17(20)-pregnene 3-acetate, 68550-73-2; 21-hydroxy-3-oxopregna-5,17(20)-diene 3-ethylene ketal, 68628-72-8; ethyl (*E*)-4α,5α-dihydroxy-3-oxopregn-17(20)-en-21-oate, 68550-74-3; ethyl 3-oxo-4α,5α,17α,20β-tetrahydroxypregnan-21-oate, 68568-35-4; 1,4-androstadiene-3,17-dione, 897-06-3; isobutylene, 115-11-7.

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Aromatic Side Chain Bromination by *N*-Bromosuccinic Imide. 5.[1] Ring Substituents and Selectivity

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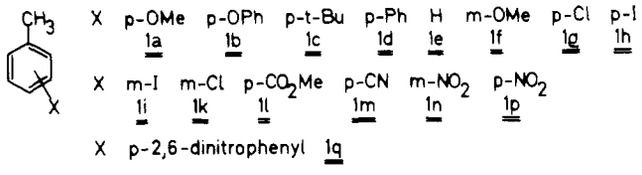
The selectivity (monobromination/dibromination) of *N*-bromosuccinic imide (NBS) toward 15 meta- and para-substituted toluenes was evaluated by ^{1}H NMR integration. Except for two substrates, selectivity and hence maximum yield correlate with Hammett σ^+ parameters. The Hammett ρ value of the reaction $XC_6H_4CH_2Br \rightarrow XC_6H_4CHBr_2$ (dibromination) is −0.88. The results demonstrate that in NBS side chain bromination substrate reactivity parallels selectivity.

Benzylic and allylic bromination, since long achieved by use of NBS,[2] is an important method to functionalize hydrocarbon molecules in phane chemistry[3] as well as in other fields. Although the reaction yields 67% benzylic bromide from toluene,[4] it is, from the angle of phane chemistry, not quite satisfying for two reasons.

(a) In multiple brominations, e.g., of xylenes or mesitylene, yields are reduced according to eq 1 (see Table I), where Y_k is the yield of bromination of a benzene with k methyl groups and Y_1 is the yield of bromination of the corresponding toluene.[5] Equation 1 applies to benzenes where adhering methyl groups are both electronically and sterically independent of one another. As a rule, this condition is met in the case of meta and para substitution.

$$Y_k = Y_1{}^k \quad (1)$$

(b) Electron-withdrawing substituents and heteroatoms affect both yield and reaction time[9] to the worse. For example, 1,3-dimethyl-2-nitrobenzene, which suffers from both restrictions, is brominated to 22% 1,3-bis(bromomethyl)-2-nitrobenzene only.[10] Hence, there is still profit in a general improvement of the preparative NBS side chain bromination method.



Results and Discussion

In order to enlighten the relevant factors, we investigated the NBS bromination of a series of meta- and para-substituted toluenes (**1a–q**).

Product Analysis. In a nonpolar solvent like tetrachloromethane, benzylic bromide **2** formed at first (eq 2) is further converted to dibromide **3** (eq 3). In the ^{1}H NMR spectrum, the benzylic protons show up at ~2.4 (**1**), ~4.5 (**2**), and ~6.6 ppm (**3**). Ring bromination, which would shift these signals by ~0.2 ppm downfield, was not detected. Substantial amounts of unconverted as well as dibrominated side products **1** and **3** indicate that the ratio $\alpha = k_1/k_2$ must be relatively low. For toluene itself (**1e**), Keefer et al.[11] calculated $\alpha = 5.5$ from competition experiments. We determined α by a more convenient method. Each substrate was treated with various amounts of NBS in refluxing CCl_4. The product mixtures were

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Table I. Yields of Bromination (NBS/CCl_4) of Some Methylated Benzenes

substrate	registry no.	k^a	yields,[b] % exptl/ref	calcd[c]	calcd[d]
toluene		1	67/4		62
m-xylene	108-38-3	2	31/6	44	39
mesitylene	108-67-8	3	23/7	30	24
3,3′,5,5′-tetramethylbiphenyl	25570-02-9	4	18/8	20	15

[a] Number of brominated methyl groups. [b] Note that experimental conditions were different for all substrates. [c] The calculation is based on the experimental yield of toluene. [d] The calculation is based on the mean experimental yield of all substrates.

