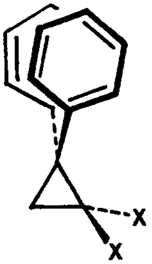
Tetrahedron Letters,Vol.23,No.16,pp 1635-1638,1982 0040-4039/82/161635-04$03.00/0
Printed in Great Britain

SYNTHESIS AND ELECTROPHILIC REACTIONS OF A CONFORMATIONALLY RIGID CYCLOPROPYLCARBINYL CATION. AN UNUSUAL SYNTHESIS OF SUBSTITUTED BENZ[A]AZULENES.

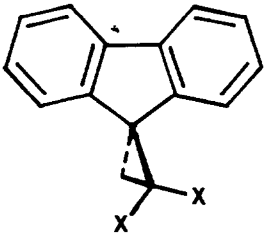
Mark E. Jason
Department of Chemistry, Amherst College, Amherst, Massachusetts 01002

Abstract: A tropylium-substituted cyclopropane has been prepared which is rigidly held in the "bisected" conformation. Its electrophilic reactions are also investigated.

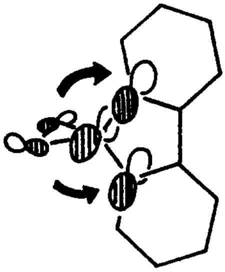
Bond length asymmetry in cyclopropanes, as induced by aromatic substituents, has recently been an object of attention in our laboratories.[1] We have observed shortening of the cyclopropane bonds *opposite* *gem*-diphenyl or 2,2'-biphenyl substitution, as in structures 1 and 2, respectively.[1b] The asymmetry in 2 has been explained in terms of cyclopropane-to-biphenyl charge transfer in analogy with the stabilization of cyclopropylcarbinyl cations. The orbital interaction, using Walsh orbitals on cyclopropane, is seen in 3.[2,3]



1a X=Cl
1b X=Br



2a X=H
2b X=Cl

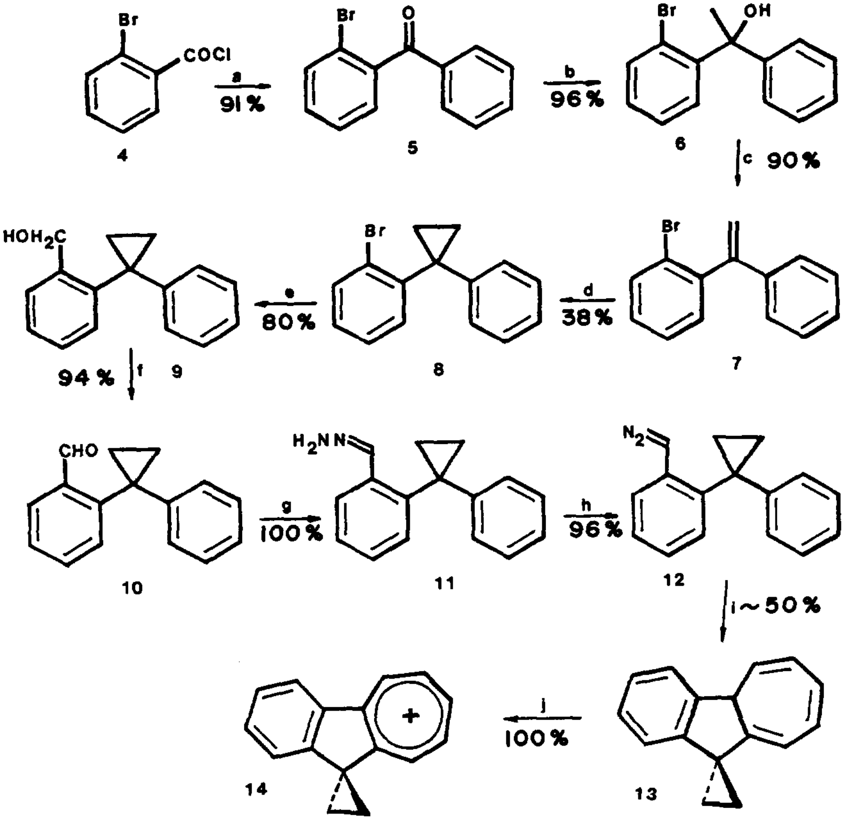


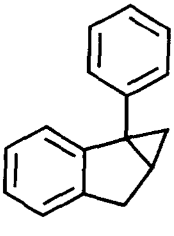
3

Our goal was to prepare a stable cyclopropylcarbinyl cation in which the geometry was frozen as close as possible to the "perpendicular."[1] Because of the attractive geometric aspects of the spirofluorene ring system, and the inherent stability of the tropylium ion, the cation 14 was selected as a promising target. Direct expansion of one of the six-membered rings of 2a has not yet succeeded. Literature procedures notwithstanding, we were unable to cleanly reduce 2a to a dihydro derivative.[4] Therefore, the synthesis in Scheme 1 was devised.[5,6]

