61. Benzo[9]annulenone. Synthesis and Acid-Induced Antiaromaticity[1])

Preliminary communication

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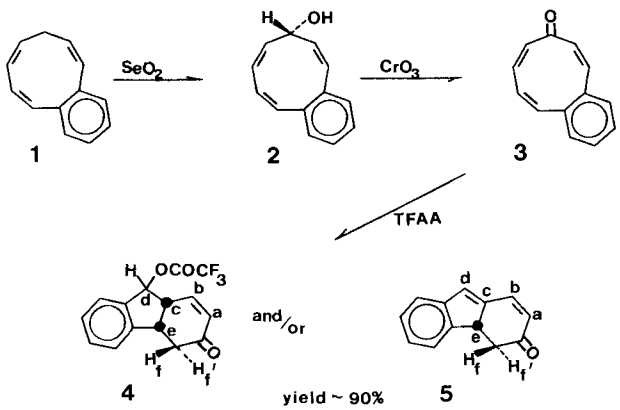
Summary

The synthesis and acid-induced pericyclization of the title substance (**3**), the simplest known [9]annulenone, are described.

The antiaromatic instability imparted on the nine-membered ring by the presence of a $4n$-π-electron ($n=2$) periphery was demonstrated several years ago in the work dealing with the generation and bond relocation of the cyclononatetraenyl cation [1]. In contrast, no information is available on the family's pseudo $4n$-π-member ($n=2$), namely the corresponding ketone ([9]annulenone) whether in the parent state or simple annulated form[3]). In the present report we describe the synthesis and induced instability of the simplest monoannulated relative, namely benzo[9]annulenone **3**.



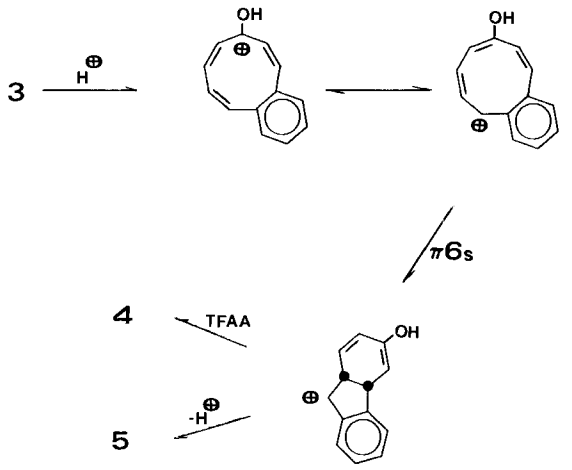
[1]) Work supported by the National Science Foundation.

[2]) On Sabbatical leave from the Department of Chemistry, Shiraz University, Shiraz, Iran.

[3]) A sterically congested (diphenyl)-substituted naphtho[9]annulenone was recently prepared in our laboratories (*A. G. Anastassiou, H. S. Kasmai & M. Sabahi*, Chem. Commun. *1979*, 1031.

0018-019X/81/2/0617-03$01.00/0

Scheme



Compound 3, [yellow solid, m.p. 83–84°. – IR. (KBr): 1625*s* (C=O). – UV. (CH_3CN): 353 (29), 335 (280), 252 (420), 244 (4100). – ^{1}H-NMR. ($CDCl_3$): 5.7–7.3 (*m*). – ^{13}C-NMR. ($CDCl_3$): 121–138; 193.9 (CO). – MS.: 182 (10%, *M*)] was prepared essentially quantitatively (*ca.* 90% after purification) from benzo-CNT (**1**) [2] *via* alcohol **2** [m.p. 85–86°; characterized by IR., UV., ^{1}H-NMR., ^{13}C-NMR and MS.]

Keeping in mind that ketone **3** is (i) largely insensitive to either air or heat, (ii) associated with a CO frequency whose value (1625 cm^{-1}) is indicative of the presence of conventional α,β unsaturation and (iii) it has NMR. characteristics which are, overall, suggestive of a strictly atropic frame, we may safely conclude that in its isolated state the molecule **3** is best viewed as a non-aromatic benzopolyene. To be sure, this result is hardly surprising insofar as the ketonic unit of the molecule is incorporated in a molecular frame which is sufficiently large as to resist the development of antiaromaticity *via* planarization.

