

Pyrene Dimerization into 1,1'-Dipyrenyl

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Abstract—Treatment of pyrene and some its derivatives with Cu(II) tetrafluoroborate or perchlorate in CH₃CN cleanly led to the formation of 1,1'-dipyrenyls. The other polycyclic hydrocarbons (anthracene, perylene) under the same conditions provide cation-radicals. 1,1'-Dipyrenyl strongly differs from pyrene in the chemical behavior: it does not undergo either formylation by Vilsmeier reaction, neither acylation (AcCl, ZnCl₂) or nitration (by pyridinium nitrate in boiling pyridine whereas the pyrene is easily involved into these reactions.

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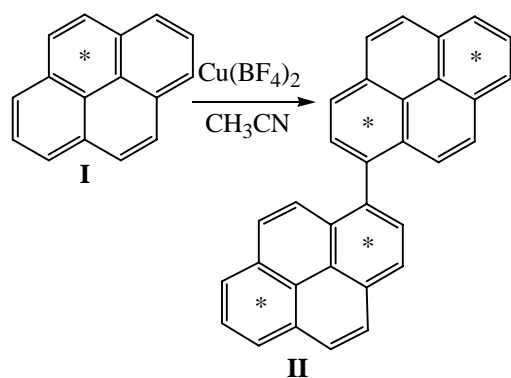
Among the multitude of polycyclic hydrocarbons we marked out [1] a group of so-called cyclic polyenes, compounds containing a diene or polyene group in the contiguous aromatic rings. The simple benzoid polycycles, for instance, naphthalene or phenanthrene, do not belong to these polyenes. On the contrary, anthracene, tetracene, pyrene, and perylene are typical examples of the cyclic polyenes. The only criterion of the membership of this group is the reaction with nitric acid generated from the pyridinium nitrate in boiling pyridine. It is presumed that the nitration action is produced by undissociated (molecular) nitric acid HO–NO₂ that adds to the terminal atoms of the heteroannular diene (positions 9 and 2 in the anthracene). Only the mentioned polyenes are involved into this reaction, whereas benzene derivatives naphthalene and phenanthrene are totally inert [1]. The difference in the reactivity exists also in other reactions, for example, practically all the cyclic polyenes readily enter into the oxidative substitution consisting in combined action of an oxidant (commonly Cu²⁺ ion) and of the oxidizable component (R[–], R', or R–R) [2, 3]. The attempts to carry out the same reactions with naphthalene were unsuccessful.

The term “cyclic polyene” should not be understood in the sense of a constant presence in the molecule of the heteroannular diene. Under the common conditions of electrophilic substitution, e.g., of nitration, there is no significant difference in behavior of between phenanthrene and anthracene, although the latter is more

active. Still in the anthracene the heteroannular diene can be manifested, but never in the phenanthrene for it should result in the loss of aromaticity of one benzoid ring. In other words, the “cyclic polyenes” only virtually exist as such, and their enhanced reactivity manifests itself but under fairly mild conditions. For instance, as we recently showed, perylene easily underwent sulfonation [Cu(SO₂R)₂], halogenation (NBS), acetoxylation [Pb(OAc)₄], thiocyanation [NaSCN, Cu(BF₄)₂], “cyanoisopropanation” (NCMe₂C[–], Cu²⁺), and arylation (ArN₂⁺).

Another easily observed difference was found in the action of ionized Cu²⁺ salts (tetrafluoroborate or perchlorate). The cyclic polyenes are readily oxidized giving strongly colored cation-radicals whereas the benzoid polycycles remain intact. The reaction can be performed on a chromatographic plate with a streak of copper salt applied from acetonitrile solution. At eluting polycycle through the copper salt streak the cyclic polyene colorizes and is retained, but the benzoid polycycle gets through unchanged.

