Alkyllithiums as Alkylating Agents: Regioselective Alkylation in the Semi-Bay Region of Polycyclic Azaarenes†

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Alkylation, especially butylation, improves the solubilities of polycyclic azaarenes (PAA) in common solvents, thus increasing their potential use as substrates for molecular recognition. Further, *n*-butylacridine derivatives are important building blocks for "hexagonal lattice" receptors, which are relatively rigid planar hosts for metal ions and organic molecules.[1−3] Several methods are available for the synthesis of polycyclic pyridines that are annelated to nonaromatic rings,[4−6] but most are not readily amenable to introduction of an alkyl group at the C-4 position of the pyridine nucleus.

In an attempt to synthesize bay region polyalkylated PAA derivatives via regioselective bay region lithiation following the recent report of Ashe et al.,[7] we found that *n*-BuLi not only lithiates the bay region[8] of PAA but also undergoes 1,4-addition to the pyridine nucleus and after the usual workup affords the *n*-butyl PAA derivative. We examined the utility of this reaction with several PAA's and various alkyllithiums and found it to be a general method for the regioselective synthesis of alkyl PAA derivatives. A typical procedure involves treatment of a solution of PAA with alkyllithium (3−4 equiv) in THF/TMEDA under an argon atmosphere at 0−5 or 0−25 °C (see Table 1) for 1.5−1.75 h followed by quenching with water to afford the alkyl PAA derivative in high isolated yield (50−94%). Use of excess RLi was essential for smooth reaction. When an equivalent amount of RLi was employed, the reaction led to a complicated mixture containing an acridan derivative[9] as the major component. In some cases (entry nos. 10, 12, 16, 19, or 20 in Table 1) even the use of excess RLi produced only acridan derivatives, some of which were aromatized with DDQ in refluxing benzene to the respective alkyl PAA derivatives.[10] The butylation was highly regioselective depending on the nature of PAA. Thus, with dibenzacridines such as compound **13**, **17**, **22**, **26**, or benzo[*a*]naphtho-[2,1-*h*]acridine (**24**), the butyl group enters at C-7 or C-14 (for compounds **17**, **24**, and **26**), respectively, as evidences by the disappearance of the sharp singlet at 8.16−8.48 in the ^{1}H NMR spectra. In contrast, the acenaphthoquinolines were alkylated exclusively in the semi-bay region of the acenaphthene moiety, which again is highly influenced by the position of the heteroatom. Thus, in compound **1**, **5**, or **9** the alkyl group attached at C-6, as indicated by the retention of the singlet at 8.48−9.29 and disappearance of the doublet at 8.44−8.51. Although the mechanism for this conversion and the reason for the observed selectivity has not been fully elucidated, the current studies are consistent with the mechanism depicted in Figure 1 (Chart 1).

There are some references on alkylation of [6]-paracyclophane[11] and in the 2- or 4-positions of pyridine moieties[12] by alkyllithiums, but to our knowledge no systematic studies on polycyclic monoazaarenes have been done so far.

All the compounds have been characterized by the usual methods (such as ^{1}H NMR and in some cases by ^{13}C NMR, MS, elemental, and X-ray crystallographic[13] analyses). In general, the method appears to be broad in scope. It affords high yields and is advantageous over Bernthsen reactions.[14] The results are summarized in Table 1.

Experimental Section

General Methods. Starting materials were prepared according to standard procedures. Butyllithiums and methyllithium were purchased from Fluka, and THF was distilled from sodium and benzophenone and TMEDA from KOH. All reactions were carried out under argon or nitrogen atmosphere. Melting points were determined with a one-side-opened glass capillary using a sulfuric acid bath apparatus and are uncorrected. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker FACF-200 FT NMR spectrometer, and chemical shifts (δ) are reported in ppm. Mass spectra were obtained on a Finnigan Mat 8230 mass spectrometer. Experimental analyses were obtained using Herecus Carlo Erba 1108 C,H,N elemental analyzer.

