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CATALYTIC HYDROGENATION OF PYRYLIUM SALTS

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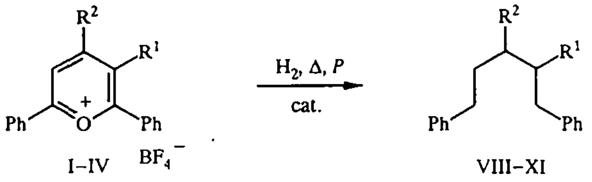
*On catalytic reduction of 2,6-diphenylpyrylium salts, hydrogenolysis occurs at the C—O bond with the formation of 1,5-diphenylpentanes. The principal direction of the hydrogenation of 9-phenyl-*sym-*octahydroxanthylium tetrafluoroborate is the formation of a mixture of products of partial and complete reduction of the heterocycle. The structure of the substances obtained was established by IR and ^{13}C NMR spectroscopy.*

Catalytic hydrogenation is a practically uninvestigated aspect of the well-studied chemistry of pyrylium salts. Up to the present time, only individual examples of similar reactions are known [1, 2]. We have studied the catalytic hydrogenation of pyrylium tetrafluoroborates (I)-(IV), differing in the number and nature of substituents, and their condensed analogs, the hydrochromylium (V) and (VI) and octahydroxanthylium (VII) tetrafluoroborates.

Reaction was carried out in an autoclave in the temperature range 40-100°C and pressure 7-12 MPa on various catalysts. It was established that pyrylium salts (I)-(IV) react with rupture of the heterocycle and the formation in high yield (80-92%) of 1,5-diphenylpentanes (VIII)-(XI). The degree of substitution and the nature of the substituents (alkyl, aryl) have practically no influence on the yield of final product.



I, VIII $R^1 = R^2 = H$; II, IX $R^1 = H$, $R^2 = Me$; III, X $R^1 = H$, $R^2 = Ph$;
IV, XI $R^1 = Me$, $R^2 = Ph$

A study has been made of the effect on the yield of hydrocarbon (X) of temperature, hydrogen pressure, and catalyst using 2,4,6-triphenylpyrylium tetrafluoroborate (III) as an example. At 40°C, the yield of 1,3,5-triphenylpentane (X) was 68%, at 50°C it had increased to 80%, and remained practically unchanged on increasing the temperature to 100°C. A further increase in temperature leads to hydrogenation of the benzene rings and the formation of a mixture of hydrocarbons separable with difficulty. On increasing the pressure from 7 to 10 MPa, the yield of product was increased by 20%. Of the catalysts investigated, Raney Ni, Pd/C, and Ni/Ru, the latter proved to be the most active (Table 1).

The catalytic hydrogenation of 2-phenyl-5,6,7,8-tetrahydrochromylium (V) and 2,4-diphenyl-5,6,7,8-tetrahydrochromylium (VI) tetrafluoroborates leads to a complex mixture of products, which we failed to separate.

On hydrogenating 9-phenyl-*sym*-octahydroxanthylium tetrafluoroborate (VII), the hydrocarbon (XII) was isolated in a yield of only 18% and the main direction of the reaction was the formation of the oxygen-containing heterocycles 9-phenyldecahydroxanthene (XIII) and 9-phenyl-dodecahydroxanthene (XIV), the combined yield of which was 51%.

The reason for the different reaction direction seemingly follows from consideration of the various stabilities towards hydrogenolysis of the C—O bond of the saturated oxygen-containing heterocycles formed. The acid released on reduction of

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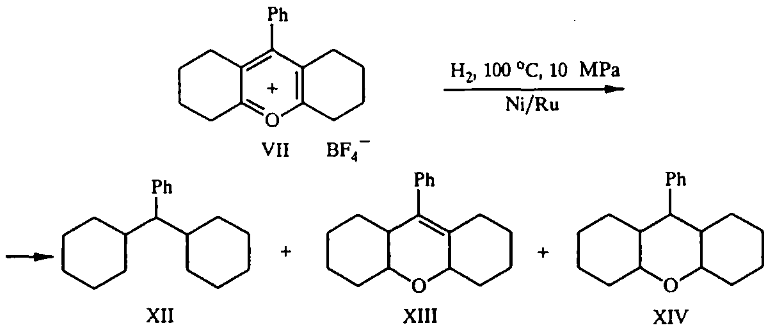
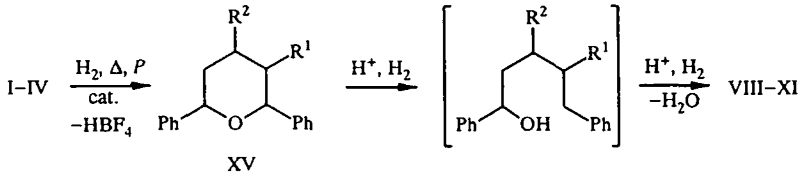


