] in the study (see Table 6).

Table 6. Competitive metalation of benzene and toluene isotopomers :
kinetic isotope effects k_H/k_D in hexane suspension (HEX) and tetrahydrofuran solution (THF).

metalation reagent						
	HEX +25°C	THF -50°C	THF -75°C	HEX +25°C	THF -50°C	THF -75°C
$LiC_4H_9 + KOC(CH_3)_3$	2.7	9.5	16	2.4	15	20
KC_4H_9	2.9	7.6	40	3.3	13	40
$KCH_2Si(CH_3)_3$	1.2	75	190	5.8	50	170

The numbers obtained for tetrahydrofuran solutions at -50°C must be regarded with caution since under these conditions butylpotassium and even LICKOR rapidly react with the solvent. At lower temperatures (-75°C), however, the difference between the two reagents becomes relevant and distinct. The isotope effects measured allow us to draw a few noteworthy conclusions :

- The numbers found with tetrahydrofuran solutions of LICKOR and butylpotassium fall in the expected range [55, 56], around 6 for benzene and 9 for toluene. The much greater values obtained with trimethylsilylmethylpotassium must be attributed to a "tunnel effect" [55].
- In hexane suspension, the isotope effects are amazingly small, averaging a value of 3. This could mean that aggregate reorganization and precomplexation [56] is a rate determining step also for the monometalation.
- All three metalating agents give rise to individually distinguishable isotope effects. The difference is of course not big, but significant, *i.e.*, beyond the limits of error (see experimental). Thus we have gathered a new piece of evidence against the frequently alleged chemical identity of the LICKOR reagent with butylpotassium. As we have already demonstrated previously, the superbase is also endowed with a very specific regioselectivity profile [57] and a remarkable inertness towards ethereal solvents [23].

If the LICKOR reagent is *not* butylpotassium, what is it then ? We wonder whether it will ever be possible to answer this question conclusively and ultimately. As a matter of fact, we have to differentiate between the reacting species and the composition of adducts or products which precipitate. As we have seen in the preceding chapters, superbase reactions can be extremely fast and generally occur under circumstances where no dynamic equilibrium is established among the various forms of organometallic oligomers and mixed aggregates. It is very difficult to investigate what happens at this stage. At the end of the reaction, when all potassium *tert*-butoxide has dissolved and a new precipitate has formed, the latter may turn out to be mainly a potassium compound, say benzylpotassium if toluene or phenylpotassium [21] if benzene was the substrate. By repetitive washing with aromatic solvents a remaining lithium component may be completely extracted [51]. All this, however, does by no means prove that only potassium and no lithium is involved in the crucial event, the hydrogen/metal exchange process. By the same token, the nature of the *in situ* generated superbase cannot be deduced from the composition of the precipitate which slowly deposits. No doubt, under carefully controlled conditions the mixing of butyllithium solutions with potassium *tert*-butoxide, *tert*-pentanolate (2-methyl-2-butanolate) or menthanolate can produce relatively pure butylpotassium [58]. The latter reagent, well known since more than half a century, [59] can be conveniently prepared in different other ways too. However, as we have pointed out on many occasions [12, 23, 57, 60, 62] it reacts less selectively and gives poorer yields than the LICKOR mixture.

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EXPERIMENTAL PART

1. General Remarks

Starting materials have been purchased from Fluka AG (Buchs), Aldrich-Chemie (Steinheim), or Merck-Schuchardt (Darmstadt), unless literature sources or details for the preparation are given. *Butyllithium* and *potassium tert-butoxide* were supplied by CheMetall, Frankfurt, and Hüls, Troisdorf. All commercial reagents were used without further purification.

Air and moisture sensitive compounds were stored in Schlenk tubes or Schlenk burettes. They were protected by and handled under an atmosphere of 99.995% pure nitrogen.