General Procedure. To an ice-cooled solution of the azarene (0.22 mmol) in dry THF (3−4 mL) and TMEDA (0.3−0.5 mL), under argon atmosphere, was added 3−4 equiv of alkyllithium solution (in hexane) dropwise. A dark reddish brown solution was formed. The mixture was stirred at 0 °C or at rt (Table 1) for 1.5−1.75 h and then decomosed with ice−water. Extraction with dichloromethane or benzene followed by usual workup afforded the crude product which was further purified by column

† Dedicated to Prof. U. R. Ghatak on the occasion of his 65th birthday.

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(7) Ashe (III), A. J.; Kampf, J. W.; Savla, P. M. *J. Org. Chem.* **1990**, *55*, 5558.
(8) Compound **17** on reaction with ~3 equiv of *n*-BuLi/THF/TMEDA at 0−5 °C followed by quenching with MeI afforded 14-*n*-butyl-7,8-dimethyl-7,14-dihydrodibenz[*a*,*h*]acridine as evident by the spectroscopic analysis: ^{1}H-NMR ($CDCl_3$) 0.78 (t, 3H, J = 7.1 Hz), 1.15−1.50 (m, 4H), 1.55−2.00 (m, 2H), 2.98 (s, 3H), 3.38 (s, 3H), 4.71 (t, 1H, J = 5.1 Hz), 7.26−7.81 (m, 10H), 8.08 (d, 1H, J = 8.3 Hz). Anal. Calcd for $C_{27}H_{27}N$: C, 88.77; H, 7.40; N, 3.80. Found: C, 88.61; H, 7.19; N, 3.63.
(9) Blout, E. R.; Corley, R. S. *J. Am. Chem. Soc.* **1947**, *69*, 763.
(10) Selected acridans were aromatized with DDQ in refluxing benzene to give excellent yields of the corresponding azaarenes. (a) Compound **14** gave 7-methyldibenz[*c*,*h*]acridine (**29**): yield 80%; mp 222−223 °C (lit. mp 222−223 °C: Porai-Koshits, A. E.; Ter-Sarkisyan, G. S. *Izvest. Akad. Nauk S.S.R., Otdel Khim. Nauk.* **1951**, 771; *Chem. Abstr.* **1952**, *46*, 8116g. The structure of **29** has also been confirmed by X-ray crystallographic analysis. (b) Product **16** afforded 7-isobutyldibenz[*c*,*h*]acridine (**31**): yield 89%; mp 148−149 °C (petroleum ether); ^{1}H NMR ($CDCl_3$) 0.90 (t, 3H, J = 7.4 Hz), 1.76 (d, 3H, J = 7.3 Hz), 2.07−2.46 (m, 2H), 4.09−4.35 (m, 1H), 7.75−7.93 (m, 8H), 8.30 (d, 2H, J = 9.5 Hz), 9.80 (dd, 2H, $J_{1,2} = J_{12,13}$ = 7.7 Hz and $J_{1,3} = J_{11,13}$ = 1.2 Hz). (c) Product **21** afforded 14-isobutyldibenz[*a*,*h*]acridine: yield 90%; mp 163−164 °C (petroleum ether); ^{1}H NMR ($CDCl_3$) 0.72 (t, 3H, J = 7.3 Hz), 1.96 (d, 3H, J = 7.2 Hz), 2.07−2.28 (m, 2H), 4.35−4.47 (m, 1H), 7.56−8.00 (m, 8H), 8.04 (d, 1H, J = 9.9 Hz), 8.40 (d, 1H, J = 9.6 Hz), 8.43 (dd, 1H, $J_{1,2}$ = 9.2 Hz and $J_{1,3}$ = 2.3 Hz), 9.53 (dd, 1H, $J_{8,9}$ = 8.0 Hz and $J_{8,10}$ = 2.2 Hz). (d) The crude product was contaminated with little fully aromatic material. Aromatization afforded 14-*n*-butyldibenz[*a*,*h*]acridine (**20**).
(11) Tobe, Y.; Jimbo, M.; saiki, S.; Kakiuchi, K.; Naemura, J. *J. Org. Chem.* **1993**, *58*, 5883.
(12) Joub, J. A.; Mill, K. and Smith, G. F. *Heterocyclic Chemistry* 3rd ed.; Chapman and Hall: London, 1993; pp 80−81 and 123.
(13) (a) Buu-Hoi, N. P. *J. Chem. Soc.* **1950**, 1146. However, the structure is not supported by any spectral data. Also, dibenz[*a*,*h*]-acridine itself melts at 223−224 °C. (b) The structure of compounds **20** and **27** have also been confirmed by X-ray crystallographic data.
(14) Klemm, L. H.; Chiang, E.; O'Bannon, G. W. *J. Heterocycl. Chem.* **1992**, *29*, 571 and ref 3 cited therein.

