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THE MECHANISM OF DEHYDRATION OF 4-HYDROXYMETHYL-12-HYDROXYTETRACYCLO[7.3.1^{2,7}.0^{6,11}]TRIDECANE

Using the semiempirical program PM3 revision of the before proposed scheme of the convertions 4-hydroxymethyl-12-hydroxytetracyclo[7.3.1^{2,7}.0^{6,11}]tridecane in a hot phosphoric acid was realized. According to new proposed scheme, where disadvantageous stages of Wagner-Meerrwein rearrangements are absent, a final product should be 4-methyl-5-oxotetracyclo [7.3.1^{2,7}.0^{6,11}]tridecane. We suggested explanation of absence of methyloxadiamantane in reaction products.

Our previous communications [1,2] described the Baeyer-Villiger oxidation of diamantanone and reduction of isomeric lactones, generated from it. In that way was synthesized 4-hydroxymethyl-12-hydroxytetracyclo[7.3.1^{2,7}.0^{6,11}]tridecane (1) and its isomer — 4-hydroxy-12-hydroxymethyltetracyclo-[7.3.1^{2,7}.0^{6,11}] tridecane (20) [3]. The last diol at heating up to 170—190 °C with 85% phosphoric acid mainly gave 3-methyl-2-oxadiamantan (22). Differently behaved 4-hydroxymethyl-12-hydroxytetracyclo[7.3.1^{2,7}.0^{6,11}] tridecane (1): it thus underwent a pinacoline similar rearrangement giving ketone. Ketone structure couldn't be exactly determine on the basis of spectral data. The suggested scheme of transformations come to an end on 3-methyl-11-oxotetracyclo[6.4.1.0^{2,6}.0^{5,10}] tridecane (8) and included consecutive stages Wagner-Meerwein rearrangement, which frequently meet in reactions of cage substances [4].

Scheme 1 is taken from work [2], it is complemented only intermediate tertiary cation (3). It is evident clear, that two 1,2-hydride shifts and two Wagner-Meerwein rearrangements are the parts of assumed process. The intermediate cationes in the scheme are isomeric, and the conditions of reaction promote to achieve the thermodynamic equilibrium. It allows with sufficient reliability to use computational methods, which was widely used for an estimation of a degree of probability of chemical transformations. In the given work was used a semiempirical method PM3 as implemented in the GAMESS [5]. The values of total energy of reaction products and intermediate compounds and states (E_{tot}, *a.u.*), and also values of conversion enthalpy (ΔE_i, kJ/mol), are below given.

We shall analyze by stages the computational data of conversions on the later proposed track (Scheme1). Primary cation (1) can be ignored as independent intermediate, as experimental results not confirm of similar particles formations even in conditions of Wagner-Meerwein rearrangements [6, 7]. Solvolytic splitting off primary hydroxyl should go synchronously with splitting off of a proton and result to alkene (10). It in experiment conditions fast enough follows via protonation-deprotonation in alkene (11). Both products (10 and 11) at convertible protonation will give the same tertiary cation (3). The following three stages will be of interest for us, as they are the acts of cation isomerisation, and therefor it is possible to neglect solvation processes. As 1,2-hydride shift (3 → 4), and following Wagner-Meerwein rearrangement processes (4 → 5 and 5 → 6) pass with absorption of energy (Table 1), and total enthalpy increments included its three stages is 119.6 kJ/mol. In a deprotonation stage (6 → 7) the computation energy deficiency is compensated by a proton solvation, which does not give to estimate. Anyway it is enough of three intermediate stages, which should be disadvantageous, to engender doubt in reliability of this scheme. Such result stimulated our searches of the alternative decisions. One of possible variants was alternative on a direction of movement of electrodeficiency centre — namely — from primary hydroxyl to secondary (Scheme 2). Thus we have assumed, that in conditions of reaction promoting dehydration, the substance (10) and, further, (11) will be formed first of all, but secondary hydroxyl, not capable to dehydration, will be split off in the second turn. Stages, determining a direction of process, will be three ones 1,2-hydride shift (12 → 13), (13 → 14) and (14 → 15). As appears from the Table 1, the values of transformation enthalpy at all three these stages have negative quantity and the total effect makes 62.4 kJ/mol. The direct migration of hydride in substance (12) from allylic position to electrodeficien carbon atom (12 → 15) is possible also, by the way, hydride ion need to overcome distance only 3,2Å. The stages (16 → 17) and (17 → 18) are migrations of double bond with value of total transformation enthalpy –17.1 kJ/mol. At last, we shall pay attention, that formed 4-methyl-5-oxotetracyclo[7.3.1^{2,7}.0^{6,11}]tri-

decane (19) on 28.2 kJ/mol is less strained in comparison with ketone (8) of the initial scheme.

