Tetrahedron Letters Vol 32, No 6, pp 773-776, 1991
Printed in Great Britain

0040-4039/91 \$3.00 +
Pergamon Press plc

AZULENE ANALOGUES OF TRIPHENYLMETHYL CATION; EXTREMELY STABLE HYDROCARBON CARBOCATIONS

Shunji Ito, Noboru Morita, and Toyonobu Asao*
Department of Chemistry, College of General Education, Tohoku University,
Kawauchi, Aoba-ku, Sendai 980, Japan

Dedicated to Professor Tetsuo Nozoe on the occasion of his 88th birthday

Abstract: A series of azulene analogues of triphenylmethyl cation, tri(1-azulenyl)-methyl cation, di(1-azulenyl)phenylmethyl cation, (1-azulenyl)diphenylmethyl cation, and their methyl and methoxycarbonyl derivatives were synthesized. Their pK_{R^+} values showed that the stability of these cations dramatically increases with the number of azulene rings, and the pK_{R^+} values of tri(1-azulenyl)methyl cation (11.3) and its trimethyl derivative (11.4) are the highest ever reported for methyl cations substituted with hydrocarbon groups.

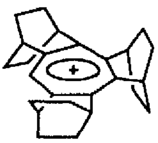
The syntheses of extremely stable cyclic hydrocarbon carbocation **1**, which consists of tropylium ion annelated with three bicyclo[2.2.2]octenes (pK_{R^+} 13.0, the highest value ever reported), and tricyclopropylcyclopropenium ion **2** (pK_{R^+} 10.0), have recently been reported.[1,2] Theoretical calculations[3] and a large dipole moment[4] of azulene suggested that azulene should stabilize cations attached at 1-position through p-p interaction as shown by tri(3-guaiazulenyl)cyclopropenium ion **3** (pK_{R^+} > 10).[5] Accordingly, tri(1-azulenyl)methyl cation **4** can be expected to show extraordionary stability by the contribution of resonance forms, e.g. **4'**.

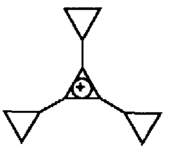
Here, we report the synthesis and the pK_{R^+} values of azulene analogues of triphenylmethyl cation **5**, tri(1-azulenyl)methyl, di(1-azulenyl)phenylmethyl, and (1-azulenyl)diphenylmethyl cations and their methyl and methoxycarbonyl derivatives. Tri(1-azulenyl)methyl cation and its 3,3',3"-trimethyl derivative show pK_{R^+} 11.3 and 11.4, respectively, the highest values as methyl cation substituted with hydrocarbon groups ever reported.

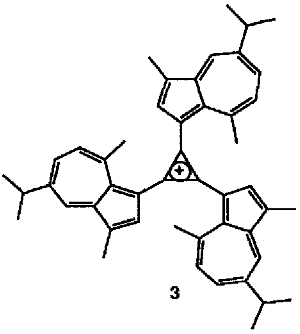
Two methods have been reported respectively for the synthesis of tri(1-azulenyl)methyl cation **4**,[6,7] but we found neither method gave the desired cation, namely, 1) the reaction of azulene with tetraethyl orthocarbonate in nitromethane in the presence of HCl was found to give polymeric cation, whose stracture has not been clarified yet, 2) the reaction of tri(1-azulenyl)methane with $Ph_3C^+PF_6^-$ was found to give not tri(1-azulenyl)methyl cation by hydride abstraction but di(1-azulenyl)-methyl cation by extrusion of one azulene ring.

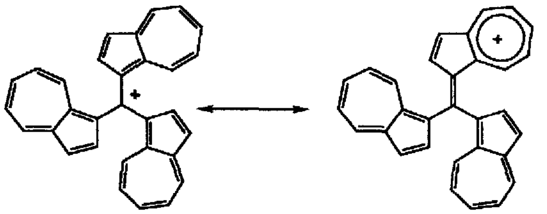
Synthesis of tri(1-azulenyl)methyl cation **4** was finally accomplished by the hydride abstraction of tri(1-azulenyl)methane with DDQ.