0022-3263/96/1961-1863$12.00/0

Table 1

entry no.	compd (no.)	reagent and condns	product[a] (yield)	mp (°C)
1	**1**	MeLi/THF/TMEDA/0−5 °C	2 (79%)	118−119
2	**1**	n-BuLi/THF/TMEDA/0−5 °C	3 (58%)	106−107
3	**1**	s-BuLi/THF/TMEDA/0−5 °C	4 (54%)	semisolid
4	**5**	MeLi/THF/TMEDA/0−5 °C	6 (82%)	207−208
5	**5**	n-BuLi/THF/TMEDA/0−5 °C	7 (63%)	132−133
6	**5**	s-BuLi/THF/TMEDA/0−5 °C	8 (69%)	154−155
7	**9**	MeLi/THF/TMEDA/0−5 °C	10 (50%)	150−151
8	**9**	n-BuLi/THF/TMEDA/0−5 °C	11 (70%)	149−150
9	**9**	s-BuLi/THF/TMEDA/0−5 °C	12 (69%)	118−119
10	**13**	MeLi/THF/TMEDA/0−5 °C	14 (94%)	156−157[10a]
11	**13**	n-BuLi/THF/TMEDA/0−rt	15 (73%)	182−183
12	**13**	s-BuLi/THF/TMEDA/0−rt	16 (63%)	semisolid[10b]
13	**17**	MeLi/THF/TMEDA/0−5 °C	18 (94%)	211−213
14	**17**	n-BuLi/THF/TMEDA/0−5 °C	19 (84%)	156−157[10d]
15	**17**	n-BuLi/THF/TMEDA/0−rt	20 (80%)	129−130[13a,b]
16	**17**	s-BuLi/THF/TMEDA/0−rt	21 (76%)	154−156[10c]
17	**22**	n-BuLi/THF/TMEDA/0−rt	23 (70%)	155−156
18	**24**	n-BuLi/THF/TMEDA/0−rt	25 (70%)	156−157
19	**26**	MeLi/THF/TMEDA/0−rt	27 (93)	218−220
20	**26**	n-BuLi/THF/TMEDA/0−rt	28 (83%)	165−166
21	**26**	s-BuLi/THF/TMEDA/0−rt	No reaction	

[a] The products were recrystallized from hexane or a hexane−chloroform mixture.

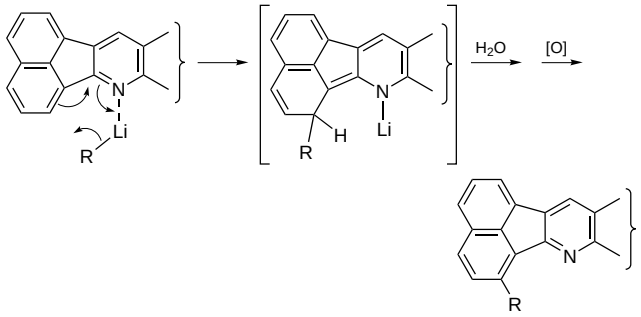


Figure 1.

chromatography (neutral Al_2O_3/petroleum ether−ethyl acetate mixture) followed by recrystallization with an *n*-hexane−$CHCl_3$ mixture.

6-Methylacenaphtho[1,2-*b*]quinoline (2): light yellowish solid; mp 118−119 °C; yield 79%; ^{1}H NMR ($CDCl_3$) 3.25 (s, 3H), 7.49−7.74 (m, 5H), 7.85 (d, 1H, *J* = 5.0 Hz), 7.89 (d, 1H, *J* = 5.6 Hz), 7.99 (d, 1H, *J* = 6.8 Hz), 8.24 (d, 1H, *J* = 8.3 Hz), 8.47 (s, 1H). Anal. Calcd for $C_{20}H_{13}N$: C, 89.89; H, 4.87; N, 5.24. Found: C, 89.66; H, 4.73; N, 5.05.

