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GENERATION AND THE AMBIDENT CHARACTER OF 9-ANTHRYLMETHYL CARBANIONS

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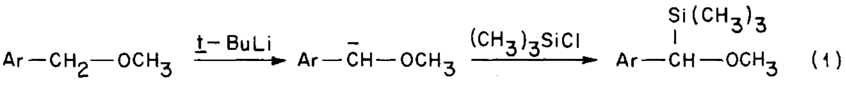
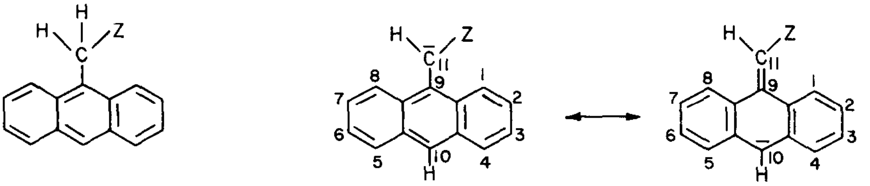
Abstract: 9-Methoxymethylanthracene, 9-trimethylsilylmethylanthracene and 9-thiomethoxymethylanthracene are converted by butyllithium reagents to α-methoxy-9-anthrylmethyl, α-trimethylsilyl-9-anthrylmethyl and 9-anthrylmethyl carbanions, respectively, which react at their C-10 and C-11 positions with appropriate electrophiles.

Various methoxymethylarenes (1, Eq 1) are deprotonated by t-butyllithium/TMEDA/Et$_2$O at -78^{o}C to methoxyarenylmethyl carbanions (2) which react with chlorotrimethylsilane to yield [methoxy(arenyl)methyl]trimethylsilanes (3, 68-100%).[1] We now report the behavior of 9-



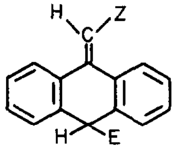
$$\underset{1}{Ar-CH_2-OCH_3} \xrightarrow{t-BuLi} \underset{2}{Ar-\overset{-}{C}H-OCH_3} \xrightarrow{(CH_3)_3SiCl} \underset{3}{Ar-\overset{Si(CH_3)_3}{\overset{|}{C}H}-OCH_3} \quad (1)$$

methoxymethylanthracene (4), 9-trimethylsilylmethylanthracene (5) and 9-thiomethoxymethylanthracene (6) with alkyllithium reagents and the reactions of the subsequent carbanions, 11a-b:13a-b, with varied electrophiles. The results reveal the extensive ambident character of simple 9-anthrylmethyl carbanions at their C-10 and C-11 positions and the potential of such systems for synthesis.[2] The study is also of note in that 6 undergoes efficient dethiomethoxylation by t-butyllithium or with lithium to give the parent 9-anthrylmethyl carbanion, 13a-b, which is then usable synthetically.

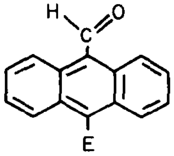


4; Z = OCH$_3$
5; Z = Si(CH$_3$)$_3$
6; Z = SCH$_3$
7; Z = C(CH$_3$)$_3$
8; Z = D
9; Z = CH$_3$
10; Z = CHOHC$_6$H$_5$
11a; Z = OCH$_3$
12a; Z = Si(CH$_3$)$_3$
13a; Z = H
11b; Z = OCH$_3$
12b; Z = Si(CH$_3$)$_3$
13b; Z = H

In the present investigation 4 and t-butyllithium (1.0-1.2 equiv) in TMEDA (1.0-1.3 equiv)/Et$_2$O at -78^{o}C are found to give 11a-b, a dark green anion, which reacts with chlorotrimethylsilane to yield, after column chromatography on silica gel, 9-methoxymethylene-10-trimethylsilyl-9,10-dihydroanthracene (14a, 40%),[3a] 9-anthraldehyde (15a) and 9-neopentylanthracene (**7**, 16-36%). Similarly, quenching the mixture from **4** and *t*-BuLi/TMEDA/Et$_2$O at -78°C with deuterium oxide (D$_2$O) results in 10-deuterio-9-methoxymethylene-9,10-dihydroanthracene (**14b**, > 55%), 9-anthraldehyde (**15b**) containing 64% D at C-10, and **7**.[3b] Formation of **14a** and **14b** clearly indicates the carbanionic activity of **11a-b** at C-10. Hydrolysis and oxidation of **14a** and **14b** during chromatography and work-up account for the production of **15**. The origin of **7** has not yet been established. Hydrocarbon **7** might arise from **4** by S$_N$2 displacement by *t*-butyllithium, radical-anion processes analogous to that to be discussed for **6**, *alpha*-elimination with capture of *t*-butyllithium or other complex processes.

