Pergamon

Tetrahedron Letters, Vol. 37, No. 28, pp. 4965-4966, 1996
Copyright © 1996 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0040-4039/96 $15.00 + 0.00

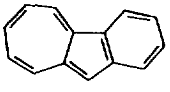
PII: S0040-4039(96)00979-3

A Novel Synthesis of β-(10-Benz[*a*]azulenyl)-α,β-unsaturated Ketones by Intramolecular Cyclization of *o*-[2-Furyl]cycloheptatrienylbenzenes

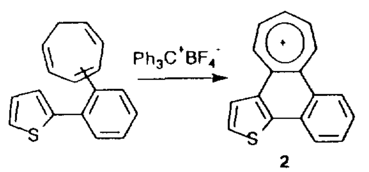
Kimiaki Yamamura*, Taihei Yamane, Masao Hashimoto, Hideyoshi Miyake[†], and Shin-ichi Nakatsuji[††]

Department of Chemistry, Faculty of Science, Kobe University, Nada, Kobe 657, Japan
[†]Department of Biofunctional Chemistry, Faculty of Agriculture, Kobe University, Kobe 657, Japan
[††]Department of Material Science, Faculty of Science, Himeji Institute of Technology, Hyogo 679-12, Japan

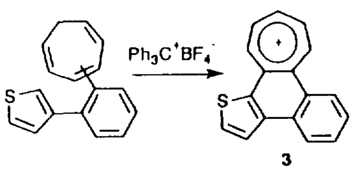
Abstract: Treatment of *o*-[2-furyl]cycloheptatrienylbenzenes with triphenylmethyl tetrafluoroborate (trityl salt) in dichloromethane gave β-(10-benz[*a*]azulenyl)-α,β-unsaturated ketones in one-pot, in which a novel cyclization involving intramolecular attack of tropylium ion to the α-position of furan ring is postulated. Copyright © 1996 Elsevier Science Ltd


1

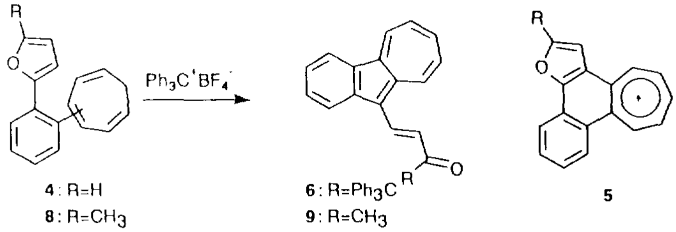
In spite of the fundamental significance of benz[*a*]azulene (1) which is a very well-known class of polycyclic nonbenzenoid hydrocarbons, the synthetic difficulties of benz[*a*]azulenes have precluded the progress in this area.[1] Here we wish to report a novel one-pot synthesis of 4-(10-benz[*a*]azulenyl)-3-butene-2-ones, β-(10-benz[*a*]azulenyl)-α,β-unsaturated ketones, from the corresponding *o*-[2-furyl]cycloheptatrienylbenzenes by treatment with trityl salt. This method should provide efficient access to a variety of α,β-unsaturated carbonyl derivatives of benz[*a*]azulene. In a previous paper, we reported on a facile synthesis of cyclohepta[*a*]thieno-[c]naphthalenylium ions (2) and (3) by the intramolecular cyclization of *o*-thienylcycloheptatrienylbenzenes using trityl salt as the hydride abstract reagent.[2] In the reaction, intramolecular Friedel-Crafts type reaction of the initially formed *o*-tropyliothienylbenzenes to form a six-membered ring was proposed. If this reaction is applied to *o*-[2-furyl]cycloheptatrienylbenzene (4), the formation of cyclohepta[*a*]furo[c]naphthalenylium ion (5) may be predicted. However, when 4, prepared from 2-trimethylstannylfuran and *o*-cycloheptatrienylbromobenzene[3], was treated with 2 equivalent of trityl salt in dichloromethane at ambient temperature for 24 hrs, black prisms of mp 295 °C were isolated instead of 5 (yield; 41.3%). These prisms showed the existence of an α,β-unsaturated carbonyl moiety in its IR spectrum. Further analysis of the compound by NMR, UV-vis, MS spectra as well as X-ray crystal analyses[4] elucidated the structure to be, to our surprise, (*E*)-1,1,1-triphenyl-4-(10-benz[*a*]azurenyl)-3-butene-2-one (6)[5] (Scheme 1).