Tetrahydrofuran was obtained anhydrous by distillation after the characteristic blue color of *in situ* generated sodium diphenylketyl [62] was found to persist. In case of poor quality it had before been pretreated with cuprous chloride [63] and potassium hydroxide pellets. *Hexane* and *benzene* were dried by careful azeotropic distillation.

Ethereal extracts were dried with sodium sulfate. Before distillation of compounds prone to radical polymerization or sensitive to acids a spatula tip of *hydroquinone* or, respectively, *potassium carbonate* was added.

The temperature of dry ice methanol baths is consistently indicated as -75°C, "room temperature" (22 - 26°C) as 25°C. *Melting ranges* (mp) are reproducible after resolidification, unless otherwise stated ("dec."), and are corrected using a calibration curve which was established with authentic standards. If no melting points are given, it means that all attempts to crystallize the liquid product have failed even at temperatures as low as -75°C. If no reduced pressure is specified, *boiling ranges* were determined under ordinary atmospheric conditions (720 ± 25 mmHg).

Whenever reaction products were not isolated, their yields were determined by *gas chromatography* comparing their peak areas with that of an internal standard and correcting the ratios by calibration factors. The purity of distilled compounds was checked on at least two columns loaded with stationary phases of different polarity. Chromosorb G-AW of 80 - 100 and, respectively, 60 - 80 mesh particle size were chosen as the support for packed analytical or preparative columns (2 or 3 m long, 2 mm inner diameter and 3 or 6 m long, 1 cm inner diameter, respectively). All packed columns were made of glass, while quartz ("fused silica") was chosen as the material for capillary columns ($\geq$ 10 m long). The type of the stationary phase used is abbreviated as SE-30 (silicon rubber), OV-17 (silicon rubber), OV-1701 (silicon rubber), C-20 M (polyethylene glycol), DB-WAX (polyethylene glycol), FFAP (polyethylene glycol + 2-nitroterephthalate) and Ap-L (Apiezon L hydrocarbon). In the case of programmed temperature increase a rate of 10 °C/min was maintained.

Infrared spectra were recorded of films if the sample was liquid at room temperature, while solid substances were embedded in potassium bromide pellets. The intensities of absorption bands are abbreviated as s (strong), m (moderate) and w (weak).

Nuclear magnetic resonance spectra of hydrogen nuclei in deuterochloroform solution were recorded at 360 MHz or, indicated by an asterisk, at 250 MHz. Chemical shifts refer to the signal of tetramethylsilane (δ = 0 ppm). The shift numbers of silylated compounds were determined relative to the residual solvent peak (CD_5H : δ = 7.16 ppm, $CHCl_3$: δ = 7.27 ppm). Coupling constants (J) are measured in Hz. Abbreviations of coupling patterns: s (singlet), d (doublet), t (triplet), hept (heptuplet), td (triplet of doublets) and m (multiplet).

Mass spectra were obtained at a 70 eV ionization potential. Whenever no molecular peak was observed under standard conditions, chemical ionization ("c.i.") in an ammonia atmosphere was applied.

Elementary analyses were performed by the laboratory of I. Beetz, D-8640 Kronach. The fictitious hydrogen percentages (% "H") were calculated as 1.008 (h + 20.027/18.015 × d)/molec. weight, where h and d stand for the number of hydrogen and, respectively, deuterium atoms in the cross formula.

2. Metalation of Benzene

a) *Suspension in hexane*: Under vigorous stirring, benzene (0.89 mL, 0.78 g, 10 mmol) and potassium *tert*-butoxide (1.1 g, 10 mmol) were added to a 1.5 M solution of butyllithium (10 mmol) in hexane (6.6 mL). After the given reaction time (see Table 2), the mixture was poured on dry ice covered with some tetrahydrofuran (10 mL). After evaporation to dryness, a known amount of *p*-toluic acid was added as an "internal standard". The residue was dissolved in 10% aqueous sodium hydroxide (20 mL) and washed with diethyl ether (2 x 15 mL). The aqueous phase was acidified (to pH 2) and extracted with diethyl ether (3 x 10 mL). The combined organic layers were treated with ethereal diazomethane until the yellow color of the latter persisted and then concentrated. The products were identified by gas chromatographic comparison with authentic samples [*e.g.*, *o*-, *m*- and *p*-bis(trimethylsilyl)benzene [64]] and their quantities determined relative to the standard (50 m OV-1701, 120 → 190 °C; 30 m DB-WAX, 120 → 250 °C).