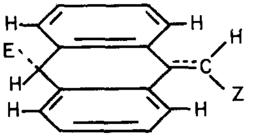


14a; $Z = OCH_3$, $E = Si(CH_3)_3$ (40%)
14b; $Z = OCH_3$, $E = D$ (55%)
14c; $Z = OCH_3$, $E = CH_3$ (75%)
14d; $Z = OCH_3$, $E = COC_6H_5$ (45%)
14e; $Z = OCH_3$, $E = CHOHCH_3$ (53%)
14f; $Z = OCH_3$, $E = CHOHC_6H_5$ (39%)
14g; $Z = OCH_3$, $E = COH(CH_3)_2$ (55%)
14h; $Z = Si(CH_3)_3$, $E = Si(CH_3)_3$ (55%)
14i; $Z = H$, $E = CH_3$ (37%)
14j; $Z = H$, $E = CHOHC_6H_5$ (20%)



15a; E = H
15b; E = D

The preparative potential of **11a-b** is illustrated further by its reactions with dimethyl sulfate, benzoyl chloride, acetaldehyde, benzaldehyde and acetone to give the isolable, analytically-pure C-10 products, **14c-g**, in the indicated yields.[3b] The significant behavior of **11a-b** thus is its electrophilic reactivity at C-10. This property of **11a-b** is similar in part to reactions of 9-anthryldiphenylmethyllithium with ethereal hydrogen chloride to give 9-diphenylmethylene-9,10-dihydroanthracene and 9-diphenylmethylanthracene in 7:3 ratio[4a] and the recent conversions[4b] of 2-(3-methyl)naphthylmethyllithium by chlorotrimethylsilane and by bromine to 2,3-dimethyl-1-trimethylsilylnaphthalene and 1-bromo-2,3-dimethylnaphthalene, respectively.[4c] The specificity of reactions of **11a-b** at its C-10 position in the present systems is presumably the result of electronic effects[5] and because of steric factors as in **16** in which *peri*-interactions are relatively minimized. Competitive nucleophilic attack at C-11 in **11a-b** as in **17** or rearrangements of **14a**-**14g** to 9-methoxymethyl-10-substituted-anthracenes are apparently inhibited by steric demands at the *peri* positions.



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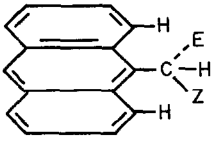

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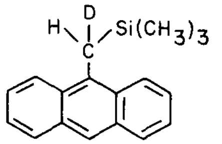
Deprotonation of **5** to **12**a-b, a deep green anion, is effected by *n*-butyllithium (1.0 equiv) in TMEDA/Et_2O at 0°C. Quenching of **12**a-b with methanol results in regeneration of **5** (100%). Methanol-O-D (CH_3OD) leads to deuteration of **12**a-b at C-11 to give 9-trimethylsilylmethylanthracene (**18**) which does not contain deuterium in the anthracene unit of the product and thus **19** was not formed initially and then rearranged to **20**. Reaction of 12a-b with chlorotrimethylsilane results however in trimethylsilylation at C-10 to give [9,10-dihydro-10-(trimethylsilylmethylene)-9-anthryl]trimethylsilane (**14**h) in 85% isolated yield. The difference in the behavior of **12**a-b in protonation and in reaction with chlorotrimethylsilane appears to be related dramatically to the differences in the steric effects at the *peri*-positions in the two systems. Reactions of **12**a-b with bulky electrophiles to give analogs of **14**i-j would thus appear to be of considerable synthetic promise.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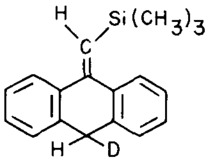
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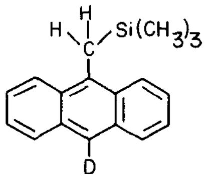
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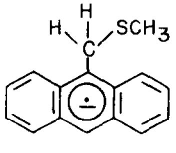
Of particular interest is that *t*-butyllithium in TMEDA/Et_2O at -78°C converts thioether **6** efficiently to the (emerald green) lithium derivative of **13**a-b.[6] The behavior of alkyllithium reagents with **6** is thus decidedly different from that with **4** and **5**. Further, lithium (3 equiv) also reacts with **6** in tetrahydrofuran at 25°C to give **13**a-b which is trapped by chlorotrimethylsilane to yield **5** (85%). The reactions of **6** with *n*-butyllithium or with lithium are the first preparations of lithio **13**a-b to be reported.[7] The mechanisms, however, by which **13**a-b are formed from **6** are as yet not clear. Routes to **13**a-b of special consideration involve electron transfer to **6** and subsequent loss of thiomethoxy free radical from 9-thiomethoxymethylanthracene radical-anion (**21**)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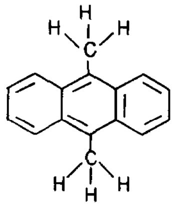
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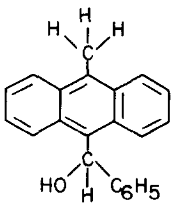
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Lithio **13**a-b reacts with deuterium oxide to give 9-methylanthracene (**8**, 88%) in which > 90% of the deuterium is in the methyl group. Similarly, **13**a-b and chlorotrimethylsilane yield **5** (91%). The behavior of **13**a-b in these systems is thus as a nucleophile with (near) exclusivity for reaction at C-11. In contrast however **13**a-b effects displacement of dimethyl sulfate to form 9-ethylanthracene (9) and 10-methyl-9-methylene-9,10-dihydroanthracene (14i) in 1:1 ratio in 73% yield. Also, benzaldehyde reacts with 11a-b, yielding, after neutralization and column chromatography, 2-(9-anthryl)-1-phenylethanol (10) and 9,10-dihydro-10-methylene-α-phenyl-9-anthracenemethanol (14j) in 3-4:1 ratios in 82-92% yields. Thus with appropriate nucleophiles 13a-b is an ambident nucleophile at C-10 and C-11. These results support the proposition that the ambident selectivity of 9-anthrylmethyl carbanions for reaction at C-10 is enhanced with relatively bulky electrophiles. Of further note is that 14i is converted by trichloroacetic acid in chloroform at 25°C to the more thermodynamically stable isomer, 9,10-dimethylanthracene (22), in 100% yield. On the other hand, trichloroacetic acid/chloroform effects cleavage of 14j to 9-methylanthracene (8, Z=H; 90%) and benzaldehyde; 9-(α-hydroxybenzyl)-10-methylanthracene (23) is not found.