6-*n*-Butylacenaphtho[1,2-*b*]quinoline (3): light yellowish solid; mp 106−107 °C; yield 58%; ^{1}H NMR ($CDCl_3$) 1.05 (t, 3H, *J* = 7.1 Hz), 1.52−1.63 (m, 2H), 1.83−1.94 (m, 2H), 3.72 (t, 2H, *J* = 7.5 Hz), 7.53−7.74 (m, 5H), 7.90 (d, 2H, *J* = 8.2 Hz), 8.03 (d, 1H, *J* = 7.0 Hz), 8.22 (d, 1H, *J* = 8.3 Hz), 8.51 (s, 1H); ^{13}C NMR ($CDCl_3$) 14.07, 22.74, 32.10, 33.52, 119.56, 125.97, 126.32, 126.77, 127.03, 128.13, 128.64, 128.34, 130.17, 131.27, 142.16. Anal. Calcd for $C_{23}H_{19}N$: C, 89.32; H, 6.15; N, 4.53. Found: C, 89.18; H, 6.00; N, 4.38.

6-*sec*-Butylacenaphtho[1,2-*b*]quinoline (4): semisolid mass; yield 54%; ^{1}H NMR ($CDCl_3$) 1.06 (t, 3H, *J* = 7.5 Hz), 1.57 (d, 3H), 1.87−1.94 (m, 2H), 4.90−5.18 (m, 1H), 7.49−7.75 (m, 5H), 7.87−8.13 (m, 2H), 8.03 (d, 1H, *J* = 6.9 Hz), 8.23 (d, 1H, *J* = 8.2 Hz), 8.51 (s, 1H). Anal. Calcd for $C_{23}H_{19}N$: C, 89.32; H, 6.15; N, 4.53. Found: C, 89.15; H, 6.00; N, 4.39.

6-Methylacenaphtho[1,2-*b*]benzo[*f*]quinoline (6): light yellow solid; mp 207−208 °C; yield 82%; ^{1}H NMR ($CDCl_3$) 3.27 (s, 3H), 7.55 (d, 1H, *J* = 8.4 Hz), 7.64−7.70 (m, 3H), 7.87 (d, 1H *J* = 8.4 Hz), 7.94−8.01 (m, 3H), 8.11 (d, 1H, *J* = 7.1 Hz), 8.16 (d, 1H, *J* = 9.2 Hz), 8.78 (d, 1H, *J* = 8.2 Hz), 9.32 (s, 1H); ^{13}C NMR ($CDCl_3$) 18.89, 120.01, 121.60, 122.63, 126.73, 126.79, 127.05, 128.09, 128.46, 128.72, 129.25, 129.82, 131.93, 132.18, 136.97. Anal. Calcd for $C_{24}H_{15}N$: C, 90.85; H, 4.73; N, 4.41. Found: C, 90.71; H, 4.51; N, 4.27.

6-*n*-Butylacenaphtho[1,2-*b*]benzo[*f*]quinoline (7): yellow solid; mp 132−133 °C; yield 63%; ^{1}H NMR ($CDCl_3$) 1.07 (t, 3H, *J* = 7.3 Hz), 1.55−1.66 (m, 2H), 1.86−1.97 (m, 2H) 3.74 (t, 2H, *J* = 7.7 Hz), 7.59−7.74 (m, 4H), 7.89−8.00 (m, 4H), 8.11−8.18 (m, 2H), 8.79 (d, 1H, *J* = 8.0 Hz), 9.33 (s, 1H); MS (*m*/*z*) 359 (M^+, 74), 344 (81), 330 (94), 317 (100), 303 (37). Anal. Calcd for $C_{27}H_{21}N$: C, 90.25; H, 5.85; N, 3.90. Found: C, 90.05; H, 5.74; N, 3.80.