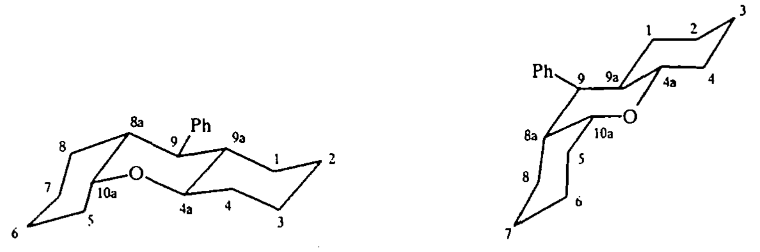
the pyrylium salt assists hydrogenolysis under the conditions studied. As is known [3], hydrogenolysis occurs readily in systems in which the oxygen is bound to a carbon atom of the benzyl type, and such compounds of the type of (XV) may arise on hydrogenation of 2,6-diphenyl substituted pyrylium salts (I)-(IV).



The hydroxanthenes (XIII) and (XIV) are stable to hydrogenolysis since they contain no labile C−O bonds. These compounds are the main products of the hydrogenation of salt (VII), but hydrocarbon (XII) is formed as a by-product.

The IR spectra of hydrocarbons (VIII)-(XII) contained only absorption bands characteristic of aliphatic (ν_{C-H} 2870-2930 cm^{-1}) and aromatic ν_{C-H} 3030-3080 cm^{-1}, δ_{C-H} 750-770, 700-710 cm^{-1}, ν_{C-C} 1600 cm^{-1}) C−C and C−H bonds. The structure of the oxygen-containing heterocycles (XIII) and (XIV) was established by ^{13}C NMR. We failed to separate these products completely, however, a certain quantity of dodecahydroxanthene (XIV) was obtained in pure form by multiple recrystallization from ethanol. Assignment of the signals in the spectrum was made taking into account data on the effect of oxygen on the chemical shifts of the carbon atoms of the heterocycle [4], and also the results of spectral investigations on the isomeric perhydroanthracenes [5].

The ^{13}C NMR spectrum of dodecahydroxanthene (XIV) contains 17 signals, which indicates its unsymmetrical structure. Low field signals at 82.77 and 76.67 ppm may only be assigned to $C_{(4a)}$ and $C_{(9a)}$ adjacent to the heteroatom. The displacement of the $C_{(9)}$ signal towards low field (52 58 ppm) is explained by the effect of the phenyl substituent bonded directly to this atom (in perhydroanthracenes, this signal is at 32-42 ppm [5]). The junction carbon atoms $C_{(8a)}$ and $C_{(9a)}$ are characterized by absorption at 43.33 ppm and 31.18 ppm respectively. The presence of a high field signal at 20.95 ppm indicates a *cis* connection of the heterocycle with one of the alicycles. Consequently, either a *cis-anti-trans* or a *cis-syn-trans* configuration may be assigned to the compound being investigated.



cis-syn-trans

cis-anti-trans

XIV

The position of the signals for the $C_{(9)}$ and $C_{(9a)}$ atoms points in favor of the *cis-anti-trans* configuration. The axial orientation of the $C_{(5)}-C_{(10a)}$ bond in the *cis-syn-trans* isomer must displace the signal of the $C_{(9)}$ atom, located in the g posi-

TABLE 1. Hydrogenation of 2,4,6-Triphenylpyrylium Tetrafluoroborate (III)

T, °C	P, MPa	Catalyst	Yield of 1,3,5-triphenylpentane (X), %
45	10	Ni/Ru	68
50	10	—"—	80
60	10	—"—	83
100	10	—"—	84
50	7	—"—	63
50	8	—"—	77
50	10	Raney Ni	74
50	10	Pd/C	67

TABLE 2. Physical Constants and Yields of the Compounds Obtained

Compound	Empirical formula	Found, % / Calculated, %		Bp, °C/mm Hg	Yield, %
		C	H		
VIII	$C_{17}H_{20}$	91,53 91,01	9,48 8,98	162...165/3	78
IX	$C_{18}H_{22}$	91,67 90,69	9,35 9,30	160...165/1	81
X	$C_{23}H_{24}$	91,50 91,30	9,63 8,76	202...204/3	84
XI	$C_{24}H_{26}$	91,23 91,75	8,53 8,25	210...214/3	92
XII*	$C_{19}H_{28}$	89,47 89,06	11,03 10,94	—	18
XIII+XIV†	—	—	—	—	51

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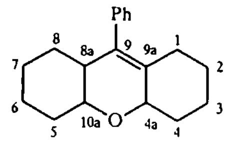
*Isolated by column chromatography: R_f 0.84 (eluent hexane–ether–acetone, 4:1:1).

