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"Highly Destabilized Carbocations," Generation and Rearrangements in the Reaction of 8,9,10,11-Tetrahydrocyclohepta[a]phenalen-6(12H)-one-12-ol and -7(12H)-one-12-ol with Sulfuric Acid

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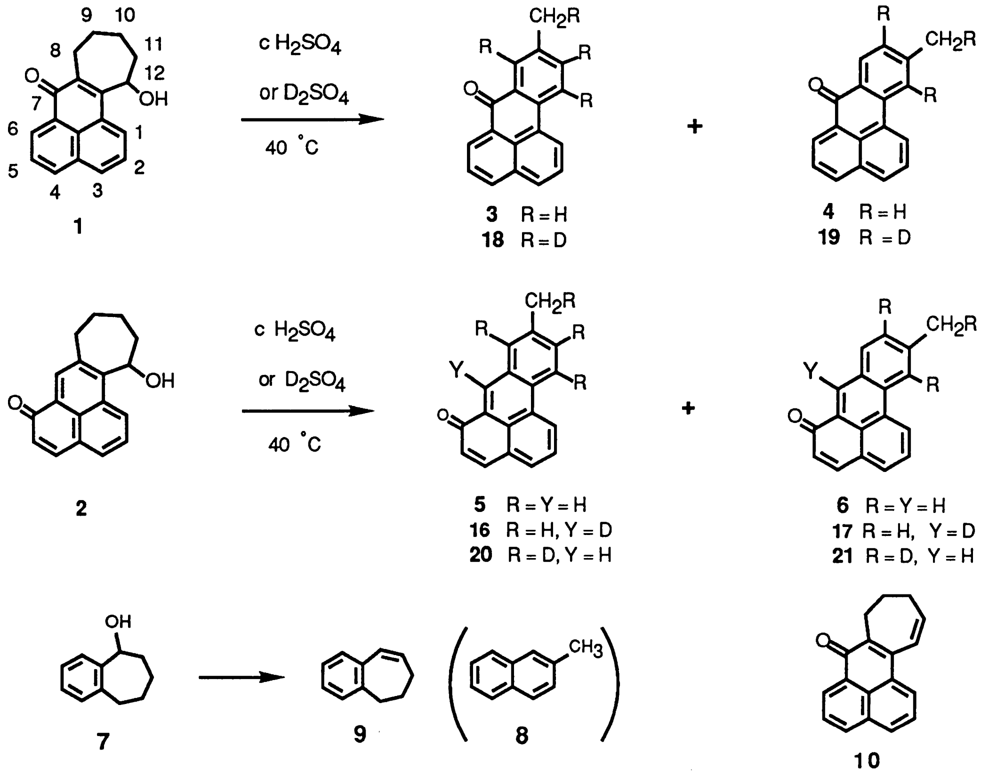
The reaction of 8,9,10,11-Tetrahydrocyclohepta[a]phenalen-6(12H)-one-12-ol and -7(12H)-one-12-ol with H_2SO_4 gave skeletally rearranged 9- and 10-methylbenz[de]anthracen-6-one and -7-one via destabilized vicinal dications.

Although aromatic dications and aliphatic dications separated by at least two carbons are often stable,[1] the "highly destabilized carbodications," where the adjacent two cation centers are substantially repulsive, have only been observed in gas phase mass spectrometric studies and in very strongly acidic conditions.[2] Then the rearrangement of such dication has not appeared so far. The present paper reports the generation and rearrangements, as the first example, of such adjacent carbodications in the reaction of 8,9,10,11-tetrahydrocyclohepta[a]phenalen-7(12H)-one-12-ol **1** and -6(12H)-one-12-ol **2**[3] with H_2SO_4, and the discussion on the mechanism based upon the deuterium labeling and related experiments.