6-*sec*-Butylacenaphtho[1,2-*b*]benzo[*f*]quinoline (8): yellow solid; mp 154−155 °C; yield 69%; ^{1}H NMR ($CDCl_3$) 0.99 (t, 3H, *J* = 7.3 Hz), 1.52 (d, 3H, *J* = 7.0 Hz), 1.81−2.00 (m, 2H), 4.92−5.02 (m, 1H), 7.54−7.74 (m, 4H), 7.89−7.99 (m, 4H), 8.12 (d, 1H, *J* = 6.7 Hz), 8.16 (d, 1H, *J* = 9.0 Hz), 8.78 (d, 1H, *J* = 7.9 Hz), 9.33 (s, 1H); ^{13}C NMR ($CDCl_3$) 12.32, 21.02, 31.02, 35.52, 120.01, 121.88, 122.64, 123.32, 126.84, 126.88, 127.11, 127.30, 128.50, 128.74, 128.95, 130.00, 130.32, 130.89, 131.91, 132.08, 132.86, 134.69, 147.00, 147.66; MS (*m*/*z*) 359 (M^+, 92), 344 (M − 15, 100), 330 (82), 317 (82), 303 (60). Anal. Calcd for $C_{27}H_{21}N$: C, 90.25; H, 5.85; N, 3.90. Found: C, 90.02; H, 5.72; N, 3.78.

6-Methylacenaphtho[1,2-*b*]benzo[*h*]quinoline (10): yellow solid; mp 150−151 °C; yield 50%; ^{1}H NMR ($CDCl_3$) 3.38 (s, 3H), 7.45−7.96 (m, 9H), 8.07 (d, 1H, *J* = 6.9 Hz), 8.56 (s, 1H), 9.50 (d, 1H, *J* = 7.9 Hz). Anal. Calcd for $C_{24}H_{15}N$: C, 90.85; H, 4.73; N, 4.41. Found: C, 90.73; H, 4.59; N, 4.29.

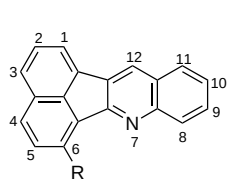
6-*n*-Butylacenaphtho[1,2-*b*]benzo[*h*]quinoline (11): greenish yellow solid; mp 149−150 °C; yield 70%; ^{1}H NMR ($CDCl_3$) 1.03 (t, 3H, *J* = 7.3 Hz), 1.59−1.70 (m, 2H), 1.97−2.04 (m, 2H), 3.81 (t, 2H, *J* = 7.6 Hz), 7.58−7.91 (m, 9H), 8.03 (d, 1H, *J* = 6.9 Hz), 8.51 (s, 1H), 9.47 (d, 1H, *J* = 7.9 Hz); ^{13}C NMR ($CDCl_3$) 14.21, 23.13, 32.81, 33.65, 120.07, 124.36, 124.70, 126.29, 126.74, 126.83, 126.90, 126.99, 127.05, 127.65, 127.72, 128.18, 128.56, 131.38, 142.10; MS (*m*/*z*) 359 (M^+, 89), 344 (M − 15, 91), 330 (100), 317 (98), 303 (63). Anal. Calcd for $C_{27}H_{21}N$: C, 90.25; H, 5.85; N, 3.90. Found: C, 90.02; H, 5.72; N, 3.78.

6-*sec*-Butylacenaphtho[1,2-*b*]benzo[*h*]quinoline (12): yellow solid; mp 118−119 °C; yield 69%; ^{1}H NMR ($CDCl_3$) 1.05 (t, 3H, *J* = 7.4 Hz), 1.60 (d, 3H, *J* = 6.9 Hz), 1.97−2.07 (m, 2H), 4.98−5.22 (m, 1H), 7.64−7.82 (m, 6H), 7.90−7.98 (m, 3H), 8.07 (d, 1H, *J* = 6.8 Hz), 8.56 (s, 1H), 9.46 (d, 1H, *J* = 8.8 Hz); ^{13}C NMR ($CDCl_3$) 12.52, 20.77, 30.84, 35.95, 119.97, 124.30, 124.67, 126.21, 126.74, 126.79, 126.92, 127.03, 127.29, 127.62, 127.70, 128.57, 132.32, 133.01, 133.68, 147.06; MS (*m*/*z*) 359 (M^+, 51), 344 (100), 330 (36), 318 (26), 303 (14), 166 (25), 159 (25). Anal. Calcd for $C_{27}H_{21}N$: C, 90.25; H, 5.85; N, 3.90. Found: C, 90.06; H, 5.77; N, 3.71.