Table 1. **Calculated volues of total energy of compounds and intemediated cationes (E_{tot}) and enthalpies its transformations (ΔE_i)**

Initial substance		End substance		Transformation enthalpy, ΔE_i, кДж/моль
№	E_{tot}, a.e.	№	E_{tot}, a.e.	
1	-95.0796	3	-83.4140	909.3
1c[1]	-95.0871	3	-83.4140	929.0
3	-83.4140	4	-83.3985	40.6
4	-83.3985	5	-83.3805	47.4
5	-83.3805	6	-83.3685	31.6
6	-83.3685	7	-83.1215	648.3
7	-83.1215	8	-83.1374	-41.4
1	-95.0796	10	-83.1249	38.2
10	-83.1249	11	-83.1350	-26.4
11	-83.1350	12	-71.4347	1000.4
12	-71.4347	13	-71.4402	-14.4
13	-71.4402	14	-71.4438	-9.5
14	-71.4438	15	-71.4584	-38.5
15	-71.4584	16	-83.1349	-937.8
16	-83.1349	17	-83.4094	1802.9
17	-83.4094	18	-83.1414	-1820.0
18	-83.1414	19	-83.1502	-22.9
1a[2]	-170.0246	3a[3]	-120.9476	470.2
3a[3]	-120.9476	4a[3]	-120.8627	223.0
4a[3]	-120.8627	5a[3]	-120.9127	-131.4
5a[3]	-120.9127	6a[3]	-120.9026	26.5
6a[3]	-120.9026	7a[3]	-120.6485	667.3
1b[4]	-170.1361	3b[5]	-120.9476	763.1
3b[5]	-120.9476	4b[5]	-120.9196	73.5
4b[5]	-120.9196	5b[5]	-120.8649	143.7
5b[5]	-120.8649	6b[5]	-120.9096	-117.4
6b[5]	-120.9096	7a[3]	-120.6485	685.6
1	-95.0796	10	-83.1249	38.2
10	-83.1249	11	-83.1350	-26.4
11	-83.1350	12	-71.4347	1000.4
12	-71.4347	13	-71.4402	-14.4
13	-71.4402	14	-71.4438	-9.5
14	-71.4438	15	-71.4584	-38.5
15	-71.4584	16	-83.1349	-937.8
16	-83.1349	17	-83.4094	-720.8
17	-83.4094	18	-83.1414	703.7
18	-83.1414	19	-83.1502	-22.9