Reactions with two or three equivalents of the bases (in 13 and, respectively, 20 mL of hexane) were carried out analogously.

b) *Solution in tetrahydrofuran*: The solvent was stripped off from a solution of butyllithium (0.10 mol) in hexane. Precooled (-75 °C) tetrahydrofuran (0.10 L), benzene (0.10 mol) and potassium *tert*-butoxide (0.10 mol) were added and the mixture was stirred at 50 °C until the alcoholate had completely dissolved. At the given intervals (see Table 2), samples (10 mL) were withdrawn and poured on dry ice. The products were isolated and analyzed as described above.

3. Metalation of Naphthalene

Metalations were carried out as described above (Sections 2a and 2b). At the indicated intervals (see Table 3), two identical samples were withdrawn. One of them was treated with excess dimethyl sulfate. After addition of propylbenzene as an internal standard, the products, in particular mono- and dimethylated naphthalene and, in addition, 1- and mainly 2-butylnaphtalene [65] were identified by gas chromatography (45 m SE-30, 120 °C [5 min] → 200 °C; 5 m, 5% Ap-L, 120 °C [15 min] → 250 °C, after 45 min → 250 °C). Authentic samples of all methyl- and dimethylnaphthalenes had been obtained from Fluka, Buchs, or Aldrich, Steinheim, except 1,7-dimethylnaphthalene which is supplied by Wiley Organics (Columbus, Ohio).

The other sample was treated with fluorodimethoxyborane [66] and alkaline hydrogen peroxide. The resulting naphthols and naphthalenediols were isolated (by extraction with aqueous sodium hydroxide, acidification and reextraction with diethyl ether), dissolved in dimethylformamide and converted to the methoxy compounds (by consecutive reaction with sodium hydride and methyl iodide). Beforehand a known amount of 4-*tert*-butylcatechol had been added as an internal standard. The products were identified by gas chromatographic comparison with authentic samples prepared from the commercially available mono- and di-hydroxynaphthalenes (1 m, 5% SE 30 and 1 m, 5% Ap-L, 150 °C [10 min] → 250 °C).

4. Metalation of *tert*-Alkylbenzenes

a) *Preparative reactions*: The reactions were carried out on a 50 mmol scale, following basically the same procedures as described for benzene (see Sections 2a and 2b). The reaction time was, however, uniformly 2 h and the acids were analyzed as such rather than as methyl esters. Yields and product ratios (see Table 5) were determined by gas chromatography (2 m, 5% Ap-L and 3 m, 5% FFAP at 150 → 200 °C in the case of C_{11} and at 200 → 240 °C in the case of C_{15} acids, using pentadecane as an internal standard).

3- and 4-*tert*-Butylbenzoic acid [46, 67]: mp 129 -130 °C and 168 - 169 °C, respectively; bp (of the mixture) 126 - 130 °C/mmHg. ^{1}H-NMR* of the *m*-isomer: 12.30 (1 H, s, broad), 8.88 (1 H, ddd, *J* 7.8, 1.9, 1.8), 8.15 (1 H, t, *J* 1.8), 7.93 (1 H, dt, *J* 7.8, 1.8), 7.40 (1 H, t, *J* 7.8), 1.37 (9 H, s). -^{1}H-NMR* of the *p*-isomer: 12.30 (1 H, s, broad), 8.05 (2 H, dt, *J* 8.2, 4.0), 7.46 (2 H, dt, *J* 8.2, 4.0), 1.34 (9 H, s).