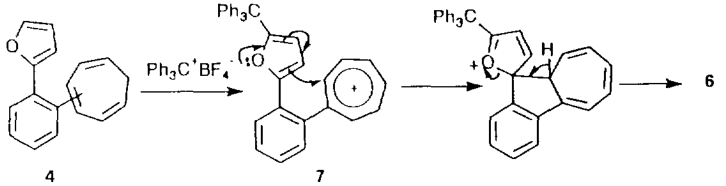
2



3



Scheme 1.



Scheme 2.

Thus a dramatic difference in the reaction product from the thiophene series described earlier[2] was observed in the furan derivative (4). Since it is well-known that the 2-position of the furan ring is much more reactive towards electrophiles than the 3-position and that furans are readily ring-opened to 1,4-diketones under acidic conditions,[6] the formation of 6 can be rationalized as shown in Scheme 2. The intramolecular cyclization reaction of the initially formed trityl substituted cation (7) happens to give the spiro-type intermediate, which can be converted to the final product by ring-opening reaction. Apparently, trityl salt acts as both an electrophile and a hydride abstract reagent in the reaction. When 5-trityl derivative of 4[5], prepared individually, was treated with an equimolar amount of trityl salt, 6 was obtained in 45.0 % yield. To ensure the reaction process further, we then subjected 5-methyl derivative of 4, i.e., *o*-[2-(5-methyl)furyl]cycloheptatrienylbenzene (8)[5] prepared from 5-methyl-2-trimethylstannylfuran[5] and *o*-cycloheptatrienylbenzene, to the reaction with an equimolar amount of trityl salt and succeeded in isolating (*E*)-4-(10-benz[*a*]azulenyl)-3-butene-2-one (9) as black needles of mp 112 °C in 40.0 % yield. The structure was established by its NMR, IR UV-vis and MS spectra as well as elemental analyses.

To our knowledge, this is the first case of such tropylium ion-mediated furan-ring-opening reaction to yield benz[*a*]azulene derivatives[7] and the successful preparation of 6 and 9 opened a route to the synthesis of various α,β-unsaturated carbonyl derivatives of benz[*a*]azulens. Further study of this novel synthesis is now in progress directed towards elaboration of the scope and limitation of this reaction.

Acknowledgement We wish to thank Miss Masuko Nishinaka for the elemental analysis and measurement of mass spectra and are grateful to Miss Yasuko Mizuta and Miss Reiko Yamamura for their kind collaboration.

References and Notes

1) Several successful studies have been achieved in recent years; Cf. M.A. O'Leary, G.W. Richardson, and D.Wege,*Tetrahedron*, **1981**, *37*, 813~823; M.E. Jason, *Tetrahedron Lett.*, **1982**, *23*, 1635~1638; K. Mizuno, K. Okada, and M. Oda, *Tetrahedron Lett.*, **1984**, *25*, 2999~3002; Y.N. Gupta and K.N. Houk, *Tetrahedron Lett.*, **1985**, *26*, 2607~2608; H. Duddeck, M. Kennedy, M.A. Mckervey, and F.M. Twohig, *J. Chem. Soc., Chem. Commun.*, **1988**, 1586~1588; M. Yasunami, T. Sato, and M. Yoshifuji, *Tetrahedron Lett.*, **1995**, *36*, 103~106 and references cited therein.

2) K. Yamamura, H. Miyake, S. Nakatsuju and I. Murata, *Chemistry Lett.*, **1992**, 1213~1216.

3) K. Yamamura, K. Nakatsu, K. Nakao, T. Nakazawa and I. Murata, *Tetrahedron Lett.*, **1979**, 4999~5002.

4) M. Hashimoto, K. Yamamura, H. Miyake and S. Nakatsuji, to be published.

5) All the new compounds described in this paper afforded satisfactory spectroscopic data as well as elemental analyses.

6) M.V. Sargent and T.M. Cresp, "Comprehensive Organic Chemistry, " Pergamon Press, **1979**, 4, 693.

7) The addition of tropylium ion to allenylsilans to afford azulene derivatives was reported; D.A. Becker and R.L. Danheiser, *J. Am. Chem. Soc.*, **1989**, *111*, 389~391.

(*Received in Japan* 11 *April* 1996; *revised* 17 *May* 1996; *accepted* 22 *May* 1996)