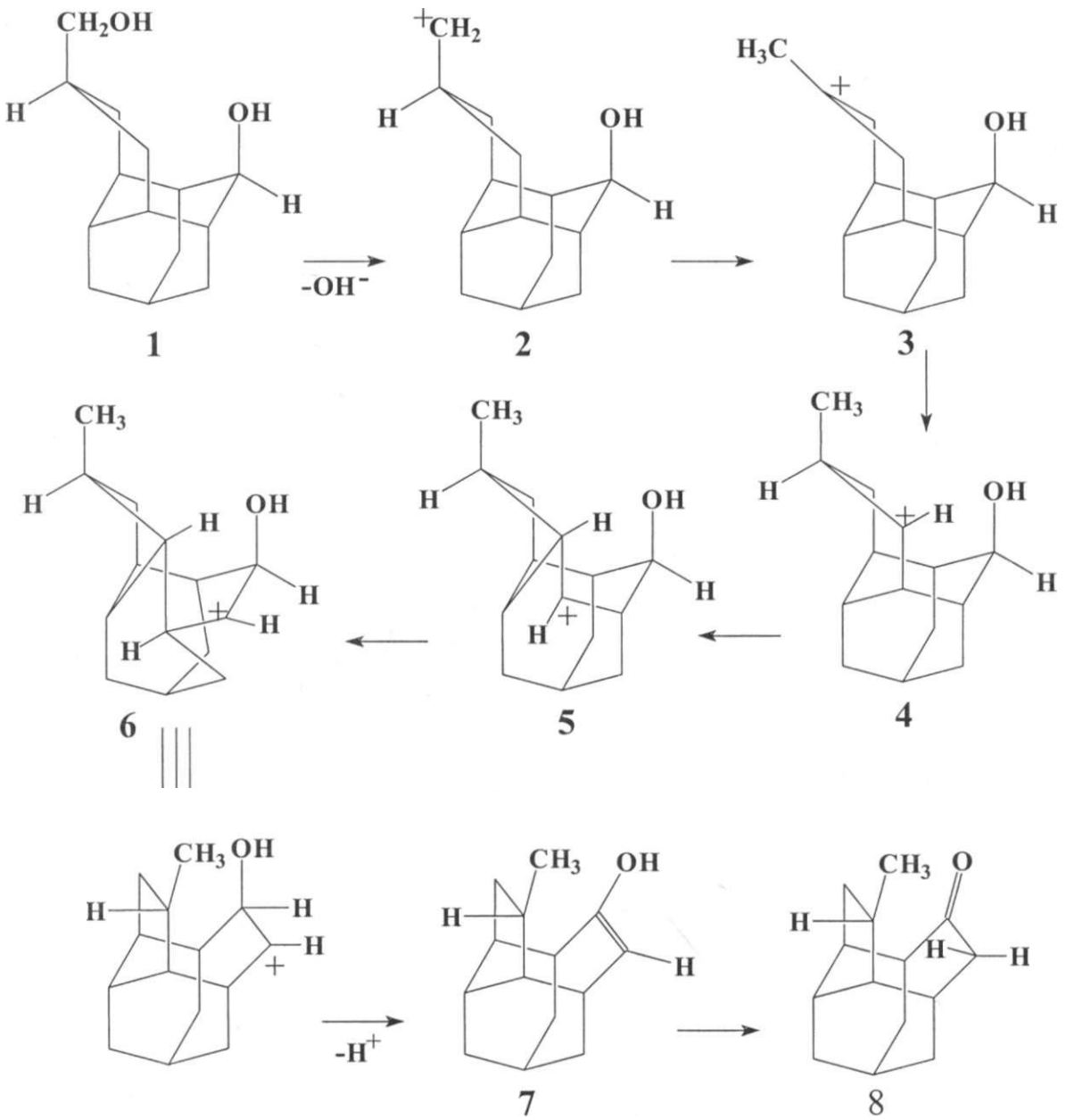
[1] X = H; R_1 = H; R_2 = OH.
[2] X = PO_3H_2; R_1 = OPO_3H_2; R_2 = H.
[3] R_1 = OPO_3H_2; R_2 = H.
[4] X = PO_3H_2; R_1 = H; R_2 = OPO_3H_2.
[5] R_1 = H; R_2 = OPO_3H_2.

Our calculations are made of the assumption, that hydroxyl during conversions not phosphorylated. For the Scheme 2 these circumstances do not play first fiddle, since in key stages just not containing hydroxyl cationic intermediates take part. Concerning the Scheme 1 it cannot be told. We checked an opportunity of the reaction passing through phosphorilated compounds and have repeated computation for completely phosphorilated initial diol (1a: X = PO_3H_2; R_1 = = OPO_3H_2; R_2 = H) [Scheme 3]. The transformations should proceed through the following intermediates: 1a → 3a → 4a → 5a → 6a → 7a. Let's consider key stages (3a → 4a), (4a → 5a) and (5a → 6a). There is sharp increase in absolute values enthalpy transformations. Two of three stages have positive enthalpy values, and the so high values for (3a → 4a) practically completely prevent from transformations according to this scheme.

So far as the spectral data do not contradict new structure ketone? 4-Methyl-5-oxotetracyklo-[7.3.1^{2,7}.0^{6,11}]tridecane (19), as well as ketone (8) relate to C_1 group of symmetry, has identical numbers of carbon atoms differing on a substitution degree, that permit of ^{13}C NMR data attributing with its structure. Moreover, the intensive ion at m/z 133 (37%) in EI mass spectra ofketone easier for interpreting as the loss of containing functional group fragment from adamantane skeleton of substance (19). Such fragmentation is characteristic for derivative of adamantane [8], whereas in the case ofketone (8), as homoadamantane derivative, ion at m/z 147 must be more intensive (but it make up only 9%).