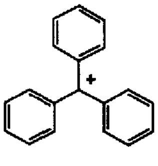
Tri(1-azulenyl)methane **6a** has been obtained by the auto-oxidation of azulene with O_2 in 3.2% yield as one of many products.[7] The compound **6a** was effectively synthesized by the reaction of 1-formylazulene with azulene under an acidic condition. A mixture of 1-formylazulene with two molar equivalents of azulene in acetic acid was stirred at room temperature for 3 days to yield tri(1-azulenyl)methane **6a** in 30% yield, accompanied with 1,3-bis[di(1-azulenyl)methyl]azulene **7** in 14% yield. Tri[1-(3-methylazulenyl)]methane **6b**[8] and tri[1-(3-methoxycarbonylazulenyl)]methane **6c**[9] were also obtained by similar reactions of 3-methyl- and 3-methoxycarbonyl-1-formylazulenes with the respective 1-methyl- and 1-methoxycarbonylazulenes in 70% and 94% yields, respectively.

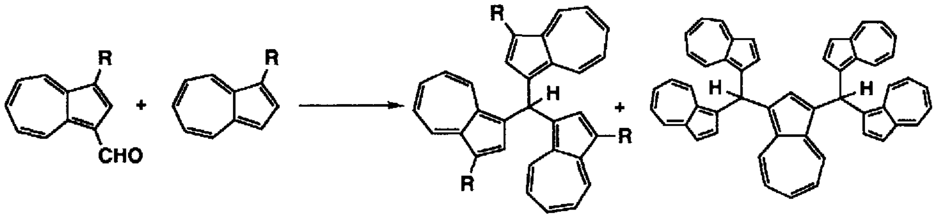

1


2


3


4 4'


5



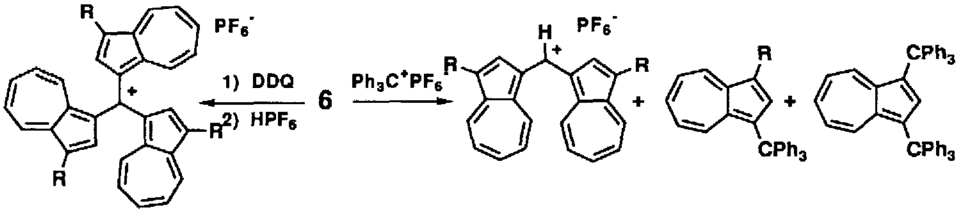
6a R = H
6b R = Me
6c R = COOMe

7

Hydride abstraction of these tri(1-azulenyl)methanes **6a**, **6b**, **6c** by the reaction with $Ph_3C^+PF_6^-$ afforded the corresponding diazulenylmethyl cations **8a**,[10] **8b**, **8c** in 98%, 98%, and 98%, yields, respectively, by extrusion of one azulene ring each, and the corresponding 1-triphenylmethylazulenes **9a**,[11] **9b** and **9c**, and 1,3-bis(triphenylmethyl)azulene **10**[11] from **6a**

However, hydride abstraction of **6a** by the reaction with DDQ in CH_2Cl_2, followed by exchange of counter anion with PF_6 by addition of 60% HPF_6 aqueous solution was found to yield tri(1-azulenyl)methyl hexafluorophosphate **4a** quantitatively as a deep-blue powder.[12] Similarly, its 3,3',3"-trimethyl- **4b** and 3,3',3"-trimethoxycarbonyl derivatives **4c** were also obtained quantitatively from the corresponding methanes **6b**, **6c**, respectively Reduction of **4a** and **4b** with $LiAlH_4$ in THF-CH_2Cl_2 afforded the corresponding triazulenylmethanes in around 20% yields

In a similar manner, di(1-azulenyl)phenylmethyl cation (**12a**) and (1-azulenyl)diphenylmethyl cation (**14a**) and their methyl (**12b**, **14b**) and methoxycarbonyl (**12c**, **14c**) derivatives were also synthesized,[9] starting from the substituted methanes (**11**, **13**) which had been obtained by the reaction[13] of the corresponding azulenes with benzaldehyde and benzhydrol, respectively

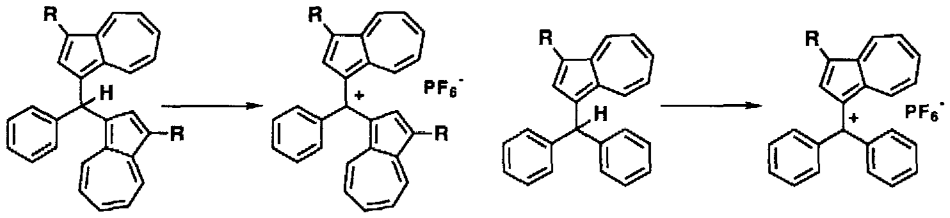


4a R = H
4b R = Me
4c R = COOMe

8a R = H
8b R = Me
8c R = COOMe

9a R = H
9b R = Me
9c R = COOMe

10



11

12a R = H
12b R = Me
12c R = COOMe

13

14a R = H
14b R = Me
14c R = COOMe

Table I pK_{R^+} Values of (1-azulenyl)methyl cations [a]

