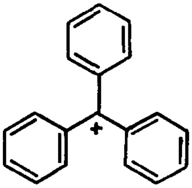
Tetrahedron Letters,Vol.25,No.28,pp 2999-3002,1984 0040-4039/84 $3.00 + .00
Printed in Great Britain

GENERATION AND NOTABLE POSITION DEPENDENT ELECTROCYCLIZATION OF CYCLOHEPTATRIENYLPHENYLCARBONIUM IONS—ELECTROCYCLIZATION OF A NORCARADIENE

Kiyoharu Mizumoto, Keiji Okada, and Masaji Oda*
Department of Chemistry, Faculty of Science, Osaka
University, Toyonaka, Osaka 560, Japan

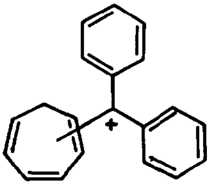
Summary: While (1- and 2-cycloheptatrienyl)phenylcarbonium ions undergo electrocyclizations through the cycloheptatriene forms giving dihydrobenz[a]azulenes, (3-cycloheptatrienyl)-diphenylcarbonium ion does through the norcaradiene form. (7-Cycloheptatrienyl)diphenylcarbnium ion undergoes a rearrangement. A possible rationalization is discussed.

Triphenylcarbonium ion 1 and tropylium ion 2 are well-known stable carbonium ions.1) The latter is more stable than the former owing to 6π electron aromatic stabilization, and hydride abstraction of cycloheptatrienes with 1 has been a useful synthetic method for tropylium ions.1) There has been, however, no report on the properties of the carbonium ions 3 ∿ 6 in which one phenyl group of 1 is replaced by a cycloheptatriene group. We were interested in their stability and reactivity which might change with the substitution position in the cycloheptatriene ring. It has been found that these cations are much less stable than 1, and that one of the four isomers rearranges and the other three isomers undergo electrocyclizations chemoselectively through either the cycloheptatriene (CHT) form or the norcaradiene (NCD) form depending on the substitution position.



1

2



3: 1-Cycloheptatrienyl-
4: 2-
5: 3-
6: 7-

Treatment of (1-cycloheptatrienyl)diphenylcarbinol 7a2) with trifluoroacetic acid in dichloromethane at -72°C displayed deep red color to suggest generation of the carbonium ion 3a.3) The color, however, faded to pale yellow-green within 2 h at this temperature. The discoloration was rapid at -40°C. From this solution was obtained 4b,9-dihydro-10-phenylbenz[a]azulene 8a4) in 98% yield. Other protic and Lewis acids were also effective for the transformation; for instance, stirring 7a with zinc chloride in dichloromethane at room temperature for 1 h gave 8a in 84% yield. No formation of hydride shifted product such as 9 was observed. Triphenylmethyl perchlorate did not abstract hydride from 7a but merely worked as an acid source giving only 8a. The cyclization appears general for (1-cycloheptatrienyl)-

phenylcarbinols: 7b and 7c yielded 8b (74%) and 8c (95%), respectively, under similar conditions. In the case of 7c, brief acid treatment afforded in addition to 8c the uncyclized olefin 11[5] which was transformed to 8c on further acid treatment. Dehydrogenation of 8a ∼ c with Pd-C in boiling ethylene glycol gave the corresponding benz[a]azulenes 10a ∼ c[6] to support the assigned structures.

(2-Cycloheptatrienyl)phenylcarbinols 12a and 12b,[2] when treated with zinc chloride at room temperature, similarly underwent cyclization to give 4b,5-dihydrobenz[a]azulenes 13a (64%) and 13b (59%),[4] respectively.

In contrast to 1- and 2-isomers, (3-cycloheptatrienyl)diphenylcarbinol 14[2] did not give dihydrobenzazulene at all on acid treatment, but did the tetracyclic hydrocarbon 15[4] stereoselectively in high yields (91%, CF_3COOH-CH_2Cl_2, -30°C; 80%, $ZnCl_2$-CH_2Cl_2, room temp.). The presence of a cyclopropane ring in 15 is clearly indicated by ^1H- and ^{13}C-NMR spectra.[4] We tentatively assign the stereochemistry as shown from steric point of view in the transition state of the conrotatory cyclization.