Thus, as we consider, there are many reasons for the benefit of reconsideration of a conclusion about structure ketone, which is formed as a result ofheating 4-hydroximethyl-12-hydroxytetracyclo[7.3.1^{2,7}.0^{6,11}] tridecane (1) in a phosphoric acid. The final determination of this problem can be get only by direct definition, for example by means of X-ray analysis, or counter synthesis.

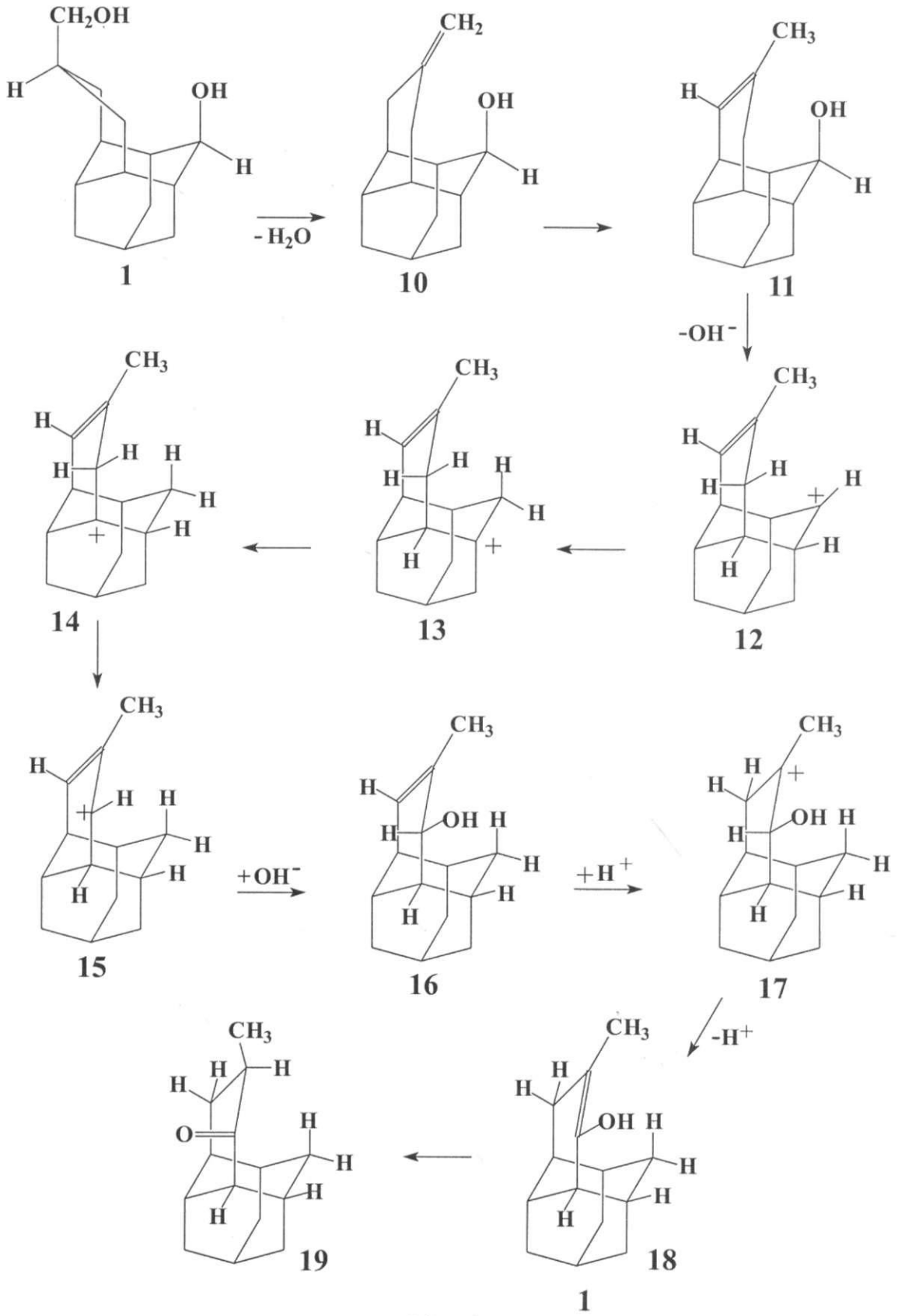
There is one more ambiguity connected to reactivity(l) and (20) in phosphoric acids. Why at essential affinity of structures they so differ on character of obtained products? We try to approach to the answer to this question, using computational methods. Thus, under Scheme 4 [2] diol (20) by transannular deprotonation via transition cation (21) mainly formed 3-methyl-2-oxadiamantan (22). From the Scheme 2: alkenes (10) and (11) by protonation double bond can yield tertiary cation, isomer of cation (21), which is also able with ring closure to form l-methyl-2-oxadiamantan. What can prevent from such process? This reaction, for example, shall not take place, if the hydroxyl will be directed to the opposite side. Suppose diol (1) isomerize yet at the first stage, allowing diol (1c: X = H, R_1 = H, R_2 = OH), for which the calculated