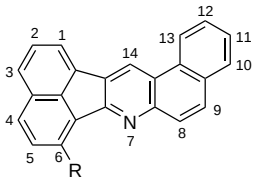
7-Methyl-7,14-dihydrodibenz[*c*,*h*]acridine (14):[10a] yellow solid (gradually turns brown); mp 156−157 °C; yield 94%; ^{1}H NMR ($CDCl_3$) 1.47 (d, 3H, *J* = 6.9 Hz), 4.38−4.50 (q, 1H, *J* = 6.9 Hz), 7.37 (d, 2H, *J* = 8.4 Hz), 7.46−7.64 (m, 6H), 7.66 (d, 2H, *J* = 7.9 Hz), 8.03 (d, 2H, *J* = 8.3 Hz).

7-*n*-Butyldibenz[*c*,*h*]acridine (30). The crude product contained compound **15** as minor impurities (10%) as observed from ^{1}H NMR. A pure sample of **30** was obtained by aromatization of the crude reaction mixture with DDQ/benzene: yellow solid; mp 182−183 °C; yield 73%; ^{1}H NMR ($CDCl_3$) 1.04 (t, 3H,

Chart 1



1 (R = H)
2 (R = Me)
3 (R = *n*–Bu)
4 (R = *s*–BU)



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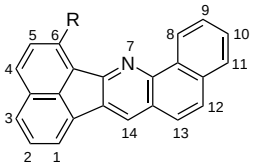
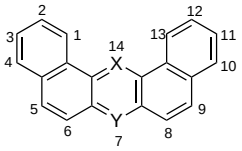
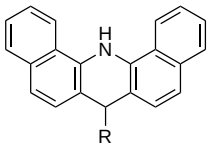
6 (R = Me)
7 (R = *n*–Bu)
8 (R = *s*–Bu)



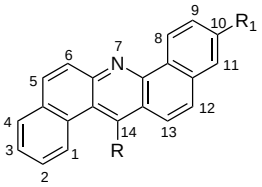
9 (R = H)
10 (R = Me)
11 (R = *n*–Bu)
12 (R = *s*–Bu)



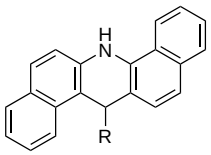
13 (X = N, Y = CH)
26 (X = CH, Y = N)



14 (R = Me)
15 (R = *n*–Bu)
16 (R = *s*–Bu)



17 (R = R_1 = H)
20 (R = *n*–Bu, R_1 = H)
22 (R = H, R_1 = OMe)
23 (R = *n*–Bu, R_1 =OMe)



18 (R = Me)
19 (R = *n*–Bu)
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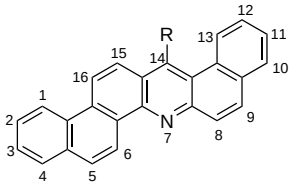

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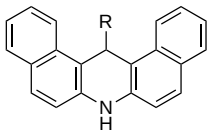
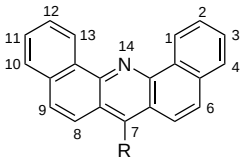


27 (R = Me)
28 (R = *n*–Bu)



29 (R = Me)
30 (R = *n*–Bu)
31 (R = *s*–Bu)

J = 7.2 Hz), 1.56−1.66 (m, 2H), 1.79−1.87 (m, 2H), 3.58 (t, 2H, J = 7.8 Hz), 7.70−7.95 (m, 6H), 7.81 (d, 2H, J = 9.3 Hz), 8.08 (d, 2H, J = 9.4 Hz), 9.78 (dd, 2H, J = 7.8, 1.3 Hz); ^{13}C NMR ($CDCl_3$) 14.01, 23.27, 27.53, 33.47, 121.90, 123.39, 125.56, 126.99, 127.19, 127.55, 128.43, 132.60, 133.41, 145.25, 145.39. Anal. Calcd for $C_{25}H_{21}N$: C, 89.55; H, 6.27; N, 4.18. Found: C, 89.34; H, 6.19; N, 4.95.