On the other hand, (7-cycloheptatrienyl)diphenylcarbinol 16[2] rapidly rearranged to triphenylethene by acids. Such a rearrangement of 7-substituted cycloheptatrienes via norcaradienes have been well precedented.[7]

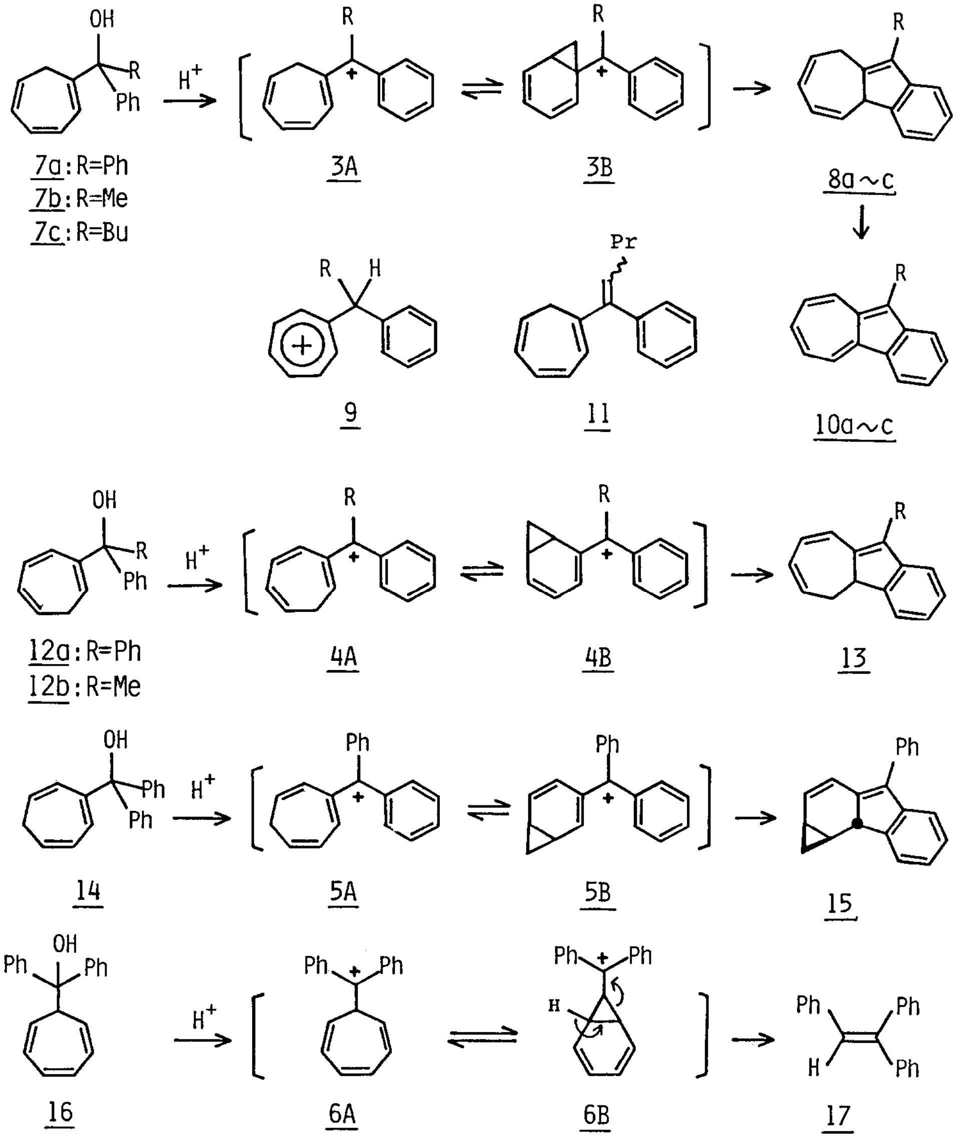
Thus, while (1- and 2-cycloheptatrienyl)phenylcarbonium ions 3 and 4 cyclize chemoselectively through the CHT forms 3A and 4A, (3-cycloheptatrienyl)diphenylcarbonium ion 5 does through the NCD form 5B (Scheme 1). It is well documented that a CHT equilibrates with a NCD and a number of factors affect the equilibrium.[8] Activation energy for the isomerization is considerably low: for the parent CHT, $\Delta G^{\ddagger}_{NCD \to CHT} = 7.2$ kcal/mol and $\Delta G^{\ddagger}_{CHT \to NCD} \simeq 11$ kcal/mol (25°C) have been reported.[9] The similar equilibria should be also present in the cation 3 ∼ 6 under the reaction conditions. In 3, cyclization would be possible only through the CHT form 3A, whereas in 4 and 5, cyclization would be possible through both the CHT and NCD forms 4A,B and 5A,B.