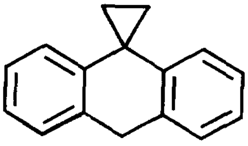
The synthesis of 14 was quite straightforward. The yields are for distilled or chromatographed products, with the exception of steps g → j. Cyclopropanation (7 → 8) was sliggish and accompanied by the formation of 1-(2'-bromophenyl)-1-phenylpropene. The conversion of 12 → 13 could have been complicated by the competition among a number of alternative carbene reactions.

SCHEME 1

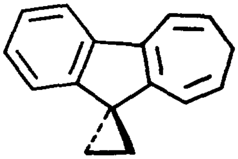




15



16



17

a) C_6H_6, $AlCl_3$; b) CH_3MgBr, Et_2O; c) Ac_2O, H_2SO_4 (cat.); d) CH_2I_2, Zn(Cu); e) Mg, Et_2O/CH_2O, f) $CrO_3\cdot 2Pyr$; g) H_2NNH_2, EtOH; h) HgO, EtONa, Et_2O; i) hν (Pyrex), CH_2Cl_2; j) $\emptyset_3C^+BF_4^-$

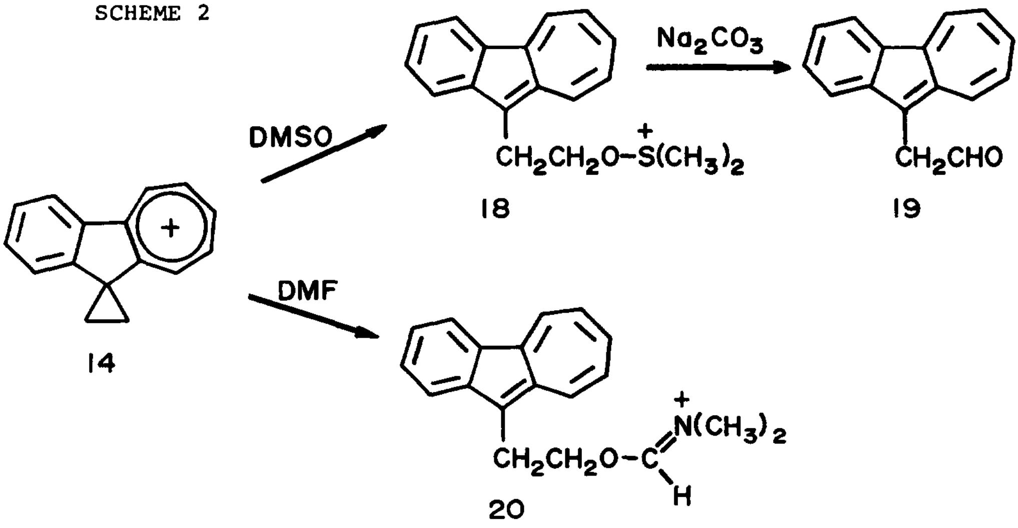
Investigation of the photolysis mixture indicated the presence of two products other than 13. The products derived from C-H insertion, 15 and 16, were each formed in approximately 5% yield, based on ^1H, ^{13}C and uv spectroscopic data. In addition, the azine derived from the diazo compound accounted for roughly 40% of the product mixture. Attempted GLC purification of 13 resulted in rearrangement to the apparently more stable isomer 17.

The cycloheptatriene 13 and tropylium ion 14 were characterized by their spectroscopic data:[8] 13 ^1H nmr ($CDCl_3$) δ7.27 (m, 4H), 6.72 (dd, 3.5 Hz, 5.0 Hz, 1H), 6.52 (m, 1H), 6.10 (m, 1H), 5.73 (m, 1H), 5.18 (dd, 4.2 Hz, 9.5 Hz, 1H), 3.64 (m, 1H), 1.34 (m, 4H); ^{13}C nmr ($CDCl_3$) 148.1, 147.0, 143.9, 130.5, 128.4, 127.4, 126.5, 125.1, 124.4, 124.0, 118.2, 111.2, 48.5, 30.4, 24.9, 22.5. The spectroscopic data for 14 are similarly straightforward: ^1H nmr (CD_3CN) δ9.6-9.5 (m, 1H), 9.0-8.4 (m, 5H), 8.0-7.5 (m, 3H), 2.7-2.4 (aa'bb', 4H); ^{13}C (CD_3CN), 175.7, 152.5, 149.3, 149.1, 148.2, 143.0, 142.1, 136.4, 129.2, 125.6, 121.0, 38.4, 26.7; uv (CH_2Cl_2) λ_{max} = 384, 350sh, 320sh, 305sh, 283, 241. Two of the quarternary sp^2 carbons were not identified in the ^{13}C nmr spectrum.

