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GENERATION AND THERMAL BOND RELOCATION OF A STERICALLY CONGESTED CYCLONONATETRAENYL ANION

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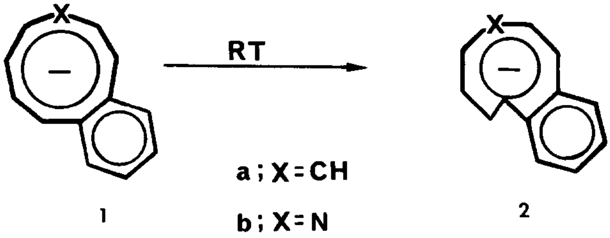
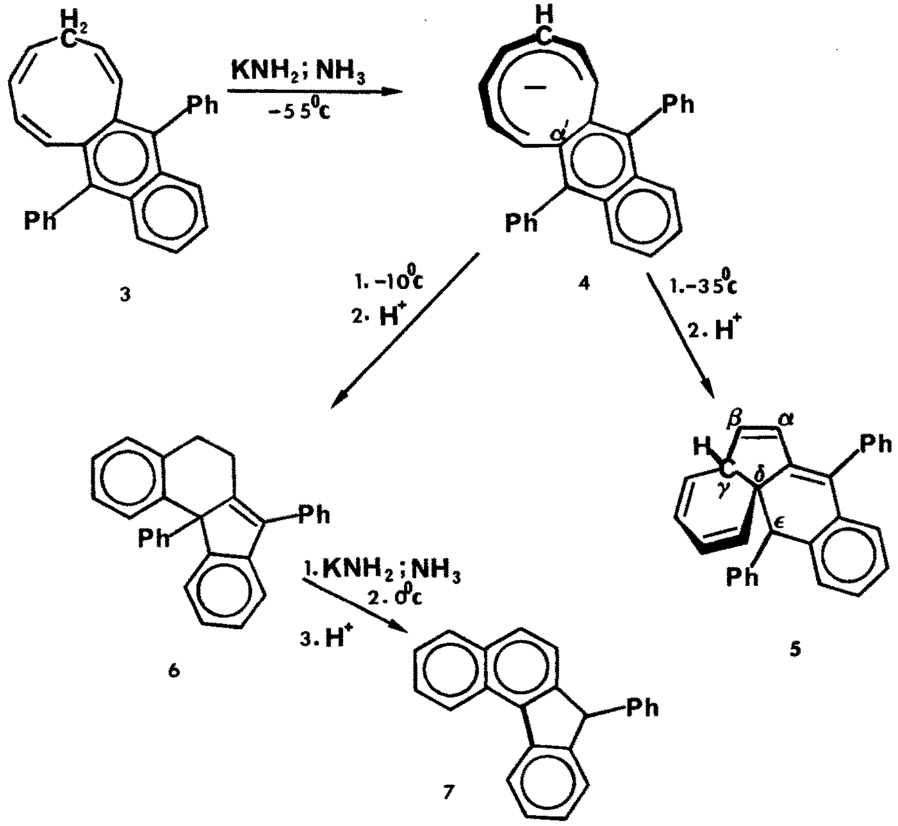
The sterically strained anion **4** was found to be thermally labile to subzero workup, readily undergoing temperature-dependent electrocyclization to a variety of tetracyclic frames.

Peri H,H interactions play a dominant role in the thermal stability of the skeletally all-cis benzo[9]annulene frame as attested by the surprising but well documented tendency of the benzocyclo nonatetraenyl anion **1a**[3] and its "aza" analog **1b**[4], to cleanly undergo cis → trans isomerization to **2** upon mild heating[5,6]. In an attempt to extend our insight into the nature and scope of this chemically productive steric effect we have generated the sterically congested naphthocyclononatetraenyl anion **4** and have examined its thermally induced chemical response.