We can hardly rationalize the interpretation that the equilibrium between 5A and 5B is shifted far to the side of 5B to cause selectively the NCD cyclization.

It has been accepted that MO coefficients play an important role in the regioselectivity, siteselectivity, and periselectivity of pericyclic reactions.[10] Therefore, we at present interpret the remarkably chemoselective cyclizations observed in 4 and 5 in terms of frontier orbital controlled electrocyclization of the pentadienyl cations that are present as a partial structure in both the CHT and NCD forms of these compounds. In this context, the reaction course is determined by the rate of cyclization, which is in turn dependent on the MO coefficients in each form. Fig. 1 shows HOMO of benzyl cation substituted hexatrienes and butadienes, the simplified models for 4 and 5, as calculated by simple HMO method. The figures indicated are the MO coefficients on the cyclizing carbons. The values lead to a suggestion that the orbital interaction between the two carbons of 4A is slightly larger than that of 4B and that of 5A is conversely much smaller than that of 5B, being consistent with the experimental results.

It is noteworthy that in view of ready availability of 1-benzoylcycloheptatriene,[11] the precursor for 7, acid induced cyclization and dehydrogenation of 7 would provide a general synthetic method for benz[a]azulenes.

Acknowledgment : This work was supported by a Grant-in-Aid for Scientific Research No. 57470020 from the Ministry of Education, Science and Culture, Japan



Scheme 1

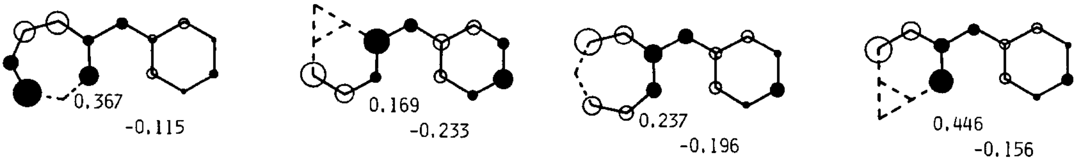


Fig.1 HOMO of benzyl cation substituted hexatrienes and butadienes by HMO method.

REFERENCES AND NOTES

1) For a review see J.L. Franklin, H.H. Freedman, and K.M. Harmon, "Carbonium Ions," Vol. I V, Ed by G.A. Olah and P.v.R. Schleyer, Wiley-Interscience, New-York, 1968 1974, Chapt. 2, 28, and 29.

2) The carbinols were prepared as follows. Reactions of 1-benzoylcycloheptatriene[11] with phenyl or alkyllithium gave 7a~c in good yields. Reactions of 3- and 7-carbomethoxy-cycloheptatriene[12,13] with phenyllithium lead successfully to 14 and 16, respectively. The preparation of 12a, however, met with difficulty: while reaction of 2-benzoylcycloheptatriene[11] with methyllithium was successful, reaction with phenyllithium gave a complex mixture of 1,4-adduct, 7a, 12a, and 14. Because of failure in forming 12a selectively under a variety of conditions, 12a was obtained by HPLC separation of the carbinol mixture. The selected physical data of some carbinols are following: 7a: 91%; mp 85-86°C; ^{1}H-NMR (100 MHz, CDCl$_3$) δ 2.42 (d, J=7 Hz, 2H), 2.58 (s, OH), 5.17 (dt, 9, 7 Hz, 1H), 5.91 (m, 1H), 6.12 (m, 1H), 6.48 (m, 2H), 7.15-7.45 (m, 10H); 12a: ca 10%; mp 115-116°C; ^{1}H-NMR (100 MHz, CDCl$_3$) δ 2.24 (t, J=7 Hz, 2H), 2.54 (br. s, OH), 5.07 (t, 7 Hz, 1H), 5.54 (dt, 9, 7 Hz, 1H), 6.18 (m, 1H), 6.62 (m, 2H), 7.28 (br. s, 10H); 14: 93%; mp 97-98°C; ^{1}H-NMR (100 MHz, CDCl$_3$) δ 2.31 (t, 7 Hz, 2H), 2.65 (Br. s, OH), 5.40 (m, 2H), 6.10 (m, 2H), 6.35 (d, 6 Hz, 1H), 7.15- 7.50 (m, 10H); 16: 97%; mp 90-91°C; ^{1}H-NMR (60 MHz, CDCl$_3$) δ 2.50 (s, OH), 2.57 (t, J=6 Hz, 1H), 5.30 (dd, 9, 6 Hz, 2H), 6.10 (br. d, 9 Hz, 2H), 6.60 (t, 3 Hz, 2H), 7.00-7.50 (m, 10).

