Tetrahedron Letters,Vol.27,No.42,pp 5159-5160,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

BENZOCALICENES AND BENZOTRIAHEPTAFULVALENES FROM CYCLOPROPARENES[1]

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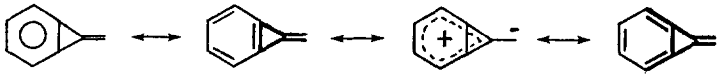
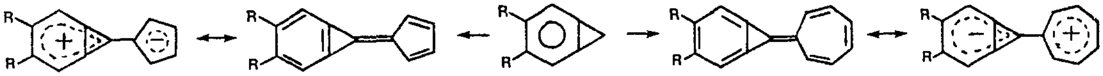
Summary: *The benzocalicenes (8)/(9) and the first triaheptafulvalenes (10)-(13) are available by Peterson olefination of the corresponding cycloproparene. Small hypsochromic shifts are noted in their uv spectra; the dipole moments of (8) and (12) are 2.6 and 1.2 Debye respectively.*

The strained ortho-bridged aromatics[2] and the cross-conjugated systems represented by the fulvalenes[3] and radialenes[4] are interesting classes of compound that continue to attract attention. The recently reported and surprisingly stable alkylidenecycloproparenes, e.g. (1),[5] combine the structural features of these groups into a single molecule. Thus the ortho-fused (1a) may be regarded simultaneously as a benzannulated methylenecyclopropene (1b), a benzannulated triafulvene (1b)↔(1c), and an unusual radialene (1d). A similar consideration of the cyclopentadienylidene homologue (4) shows that the 'electron-sink' should stabilise charge separation further when compared with (1c). By comparison the electron-donating ability of the cycloheptatrienylidene moiety, coupled with the known stability of the cycloproparenyl anion,[5,6] could neutralise or even reverse such polarity in fulvalene (6). Thus the cycloproparenylidene substructure in these fulvalenes is of particular interest as an ambiphile capable of stabilising both positive and negative charge. We now provide the first account of fulvalenes that contain this structural subunit, namely (8)-(13), and note that (10)-(13) are the first triaheptafulvalene derivatives reported.



1a 1b 1c 1d

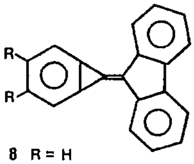


4 R = H
5 RR = benzo

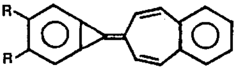
2 R = H
3 RR = benzo

6 R = H
7 RR = benzo

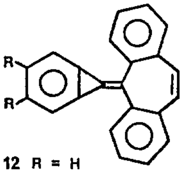
Trimethylsilylation of the cycloproparene (2) or (3), treatment with base, and reaction of the ensuing anion with an aryl ketone provides alkylidenecycloproparenes by Peterson olefination.[5] Such reactions employing fluorenone give the benzocalicenes (8) (22%)[7] and (9) (96%) as coloured crystalline solids.[8] The facile dimerisation of cyclopentadienone prevents analogous preparation of the parent benzocalicenes (4) and (5). Whilst tropone is readily available, reactions with it have thus far failed to provide the triaheptafulvalenes (6) and (7). However, the use of benzo-[4,5]- and dibenzo[2,3:6,7]-tropone lead to (10) and (11), and (12) and (13) respectively.[9] It was noted earlier that the reactions are more efficient with (3);[5] the present study is no exception.



8 R = H
9 RR = benzo



10 R = H
11 RR = benzo



12 R = H
13 RR = benzo

Fulvalenes (11) and (13) are isolated in yields of 51 and 87% whereas (10) and (12) are obtained in only 9 and 11% yield respectively.

Fulvalenes (8)-(13) show a three-membered ring vibration at ∿1780 cm^{-1} in the infrared and display distinct quaternary carbon resonances for the linking double bond atoms in the range 105-120 ppm. Furthermore, each of (8)-(13) show small (3-7 nm) hypsochromic shifts in their long wavelength ultraviolet maxima[8,9] on changing the solvent from cyclohexane to acetonitrile. These shifts typify those recorded for other polar fulvalenes.[3,10] The dipole moments of (8) and (12) have been measured as 2.6 and 1.2 Debye respectively. Thus there is a significant contribution to the structure of (8) from its polar form, c.f. (4), as is expected for such a calicene.[11] On the other hand, the small dipole moment of (12) clearly implies a much reduced polar contribution with concomitant enhancement of polyolefin character. The dipole that is present in (12) however, cannot be assigned unequivocally to lie in the direction depicted for parent (6).

Acknowledgements: Financial support in Wellington from the NZ Universities Grants Committee and in Utah from the NSF (Grant CHE 84-19099) is gratefully acknowledged.

References and Footnotes:

1. Studies in the Cycloproparene Series. For the previous part see reference 5a.
2. Halton, B. *Ind. Eng. Chem. Prod. Res. Dev.* 1980, *19,* 349-64.
3. Prinzbach, H.; Knothe, L. *Pure Appl. Chem.* 1986, *58,* 25-38; Prinzbach, H. *Ibid.* 1971, *28,* 281-329; Neuenschwander, M. *Ibid.* 1986, *58,* 55-66, and references cited.
4. Stehling, L.; Wilke, G. *Angew. Chem. Int. Ed. Engl.* 1985, *24,* 496-7.
5. (a) Halton, B.; Randall, C.J.; Gainsford, G.J.; Stang, P.J. *J. Am. Chem. Soc.* 1986, *108,* 0000. (b) Halton, B.; Randall, C.J.; Stang, P.J. *Ibid.* 1984, *106,* 6108-10.
6. Eaborn, C.; Eidenschink, R.; Harris, S.J.; Walton, D.R.M. *J. Organomet. Chem.* 1977, *124,* C27-9; Eaborn, C. *Ibid.* 1980, *192,* 155-61.
7. New compounds gave satisfactory microanalytical and/or high resolution mass, and spectral data.
8. (8): mp 176-8°; λ_{max} (C_6H_{12}) 438.5 (4.63), 411 (4.57), 392 (4.40), (CH_3CN) 432 (4.51), 407.5 (4.56), 388 nm (log ε 4.40). (9): mp 259-60°; λ_{max} (C_6H_{12}) 470.5 (5.00), 435.5 (4.79); (CH_3CN) 466.5 (4.87), 433.5 nm (log ε 4.73).
9. (10): mp 128-9°; λ_{max} (C_6H_{12}) 451.5 (4.79), 439 (4.55), 419 (4.69), 394 (4.34); (CH_3CN) 444 (4.64), 433 (4.48), 414 (4.61), 391 nm (log ε 4.33). (11): mp 232° dec.; λ_{max} (C_6H_{12}) 475 (4.92), 458 (4.35), 438 (4.58), 407 (4.09); (CH_3CN) 470 (4.93), 454 (4.45), 434 (4.63), 404 nm (log ε 4.17). (12): mp 158-58.5°; λ_{max} (C_6H_{12}) 383 (4.31), 308 (3.82); (CH_3CN) 376 (4.30), 299 nm (log ε 3.89). (13): mp 180-1°; λ_{max} (C_6H_{12}) 473 sh (3.21), 414 (4.29), 336 (3.82); (CH_3CN) 468 sh (3.36), 411 (4.39), 340 nm sh (log ε 3.60).
10. Prinzbach, H.; Fischer, U. *Helv. Chim. Acta* 1967, *50,* 1669-92.
11. Prinzbach, H.; Woischnik, E. *Helv. Chim. Acta* 1969, *52,* 2472-6.

(Received in UK 26 August 1986)