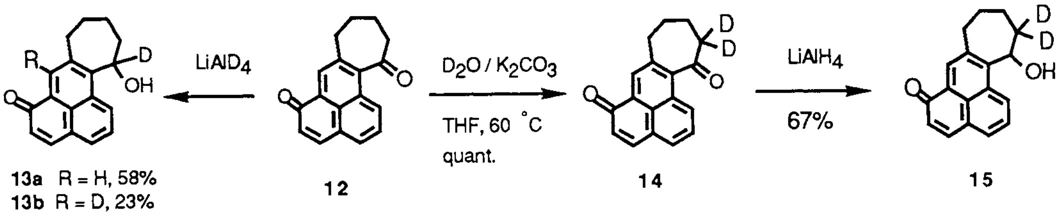
The experimental results are described as follows (Scheme 1). i) The reaction of **1** in H_2SO_4 at 45 °C for 45 min gave two isomers 9- and 10-methyl-benz[de]anthracen-7-ones (**3**[4] and **4**,[5] respectively) both in 36% yield. ii) The reaction of the positional isomer **2** containing the carbonyl group on the 6-position with H_2SO_4 under the same conditions as above also gave two isomers 9- and 10-methylbenz[de]anthracen-6-ones, **5** and **6**, in 25% and 57% yields, respectively.[6] iii) The reaction of a similar system 2,3-benzo-2-cyclohepten-1-ol **7**, having no phenalenone moiety, under the same conditions did not give **8** but only dehydrated compound **9** in 57% yield. iv) The reaction of an alternate compound 8,9,10,-trihydrocyclohepta[a]-phenalen-7-one **10**[3] with H_2SO_4 under the same conditions as above gave the rearranged products **3** and **4** in 46% and 23% yields, respectively, as in



Scheme 1.

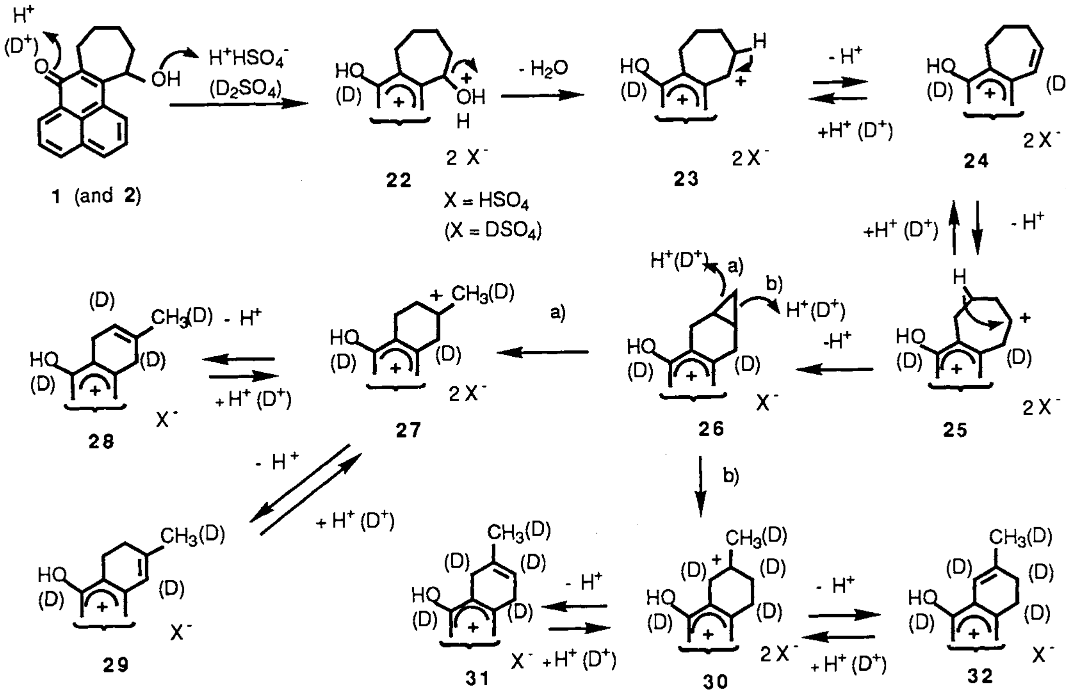
the case of **1**, where the cation center is expected to be formed at 11-position first as **25** by the protonation, rather than at 12-position in **23** due to the electronic repulsion between the two adjacent positive charges. v) Only **10** was obtained by the reaction of **1** with other acids such as polyphosphoric acid and a catalytic amount of p-toluenesulfonic acid in refluxing benzene. The use of a Lewis acid $AlCl_3$ gave unchanged starting material along with some decomposed products. vi) The individual reactions of **3**, **4**, **5**, and **6** in H_2SO_4 under the same conditions as above gave unchanged starting materials. vii) The ^1H NMR monitoring experiments of **1** in sulfuric acid-d_2 (D_2SO_4) showed the down field shifts for phenalenone moiety (cationic species) and gradual formation of methyl groups. viii) The deuteration on aromatic rings of **3**-**6** in D_2SO_4 at 50 °C, although actually occurs, was too slow at 9- and 10-positions to detect. The following are revealed by the above results; 1) The independence of the carbonyl position in phenalenone of **1** and **2** from the rearrangement. 2) The necessity of adjacent fused phenalenium dication for the carbocation shift in the initially formed cation **23** to form more stable **25** followed by the subsequent skeletal rearrangements. 3) The specificity of H_2SO_4 for these rearrangements. 4) Formation of only two methyl isomers from corresponding alcohols and that the methyl group does not migrate after aromatization.