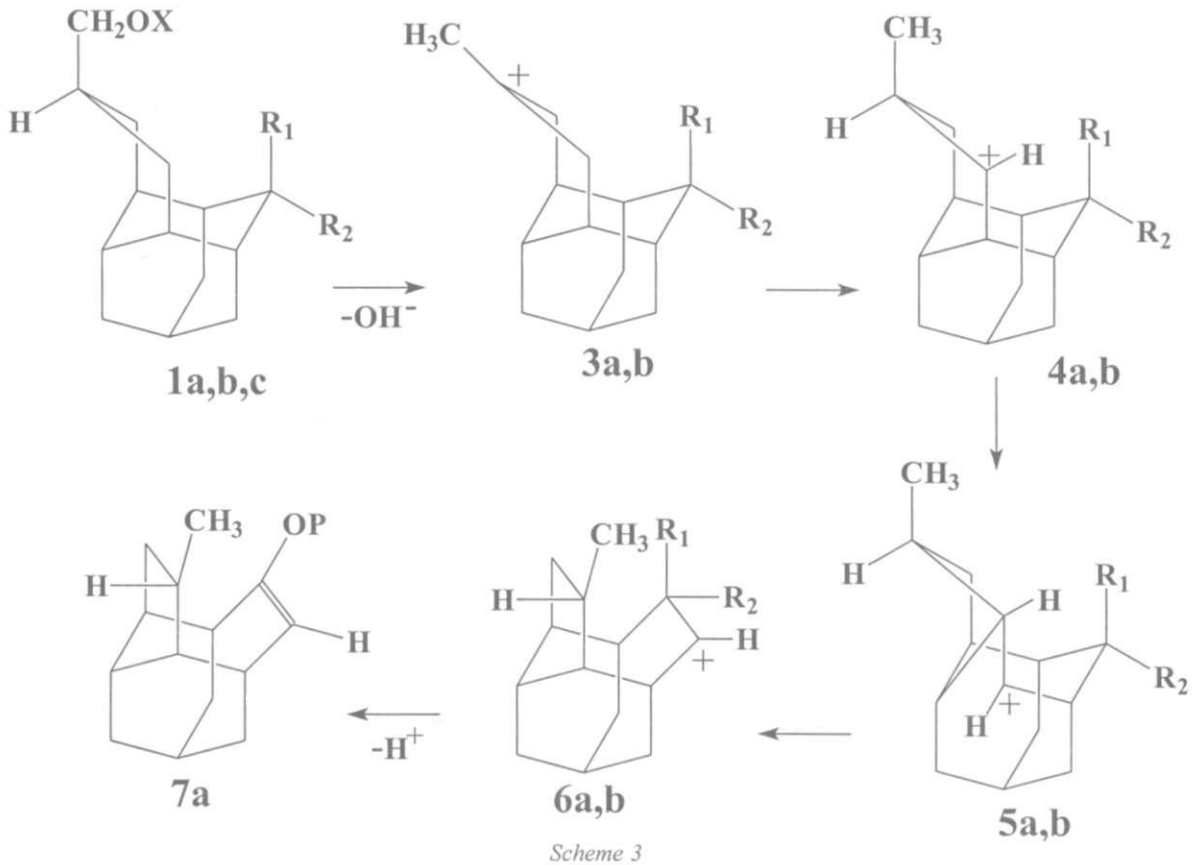
Scheme 1

values E^{tot} on 19.7 kJ/mol is less, than for initial diol. Though this isomerization is thermodynamic favorable, it is poorly probable, that such reaction take place in the concentrated phosphoric acid. Likely the substitution of hydroxyl by phosphate group become The value of total energy of diphosphate (1b: X = = PO^3H^2; R^1 = H; R^2 = OPO^3H^2) is smaller by 292.9 kJ/mol than its for diphosphate (1a: X = PO^3H^2; R^1 = OPO^3H^2; R^2 = H). It could stimulate during phosphorylation fast formation diphosphate (1b), it is incapable of conversion to 1-methyl-2-oxadiamantane. However now we have to repeat our computation likely Scheme 1, but for phosphorylated derivatives of diol (1). In the pathway 1b → 3b → 4b → 5b → 6b → 7a (Scheme 3) at the two first key stages from three [(3b → 4b), (4b → 5b) and (5b → 6b)] the values of conversion enthalpy are positive (mounting to 143.7 kJ/mol for 3b → 4b). Therefor, the formation of ketone (8) is improbable as well as via phosphorylation pathway.

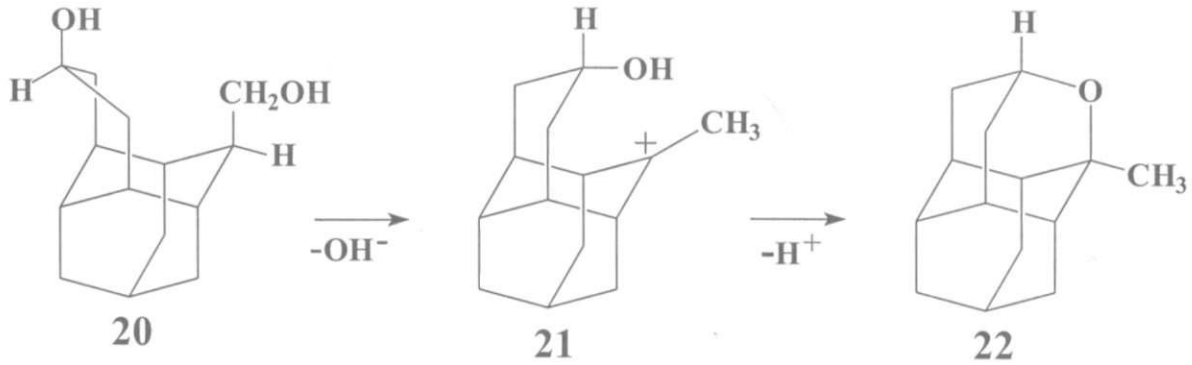
Thus results of computations allow to make the assumption, that heating of 4-hydrohymethyl-12-hydrohytetracyklo[7.3.$1^{2,7}$.$0^{6,11}$]tridecane (1) with the concentrated phosphoric acid yields 4-methyl-5-oxotetracyklo[7.3.$1^{2,7}$.$0^{6,11}$]tridecane (19), and this process proceeds via phosphorylated transition structures and at early steps secondary hydroxyl upon S^N2 mechanism is replaced on phosphoryle.