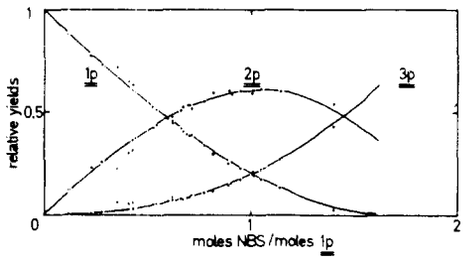


Figure 1. Relative product composition in the bromination of *p*-nitrotoluene as a function of consumed amount of NBS (dots). The graphs correspond to $\alpha = k_1/k_2 = 3.418$ (see Table II).

analyzed by ^1H NMR integration. In Figure 1, the relative product composition for *p*-nitrotoluene (**1p**) vs. the consumed amount of NBS is plotted.

$$\underset{1}{ArCH_3} \xrightarrow{k_1} \underset{2}{ArCH_2Br} \tag{2}$$

$$\underset{2}{ArCH_2Br} \xrightarrow{k_2} \underset{3}{ArCHBr_2} \tag{3}$$

Selectivity Evaluation. Since in the Goldfinger scheme (eq 4–6)[12] now generally accepted as the operative mechanism[13] the bromine concentration is approximately steady in

$$ArCH_2X + Br\cdot \rightarrow Ar\dot{C}HX + HBr \tag{4}$$

$$HBr + NBS \rightarrow Br_2 + \text{succinic imide} \tag{5}$$

$$Ar\dot{C}HX + Br_2 \rightarrow ArCHXBr + Br\cdot \tag{6}$$

$$X = H, Br$$

the course of the reaction, and since allylic bromination is known to be first order in substrate and zero order in NBS,[14] we regard eq 2 and 3 as consecutive (pseudo)monomolecular reactions, which are governed by eq 7–9.[15] For each set of relative product composition, an α value was computed iteratively from eq 7–9.

$$Y_1 = e^{-k't} \tag{7}$$

$$Y_2 = \frac{k'}{k'' - k'}(e^{-k't} - e^{-k''t}) \tag{8}$$

$$Y_3 = 1 - \frac{k''e^{-k't} - k'e^{-k''t}}{k'' - k'} \tag{9}$$

Y_u = relative yield of compound u (u = **1**, **2**, or **3**)
k' and k'' = rate constants

Table II. Selectivity Ratio $\bar{\alpha}$ and Maximum Yield for NBS Bromination of Toluenes 1a–p

compd	$\bar{\alpha}^a$	s	Δ/s	b	Y, %
1a	6.315	0.781	1.511	8/8	70.7
1b	9.25[c]			3/5	76.5
1c	8.726	1.184	1.560	7/12	75.5
1d	10.977	0.677	0.971	4/4	78.7
1e	7.653	0.958	1.883	10/10	73.6
1f	6.539	1.200	1.792	7/10	71.2
1g	6.583	1.083	1.663	11/11	71.4
1h	10.804	1.909	1.211	5/7	78.4
1i	4.958	0.455	1.541	8/8	66.7
1k	3.911	0.297	1.747	8/8	62.6
1l	6.360	0.502	1.382	8/8	70.8
1m	1.096	0.336	1.926	6/7	38.5
1n	2.775	0.289	1.955	8/8	56.3
1p	3.418	0.238	1.816	18/24	60.2

[a] Selection criteria: $s/\bar{\alpha} \leq 0.2$ (s = mean deviation) *and* $\Delta/s \leq 2$ ($\Delta = |\alpha - \bar{\alpha}|_{max}$). [b] Number of α values finally used for $\bar{\alpha}$/total number of α values. [c] From a graphically estimated Y value. $\bar{\alpha}$ is not used for eq 11 and 13.

In order to overcome the notorious inaccuracy of NMR integration, we determined 4–24 α values for each toluene and calculated the mean value $\bar{\alpha}$ (see Table II) by a selection method described by Schmid et al.[16] $\bar{\alpha}$ reflects the selectivity[17] bromine exhibits toward a mixture of $ArCH_3$ and $ArCH_2Br$ and is therefore a measure for the maximum yield Y (Table II), to which it is related by eq 10.

$$Y = \frac{\bar{\alpha}}{1 - \bar{\alpha}}\left(e^{-\bar{\alpha}\ln[\bar{\alpha}/(\bar{\alpha}-1)]} - e^{-\ln\bar{\alpha}/(\bar{\alpha}-1)}\right) \tag{10}$$

Correlations. Log $\bar{\alpha}$ yields to eq 11 (correlation coefficient $r^2 = 0.852$; see Figure 2).