To determine the origin of the methyl proton(s) and the methyl group,



Scheme 2.

the labeled compound having two deuteriums on 11-position **15** or a deuterium on the 12-position (**13a**, **13b**) were prepared from **12**[3)] by the conventional means as shown in Scheme 2, and subjected to the reaction under the same conditions as above. The rearranged compounds **5** and **6** from **15**, and **16** and **17** from **13b** did not retain deuterium on the methyl group. The reaction was also performed in D_2SO_4 by using **1** and **2** to know the positions where the deuteriums are incorporated. The reaction of **1** with D_2SO_4 gave deuterated compounds **18** and **19** both in 37% yield. Similarly, the reaction of **2** with D_2SO_4 under the same conditions as above gave deuterated compounds **20** and **21** in 26% and 57% yields, respectively. The methyl groups contained one deuterium and the newly formed benzene moieties possessed deuteriums on the adjacent positions of the methyl group. A reasonable explanation for these results is that the reaction proceeds through three-membered-ring intermediates formed from the cation in which the cationic center is located at the 11-position, followed by the ring opening by protonation[7)] to yield two isomers according to two different



Scheme 3.

bond cleavage pathways a) and b), and the reversible protonation on the adjacent positions of methyl group as shown in Scheme 3. This is new evidence for the reversible protonation in the migration of the cationic center (12- to 11-position) to adjacent position but not commonly accepted 1,2-hydride shift.8) The final dehydrogenation of rearranged compounds to aromatize is due to the strong oxidation ability of H_2SO_4,9) since the reaction of **2** with trifluoromethanesulfonic acid, a weeker oxidant than H_2SO_4, gave a complex mixture of rearranged dihydro-compounds of **5** and **6**. Then a plausible reaction mechanism is tentatively illustrated in Scheme 3.

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6) Selected physical properties of new compounds.

5: yellow needles, mp 154-155 °C(CH_2Cl_2-hexane); IR (KBr): 3050w, 1645vs, 1620s, 1580vs, 1258m, 1128m, 841s cm^{-1}; ^{1}H-NMR (90 MHz, $CDCl_3$, TMS) δ =8.96(s, 1H), 8.63 (d, J=8.6 Hz, 1H), 7.95 (s, 1H), 7.81 (d, J=9.90 Hz, 1H), 7.72 (m, 3H), 6.75 (d, J=9.90 Hz, 1H), 2.62 (s, 3H); MS(70 eV): m/z 244 (M^+, 100%).

6: yellow needles, mp 166-167 °C (hexane-CH_2Cl_2); ^{1}H NMR(90 MHz, $CDCl_3$, TMS) δ =9.10 (s, 1H), 8.91 (dd, J=7.80 & 1.80 Hz, 1H), 8.63 (d, J=1.32 Hz, 1H), 8.18 (d, J=8.30 Hz, 1H), 7.91 (d, J=9.90 Hz, 1H), 7.85 (m, 2H), 7.66 (dd, J=8.30 & 1.32 Hz, 1H), 6.85 (d, J=9.90 Hz, 1H), 2.79 (s, 3H); MS(70 eV): m/z 244 (M^+, 100%).

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