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A [9]ANNULENONE DERIVATIVE

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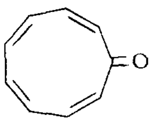
In the series of the monocyclic conjugated ketones, called annulenones,[1] the [3], [5] and [7] members or their derivatives have been rather extensively studied. Recently, the [11],[2] [13],[1] [15][3] and [17][4] members of the series have been reported. The only missing member is the nine-membered ring ketone, [9]annulenone 1,[5] the π-electron analog of cyclopentadienone.[6] We wish to report the preparation and properties of the dibenzo derivative of 1, as well as a versatile route to derivatives of the corresponding hydrocarbon 11H-dibenzo[a, c]cyclononatetraene (DBCNT) (2).[7]

Ozonolysis of 2,3-dihydro-1H-cyclopenta[l]phenanthrene[8] (3) yielded the diketone 4,[9] mp 190° (EtOH, 90%); mass spectrum, m/e 250 (M), 222 (M-CO), 194 (M-2CO) and 152 (100%); $\nu_{max}^{CHCl_3}$ (cm^{-1}) 1670, 1680 (C = O); λ_{max}^{EtOH} 230 (ε 16,250) and 285 nm sh (2,200); nmr ($CDCl_3$) δ = 7.54 ppm (8H, m), 2.56 (4H, m) and 1.9 (2H, m). Treatment of 4 with PhLi in ether afforded 80% of the corresponding diol 5,[9] mp 180° (benzene-hexane); mass spectrum, m/e 406 (M), 388 ($M-H_2O$) and 370 ($M-2H_2O$); $\nu_{max}^{CHCl_3}$ (cm^{-1}) 3400 (OH); λ_{max}^{EtOH} 254 (ε 1,250) and 260 nm (1,240). The nmr spectrum shows signals at δ = 8.08 (2H, dd, J = 8.2 Hz assigned to protons



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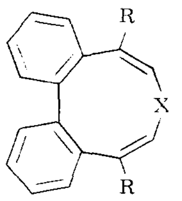
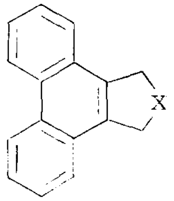


2 X = CH_2, R = H

6 X = CH_2, R = Ph

7 X = C=O, R = Ph



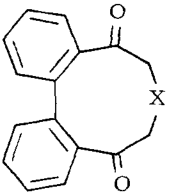
3 X = CH_2

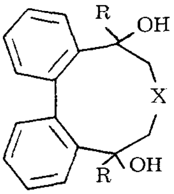
8 X = C=O

H_4 and H_5 of the biphenyl system), 7.2 (4H, m H_2, H_3, H_6 and H_7), 7.16 (10H, broad singlet, 6.4 (2H, dd, J = 8.2 Hz, assigned to protons H_1 and H_8 facing the phenyl rings and thus shielded) and 2.15 (8H, m, alicyclic and hydroxyl protons).[10] Dehydration of **5** with *p*-toluenesulfonic acid in benzene and chromatography on silica-gel afforded **6**,[9] a 9,13-diphenyl derivative of DBCNT (**2**) in 70% yield, mp 113° (hexane): mass spectrum, m/e 370 (M), 356 (M-CH_2), 278 and 215 (100%); λ_{max}^{EtOH} 245 (ε 22,000), 265 (15,400) and 317 nm (90); nmr ($CDCl_3$) δ = 7.13 (18H, m, aromatic), 5.95 (2H, t, H_{10} and H_{12}, J = 6.0 Hz) and 3.0 (2H, t, allylic H_{11}, J = 6.0 Hz),[10] Dreiding models indicate the molecule of **6** to be nonplanar and dissymmetric, so that the observed equivalence of the allylic protons at room temperature points to a rapid ring inversion.[11]