$$\log\bar{\alpha} = 0.90 - 0.50\sigma^+ \tag{11}$$

Whereas meta substituents respond equally well to σ ($r^2 = 0.98$) and σ^+ [18] ($r^2 = 0.97$), para substituents definitely prefer σ^+ ($r^2 = 0.84$) over σ ($r^2 = 0.64$). This is in line with the postulate of a polar transition state **4**.[13]

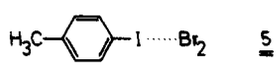
$$\underset{4}{[R\text{-}H\cdot X \leftrightarrow R\text{-}H\text{-}X^{\delta+}\ {}^{\delta-} \leftrightarrow R\cdot H\text{-}X]}$$

According to Walling,[9] the bromination reaction 2 follows the Hammett relation shown in eq 12. From eq 11 and 12, the Hammett relation for reaction 3 can be deduced (see Figure 2); $r^2 = 0.94$ indicates a good correlation.

$$\log k_1/k_{1H} = -1.38\sigma^+ \tag{12}$$

$$\log k_2/k_{2H} = -0.88\sigma^+ \tag{13}$$

Compounds Resisting Correlations. For still unknown reasons, *p*-methoxytoluene (**1a**) and *p*-cyanotoluene (**1m**) escape both from eq 11 and 13, adopting far too small $\bar{\alpha}$ values. These two substrates were not used in the correlations 11 and 13. Also, *p*-iodotoluene (**1h**) drops out of line, although to a less degree and in the opposite direction. To account for this behavior, one might consider an adduct **5** like that observed with chlorine and iodobenzene.[19]



5

Bromine association to iodotoluene could affect the "reagent part" (bromine) as well as the "substrate part" (iodotoluene). The first effect should work with *m*-iodotoluene too, but is definitely not observed. Also, addition of iodobenzene

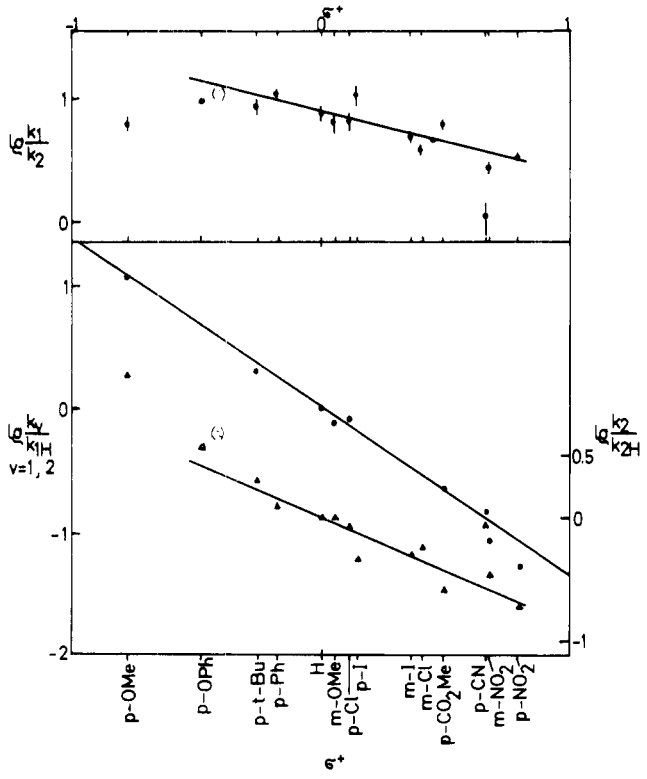


Figure 2. Bottom: Hammett plots of reactions 2 (left scale) and 3 (right scale). The latter graph is adjusted to the left scale in such a way that all rate constants can be compared directly. Top: plot of selectivity ratio α vs. σ^+. (a) See Table I, footnote *c*.

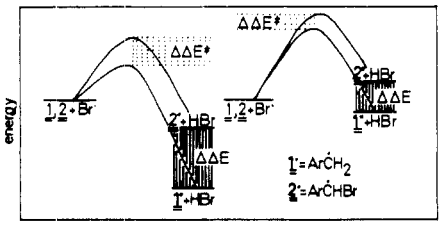


Figure 3. Energy profiles for the bromination of toluenes: (left) with electron-releasing ring substituent; (right) with electron-withdrawing ring substituent.

in the bromination of *p*-nitrobenzene does not improve the selectivity at all.

The second effect might alter the σ^+_p value of the iodo substituent to a lower, i.e., a "more selective", one. Yet, the ^{13}C NMR spectrum of iodobenzene does not reflect any changes in the electron densities of the ring atoms on bromine addition.