3) ^{1}H-NMR spectrum of this solution at -70°C suggested a rapid equilibrium between 3a and 7a, and NMR observation of 3a itself has not yet been successful.

4) 8a: mp 124-125°C; ^{1}H-NMR (100 MHz, CDCl$_3$) δ 3.41 (m, 2H), 4.42 (br. s, 1H), 5.75-6.20 (m, 4H), 7.05-7.55 (m, 9H); 13a: mp 91.5-93.0; ^{1}H-NMR (100 MHz, CDCl$_3$) δ 2.46 (dd, J=16, 13 Hz, 1H), 2.98 (m, 1H), 3.80 (dd, 13, 3 Hz, 1H), 5.65-6.05 (m, 3H), 6.47 (d, 11 Hz, 1H), 7.10-7.50 (m, 9H); 15: mp 61.5-62.5°C; ^{1}H-NMR (100 MHz, CDCl$_3$) δ 0.12 (dt, J=5.5, 4, 4 Hz, 1H), 0.96 (ddd, 8, 8, 4 Hz, 1H), 1.52 (m, 1H), 1.92 (dddd, 8, 8, 5.5, 5.5 Hz, 1H), 3.81 (d, 5.5 Hz, 1H), 6.24 (dd, 10, 4 Hz, 1H), 6.38 (dd, 10, 1 Hz, 1H), 7.10-7.60 (m, 9H); ^{13}C-NMR (22.49 MHz, CDCl$_3$) δ 10.85, 12.58, 15.40, 46.11, 119.57, 119.84, 122.82, 124.99, 126.83, 127.27, 128.46, 128.84, 134.74, 135.12, 137.07, 139.62, 145.20, 145.63.

5) 11: this compound is a *ca* 2:1 mixture of geometrical isomers as judged by ^{1}H-NMR spectrum (100 MHz, CDCl$_3$) δ 0.8-1.0 (m, 3H), 1.2-1.6 (m, 2H), 1.8-2.2 (m, 2H), 2.32 (d, J=7 Hz, 0.7H), 2.59 (d, 7 Hz, 1.3H), 5.2-6.7 (m, 6H), 7.0-7.5 (m, 5H).

6) 10a: 67%; mp 100-102°C (lit.[14] 99°C); 10b: 45%; mp 79-80°C (lit.[15] 80°C); 10c: 29%; green oil; ^{1}H-NMR (60 MHz, CCl$_4$) δ 0.7-2.0 (m, 7H), 3.09 (t, J=7 Hz, 2H), 6.5-8.4 (m, 9H).

7) a) R. Grigg, R. Hayes, and A. Sweeney, J. Chem. Soc. (D), 1248 (1971); b) J. Hambrecht, H. Straub, and E. Mueller, Chem. Ber., 107, 2985 (1974); c) M. Ogawa, M. Sugishita, M. Takagi, and T. Matsuda, Tetrahedron, 31, 299 (1975).

8) a) For a review see E.N. Marvell, "Thermal Electrocyclic Reactions," Academic Press, New York, 1980, Chapt. 7; b) K. Takahashi, K. Takase, and H. Toda, Chem. Lett., 979 (1981); c) K. Takeuchi, H. Fujimoto, and K. Okamoto, Tetrahedron Lett., 4981 (1981).

9) M.B. Rubin, J. Am. Chem. Soc., 103, 7791 (1981).

10) I. Fleming, "Frontier Orbitals and Organic Chemical Reactions," Wiley-Interscience, New York, 1976.

11) J.A. Blair and C.J. Tate, J. Chem. Soc. (C), 1592 (1971).

12) K. Konrow, J. Am. Chem. Soc., 81, 5461 (1959).

13) P.L. Pauson and K.H. Todd, J. Chem. Soc. (C), 2636 (1970).

14) W. Treibs and A. Stein, Ann., 572, 165 (1951).

15) M.A. O'leary, G.W. Richardson, and D. Wege, Tetrahedron, 813 (1981).

(Received in Japan 29 March 1984)