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CYCLOPROPA[E]CYCLOBUTA[B]NAPHTHALENE AND CYCLOPROPA[B]ANTHRACENE

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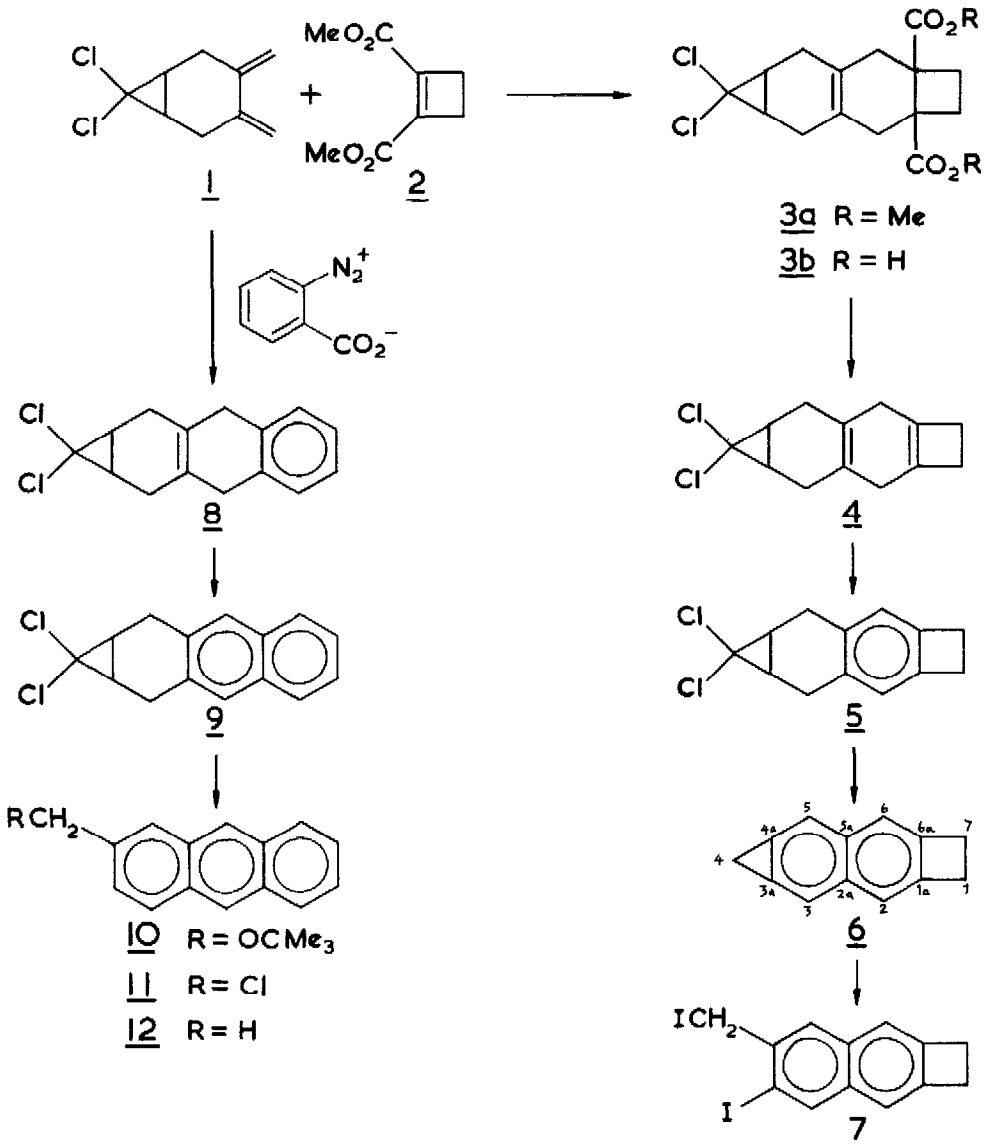
We have recently suggested that 7,7-dichloro-3,4-dimethylene bicyclo[4.1.0]heptane (1) should be a valuable precursor for the synthesis of a variety of aromatic systems annelated with 3-membered rings.[1] We would now like to substantiate this suggestion by describing both the transformation of 1 into cyclopropa[e]cyclobuta[b]naphthalene (6) and our attempts to prepare cyclopropa[b]anthracene (13).