Application of the Leffler–Hammond Postulate. We find that more reactive toluenes are brominated not only faster[9] but also with greater selectivity. To put this in terms of the Leffler–Hammond postulate,[17] electron withdrawal through the ring makes the benzylic radicals in reactions 2 and 3, respectively, energetically less favorable *and* diminishes the difference between their ground state energies (see Figure 3).

Since log k is linearly related to the activation energy, the bottom section of Figure 2 reflects the relative position of all activation energies involved on an appropriate negative energy scale.

Although side chain bromination is more selective than chlorination, its selectivity factor α is still relatively low (3–11; see Table II), thus giving rise to troublesome preparations. The Leffler–Hammond postulate predicts that making the reactions 2 and 3 less exothermic (more endothermic) increases the difference of the respective activation energies and hence the selectivity. Electron-withdrawing substitution fails to fulfill this prediction. Presently, we are engaged in the investigation of more prospective means to gain better selectivity.

Experimental Section

Materials. We employed Baker grade NBS and Merck azabis(isobutyro)nitrile (AIBN). Tetrachloromethane was stored over $CaCl_2$ and decanted. *p*-Methoxytoluene, *p*-*tert*-butyltoluene, *p*-chlorotoluene, and *m*- and *p*-nitrotoluene are commercially available. *m*-Chlorotoluene, *p*-cyanotoluene, and *m*- and *p*-iodotoluene were prepared from toluidine by Sandmeyer reactions.[20] *m*-Cresol was methylated by dimethyl sulfate to *m*-methoxytoluene.[20] By a Gomberg reaction, *p*-toluidine and benzene gave *p*-phenyltoluene (4-methylbiphenyl).[21] *p*-(Carboxymethyl)toluene was synthesized in four steps from *p*-toluidine.[20] *p*-Phenoxytoluene was prepared from *p*-cresol and bromobenzene.[22] *p*-(2,6-Dinitrophenyl)toluene was prepared from iodotoluene and 1,3-dinitrotoluene in the presence of quinoline and copper oxide.[23] All toluenes were pure according to ^1H NMR spectra and melting point or refractive index.

Procedure. Approximately 8 mmol of substrate was dissolved in 20 mL of tetrachloromethane. A 7–9 mmol amount of NBS and 5 mg of AIBN were added. The mixture was stirred and illuminated by a 200-W bulb, which sufficed to reflux the solvent. As soon as all of the NBS was converted to succinic imide (which lasted from 10 min to 48 h, depending on the substrate), the reaction mixture was cooled to 30 °C.

In order to check bromine–iodobenzene association, 1 mL of iodobenzene was added to eight runs prepared with *p*-nitrotoluene in the usual way.

Analytical. ^1H NMR samples were taken from the crude reaction mixtures. The spectra were recorded on a Varian EM 360 spectrometer. Each spectrum was integrated five to ten times. After allowing for the different number of benzylic protons, the relative product composition was calculated from the average integration values. α was computed on a Wang 2000. The carbon-13 spectra were recorded on a Bruker WP 80 spectrometer (solvent $CDCl_3$).

Acknowledgment. We are indepted to Drs. R. Sievers and R. Hundt, who supported the computational program and computing time, and to Messrs. K. von der Wettern and F. Speckenbach and Miss R. Michels, who prepared a great number of the substrates and performed some of the experiments.

Registry No.—**1a,** 104-93-8; **1b,** 1706-12-3; **1c,** 98-51-1; **1d,** 644-08-6; **1e,** 108-88-3; **1f,** 100-84-5; **1g,** 106-43-4; **1h,** 624-31-7; **1i,** 625-95-6; **1k,** 108-41-8; **1l,** 99-75-2; **1m,** 104-85-8; **1n,** 99-08-1; **1p,** 99-99-0; **1q,** 23621-60-5; NBS, 128-08-5.