Further study of electrical and steric factors on the reactions of arylmethyl carbanions with varied electrophiles is in progress.

Acknowledgement: This research was supported by the National Science Foundation.

References and Notes

1. (a) Such derivatives include 1-and 2-methoxymethylnaphthalenes, 1-methoxymethylanthracene, 9-methoxymethylphenanthrene and 1-methoxymethylpyrene.[1b] (b) T. A. Engler and H. Shechter, Tetrahedron Lett., 2715 (1982).
2. The C-10 ring positions of 9-anthryldiphenylmethyl cations, 9-anthrylmethyl halides and 9-anthrylmethyltrimethylammonium salts are highly reactive to nucleophiles. (b) M. Nojima, M. Takagi and S. Kusabayashi, J. Chem. Soc., Perkin 1, 2941 (1979). (c) M. Takagi, M. Nojima and S. Kusabayashi, J. Am. Chem. Soc., 104, 1636 (1982). (d) F. Ogata, M. Takagi, M. Nojima and S. Kusabayashi, ibid., 103, 1145 (1981). (e) M. Takagi, M. Nojima and S. Kusabayashi, J. Chem. Soc., Perkin 1, 2637 (1981). (f) H. D. Becker, K. Andersson and K. Sandros, J. Org. Chem., 45, 4449 (1980). (g) H. D. Becker, K. Sandros and K. Andersson, ibid., 44, 1336 (1979). (h) G. Felix, R. Lapouyade, A. Castellen and H. Bouas-Laurent, Tetrahedron Lett., 409 (1975). (i) C. W. Jaeger and N. Kornblum, J. Am. Chem. Soc., 94, 2545 (1972).
3. (a) All new compounds or their derivatives from the present research gave proper spectra, analyses and/or exact masses. (b) In the preparations of 11a-b from 4 and t-butyllithium, 7 is always produced.
4. (a) M. Nojima, M. Takagi and S. Kusabayashi, J. Chem. Soc., Perkin 1, 2948 (1979). (b) R. H. Mitchell, T. W. Dingle and R. V. Williams, J. Org. Chem., 48, 903 (1983). (c) After submittal and review of the present manuscript, M. Takagi, M. Nojima and S. Kusabayashi, J. Am. Chem. Soc., 105, 4676 (1983) reported the results of a major study of protonation and alkylation of ambident (9-anthryl)arylmethyl anions. The conclusions from the present investigation are essentially identical with the latter publication.
5. (a) Simple Huckël calculations indicate that the C-10 ring position in 11a-b is the site of highest electron density (1.317 vs 1.149 at the C_{11} position). (b) H. H. Greenwood, "Computing Methods in Quantum Organic Chemistry," Wiley-Interscience, New York, 1972. The parameters used were $\alpha^1 = \alpha_o + H_x\beta_o = 2$ and $\beta_{c-x} = k_{c-x}\beta_o = 0.8$. To account for the nonplanarity of 11 a-b, β was further corrected to $\beta^1 = \beta_{c-x} \cos 20^o$.
6. Efforts to deprotonate 6 effectively with lithium diisopropylamide, lithium 2,2,6,6-tetramethylpiperidide, methyllithium and n-butyllithium in TMEDA, ethyl ether or tetrahydrofuran at a variety of temperatures have failed.
7. 9-Trimethylsiloxymethylanthracene is also converted to 13a-b by lithium in tetrahydrofuran.

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