Scheme 2



Scheme 3



Scheme 4

1. *Ondráček J., Janků J., Novotný J.* et al. The Bayer—Villiger oxidation of Diamantanone and the structure of 11-oxo-10-oxapentacyclo[7,4,1,1,$1^{4,13}$,$0^{2,7}$,$0^{6,12}$]pentadecane // Collect. Czech. Chem. Commun.— 1989.— Vol. 54.— P. 3260—3266.
2. *Янку И., Голованюк А. Н., Цыбульский А. В.* и др. Синтез 10- и 11-окса-2(3)-гомодиамантана // Журнал орг. химии.— 1990.— Т. 26.— № 6.— С. 1366—1368.
3. *Janků J., Isaev S. D., Cibulskii L. Vol., Vodicka L., Yurchenko A. G.* Reaction of isomeric oxo-2(3)-oxohomodiamantanes. Dehydration of tetracyclic diols with concentrated phosphoric acid // Collect. Czech. Chem. Commun.— 1990.— Vol. 55.— P. 2475—2480.
4. *Багрий Е. И.* Адамантаны. Получение, свойства, применение.— М.: Наука, 1989.— 264 с.
5. *Schmidt M. W., Baldridge K. K., Boatz J. A.* et al. General Atomic and Molecular electronic-structure system // J. Comput. Chem.— 1993.— Vol. 14.— P. 1347—1363.
6. *Степанов Ф. Н., Гуц С. С.* Адамантан и его производные. XVI. Об электролизе адамантил-1-уксусной и гомоадамантан-3-карбоновой кислот // Журн. орг. химии.— 1968.— Т. 4.— № 11.— С. 1933—1936.
7. *Степанов Ф. Н., Гуц С. С.* О некоторых перегруппировках производных адамантана // Изв. АН СССР. Сер. химия.— 1970.— № 2.— С. 430—434.
8. *Вульфсон Н. С., Заикин В. Г., Микая А. И.* Масс-спектрометрия органических соединений.— М.: Химия, 1986.— 312 с.