We found a quite different reaction with copper (II) tetrafluoroborate in the pyrene series. The light-blue acetonitrile solution of the copper salt immediately decolorized on adding it to the pyrene solution in acetonitrile, and simultaneously started the formation of a colorless finely crystalline precipitate of 1,1'-dipyrenyl. The yield of dipyrenyl (**II**) from pure pyrene was 70%, and about 20% of the initial pyrene additionally



* Rings with an aromatic π -electrons sextet.

dimerized after the separation. The pyrene containing fluoranthene and brazane dimerized in the same way, and the impurities remained intact.

The dimerization occurred only in acetonitrile or solvents containing a cyano group. In ethyl acetate reaction of pyrene and $\text{Cu}(\text{BF}_4)_2$ resulted in formation of a dark solution, but the specific precipitate of dipyrenyl insoluble also in ethyl acetate did not form at all, and the dimerization started only at adding an equal amount of acetonitrile. A similar effect of acetonitrile was also observed in oxidative substitution of perylene.

The substituted pyrenes lacking electron-acceptor substituents dimerized similarly to pyrene, therewith derivatives like 1-ethylpyrene provide an isomer mixture of the dimerization products. 1-Acetyl-, 1-formyl-, and 1-nitropyrenes did not undergo dimerization.

When the fragment of four pyrene rings is contained in the structure of another polycycle, for example, of anthanthrene (6 rings), our preliminary findings suggest that the dimerization also occurs. The naphtho derivatives of pyrene are also involved into the dimerization.

The polycycle dimerization may be observed directly on a chromatographic plate. Dimerizing polycyclic compound passing through the zone of copper(II) tetrafluoroborate changes, and further elution reveals the dimer that is less soluble and is slower eluted than the initial polycycle. The dimer commonly possesses a strong fluorescence; when the initial polycycle is colored, the arising dimer is lighter, colorless or light yellow. These findings permit a fast analysis of polycyclic hydrocarbons or their transformation products: the substances are preliminary separated by chromatography, then at cross-flow chromatography the elution is performed through a band of applied (from acetonitrile) copper tetrafluoroborate. At the contact point form colored cation-radicals; compounds with electron-acceptor substituents pass unchanged, and the derivatives

of pyrene structure dimerize giving strongly fluorescing compounds. The latest data demonstrated that porphyrins easily provided cation-radicals; for instance, tetraphenylporphin formed a bright-green cation-radical very stable under common conditions, whereas the substituted pyrroles present as impurities and pyrrole proper converted into insoluble black polymers. Certain arenas, mainly with electron-donor properties, dimerize at the anode; the yield of diarenes is as a rule low [4].

After discovering pyrene dimerization effected by $\text{Cu}(\text{BF}_4)_2$ we hoped to perform in the same way also dimerization of the other polycyclic hydrocarbons (cyclic polyenes). However the experiments showed that neither anthracene nor perylene, nor other polycycles underwent dimerization. The reaction occurring only in the presence of nitriles (usually of acetonitrile) stopped at the stage of intensively colored cation-radicals; at heating in the presence of water introduced with the hydrated copper salt the cation-radicals converted into the corresponding quinones. Promising results were obtained in cross-coupling reactions, for instance, a mixed condensation of two arenas was observed in pairs perylene (I)-1,3-dimethoxybenzene and pyrene-*N*-ethylcarbazole.

The properties of 1,1'-dipyrenyl (above all chemical) are sharply distinguished from pyrene characteristics. The reactive arenes polymerize at treatment with $\text{Cu}(\text{BF}_4)_2$ in acetonitrile, for example, azulene and pyrrole immediately form black insoluble polymers. The finding that the pyrene reaction ended at the dimer stage and did not result in polymerization was already an indication that the oxidation potential of the dimer is a lot higher than that of pyrene. (Because of the low solubility of 1,1'-dipyrenyl we failed to perform direct measurement of its oxidation potential; it is yet clear that the potential was significantly higher than that of pyrene and approached the values characteristic of benzoid polycycles). Nonetheless, existing data suggest that diaryls are oxidized more readily than the corresponding monomers, and their reactivity also grows (see, e.g., benzene-diphenyl, and naphthalene-1,1'-dinaphthyl). However the 1,1'-dipyrenyl remained unchanged in Vilsmeier formylation reaction (*N*-methylformanilide and POCl_3 in dichlorobenzene [5]), was not acylated in the presence of ZnCl_2 (the reaction was successful with AlCl_3), and remained intact at the nitration with pyridinium nitrate in boiling pyridine [1]. The dipyrenyl behavior in the latter reaction indicated that the substance lost the quality of pyrene. The reactions were carried out under the conditions [1, 5] of dipyrenyl complete solubility, yet it