†Characterized by data of ^{13}C NMR spectra.

tion, towards high field. However, in the spectrum of the compound being investigated, this signal appears at low field and consequently does not experience this effect. At the same time, we noted a high field displacement of the $C_{(9a)}$ signal to 39.18 ppm ($C_{(8a)}$ 43.33 ppm), which is explained by the effect of the axially oriented $C_{(8)}-C_{(8a)}$ bond in the *cis-anti-trans* isomer.

By comparing the spectra of mixtures of compounds (XIII) and (XIV) with the spectrum of compound (XIV) alone it is possible to separate out the chemical shifts of the carbon atoms in 9-phenyldodecahydroxanthene (XIII). The $C_{(9)}$ and $C_{(9a)}$ atoms, being in the sp^2 hybrid state, absorb at 134.86 and 133.16 ppm. The junction atoms $C_{(4a)}$, $C_{(8a)}$, and $C_{(10a)}$ are characterized by chemical shifts of 78.33, 78.25, and 44.02 ppm respectively. The signals of the $C_{(1)}$ to $C_{(8)}$ atoms lie in the region from 34.79 to 24.46 ppm. The high field signal at 24.46 ppm indicates a *cis* junction of the heterocyclic and alicyclic rings.



XIII

EXPERIMENTAL

The IR spectra were described on a Specord M-80 spectrometer in a thin film for liquid substances and in the form of Nujol or hexachlorobutadiene mulls for crystalline substances. The ^{13}C NMR spectra were drawn on a Varian FT 80A spectrometer, operating frequency was 20 MHz. TMS was used as internal standard, solvent was deuterochloroform.

The initial pyrylium salts were synthesized by the procedure in [6].

Hydrogenation of Pyrylium Salts (general procedure). The pyrylium salt (12.5-14 mmole), ethanol (80 ml), and catalyst (0.5-1 g) were placed in an autoclave of capacity 150 ml. The initial hydrogen pressure was 7-10 MPa and the temperature 0-100°C. The process was complete after 4 h and the catalyst was separated by filtration. The ethanol was distilled off under reduced pressure. Hydrocarbons (VIII)-(XI) were distilled in vacuum.

Hydrocarbon (XII) was separated from the mixture of compounds (XIII) and (XIV) by chromatography on a column (1 = 40 mm, d = 1.5 cm of Al_2O_3 of activity grade III, eluent hexane) in 18% yield. Compounds (XIII) and (XIV) were washed from the column with a mixture of hexane–ether, 5:1. ^{13}C NMR spectra: (XIV) 82.74 ($C_{(4a)}$); 76.67 ($C_{(10a)}$); 52.58 ($C_{(9)}$); 43.27 ($C_{(8a)}$); 39.10 ($C_{(9a)}$); 32.91; 32.38; 29.19; 26.03; 25.41; 21.64; 20.95 ($C_{(1)}$ to $C_{(8)}$); 141.84; 128.78; 128.03; 125.87 ppm, benzene ring carbon atoms. (XIII) 134.86 ($C_{(9)}$); 133.16 ($C_{(9a)}$); 78.33 ($C_{(4a)}$); 76.25 ($C_{(10a)}$); 44.02 ($C_{(8a)}$); 34.79; 32.95; 29.34; 28.96; 27.00; 26.12; 24.46 ($C_{(1)}$ to ($C_{(8)}$); 138.74; 128.78; 128.03; 125.87 ppm, benzene ring carbon atoms.

The physical constants and yields of the compounds obtained are given in Table 2.

REFERENCES

1. A. P. Kriven'ko, O. V. Fedotova, P. V. Reshetov, and V. G. Kharchenko, Khim. Geterotsikl. Soedin., No. 12, 1652 (1984).
2. G. Mihai and T. S. Balaban, Z. Naturforsch. B, **41**, No. 4, 502 (1986).
3. P. N. Rylander, Catalytic Hydrogenation in Organic Synthesis, Academic Press, Orlando (1979).
4. J. B. Lambert, D. A. Netzel, Hsiang-ning Sun, and K. K. Lilianstrom, J. Am. Chem. Soc., **98**, No. 13, 3778 (1976).
5. D. K. Dalling and D. H. Grant, J. Am. Chem. Soc., **96**, No. 6, 1827 (1974).
6. J. A. Van Allen and G. A. Reynolds, J. Org. Chem., **33**, No. 3, 1102 (1968).