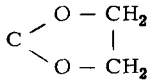
The synthesis of the dibenzo[9]annulenone derivative **7** was achieved by an analogous route starting from **8**.[8] Treatment of **8** with ethylene glycol and TsOH gave the ketal,[12] and its ozonolysis gave the triketone monoketal **9**,[9] mp 132° (EtOH, 90%): in the ir the carbonyl absorption appears at 1670 cm^{-1}; λ_{max}^{EtOH} 245 (ε 4,800) and 282 nm (800); nmr ($CDCl_3$) ppm δ = 7.60 (8H, m), 3.96 (4H, s, ketal protons) and an AB quartet (δ_A = 3.10, δ_B = 2.75, J_{AB} = = 14 Hz, 4H, assigned to the alicyclic protons).[13] Treatment of **9** with PhLi yields the diol **10**,[9] mp 217° (70%; cyclohexane); $\nu_{max}^{CHCl_3}$ (cm^{-1}) 3400 (OH), 780, 750 and 700; λ_{max}^{EtOH} 257 (ε 4,200) and 325 nm sh (280). The nmr spectrum was similar to that of **5**: δ = 8.22 (2H, dd, J = 8.2 Hz, assigned to H_4 and H_5), 7.2 (4H, m, $H_{2,3,6,7}$), 7.05 (10H, broad singlet, phenyl protons), 6.28 (2H, dd, J = 8.2 Hz), 4.86 (2H, m, OH), 4.1 (4H, s, ketal protons) and an AB quartet (δ_A = 2.91, δ_B = 2.40 ppm, J_{AB} = 15.2 Hz).[10,13] Reaction of **10** with *p*-toluenesulfonic acid afforded the desired 9,13-diphenyl-11H-dibenzo[a, c]cyclononatetraene-11-one (**7**),[9] mp 193° (chromatography on silica-gel); mass spectrum, m/e 384 (M), 356 (M-CO), 330, 279 and 254 (100%); $\nu_{max}^{CHCl_3}$ (cm^{-1}) 1605 (C = O);[15] λ_{max}^{EtOH} 229 sh (ε 28,000), 252 (13,300) and 309 nm (18,200). The uv spectrum is in good agreement with the uv spectra of other unsaturated nine-membered ring ketones,[16] but shows higher intensity bands due to the higher degree of conjugation. The nmr spectrum shows signals at δ = 7.30 (18H, m), 6.63 ppm (2H, s, vinylic H_{10} and H_{12}).

The [9]annulenone is a 4n+3 ring system and could be expected, if planar, to sustain a paramagnetic ring current, which would shift the vinylic protons H_{10} and H_{12} to higher field.[17] By comparison with literature data[16] it appears that the vinylic absorption is not shifted and no ring current is present; we could, therefore, assume that the molecule is not planar.[18]

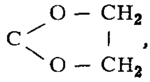




4 X = CH_2

9 X =

$C\langle{}^{O-CH_2}_{O-CH_2}$

5 X = CH_2, R = Ph

10 X =

$C\langle{}^{O-CH_2}_{O-CH_2}$, R = Ph

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2. W. Grimme, J. Residorff, W. J. Junemann and E. Vogel, J. Am. Chem. Soc., 92, 6335 (1970).
3. G. P. Cotterrell, G. H. Mitchell, F. Sondheimer and G. M. Pilling, J. Am. Chem. Soc., 93, 259 (1971).
4. a) G. W. Brown and F. Sondheimer, J. Am. Chem. Soc., 91, 760 (1969).
   b) J. Griffiths and F. Sondheimer, ibid., 91, 7519 (1969).
5. Previous attempts of preparation have failed:
   a) O. L. Chapman and J. Meinwald, J. Org. Chem., 23, 162 (1958);
   b) K. Hafner, The 3rd Jerusalem Symposium on Aromaticity, Pseudoaromaticity, Antiaromaticity, Jerusalem, 1970, p. 256.
6. E. W. Garbisch and R. F. Sprecher, J. Am. Chem. Soc., 91, 6785 (1969).

7. a) M. Rabinovitz, A. Gazit and E. D. Bergmann, Chem. Comm. 1430 (1970);
   b) P. J. Garratt and K. A. Knopp, Chem. Comm. 1215 (1970).
8. A. C. Cope, L. Field, D. W. H. MacRowell and M. E. Wright, J. Am. Chem. Soc., 78, 2547 (1956). The compound is commercially available from Aldrich Chemical Co.
9. All new compounds gave satisfactory C- and H- analyses.
10. The assignment was confirmed by double irradiation experiments.
11. The ring inversion of cyclononatetraene could not be frozen even at −130°;[14] no change was observed in 2 at −80°.[7a]
12. The uv spectrum of the ketal was typical for a phenanthrene derivative; nmr δ ($CDCl_3$) = 8.75 (2H, m), 7.75 (6H, m), 4.11 (4H, s, ketal protons) and 3.60 (4H, s, allylic protons); mass spectrum, m/e 276 (M).
13. Variable temperature studies are under way.
14. K. Hajo and S. Masamune, J. Am. Chem. Soc., 92, 6690 (1970).
15. The [11], [13], [15] and [17] annulenones display a carbonyl absorption at 1600 – 1630 cm^{-1}.[1-4] Also tropone derivatives absorb close to this region.
16. J. Ciabattoni and G. H. Berchthold (J. Org. Chem., 31, 1336 (1966)) prepared cyclononadienone and -trienon derivatives. These compounds absorb in the ir at 1610 – 1620 cm^{-1} and show high intensity bands in the uv λ_{max}^{EtOH} 228 (ε 19,800), 283 nm (10,600) and at 227 (14,200), 305 nm (17,200), respectively; their vinylic protons absorb at δ ($CDCl_3$) = 6.83 and 6.46 respectively.
17. [17]*Annulenone was found to sustain such a ring current,*[4] while the high field shift of the vinylic protons in [5]annulenone was attributed to other effects.[6] [13]Annulenone has no protons directly attached to the ring, and no effect can be observed.[1]
18. Compound 6 is probably rapidly inverting at room temperature. This point is under investigation.