Replacing a benzene ring in 2a with the tropylium cation in 14 deshields the methylene carbons of the cyclopropane by 8.4 ppm. This shift is intermediate between that of a stabilized cyclopropylcarbinyl cation (~40 ppm) and p-nitrophenylcyclopropane (~2 ppm)[9], indicating a sizable shift of electron density away from the cyclopropane ring.

The cyclopropyltropylium salt 14 can be viewed, in the nomenclature of Danishefsky, as a "spiroactivated" cyclopropane[10] in which the electron withdrawing functionality is a cation rather than two carbonyl groups. It is thus only mildly surprising that dissolving 14 in DMSO or DMF results in nucleophilic attack upon the cyclopropane ring, with subsequent cleavage of a carbon-carbon bond. The ^1H nmr and particularly the uv spectra[11] are consistent with the conversion of 14 into benz[a]azulene derivatives, as outlined in Scheme 2. The identity of 18

SCHEME 2



(^{1}H nmr shows two triplets centered at δ3.63 (J=7 Hz) and 2.67 (J=7 Hz)) is further supported by its conversion to the aldehyde, 19, with sodium carbonate (δ8.85 (J=2 Hz) and 3.47 (J=2 Hz) for the OHC-CH$_2$- fragment).[12] The nucleophilic reactions of 14 will be the subject of a future communication.

The carbene insertion reactions of o-(phenylmethyl)phenyldiazomethanes have led to the benz[a]azulene architecture. Synthesis of a wide variety of specifically substituted benz[a]azulenes should be possible with this procedure, given the wide range of synthetically available benzophenones.

Acknowledgements: I would like to thank the Department of Chemistry, Cornell University, for a most pleasant and fruitful sojourn, especially Mel Goldstein and Roald Hoffmann for their kindness and patience.

References:

1. a) Jason, M. E.; Ibers, J. A. J. Am. Chem. Soc., 1977, 99, 6012; b) Jason, M. E.; Gallucci, J. C.; Ibers, J. A. Isr. J. Chem., 1981, 21, 95.
2. Jorgensen, W. L.; Salem, L. The Organic Chemist's Book of Orbitals, Academic Press, New York, 1973, p. 153.
3. Allen, F. H. Acta Cryst., 1980, B36, 81.
4. Harvey, R. G.; Fu, P. P.; Rabideau, P. W. J. Org. Chem., 1976, 41, 2706.
5. References to individual steps: a) 8 Simmons, H. E.; Cairns, T. L.; Vladichick, S. A.; Hoiness, C. M. Org. Reac., 1973, 20, 1; b) 9 Vogel, A. I. Practical Organic Chemistry, 3rd ed., Longmans, London, 1956, p. 318; c) Ratcliffe, R.; Rodehorst, R. J. Org. Chem., 1970, 35, 4000; d) 11 Gutsche, C. D.; Johnson, H. E. J. Am. Chem. Soc., 1955, 77, 5933; e) 12 Miller, J. B. J. Org. Chem., 1959, 24, 560; 13 ref 5d; f) 14 Dauben, H. J. Jr.; Honnen, L. R.; Harmon, K. M. J. Org. Chem., 1960, 25, 1442.
6. Experimental and spectroscopic details will be published. Preprints available from author.
7. The azine can be recycled by treatment with excess hydrazine: ref 5d.
8. a) O'Leary, M. A.; Wege, D. Tetrahedron Lett., 1978, 2811; b) Butler, D. N.; Gupta, I. Can. J. Chem., 1978, 56, 80; c) Nakazawa, T.; Murata, I. J. Am. Chem. Soc., 1977, 99, 1996; d) Egger, K. W.; Moser, W. R. J. Phys. Chem., 1967, 71, 3699.
9. a) Kitching, W.; Adcock, W.; Aldous, G. J. Org. Chem., 1979, 44, 2652; b) Kusuyama, Y.; Dyllick-Brenzinger, C.; Roberts, J. D. Org. Mag. Res., 1980, 13, 372.
10. Danishefsky, S.; Singh, R. K. J. Am. Chem. Soc., 1975, 97, 3239.
11. a) Nunn, J. R.; Rapson, W. W. J. Chem. Soc., 1949, 825; b) Wege, D. private communication.
12. Kornblum, N.; Jones, W. J.; Anderson, G. J. J. Am. Chem. Soc., 1959, 81, 4113.

(Received in USA 26 May 1981)