Compounds	4	1 2	8	1 4	5
a, R=H	11 3	10 5	7 3	3 0	-6
b, R=Me	11 4	10 8	8 7	3 7	
c, R=COOMe	10 3	3 4	2 1	0 08[b]	

[a] Measured at 24 °C in buffered solution in 50% aqueous MeCN

[b] Measured in H_2SO_4-H_2O system

The pK_{R^+} values of all cations obtained here were determined spectrophotometrically at 24 °C in buffer solutions prepared in 50% aqueous MeCN, and are shown in Table I The pK_{R^+} values dramatically increase with the number of azulene rings As expected, the methyl substituent slightly increases the value and the methoxycarbonyl group decreases the stability of the cation The pK_{R^+} values of tri(1-azulenyl)methyl cations **4a** (11 3), **4b** (11 4), and **4c** (10 3) are higher by 4 0, 2 7 and 8 2 pK_{R^+} unit than those of the corresponding di(1-azulenyl)methyl cations **8a**, **8b**, **8c**, and the value of **4a** is 17 7 pK_{R^+} unit higher than that of triphenylmethyl cation (pK_{R^+} -6 4)[14] The pK_{R^+} of **4b** is the highest values as a methyl cation substituted with hydrocarbon groups ever reported

Table I also shows that the methoxycarbonyl group particularly destabilizes di- and monoazulenylmethyl cations as observed in **8c**, **12c**, and **14c** However, there is a small difference in pK_{R^+} values between **4a**,**b**, and **4c**, compared to others The small difference in tri(1-azulenyl)methyl cations can be explained in terms of sterical protection of the cation from an attack of bases by large azulene rings Therefore, it is considered that the extreme stability of tri(1-azulenyl)methyl cations mainly depends on the contribution of the resonance structure **4'** and to some extent on the steric effect of azulene rings

References and Notes

(1) K Komatsu, H Akamatsu, Y Jinbu, and K Okamoto, *J Am Chem Soc*, **110**, 633 (1988)

(2) (a) K Komatsu, I Tomioka, and K Okamoto, *Tetrahedron Lett*, **21**, 947 (1980) (b) R A Moss and R C Munjal, *ibid*, **21**, 1221 (1980) (c) R A Moss, S Shen, K Krogh-Jesperson, J A Potenza, H J Schugar, and R C Munjal, *J Am Chem Soc*, **108**, 134 (1986)

(3) (a) See, K -P Zeller, in Houben-weyl, "*Methoden der Organischen Chemie*" Ed by E Muller, Georg Thiem Verlag, Stuttgart, 1985, Vol 5, Part 2c, 127 (b) J O Morley, *J Am Chem Soc*, **110**, 7660 (1988)

(4) A J Anderson, Jr, and B M Steckler, *J Am Chem Soc*, **81**, 4941 (1959)

(5) I Agranat and E Aharon-Shalom, *J Org Chem*, **41**, 2379 (1976) Triphenylcyclopropenium ion shows a pK_{R^+} of 3 4, R C Kerber and C -M Hsu, *J Am Chem Soc*, **95**, 3239 (1973)

(6) K Hafner, H Pelster, and J Schneider, *Liebigs Ann Chem*, **650**, 62 (1961)

(7) S Takekuma, Y Matsubara, H Yamamoto, and T Nozoe, *Nippon Kagaku Kaisi*, **1988**, 157

(8) The compound **6b** has been obtained by the auto-oxidation of 1-methylazulene in 4 3% yield, S Takekuma, Y Matsubara, H Yamamoto, and T Nozoe, *Bull Chem Soc Jpn*, **60**, 3721 (1987)

(9) All new compounds were characterized by their IR, UV, ^1H NMR, and ^{13}C NMR spectral data and elemental analyses and/or mass spectroscopy

(10) E C Kirby and D H Ried, *J Chem Soc*, **1960**, 494, **1961**, 1724

(11) K Hafner, A Stephan, and C Bernhard, *Liebigs Ann Chem*, **650**, 42, (1961)

(12) All carbocations obtained in this paper were found to exist in an equilibrium with their conformational isomers (symmetrical and unsymmetrical propeller conformers) by the inspection of variable temperature NMR spectra

(13) Von H Franke and M Muhlstadt, *J Prakt Chem*, **35**, 249 (1967)

(14) E M Arnett and R D Bushick, *J Am Chem Soc*, **86**, 1564 (1964)

(Received in Japan 24 October 1990)