7-*sec*-Butyl-7,14-dihydrodibenz[*c*,*h*]acridine (16). The compound was obtained as a semisolid mass (63%) which gradually turned brown upon exposure. It was immediately aromatized with DDQ in refluxing benzene to furnish **31**[10b] in 89% yield.

14-Methyl-7,14-dihydrodibenz[*a*,*h*]acridine (18): dark colored solid; mp 211−214 °C; yield 94%; ^{1}H NMR ($CDCl_3$ + DMSO-d_6) 1.20 (d, 3H, J = 6.8 Hz), 4.75 (q, 1H, J = 6.8 Hz), 7.11−7.35 (m, 4H), 7.44 (d, 1H, J = 8.9 Hz), 7.53−7.66 (m, 4H), 7.85 (d, 1H, J = 8.4 Hz), 7.89 (d, 1H, J = 9.4 Hz), 8.04 (dd, 1H J = 7.8, 0.9 Hz); ^{13}C NMR ($CDCl_3$, DMSO-d_6) 24.07, 32.32, 114.63, 116.96, 118.10, 119.78, 120.10, 120.73, 121.10, 121.81, 124.32, 124.49, 125.75, 126.55, 127.57, 127.88, 129.11, 130.81, 132.16, 132.75, 135.91. Anal. Calcd for $C_{22}H_{17}N$: C, 89.49; H, 5.76; N, 4.74. Found: C, 89.27; H, 5.57; N, 4.63.

14-*n*-Butyldibenz[*a*,*h*]acridine (20): light yellow solid; mp 129−130 °C (lit.[13a] mp 223−224 °C); ^{1}H NMR ($CDCl_3$) 1.18 (t, 3H, J = 7.3 Hz), 1.75−1.90 (m, 2H), 2.13−2.50 (m, 2H), 3.55 (t, 2H, J = 8.0 Hz), 7.65−7.96 (m, 7H), 7.84 (d, 1H, J = 9.5 Hz), 8.09−8.13 (br, t, 2H, J = 9.5 Hz), 8.52−8.65 (t, 1H, J = 8.1 Hz), 9.55 (d, 1H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$) 13.98, 23.33, 31.56, 32.82, 122.14, 124.43, 125.66, 126.26, 126.88, 127.21, 127.53, 128.12, 128.69, 129.15, 130.05, 131.50, 133.29; MS (*m*/*z*) 335 (M^+, 100), 292 (73).

14-*sec*-Butyl-7,14-dihydrodibenz[*a*,*h*]acridine (21):[10c] brownish solid; mp 154−156 °C; yield 76%; ^{1}H NMR ($CDCl_3$) 0.60 (d, 3H, J = 6.7 Hz), 1.03 (t, 3H, J = 7.1 Hz), 1.18−1.33 and 1.61−1.75 (m, 2H), 1.85−1.93 (m, 1H), 4.83 and 4.95 (d, 1H, J = 3.8 Hz, 2.8 Hz), 6.87 (brs, 1H), 7.14 (d, 1H, J = 8.7 Hz), 7.15 (d, 1H, J = 8.7 Hz), 7.29−7.56 (m, 5H), 7.68 (d, 1H, J = 8.7 Hz), 7.76−7.92 (m, 3H), 8.04 (d, 1H, J = 8.5 Hz).

