Fragmentation of 1-hydroxy-2-(5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl)-1-phenylethyl cation in superacid

S. A. Osadchii,[a]* *M. D. Stanescu*,[b] *V. I. Mamatyuk*,[a] *and V. G. Shubin*[a]

[a]*Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, 7 prosp. Akad. Lavrent'eva, 630090 Novosibirsk, Russian Federation. Fax: +7 (383 2) 354 752*

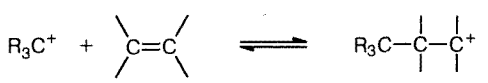
[b]*Department of Organic Chemistry, Bucharest Polytechnic Institute, 76206 Bucharest, Romania*

The 1-hydroxy-2-(5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl)-1-phenylethyl cation generated under "long life" conditions undergoes fragmentation to afford 5*H*-dibenzo[*a*,*d*]cycloheptenyl- and methylphenylhydroxycarbinyl cations but does not undergo carbocationic cyclization.

Key words: ethyl cation, 5*H*-dibenzo[*a*,*d*]cycloheptene, 5*H*-dibenzo[*a*,*d*]cycloheptenylium cation, fragmentation, superacid.

The key step in cationic polymerization, *i.e.*, the formation of a carbocation—olefin adduct, is a reversible process (Scheme 1).[1] The reverse reaction (heterolytic fragmentation) is a widespread type of organic reaction.[2] The carbocation being eliminated plays the role of a leaving group in the fragmentation (elimination), and so the fragmentation rate depends on the stability of the former.

Scheme 1

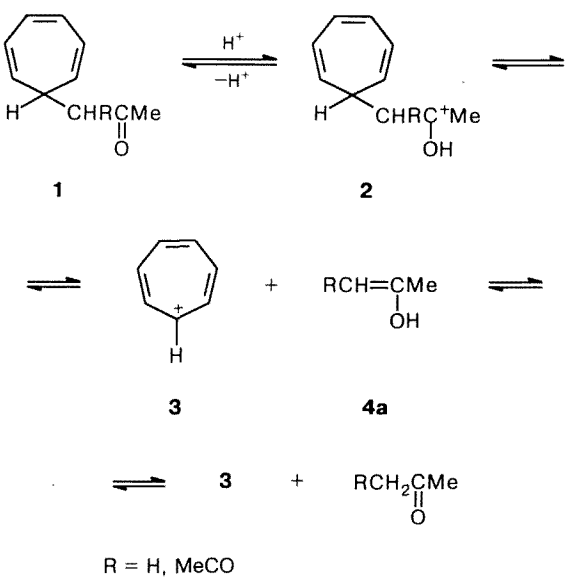


The high stability of tropilium cation (**3**) as a "leaving group" was considered to be the reason for fragmentation of cations **2**, the assumed intermediates of acidic cleavage of ketones (**1**) (Scheme 2).[3]

As has been determined earlier,[4] the equilibrium in a similar system under similar conditions (Scheme 3) is almost completely shifted to the left. This probably results from the fact that 5*H*-dibenzo[*a*,*d*]cycloheptenyl cation (**7**) has significantly lower relative stability than tropilium ion **3** ($\Delta\Delta pK_{R^+} = 8.45$).[5]

Therefore, one may assume that the predominant path for the transformation of cation **6**, the protonated form of ketone **5**, in a strongly acidic medium (*cf.* the data on the basicity of 1-phenylethanone[6]) is not fragmentation (see Scheme 3, path *a*) but carbocationic cyclization with the formation of the corresponding benzyl ions (**10**) (path *b*) (*cf.* Ref. 7).

Scheme 2



R = H, MeCO

To check this assumption, we attempted to generate the 1-hydroxy-2-(5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl)-1-phenylethyl cation (**6**) by the protonation of 2-(5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl)-1-phenylethanone (**5**) in a superacidic medium and to study its reactivity.

