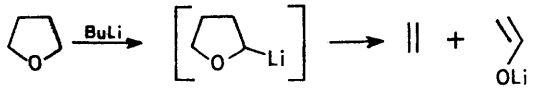
A Simple Synthesis of Anthracenes

By Ian Fleming * and Talat Mah, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

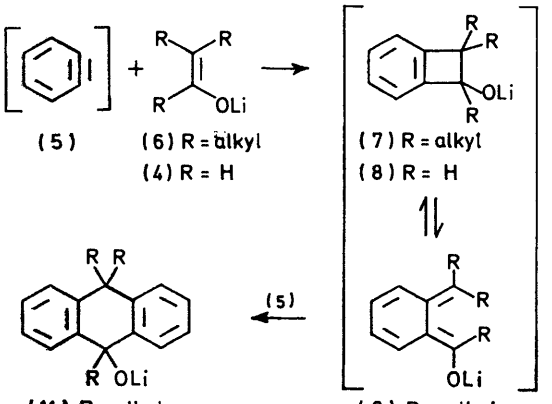
Anthracene is easily prepared in one operation from bromobenzene by using *N*-lithio-2,2,6,6-tetramethylpiperidine in tetrahydrofuran. The sequence of reactions involves benzyne and the enolate ion of acetaldehyde. The reaction is general for the synthesis of 9,10-unsubstituted anthracenes.

TETRAHYDROFURAN (THF) (1) is known [1] to react with strong bases like butyl-lithium, and the product (2) is known to decompose by a retro-cycloaddition to give ethylene (3), and the enolate ion (4) of acetaldehyde.



(1) (2) (3) (4)

Enolate ions (6) are known [2] to react with benzyne (5) to give dihydrobenzocyclobutenes (7), and the dihydrobenzocyclobutenes are known to decompose by an electrocyclic opening to give *o*-xylylenes (9), which are

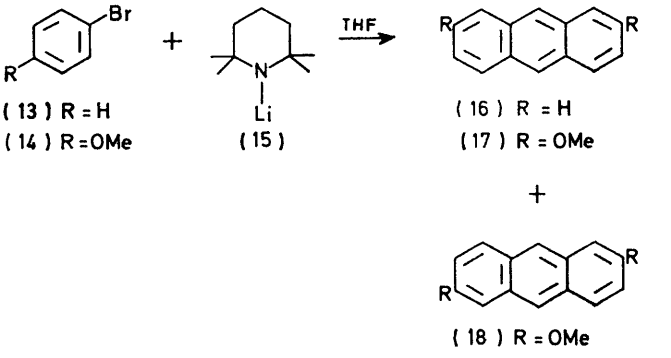


(5) (6) R = alkyl, (4) R = H (7) R = alkyl, (8) R = H

(11) R = alkyl, (12) R = H (9) R = alkyl, (10) R = H

trapped by the benzyne to give dihydroanthracenols (11). By putting these known reactions together we have found a very simple ' one-pot ' synthesis of symmetrical 9,10-unsubstituted anthracenes.

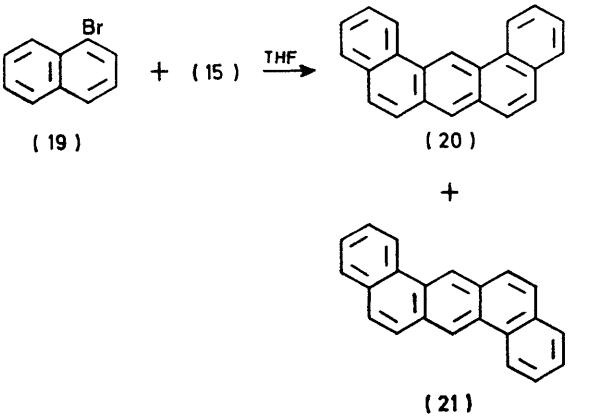
When bromobenzene (13) is added to a solution of a four-fold excess of *N*-lithio-2,2,6,6-tetramethylpiperidine (15) [3] in warm THF, the major neutral product is anthracene (16) (63% based on bromobenzene). Similarly, *p*-bromoanisole (14) gave a 1 : 1 mixture of the two



(13) R = H, (14) R = OMe (15) (16) R = H, (17) R = OMe

(18) R = OMe

anthracenes (17) and (18) (66%) and 1-bromonaphthalene gave a 1 : 1 mixture of the dibenzanthracenes (20) and (21) (84%). That the pathway followed is the sequence (5) + (4) ⟶ (8) ⟶ (10) ⟶ (12) ⟶ (16) is shown by the following observations. (i) The base (15) is



(19) (20) (21)

made from butyl-lithium and tetramethylpiperidine: when care is taken not to let the temperature rise during

[1] R. B. Bates, L. M. Kroposki, and D. E. Potter, *J. Org. Chem.*, 1970, **37**, 560.
[2] P. Caubere, *Accounts Chem. Res.*, 1974, **7**, 301.
[3] R. A. Olofson and C. M. Dougherty, *J. Amer. Chem. Soc.*, 1973, **95**, 582.

this preparation, the base (15) does not attack the THF. Thus none of the enolate (4) is produced and there is no anthracene in the products. (ii) However, anthracene was produced if this carefully prepared mixture was warmed (1 min under reflux is more than adequate). For preparative purposes, it is easy simply to mix the butyl-lithium and the tetramethylpiperidine without cooling: the exothermic reaction then allows the formation of enough of the enolate ion (4). The temperature at which the actual reaction is done is less important: even at 0°, some anthracene was produced, but yields were better above room temperature, presumably because of the need to speed up the reaction (8) ⟶ (10). (iii) In no other solvent (diethyl ether, dibutyl ether, diglyme, and dioxan were tried) is anthracene one of the products. (iv) By mixing the butyl-lithium with an excess of tetramethylpiperidine at −78°, and then warming the reaction mixture before adding the bromobenzene, we still got a good yield of anthracene. There would be no butyl-lithium present under these conditions; evidently *N*-lithiotetramethylpiperidine (15) is a strong enough base to decompose the THF.