was recovered practically unchanged from the reaction mixtures. The pyrene proper readily entered into these reactions.

Dipyrenyl possesses intensive blue fluorescence in solution and in solid state, it is insoluble in concn. H_2SO_4 , the characteristic feature of benzoid polycycles. The reduced reactivity of an aromatic compound is commonly regarded as indication of a decreased electron density on the molecule; the latter feature in its turn results in some enhancement of the vibration frequency of C–H in aromatic ring as seen in the IR spectra and in the downfield shift of signals in the ^1H NMR spectra, whereby the frequencies of the out-of-plane C–H vibrations in the IR spectrum of dipyrenyl are increased: 846 (pyrene), 853 and 860 cm^{-1} (1,1'-dipyrenyl). The higher frequencies were observed also for two other bands in the region 700–770 cm^{-1} .

In the ^1H NMR spectrum of 1,1'-dipyrenyl as compared with the spectrum of pyrene the proton signals are shifted both downfield [doublets at 8.37 and 8.26, for pyrene 8.20 ppm (d, $\text{H}^{1,3,5,8}$)] and upfield [doublets at 7.89 and 7.67, for pyrene 8.03 ppm (t, $\text{H}^{2,7}$)]. All these data suggest that in the dipyrenyl appear more benzoid aromatic sextets than in two molecules of the initial pyrene (see the scheme), and just this increase is the driving force of pyrene dimerization. However the possibility of the polycycle existence in two forms distinguished by the number and position of the aromatic sextets seems doubtful. The calculations (Hyper Chem) suggest that both pyrene fragments are located in one plane, and the intensive fluorescence and the high melting point also evidence the planar structure of the dipyrenyl. However the anthracene dimer (9,9'-dianthryl) did not possess analogous planar structure, the number of aromatic sextets did not increase, and consequently the dimer did not form. The same is also valid for perylene. In our investigation on electrolumiphors synthesis the 1,1'-dipyrenyl was the first among the polycyclic hydrocarbons endowed with the electroluminescence qualities. An interesting feature of the substance is its ability to recrystallize even in a thin film (0.5 μ) under the effect of heat generated by electric current passage. A visual model of the process is the formation of transparent crystals vertically standing on a heated surface. Under conditions of electroluminescence observation the recrystallization in a thin layer obtained by vacuum deposition between two electrodes (I_2O_3 and Al) gradually violates the electric contact, and the film stops to luminesce. The most striking fact consists in

the spontaneous recovery of the contact after some time, and the film then shows the initial electroluminescent characteristics. In the other words, the film “remembers” the primary electric impact.

The known [6] pyrene dimerization under the treatment of periodic acid in the aqueous acetic acid is accompanied with side products formation. Surely this reaction is not based “on a specific ability of the oxidant to form associates with pyrene molecules” but merely on the single-electron oxidation of pyrene. The application to the dimerization of typical single-electron oxidants like $\text{Cu}(\text{BF}_4)_2$ is far more efficient. In the synthesis of 1,1'-dipyrenyl from 1-bromopyrene by Ullman reaction the yield was 20% [7].

EXPERIMENTAL

Mass, ^1H NMR, and IR spectra were obtained on instruments Kratos MS-890, Bruker WD-200 SY (200 MHz), and UR-20 respectively.