According to ^{1}H NMR data, the starting ketone **5** in $CDCl_3$ at ~20 °C consists of two conformers in ≈13 : 1 ratio.* A comparison of chemical shifts of the CH_2 and

* The minor conformer has not been determined earlier.[4,13]

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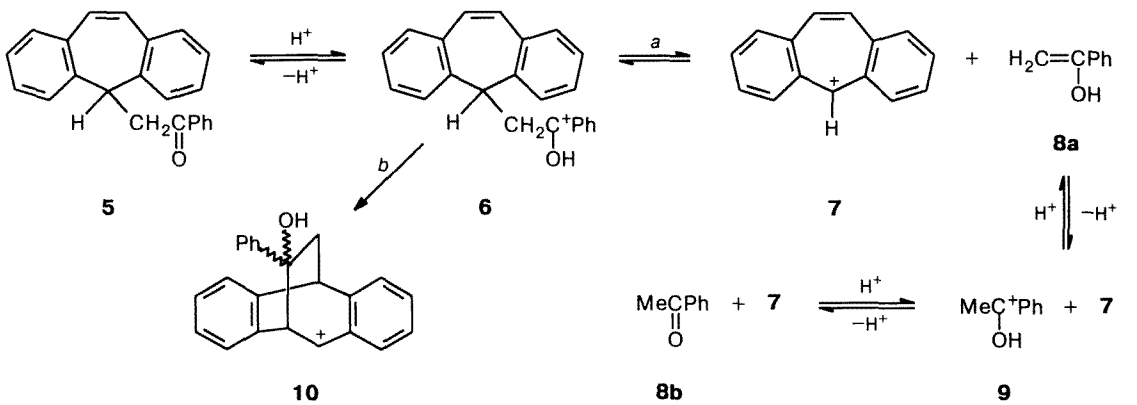
Scheme 3



5-CH groups with those of the known 5-substituted 5*H*-dibenzo[*a*,*d*]cycloheptenes[8] allowed us to attribute the signals in the ^{1}H NMR spectrum obtained and to determine that the orientation of the bulky $PhCOCH_2$ substituent at the C(5) atom in the predominant conformer ($\mathbf{5}_{ax}$) is axial (Scheme 4, *cf.* Ref. 8).

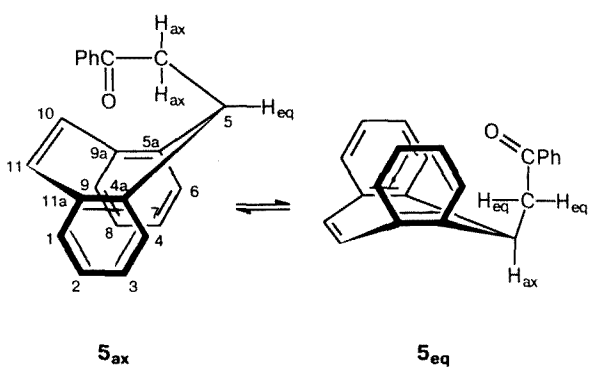
The protonation of ketone **5** at the oxygen atom may possibly afford cation **6** in the form of an equilibrium mixture of the $\mathbf{6}_{ax}$ and $\mathbf{6}_{eq}$ conformers, but only one of these ($\mathbf{6}_{ax}$) has an arrangement of the carbocationic center and the C(10)=C(11) bond favorable for cyclization, *i.e.* converging arrangement with proper orbital orientation.

The ^{1}H NMR spectrum of an acidic solution of ketone **5** (HSO_3F—SO_2FCl—CD_2Cl_2, −80 °C) contains signals of two conformers of 1-hydroxy-2-(5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl)-1-phenylethyl cation **6** in a ≈ 13 : 1 ratio. The signals were assigned by analogy with conformers $\mathbf{5}_{ax}$ and $\mathbf{5}_{eq}$ (*cf.* Ref. 8).

Increasing the temperature of the solution to −40 °C leads to a rapid decrease in the intensity of signals in the ^{1}H NMR spectrum of cation **6** ($\tau_{1/2}$ = 5 min) and to the appearance of signals of 5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl and methylphenylhydroxycarbinyl cations (cations **7** and **9**, respectively), whose ^{1}H NMR spectra are known.[9,10] After keeping the solution at −20 °C for 5 min, only signals of cations **7** and **9** (in 1 : 1 molar ratio) are observed. The signals corresponding to other carbocations were not found.