Significantly, the situation changes drastically when **3** is exposed to strong acid. In specific terms, we find that mild treatment (0°) of **3** with trifluoroacetic acid (TFAA) readily triggers deep seated rearrangement to a benzobicyclo [4.3.0]frame isolated in the form of keto fluoroester **4** [colorless liquid. – IR. (neat): 1780*s* (fluoroacetate), 1680 (C=O). – ^{1}H-NMR. ($CDCl_3$): 2.90 (*d*, J=6.0, 1 H, H′–C(f); 2.95 (*d*, J=4.5, 1 H, H–C(g)); 3.52 (*m*, 1 H, H–C(c)); 4.16 (*m*, J(e,f′)=6.0, J(e,f)=4.5, J(c,e)=5.0, 1 H, H–C(*e*)); 6.00 (*d*×*d*, J(a,b)=10.5, J(a,c)=2.5, 1 H, H–C(a)); 6.20 (*d*, J=2.0, 1 H, H–C(d)); 6.50 (*d*×*d*, J(a,b)=10.5, J=3.0, 1 H, H–C(b)); 7.2–7.6 (*m*, 4 H, aromatic). – ^{13}C-NMR. ($CDCl_3$; H-coupled): 38.00 (*t*, J=129, C(f)); 40.09 (*d*, J=126); 46.35 (*d*, J=129); 84.57 (*d*, J=158, C(d)); 123.7–145.0 (sp^2-centers); 196.25 (*s*, CO). – MS.: 296 (1.6%, *M*)] or unsaturated ketone **5** [m.p. 83–84°. – IR. (KBr): 1660*s* (C=O). – UV. (CH_3CN): 344 (29,600), 332 (36,000), 245 (20,500), 238 (23,200), 232 (22,300). – ^{1}H-NMR. ($CDCl_3$): 2.25 (*d*×*d*, J(e,f′)=13.7, J(f,f′)=15.4, 1 H, H–C(f′)); 3.25 (*d*×*d*, J(e,f)=6.0,

$J(f,f')=15.4$, 1 H, H–C(f)); 4.00 ($d\times d$, $J(e,f)=6.0$, $J(e,f')=13.7$, 1 H, H–C(e); 6.00 (d, $J(a,b)=10.0$, 1 H, H–C(a)); 6.95 (s, 1 H, H–C(d)); 7.60 (m, 5 H, aromatic). – ^{13}C-NMR. ($CDCl_3$; H-coupled): 42.01 (t, $J=135$, c(f)); 47.98 (d, $J=127$, c(e)); 122.8–140.0 (sp^2-centers); 192.96 (s, CO). – MS.: 182 (100%, M)] depending on work-up conditions[4]).

Operationally, the acid catalyzed pericyclization of **3** to **4** or **5** may be rationalized as shown in the *Scheme*, the necessary driving force being of course supplied by the development of a π-destabilized (pseudoantiaromatic) system. The significance of antiaromatic destabilization and the relative unimportance of possible steric factors in the conversion of **3** to **4** or **5** under mild (0°), acid catalysis emerges all the more striking when one considers that the corresponding $(4n+2)$-π-member of this benzannulated family, *i.e.*, benzo-CNT anion, is well known to be both strongly diatropic (^{1}H-NMR.) and highly resistant to pericyclization [3].

REFERENCES

[1] *A. G. Anastassiou & E. Yakali*, Chem. Commun. *1972*, 92.
[2] *A. G. Ansatassiou, S. S. Libsch & R. C. Griffith*, Tetrahedron Lett. *1973*, 3103.
[3] *A. G. Anastassiou & R. C. Griffith*, J. Am. Chem. Soc. *96*, 611 (1974).

[4]) Under certain basic work-up conditions, keto ester **4** readily hydrolyzes to yield the corresponding alcohol isolated as a white solid, m.p. 123–124° and characterized through fully consistent spectroscopic [IR., UV., ^{1}H-NMR., ^{13}C-NMR. and MS.] data.