The potentially aromatic (10π) naphtho[9]annulenyl system shown in **4** was produced upon exposure of conjugate acid **3**[7] to KNH_2 in liquid ammonia at -55°C. Anion **4** was found to be significantly more labile thermally than its less congested relative **1a**[3,5], defying NMR observation and rapidly undergoing deep-seated bond relocation instead of the anticipated cis → trans isomerization previously encountered with 1(a,b)[5,6]. Specifically, what one finds is that exposure of anion 4, generated at -55°C and allowed to stand at -35°C for 1-2 hours, to aqueous methanol (-35°C) yields not the anticipated conjugate acid 3 but rather the interesting "spiro"-like tetracycle depicted in 5 (mp. 187-188°C) whose structure consistently follows from conventional spectroscopic analysis ['H-NMR (200 MHz, $CDCl_3$)δ 7.7-6.9 (14H,m), 6.50 (1H,dd,J = 5.7,2.9Hz,H^{α} or H^{β}), 6.0 (1H,dd,J = 5.7,2.5Hz,H^{α} or H^{β}), 5.83 (1H,dd,J = 9.8,5.0Hz,"butadiene"), 5.6-5.4 (3H,m, "butadiene"), 4.08 (1H,s,H^{ϵ}), 3.45 (1H,dt,J = 2.7,2.5Hz,H^{γ}); ^{13}C-NMR (20 MHz, H-coupled, $CDCl_3$)δ_{TMS} 151-122 ("sp^2" centers), 58.14 (d,J_{CH} = 127Hz,C^{ϵ}), 5.73 (d,J_{CH} = 135Hz,C^{γ}), 47.31 (s,C^{δ}); MS (70eV) μ/e 370 (M^+, 100%)] and was further confirmed, unequivocally, through X-ray crystallography[8].



Interestingly, the nature of the thermal bond reorganization incurred by anion **4** is strictly temperature dependent insofar as warming the initial solution to ca -10°C prior to exposing it to aqueous methanol at -35°C, leads, cleanly not to **5** but to an isomeric tetracycle **6** [mp. 180-181°C; 'H-NMR (80 MHz, $CDCl_3$)δ 7.8-7.0 (18H,m), 3.0-2.5 (4H,m); ^{13}C-NMR (50 MHz, H-coupled, $CDCl_3$)δ 150-13 (8 singlets, quaternary "sp^2" centers), 130-120 (tertiary "sp^2" centers), 64,12 (s,C^{α}), 29.83 (t, J_{CH} = 133Hz, CH_2carbon), 22.95 (t,J_{CH} = 130Hz,CH_2carbon); MS(70eV) μ/e 370 (M^+, 74%)]. Particularly revealing of structure **6** is, of course, the ^{13}C-NMR spectrum which establishes the presence of three "aliphatic" carbon centers, two of which are secondary (CH_2) and one quaternary.

Exploring further, one discovers that exposure of either tricycle **3** or tetracycle **6** to KNH_2 in liq. NH_3 at ca.0°C followed by quenching with aqueous methanol at -35°C leads to the extrusion of one of the phenyl appendages with attendant aromatization and the formation of benzofluorene **7** (mp. 151-152°C) identical in all respects (mmp., 'H-NMR, IR, UV) with a synthetic sample[9] prepared[9b] from PPA-induced coupling of α-tetralone with benzophenone.

Concluding, it may be well worth stressing that the thermal instability of **4** leading to its operationally unexceptional[10] conversion to **5** may reasonably be viewed to derive from the sterically induced inability of the molecule's nine-membered moiety to achieve planarity and thus to delocalize its charge in attainment of its 10π "aromatic" potential.

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References and Notes

(1) Syracuse University.

(2) University of Petroleum and Minerals.

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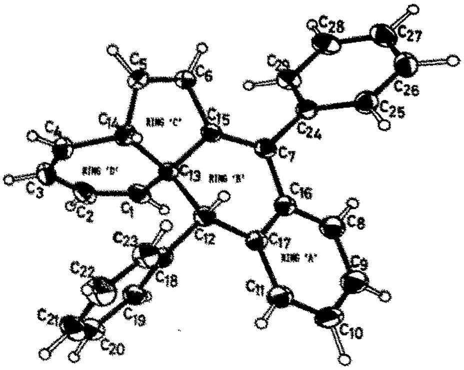
(8) Full details of this X-ray study (Fig. A) conducted at the University of Petroleum and Minerals by Professor M. Haque and his group will be published elsewhere.



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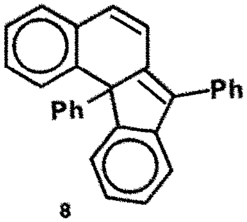
(10) While work relating to the operational details of the various transformations described in this report is currently in progress, it is perhaps worth noting at this early stage that (i) tetracycle **4** may readily be viewed to form upon intramolecular attack by the initially formed anion of **3** onto the α' center of the naphthalene appendage and (ii) a substance (mp.152-153°C), isolated on one occasion as a major byproduct during the preparation of **6** and believed to possess (^{1}H-,^{13}C-NMR,MS) structure **8** may well represent the key intermediate in the base induced conversion of **6** to **7**.



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