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Markownikoff Two-Step Hydrolithiation of α-Olefins. Transformation of Secondary and Tertiary Alkyl Phenyl Sulfides to the Relevant Alkyllithium Reagents

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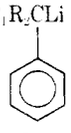
The transformation of a number of α-olefins to the relevant secondary and tertiary alkyllithium reagents has been accomplished in two steps by first converting them to the corresponding alkyl phenyl sulfides through their acid-catalyzed reaction with thiophenol, and second by cleaving the sulfides with lithium in tetrahydrofuran (THF). The overall yields ranged from ~35 to 80%, based on the isolated carboxylic acids after carbonation. Secondary and tertiary benzylic alkyl phenyl sulfides have been synthesized by alternative routes and cleaved by lithium naphthalene to the corresponding benzylic type organolithium reagents. Some of them were converted to other organoalkali reagents; e.g., $Ph_2C(CH_3)M$ (M = Li, Na, K), $LiCH(Ph)(CH_2)_nCH(Ph)Li$ (n = 3,4,5,6,10), $LiOC(Ph)(R)CH(Ph)Li$ (R = CH_3, Ph), and $LiOCH_2CH_2CH(Ph)Li$. The latter two examples represent cases of dianions formally equivalent to those derived from two-electron reductive opening of oxirane and oxetane rings, respectively. The lithiooxy sulfide PhCH(OLi)CH(Ph)SPh underwent a facile C–S as well as C–O bond fission by lithium naphthalene and was transformed to stilbene dianion $(PhCH{=}CHPh)^{2-}$.

The conventional method of preparation of organolithium reagents depends almost exclusively on the availability of the corresponding chlorides and bromides.[1] Metalation by simple organolithium and organosodium compounds is an alternative method for preparing metal derivatives of aromatic compounds.[2] The synthesis of metal derivatives such as **1** by



1, R = Li, Na, K

these two methods may present some difficulties. The metalation method is limited by the lack of regiospecificity because it usually gives rise to complex mixtures of side chain as well as ring metalated products, and the conventional method is seldom usable due to Wurtz coupling reaction.

One of the most reliable methods for preparing organoalkali reagents of unambiguous structure is the metalative cleavage reaction shown in eq 1.[3] However, ethers of this type are not as readily available as thioethers.

$$PhC(CH_3)_2OCH_3 \xrightarrow{Na\text{–}K} PhC(CH_3)_2K + CH_3OK \quad (1)$$

Recently, we reported[4] the transformation of α-olefins to the corresponding primary alkyllithium reagents by the two-step sequence shown in eq 2. Here we wish to describe the preparation of secondary and tertiary organolithiums by means of the process of eq 3.

$$R_1R_2C{=}CH_2 + PhSH \xrightarrow{R\cdot} R_1R_2CHCH_2SPh \xrightarrow[THF]{Li} R_1R_2CHCH_2Li + PhSLi \quad (2)$$

$$R_1R_2C{=}CH_2 + PhSH \xrightarrow{H^+} R_1R_2C(CH_3)SPh \xrightarrow[THF]{Li} R_1R_2C(CH_3)Li + PhSLi \quad (3)$$

The acid-catalyzed addition of thiophenol to α-olefins is almost as facile as the first step of eq 2. The fundamental difference, of course, lies in the orientation of the addition which gives the Markownikoff adduct.

Besides the fact that sulfides can be more readily accessible through the first reaction of eq 3 than the corresponding ethers, an additional advantage is offered by the more facile cleavability of C–S vs. C–O bonds by either alkali metals or aromatic radical anions.[4] Thus, the cleavage step in eq 3 can be run at low temperatures, where the highly reactive secondary and tertiary organolithium reagents can survive without reacting with the THF medium[5] in which they are prepared. It should be pointed out that the steps of eq 3 accomplish the addition of lithium hydride to an olefin in the Markownikoff orientation.

Since secondary and tertiary alkyl phenyl sulfides are available through alternative routes, we have synthesized a number of them and studied their transformation to the corresponding alkyllithium reagents. A small number of them have also been converted to the corresponding organosodium or organopotassium reagents.

Results and Discussion

Perchloric acid (70%), $pK_a = -10$, was used as a catalyst for the addition of thiophenol to α-olefins. The secondary and tertiary alkyl phenyl sulfides thus formed were isolated in yields ranging from about 65 to 90% (see Table I). Olefins such as 1,1-diphenylethylene and styrenes had to be reacted with thiophenol under an inert atmosphere; otherwise, the product was contaminated with the anti-Markownikoff adduct which could not be separated by distillation. Olefins, which on protonation give a tertiary carbenium ion, react exothermically with thiophenol in the presence of 70% perchloric acid.[6] In contrast, olefins of the type $RCH{=}CH_2$ appear to be less reactive than the previously mentioned ones. In the latter case, higher reaction temperatures and longer reaction times had to be employed in order to obtain secondary alkyl phenyl sulfides in satisfactory yields.

The cleavage of secondary and tertiary alkyl phenyl sulfides

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