10-Methoxy-16-*n*-butyldibenz[*c*,*h*]acridine (23): light yellowish solid; mp 155−156 °C; yield 70%; ^{1}H NMR ($CDCl_3$) 1.18 (t, 3H, J = 7.2 Hz), 1.75−1.86 (m, 2H), 2.16−2.24 (m, 2H), 3.78 (t, 2H, J = 8.1 Hz), 4.00 (s, 3H), 7.28 (d, 1H, J = 2.6 Hz), 7.39 (dd, 1H, J = 8.9, 2.5 Hz), 7.64−7.72 (m, 2H), 7.75−7.80 (d, 1H, J = 9.4 Hz), 7.91−7.97 (m, 2H), 8.13−8.17 (d, 2H, J = 9.4 Hz), 8.57−8.62 (dd, 1H, J = 8.7, 2.7 Hz), 9.48 (d, 1H, J = 8.9 Hz); MS (*m*/*z*) 365 (M^+, 100), 336 (39), 322 (78), 291 (44), 279 (78). Anal. Calcd for $C_{26}H_{23}NO$: C, 85.48; H, 6.30; N, 3.80. Found: C, 85.31; H, 6.21; N, 3.69.

14-*n*-Butylbenzo[*a*]naphtho[2,1-*h*]acridine (25): light yellowish solid; mp 156−157 °C, yield 70%; ^{1}H NMR ($CDCl_3$) 1.21 (t, 3H, J = 7.3 Hz), 1.75−1.93 (m, 2H), 2.14−2.32 (m, 2H), 3.83 (t, 3H, J = 8.3 Hz), 7.66−7.77 (m, 4H), 7.91−8.16 (m, 5H), 8.40 (d, 1H, J = 9.7 Hz), 8.60 (dd, 1H, J = 9.0, 2.5 Hz), 8.77 (dd, 1H, J = 7.3 Hz), 8.78 (d, 1H, J = 9.7 Hz), 9.64 (d, 1H, J = 9.0 Hz); ^{13}C NMR ($CDCl_3$) 13.87, 23.23, 31.31, 32.65, 121.63, 122.49, 123.14, 126.16, 126.46, 126.74, 127.50, 128.02, 128.73, 128.95, 129.99, 130.29, 131.54, 133.03, 133.33; MS (*m*/*z*) 385 (M^+, 100), 342 (88), 280 (85). Anal. Calcd for $C_{29}H_{23}N$: C, 90.39; H, 5.97; N, 3.64. Found: C, 90.27; H, 5.90; N, 3.53.

14-Methyl-7,14-dihydrodibenz[*a*,*j*]acridine (27):[13b] colorless solid; mp 218−220 °C; yield 93%; ^{1}H NMR ($CDCl_3$) 1.48 (d, 3H, J = 6.8 Hz), 4.80 (br s, 1H), 5.63 (q, 1H, J = 6.8 Hz), 7.01

(d, 2H, J = 8.7 Hz), 7.36 (t, 2H, J = 7.3 Hz), 7.58 (dd, 2H, J = 8.6, 1.2 Hz), 7.65 (d, 2H, J = 8.7), 7.73 (d, 2H, J = 8.5 Hz). Anal. Calcd for $C_{22}H_{17}N$: C, 89.49; H, 5.76; N, 4.75. Found: C, 89.25; H, 5.57; N, 4.60.

The structure has also been confirmed by X-ray crystallographic data. (An attempt to aromatize compound **27** with DDQ or Pd−C produced dibenz[*a*,*j*]acridine).

14-*n*-Butyl-7,14-dihydrodibenz[*a*,*j*]acridine (28): light brown solid; mp 165−166 °C; yield 83%; ^{1}H NMR ($CDCl_3$) 0.62 (t, 3H, J = 6.9 Hz), 0.97−1.06 (m, 4H), 1.83−1.93 (m, 2H), 4.77 (s, 1H), 5.71 (t, 1H, J = 4.7 Hz), 7.03 (d, 2H, J = 8.7 Hz), 7.35 (t, 2H, J = 7.6 Hz), 7.56 (t, 1H, J = 7.6 Hz), 7.68 (d, 2H, J = 8.6 Hz), 7.81 (d, 2H, J = 7.8 Hz), 8.26 (d, 2H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$) 13.91, 23.02, 27.54, 116.21, 121.92, 122.68, 126.51, 127.56, 128.79, 130.18. Anal. Calcd for $C_{25}H_{23}N$: C, 89.02; H, 6.82; N, 4.15. Found: C, 88.90; H, 6.75; N, 3.94.

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