3.5-Di-*tert*-butylbenzoic acid [68]: mp 173 -174 °C; sublimation 120 - 125 °C/0.25 mmHg. - ^{1}H-NMR: 8.01 (2 H, d, *J* 2.1), 7.71 (1 H, t, *J* 2.0), 1.34 (18 H, s).

3- and 4-(1-Methylcyclopropyl)benzoic acid: mp 106 - 107 °C and 157 - 160 °C, respectively; bp (of the mixture) 126 - 129 °C/1mmHg. - Analysis calc. for $C_{11}H_{12}O_2$ (176.21) C 74.98, H 6.86; found C 75.15, H 6.86%. - ^{1}H-NMR* of the *m*-isomer: 7.98 (1 H, t, *J* 1.8), 7.90 (1 H, dt, *J* 7.8, 1.7), 7.46 (1 H, dt, *J* 8.0, 1.8), 7.36 (1 H, t, *J* 8.0), 1.44 (3 H, s), 0.9 (2 H, m), 0.8 (2 H, m). - ^{1}NMR* of the *p*-isomer: 8.0 (2 H, m), 7.28 (2 H, dt, *J* 8.5, 1.6), 1.45 (s, 3 H), 0.9 (2 H, m), 0.8 (2 H, m).

The starting material, (1-methylcyclopropyl)benzene [69] was prepared by reduction of (2,2-dichloro-1-methylcyclopropyl)benzene [69] with sodium in refluxing ethanol; 74%; bp 66 - 69 °C/11 mmHg; n_D^{20} 1.5148; Analysis: calc. for $C_{10}H_{12}$ (132.21) C 90.85, H 9.15; found C 91.13, H 9.25%.

b) *Competition kinetics*: Under vigorous stirring, benzene (2.5 mmol), the *tert*-alkylbenzene (10 mmol) and potassium *tert*-butoxide (2.0 mmol) were added to a roughly 1 *M* solution of butyllithium (2.0 mmol) in hexane (at 25 °C) or tetrahydrofuran (at -50 °C). After 1 h, the mixture was poured on dry ice and known amounts of cyclooctane and *p*-toluic acid were added as internal standards. The acids were extracted with ice cold 10% aqueous sodium hydroxide (3 x 10 mL), the neutral material with *tert*-butyl methyl ether (3 x 10 mL) which was thoroughly washed with ice water (5 x 20 mL). The amounts of unconsumed benzene and *tert*-alkylbenzene were indirectly determined as the difference between the initial amounts and the amounts of products, benzoic acid and *tert*-alkylbenzoic acids (*m*- and *p*-isomers), as identified by gas chromatography (for conditions, see the preceding Section 4a). On this basis, relative rate constants $k_{rel} = k_A/k_B$ (A = alkylbenzene, B = benzene) were calculated using the well known formula [70]:

$$\frac{k_A}{k_B} = \frac{\ln [A]^{\text{before}} - \ln [A]^{\text{after}}}{\ln [B]^{\text{before}} - \ln [B]^{\text{after}}}$$

Splitting up the total rate in regioisomeric channels (multiplication with the isomer composition coefficients) and statistical correction (division by 2 for *m*-positions and by 6 for benzene) gave the partial rate factors mentionned in the text.

As a cross-check, a mixture of *tert*-butylbenzene and triisopropylsilylbenzene was treated with an insufficient amount of butyllithium and potassium *tert*-butoxide. This time it was possible to measure directly the consumption of both substrates. The rate ratios thus derived (1.03 in hexane and 0.56 in tetrahydrofuran) agree well with those calculated from the data collected in Table 5.