Thus, the assumption about the possibility of carbocationic cyclization of ion **6** was not confirmed. Fragmentation is the only way for its transformation in a superacidic medium. The possible reason for this is a sufficiently high stability of the cations **7** and **9** formed.

Scheme 4



$\mathbf{5}_{ax}$ $\mathbf{5}_{eq}$

Experimental

^{1}H and ^{13}C NMR spectra of ketone **5** and cation **6** were recorded on a Bruker AC 200 instrument (200.13 MHz for ^{1}H NMR and 50.32 MHz for ^{13}C NMR spectra). ^{13}C NMR spectra were obtained under conditions that totally suppressed ^{13}C—^{1}H coupling and with non-resonance irradiation of protons. The internal standards used were $CHCl_3$ (δH 7.24) and $CDCl_3$ (δC 76.9) for neutral compounds and methylene chloride (δH 5.33, δC 53.3) for ions.

The molecular mass and elementary composition of ketone **5** were determined using a Finnigan MAT 8200 high resolution mass spectrometer.

Protonation of carbocations was carried out using HSO_3F and SO_2FCl purified by the known procedure.[11] The procedure for withdrawing samples of solutions of the salts for spectral studies was described earlier.[12]

2-(5*H*-Dibenzo[*a*,*d*]cyclohepten-5-yl)-1-phenylethanone (5) was synthesized by the known procedure[4] from 5*H*-dibenzo[*a*,*d*]cycloheptenilium perchlorate[10] and 1-phenylethanone (*cf.* Ref. 13). The mass spectrometrically determined mass M was 310.1354; the elementary composition was $C_{23}H_{18}O$. ^{1}H NMR ($CDCl_3$), the predominant conformer with equatorial arrangement of H(5), δ: 3.57 (d, 2 H, CH_2, J = 7 Hz); 5.05 (t, 1 H, H(5), J = 7 Hz); 7.12 (s, 2 H, H(10), H(11)); 7.15—8.25 (m, 13 H, protons of aromatic rings); the minor conformer with axial arrangement of H(5): 4.20 (2 H, CH_2); 4.33 (1 H, H(5), AB_2 system, J = 7 Hz); the other signals overlap. The signals of

the minor conformer are difficult to find in the ^{13}C NMR spectrum (25 °C, 10 % solution in $CDCl_3$) due to their low intensities. ^{13}C NMR, the predominant conformer with equatorial arrangement of H(5), δ: 39.1 (t, CH_2); 48.9 (d C(5)); 126.5 (d), 127.5 (d), 127.6 (d), 128.3 (d), 129.4 (d), 129.6 (d), 130.9 (d, C(1)—C(4), C(6)—C(11), C_o and C_m Ph); 132.9 (d, C_p Ph), 133.7 s, 140.0 (s, C(4a), C(5a), C(9a), C(11a)), 136.8 (s, C_{ipso} Ph), 198.1 (s, C=O).

1-Hydroxy-2-(5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl)-1-phenylethyl cation (6). A solution of ketone **5** (0.089 g) in CD_2Cl_2 (0.18 mL) was cooled to −100 °C, and then SO_2FCl (0.38 mL) cooled to −100 °C was added dropwise with stirring. An HSO_3F—SO_2FCl mixture (0.38 mL, 1 : 4 v/v) cooled to −100 °C was added dropwise with stirring to the solution obtained. The mixture was stirred for 5 min at −100 °C. ^1H NMR (−80 °C), the predominant conformer with equatorial arrangement of H(5), δ: 3.81 (d, 2 H, CH_2, J = 7 Hz); 4.67 (t, 1 H, H(5), J = 7 Hz); 6.9—8.9 (m, 15 H, H(1)—H(4), H(6)—H(11), Ph); 14.3 (br, 1 H, OH); the minor conformer with axial arrangement of H(5): 4.0—4.2 (m, 3 H, CH_2 and H(5)); the other signals overlap. ^{13}C NMR, δ: 38.2 (t, CH_2); 56.1 (d, C(5)); 128—138 (m) and 144.9 (d, carbon sp^2-atoms); 218.4 (C^+).

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