EXPERIMENTAL

Anthracene (16).—Bromobenzene (0·45 g, 2·8 mmol) was added under nitrogen to a mixture of 2,2,6,6-tetramethylpiperidine (2·1 ml, 12 mmol) and n-butyl-lithium (5·1 ml of a 15% solution in hexane, 12 mmol) in dry tetrahydrofuran (30 ml) freshly brought to reflux temperature. The mixture immediately went dark brown. After heating under reflux for 0·5 h, the tetrahydrofuran was evaporated off, and the solid residue was taken up in ether and washed with water. The aqueous layer contained only a trace of phenol. The ether layer was washed with dilute hydrochloric acid and water, and dried (Na_2SO_4). The aqueous layer contained *N*-phenyl-2,2,6,6-tetramethylpiperidine (10%, estimated by n.m.r.) together with 2,2,6,6-tetramethylpiperidine. Evaporation of the ethereal solution gave anthracene (0·27 g), which crystallised from chloroform–methanol to give plates (0·16 g, 63%), m.p. 214—216° (lit.,[4] 216°), identical with authentic anthracene (mixed m.p., n.m.r., t.l.c., and g.l.c.).

Variations in the Reaction Conditions.—The reaction was carried out as described above, but with the following modifications. (i) When the butyl-lithium and the tetramethylpiperidine were mixed slowly at 0° and the reaction carried out at 20°, there was no anthracene formed, and *N*-phenyl-2,2,6,6-tetramethylpiperidine was the major product (75% by n.m.r.). (ii) When the butyl-lithium and the tetramethylpiperidine were mixed at reflux temperature and then cooled to 0° before adding the bromobenzene, anthracene was formed (40%, pure). We were not able to isolate dihydrobenzocyclobutanol. (iii) The other solvents listed in the text were used in place of THF; no anthracene was detected (g.l.c.) in the products. (iv) When butyl-lithium (5 mmol) and tetramethylpiperidine (6 mmol) were mixed at −78° and then the mixture was brought to reflux temperature before adding the bromobenzene (1 mmol), the yield of anthracene was the same as in the original reaction.

2,6- (18) *and* 2,7-*Dimethoxyanthracene* (17).—The reaction was carried out in the way described above, except that *p*-bromoanisole (14) (2 mmol) was used in place of bromobenzene. The neutral products solidified (0·26 g, 78% crude). N.m.r. analysis at this stage indicated that the two anthracenes (17) and (18) were present in essentially equal amounts and were essentially the only neutral products. Fractional crystallisation using 95% ethanol followed by chloroform gave 2,6-dimethoxyanthracene (18) as plates, m.p. 256° (lit.,[5] 255—256°), τ ($CDCl_3$) 1·79 (2H, s), 2·14 (2H, d, *J* 10 Hz), 2·7—2·95 (4H, m), and 6·05 (6H, s). The mother liquors gave 2,7-dimethoxyanthracene (17), 205—210° (from AcOH) (lit.,[5] 216—217°), which we could not obtain completely free of its isomer. Nevertheless it was easily identified by its n.m.r. spectrum: τ ($CDCl_3$) 1·77 (1H, s), 1·89 (1H, s), 2·15 (2H, d, *J* 10 Hz), 2·65—3·02 (4H, m), and 6·05 (6H, s).

Dibenz[a,h]*anthracene* (21) *and Dibenz*[a,j]*anthracene* (20).—When 1-bromonaphthalene (2 mmol) was used in the general reaction described above, a 1 : 1 mixture of the two disubstituted anthracenes (20) and (21) was obtained (0·387 g, 84%). Fractional crystallisation, using chloroform followed by benzene, gave dibenz[*a,h*]anthracene as plates, m.p. 262—263° (lit.,[6] 262°), τ ($CDCl_3$) 0·91 (2H, s), 1·18 (2H, dd, *J* 7 and 2·5 Hz), and 2·0—2·5 (10H, m); $\lambda_{max.}$ (dioxan) 281 (log ε 4·83), 289 (5·06), 299 (5·24), 323 (4·28), 335 (4·18), 351 (4·13), 374 (3·1), 385 (2·80), and 395 nm (3·06) (essentially identical with the literature [6] values); picrate, m.p. 212—214° (lit.,[6] 214°). The mother liquors gave silky needles of dibenz[*a,j*]anthracene, m.p. 195—197° (from AcOH) (lit.,[6] 196°), τ ($CDCl_3$) 0 (1H, s), 1·00 (2H, dd, *J* 8 and 1·5 Hz), 1·65 (1H, s), and 2·0—2·4 (10H, m); $\lambda_{max.}$ (benzene) 293 (log ε 4·74), 306 (5·0), 326 (4·23), 338 (4·13), 341 (4·14), 353 (3·76), 375 (2·63), 385 (2·45), and 396 nm (2·15) (essentially identical with the literature [6] values); picrate, m.p. 208—210° (lit.,[6] 210°).

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[6] E. Clar, ' Polycyclic Hydrocarbons,' Academic Press, New York, 1964, vol. I, pp. 329—341.