Diels-Alder addition of the diester 2 to the diene 1 in benzene at 60° for 24 h [2] gave the adduct 3a, pale yellow crystals, m.p. 131-134°, 75%,[3] the spectral data being in accord with the assigned structure.[4] Saponification with aqueous ethanolic KOH for 24 h under reflux gave the diacid 3b, m.p. 205-210° dec, 75%.[3] Electrolysis of a solution of 3b in aqueous pyridine containing 2.5 equivalents of Et_3N [5] gave, after chromatography on basic Al_2O_3, compound 4 in 20% yield as a white solid [4] contaminated with some of its oxidation product 5. Treatment of this mixture with pyridine hydrobromide perbromide followed by chromatography on basic Al_2O_3 gave 5 as white crystals, m.p. 88-90°, 55%.[3,4,6] Reaction of 5 (72 mg, 0.3 mmole) with excess KO*t*-Bu (800 mg, 7 mmole) in THF (7 ml) under N_2 for 18 h [7] gave, after chromatography on Al_2O_3 and subsequent sublimation, cyclopropa[e]cyclopropa[b]naphthalene (6), white crystals, m.p. 144-146°, 50%. The mass spectrum (70 eV) showed m/e 166 (M^+, 100%), 165 (M^+-1, 95%), high resolution 166.0780 ($C_{13}H_{10}$ requires 166.0782). The ^{1}H NMR spectrum ($CDCl_3$) had four singlets at τ 6.72 (4H, H^1, H^7), 6.55 (2H, H^4), 2.53 (2H) and 2.48 (2H). The ^{13}C NMR spectrum had seven singlets at 144.3 ppm (C-1a, 6a), 136.2 (C-2a, 5a), 122.1 (C-3a, 4a), 121.5 (C-2, 6), 112.7 (C-3, 5), 29.3 (C-1, 7) and 19.3 (C-4), with ^1J C-1,H 138.5 Hz and ^1J C-4,H 170 Hz.[8] The electronic spectrum showed a maximum at 226.5 nm (ε 83,500) and two bands with maxima at 256 nm (ε 3120), 267 (4830), 288 (5630), 297 (1910), 304 (2210), 310 (3620) and 324 (5430).

Treatment of 6 with iodine in $CHCl_3$ gave the di-iodide 7, yellow crystals, mp 140-142°, in 90% yield.[3,4]

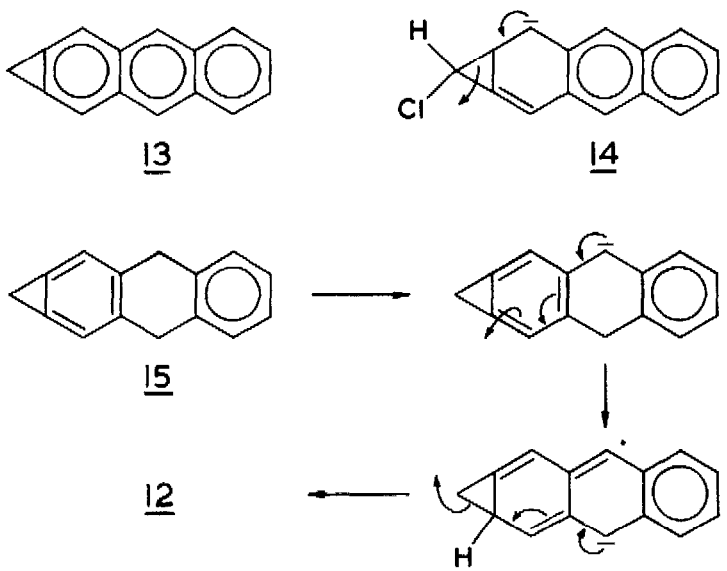


Compound 6 is stable at low temperature in the crystalline state but decomposes completely after 24 h in $CHCl_3$ solution at room temperature. The ^{13}C NMR chemical shifts of C-3,5 suggest that the cyclopropanated aromatic ring is more strained than that in dicyclopropa[b,e]naphthalene [9] or benzocyclopropene [10] but less than that in cyclopropa[4,5]benzocyclobutene.[1] The electronic spectrum of 6 is very similar to that of dicyclopropa[b,e]naphthalene,[11] both showing enhanced intensity of the longwavelength bands.

Reaction of 1 with benzenediazonium 2-carboxylate in CH_2Cl_2 for 2½ h under reflux gav

8, pale yellow crystals, mp 129-130°, 60%.[3,4] Treatment of 8 with pyridinium hydrobromide perbromide in THF under N_2 for 1 h followed by chromatography on silica gel gave 9, white crystals, mp 180-182°, 60%.[3,4] Reaction of 9 with 20 molar equivalents of KO*t*-Bu in THF under N_2 for 18 h gave the ether 10, pale yellow crystals, mp 142-145°, 40%,[3,4] and not the desired cyclopropa[b]anthracene (13). When 9 was treated with 2 molar equivalents of KO*t*-Bu for 2 h then the chloride 11, mp 192-195°, was isolated in 40% yield.[6,12,13] An alternative route to 13 could be via the corresponding dihydroderivative and in order to explore this approach 8 was reacted with 2.5 molar equivalents of KO*t*-Bu in DMSO under N_2 for 15 min, but only 2-methylanthracene (12), pale yellow crystals, mp 205-206 (lit.[14] 209-209.5°) was obtained, 40%.