5. Metalation of Triisopropylphenylsilane

a) *Preparative reaction*: The reactions were carried out as described for *tert*-alkylbenzenes (Section 4a). The regioisomeric composition of the crude product (*m*/*p* = 28 : 74) was determined by gas chromatography (2 m, 5% ApL, 200 → 240 °C; 3 m, 5% FFAP, 200 → 240 °C). Subsequently the acids formed under heterogeneous conditions in hexane were extracted and isolated by distillation; bp 127 - 130 °C/0.2 mmHg. - Analysis: calc. for $C_{16}H_{26}O_2Si$ (278.47) C 69.01, H 9.41; found C 69.53, H 9.42%. - ^{1}H-NMR* of the *m*-isomer [mp 121 - 123 °C]: 8.24 (1 H, t, *J* 1.3), 8.1 (1 H, m), 7.72 (1 H, dt, *J* 7.5, 1.3), 7.45 (1 H, t, *J* 7.5), 1.46 (3 H, hept, *J* 7.5), 1.09 (18 H, d, *J* 7.5). -^{1}H-NMR of the *p*-isomer [mp 157 - 159 °C]: 8.11 (2 H, d, *J* 8.3), 7.64 (2 H, d, *J* 8.3), 1.44 (3 H, hept, *J* 7.5), 1.09 (18 H, d, *J* 7.5).

b) *Competition kinetics*: The same procedure was applied as described for *tert*-alkylbenzenes (Section 4b) except that benzene and the silane were used in equal amounts (5.0 mmol each together with 2.0 mmol butyllithium and 2.0 mmol potassium *tert*-butoxide). The gas chromatographic conditions were as previously described (Sections 4.a and 4.b). In addition a 2 m, 5% OV-17 column was employed.

c) *Preparation of the starting material*: Benzene (8.9 mL, 7.8 g, 0.10 mol) was metalated with butyllithium and potassium *tert*-butoxide (0.10 mol each) in hexane (see Section 2a), chlorotriisopropylsilane (21 mL, 19 g, 0.10 mol) was added and the mixture stirred 2 h at 25 °C. Immediate distillation afforded a viscous colorless liquid which solidified; 57%; mp 22 - 25 °C; bp 93 - 94 °C/0.2 mmHg. - ^{1}H-NMR: 7.5 (2 H, m), 7.3 (3 H, m), 1.41 (3 H, hept, *J* 7.5), 1.08 (18 H, d, *J* 7.5). - Analysis: calc. for $C_{15}H_{26}Si$ (234.46) C 76.84, H 11.18; found C 76.87, H 11.16%.

6. Metalation of Perdeuterobenzene

a) *Preparative reactions*: Hexadeuterobenzene (8.4 g, 100 mmol, 99% isotopic purity) was added to the mixture of butyllithium (100 mmol) and potassium *tert*-butoxide (100 mmol) in hexane (65 mL). After 1 h of vigorous stirring, the electrophile (carbon dioxide, *N*,*N*-dimethylformamide or fluorodimethoxyborane, the latter followed by treatment with alkaline hydrogen peroxide) was added and the products isolated by extraction and fractional distillation or crystallization. The yield of benzaldehyde increased significantly if a precooled (-75°C) solution of lithium bromide (100 mmol) was added prior to dimethylformamide.

$[^2H_5]$Benzoic acid [71]: 62%; mp 119 - 120 °C. - **$[^2H_5]$Benzaldehyde** [72]; 58%; bp 72 - 73 °C/22 mmHg; n_D^{20} 1.5433; IR: 2820 + 2750 + 2705 (w, ν[(O=)C-H]), 2280 (w, ν[(C=)C-D]), 1700 (s, ν[C=O], 1565 (m, ν[C=C]), 1145 (s), 875 + 840 + 815 + 770 (w/m, δ[=C-D]). - Analysis: calc. for C_7HD_5O (111.15) C 75.64, "H" 5.95; found C 75.66, "H" 5.66%. - **$[^2H_6]$Benzaldehyde** [72]: 53%; bp 60 - 62 °C/12 mmHg; n_D^{20} 1.5433; IR: 2280 (w, ν[(C=)C-D], 2100 (m, ν[(O=)C-D]), 1680 (s, ν[C=O]), 1560 (m, ν[C=C]), 1175 (s), 870 + 835 + 815 + 750 (w/m, δ[=C-D]). - Analysis: calc. for C_7D_6O (112.16) C 74.96, "H" 5.99; found C 75.07, "H" 5.64%; **$[^2H_5]$Phenol** [73]: 47%; mp 40 - 42 °C/11 mmHg (isolated by steam distillation).