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МЕХАНІЗМ ДЕГІДРАТАЦІЇ 4-ГІДРОКСИМЕТИЛ-12-ГІДРОКСИТЕТРАЦИКЛО[7.3.1.^{2,7}.0^{6,11}]ТРИДЕКАНА

Використовуючи напівемпіричну квантово-хімічну програму PM3, зроблена ревізія запропонованої раніше схеми перетворень 4-гідроксиметил-12-гідрокситетрацикло[7.3.1.^{2,7}.0^{6,11}]тридекану в гарячій фосфорній кислоті. Згідно з новою схемою, в якій відсутні термодинамічно невигідні стадії перегрупування Вагнера-Мейвейна, кінцевим продуктом має бути 4-метил-5-оксотетрацикло[7.3.1.^{2,7}.0^{6,11}]тридекан. Запропоновано пояснення причин відсутності у продуктах реакції циклічних ефірів, як це має місце у випадку ізомерного 4-гідрокси-12-гідроксиметилтетрацикло[7.3.12.$^{7.06,11}$]тридекана.

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Гребенюк А. Г.

КВАНТОВО-ХІМІЧНЕ ДОСЛІДЖЕННЯ УТВОРЕННЯ ІОННИХ СТРУКТУР У МОЛЕКУЛЯРНИХ АСОЦІАТАХ ПЕНТАХЛОРИДУ ФОСФОРУ

Методом СУП МО ЛКАО у напівемпіричному наближенні PM3 розраховано рівноважну геометрію й ентальпію утворення молекулярних та іонізованих асоціатів пентахлориду фосфору. Виявлено, що мінімальний зародок кристалічної фази складається принаймні з восьми формульних одиниць.

Сучасна хімія неорганічних сполук багато уваги приділяє дослідженню будови та властивостей частинок речовини, розміри яких є проміжними між молекулами та кристалами і вимірюються нанометрами. Найважливішою рисою таких об'єктів є можливість структурно-хімічних перетворень, зумовлених зміною їхніх розмірів. Саме до таких сполук належать галогеніди [1], зокрема, пентахлорид фосфору [2, 3]. Пропонована стаття присвячена дослідженню особливостей просторової та електронної будови, а також енергетики малих частинок цієї речовини, які можуть брати участь у процесах утворення твердої фази.

Квантово-хімічні розрахунки виконано напівемпіричним методом СУП МО ЛКАО PM3 [4, 5], який добре зарекомендував себе у дослідженнях гіпервалентних структур та міжмолекулярної взаємодії, задопомогою програми [6]. Результати розрахунків наведено в таблицях 1 та 2.

У газоподібному стані пентахлорид фосфору складається переважно з мономерів, з невеликою домішкою димерних молекул, тоді як у твердому стані за нормальних умов — з іонів $[PCl^4J^+$ та $[PCl^6]^-$, хоча при охолодженні до 90 ^{0}K можливе утворення твердої форми речовини, кристалічна гратка якої складається з окремих молекул [3].

За даними [7, 8], молекула PCl^5 має форму тригональної біпіраміди з довжиною аксіального зв'язку P—Cl 212, а екваторіального — 202 пм; ентальпія утворення її становить -371 кДж/моль. Розрахунок методом PM3 цілком задовільно відтворює ці величини (відповідно 209, 205 пм та -467 кДж/моль). Кристалічний пентахлорид фосфору утворює тетрагональні кристали [9], побу-