Since the ether 10 can be obtained from the chloride 11,[15] the two primary products of these reactions are 11 and 12, which must arise from different intermediates. Whereas 11 is probably derived from the anion 14, 12 may come from the dehydroanthracene derivative 15 which is then converted to 12 by ring opening via the anion intermediate shown.[16]



13 14

15

12

The failure to form 13 under considerably less vigorous conditions than those required to prepare 6 or cyclopropa[b]naphthalene [7] may reflect a greater degree of bond fixation in 13,[17] which increases the contribution of the dimethylenecyclopropane structure.[18] Alternative routes to 13 are being investigated.

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References and Notes

1. D. Davalian and P.J. Garratt, J. Amer. Chem. Soc., 97, 6883 (1975).
2. R.P. Thummel, J.C.S. Chem. Comm., 899 (1974).
3. Satisfactory microanalytical and/or high resolution mass spectral data have been obtained for this compound.
4. ^{1}H NMR ($CDCl_3$, τ): 3a, 6.30 (s, 6H, CH_3), 7.2 - 7.8 (m, 8H), 7.8 - 8.2 (m, 4H), 8.3 - 8.6 (m, 2H); 4, 7.48 (s, 4H), 7.56 (s, 4H), 7.79 (m, 4H); 8.10 (m, 2H); 5, 3.14 (s, 2H), 6.4 - 7.6 (m, 4H), 6.92 (s, 4H), 7.95 (m, 2H); 7, (CCl_4) 1.72 (s, 1H), 2.14 (s, 1H), 2.70 (s, 1H), 2.77 (s, 1H), 5.34 (s, 2H), 6.67 (s, 4H); 8, 2.88 (s, 4H), 6.80 (bs, 4H), 7.72 (m, 4H), 8.19 (m, 2H); 9, 2.50 (m, 6H), 6.60, 7.24 (A_2B_2, 4H), 7.97 (m, 2H); 10, 1.67 (s, 2H), 2.07 (m, 4H), 2.60 (m, 3H), 5.40 (s, 2H), 8.63 (s, 9H); 11, 1.60 (s, 2H), 1.97 (m, 4H), 2.53 (m, 3H), 5.17 s, 2H); 12, 1.67 (d, 2H), 2.13 (m, 4H), 2.62 (m, 3H), 7.47 (s, 3H).
5. See P. Radlick, R. Klem, S. Spurlock, J.J. Sims, E.E. van Tamelen, and T. Whitesides, Tetrahedron Letters, 5117 (1968).
6. λ_{max} (hexane), nm (ε): 5, 220 (5100), 266 (2000), 271 (2760), 275 (3350), 281 (3370); 11, 256 (ca 100,000), 325 (ca 900), 339 (ca 1400), 353 (ca 1900), 363 (ca 1600).
7. W.E. Billups and W.Y. Chow, J. Amer. Chem. Soc., 95, 4099 (1973).
8. The assignment to the ^{13}C absorptions of 6 were made on the basis of comparison with those of benzocyclopropene and benzocyclobutene and from relative peak heights.
9. J. Ippen and E. Vogèl, Angew. Chem. Int. Ed. Engl., 13, 736 (1974).
10. H. Günther, G. Jikeli, H. Schmickler, and J. Prestien, Angew. Chem. Int. Ed. Engl., 12, 762 (1973).
11. Dicyclopropa[b,e]naphthalene has maxima in the electronic spectrum (cyclohexane) at 226 nm (ε 74, 200), 273 (7050), and 326 (6000).[9]
12. A. Streitwieser and C. Perrin, J. Amer. Chem. Soc., 86, 4938 (1964).
13. As far as we can ascertain no data have been reported for this compound.
14. E.L. Martin, J. Amer. Chem. Soc., 58, 1439 (1936).
15. This conversion was carried out in a separate experiment.
16. For a related discussion in the phenanthrene series see W.E. Billups, L.P. Lin, and W.Y. Chow, J. Amer. Chem. Soc., 96, 4026 (1974).
17. See E. Clar, Polycyclic Hydrocarbons, Academic Press, London, 1964, Vol. 1, p.32 et seq.
18. Dimethylenecyclopropane is itself a relatively unstable compound.[19]
19. R. Bloch, P. Le Perchec, and J.-M. Conia, Angew. Chem. Int. Ed. Engl., 9, 798 (1970).