If bifunctional derivatives were the targets, hexadeuterobenzene (100 mmol) was metalated 3 h with three equivalents of butyllithium and potassium *tert*-butoxide in hexane (10 mL). Terephthalic acid and hydroquinone were separated from their regioisomers and monosubstituted benzenes by fractional crystallization from water and acetone (at 0 °C), respectively. The aldehydes were purified and isolated by preparative gas chromatography (3 m, 10% C-20 M, 200 °C).

$[^2H_4]$Terephthalic acid [74]: 12%; mp > 300 °C (subl.). - **$[^2H_4]$Isophthalaldehyde**: 12%, mp 85 - 86 °C. - IR: 2870 + 2800 (w, ν[C-H]), 1695 (s, ν[C=O]), 1570 + 1410 (m, ν[C=C]), 1040 + 1000 + 850 + 835 + 795 + 775 (m, δ[C-D]). - Analysis: calc. for $C_8H_2D_4O_2$ (138.16) C 69.55, "H" 4.70; found C 69.32, "H" 4.67%. - **$[^2H_4]$Terephthalaldehyde**: 13%; mp 108 - 109 °C. - IR: 2860 + 2775 (w, ν[C-H]), 1690 (s, ν[C=O], 1420 (w, ν[C=C]), 1110 + 860 (m, δ[C-D]). - Analysis: calc. for $C_8H_2D_4O_2$ (138.16) C 69.55, "H" 4.70; found C 69.74, "H" 4.60%. - **$[^2H_4]$Hydroquinone** [75]: 11%; mp 171 - 173°C (isolated by crystallization from acetone at -75 °C).

b) *Isotope effect measurements*: The organometallic reagent (5.0 mmol) was dissolved in hexane (4.0 mL) or precooled (-75°C) tetrahydrofuran (4.0 mL). Under vigorous stirring an "internal standard" (cyclooctane or cyclodecane) and an equimolar mixture of benzene and hexadeuterobenzene 10 mmol each) of toluene and octadeuterotoluene (10 mmol each) were added. After 10 min at 25°C, 30 min at -50°C or 5 h at -75°C, the solution was poured on dry-ice. The acids were extracted by alkaline washing (3 x 2 mL 10% aqueous sodium hydroxide) and the concentration of the unconsumed isotopomers determined by gas chromatography using separately two capillary columns loaded with stationary phases of different polarity (25 m OV-17 and 50 m Ap-L; temperatures: benzene 45°C, toluene 50°C). As expected [76], the undeuterated hydrocarbons were longer retained than the perdeuterated analogs. The isotopic composition was also elucidated by GC-coupled mass spectrometry (at 10 eV ionization).

The k_H/k_D ratios listed in Table 6 are averages from 2 - 6 individual runs. Standard deviations were in the order of 3% of the absolute value; the biggest span between two extreme numbers belonging to the same set was roughly 24%. As a double check, several reactions were repeated, the metalated intermediates were intercepted and the yields as well as the isotopic composition of the resulting silanes were quantified by gas chromatography (conditions: see above, temperatures: trimethylphenylsilane 90°C, benzyltrimethylsilane 120°C) and mass spectrometry. These data allowed then to calculate the consumption of un- and perdeuterated substrates. The isotope effects obtained by this indirect and the previous direct approach coincided within reasonable limits.

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