1,1'-Dipyrenyl. To a solution of 20.2 g (0.1 mol) of pyrene (content of the main substance 99%) in 200 ml of boiling acetonitrile was added gradually at vigorous stirring a solution of 35 g of $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ in 50 ml of acetonitrile. After adding each portion of the solution the reaction mixture for a short time turned dark and then decolorized, and fine crystals of dipyrenyl precipitated. To the mixture was added by portions 6 g of copper subcarbonate till the end of frothing caused by CO_2 liberation. Then for 10 min the mixture was cooled to 30–40°C, the precipitate was filtered off and washed with acetonitrile (2×10 ml). The colored acetonitrile filtrate contained the inorganic salts and 1,6-pyrenequinone. The dipyrenyl precipitate was washed from the initial pyrene by stirring with 30 ml of acetone followed by filtration and washing of the precipitate with acetone. To remove the copper salt impurity the precipitate was stirred with a solution of 5 ml of acetic acid in 50 ml of hot water, then filtered, washed with water, with acetic acid till the washings were colorless, then with acetone, and dried. Yield 14 g (70%), mp 333°C (327–328°C [6]). Before melting (320–325°C) the powder of the substance turns into transparent plates vertically standing on the hot surface.

UV spectrum (benzene) λ_{max} , nm: 285, 315, 330, 346 (identical to the spectrum published in [7]). IR spectrum (mull in mineral oil), cm^{-1} : 3060, 3040 ($\nu_{\text{C-H}}$), 1600, 1466, 1386, 1233, 1174, 1150–1080, 966, 860–853 ($\gamma_{\text{C-H}}$), 833, 773, 766, 723, 713, 687, 647, 637, 550.

^1H NMR spectrum (CDCl_3), δ , ppm: 8.37 d (2H), 8.26 d (2H), 8.20 d (4H), 8.16 d (4H), 8.04 t (2H, $\text{H}^{7,7}$), 7.89 d (2H). Mass spectrum, m/z : 402 [M] $^+$, 400 [$M - 2\text{H}$] $^+$, 200 [$0.5 M$] $^+$. ^1H NMR spectrum of pyrene (CDCl_3), δ , ppm: 8.20 d (4H, $\text{H}^{1,3,6,8}$), 8.10 (4H, $\text{H}^{4,5,9,10}$), 8.03 (2H, $\text{H}^{2,7}$).

From the acetonitrile filtrate after diluting with water, extraction with toluene, and chromatography (SiO_2 , CH_2Cl_2 –ethyl acetate) we isolated 10 mg of 1,6-pyrenequinone identical to a standard sample. The dilution with water of acetone washings resulted in precipitation of a solid that was subjected to chromatography on a short column packed with SiO_2 to isolate 4.5 g of pyrene, mp 150°C .

The dimerization of 4 g of unreacted pyrene was carried out by a simplified procedure. To a hot solution of pyrene in 40 ml of acetonitrile was gradually added at stirring 7 g of $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ in 5 ml of acetonitrile, the mixture was heated for 5 min at stirring, then 20 ml of heptane was added, the dipyranyl precipitate floated to the boundary of the layers. The majority of the heptane solution was decanted, and the blue acetonitrile solution with the floating precipitate was filtered. The precipitate on the filter was washed with toluene (2×20 ml), acetonitrile-toluene filtrate was separated, the precipitate was

washed with water, with acetone, and dried. We obtained 2.4 g of chromatographically pure dipyranyl as light-blue powder. The toluene solution was separated from the acetonitrile solution and combined with the heptane solution, washed with water, and passed through a bed of SiO_2 (3 cm) to remove the impurity of yellow perylenequinone. We isolated 1.4 g of pyrene, mp 150°C . According to TLC data (heptane–toluene, 3:1) alongside the pyrene (greenish fluorescence) just below pyrene was located a substance with blue fluorescence (brazane).

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