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π-AROMATIC COMPLEXES OF METAL CARBONYLS IN THE PYRYLIUM SALT SERIES

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By the reaction of lithium derivatives of cyclopentadienylmagnesiumtricarbonyl, cyclopentadienylrheniumtricarbonyl, and benzenechromiumtricarbonyl with 2,6-disubstituted pyrylium salts the corresponding 4H-pyrans have been synthesized, and the oxidative dehydration of these has given pyrylium cations containing the stated organometallic groups in position 4. It has been shown that the π-complexes obtained readily exchange the oxygen of the pyrylium ring for other heteroatoms with the formation of heterocyclic compounds with metallocarbonyl substituents.

Recently, the investigation of π-complexes of transition metals with heterocyclic compounds has received considerable development [1, 2]. At the same time, π-complexes based on pyrylium salts have been studied less than others and are represented by only individual examples of the formation of ferrocene- and cymantrene-containing derivatives [3-7]. The introduction of organometallic substituents into pyrylium cations, which are distinguished by a diversity of transformations, opens up possibilities for the investigation of the mutual influence of these groupings and for the production of new metal-containing heterocyclic compounds.

In view of this, we have obtained previously unknown pyrylium cations containing in the γ-position π-aromatic ligands coordinated with carbonyls of Mn, Re, and Cr and have studied some of their properties. To synthesize the π-complexes mentioned we used the general method of alkylating γ-unsubstituted pyrylium cations with organometallic compounds leading to substituted 4H-pyrans followed by their dehydrogenation to the corresponding pyrylium salts. Thus the action of cymantrenyllithium on 2,6-disubstituted pyrylium cations gives the 4H-pyrans (I) and (II) in high yield.

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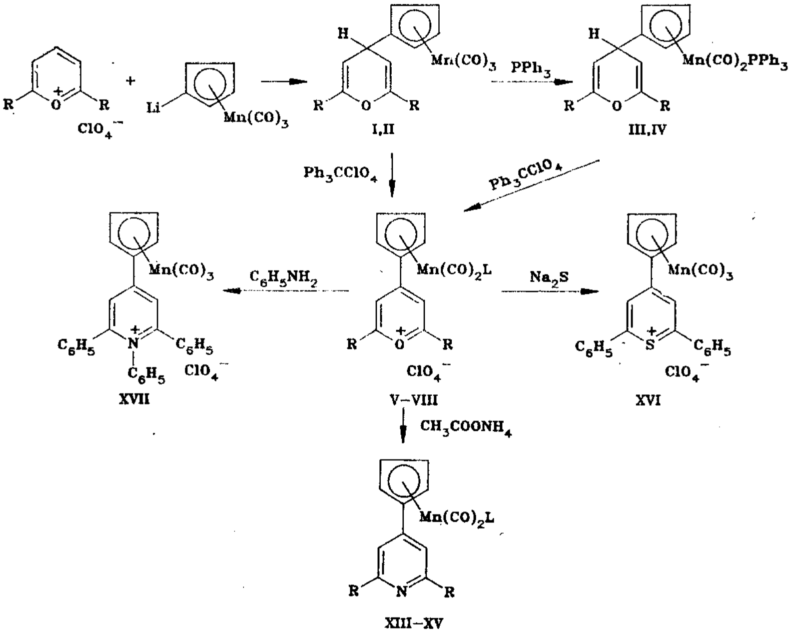
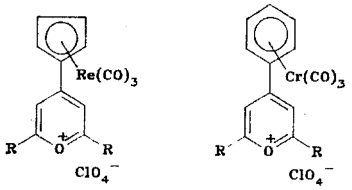


I, III, V, VI, XIII, XIV R=$(CH_3)_3C$; II, IV, VII, VIII, XV R=C_6H_5; V, VII, XIII, XV L=CO; VI, XIV L=PPh_3

In these compounds the UV-radiation-induced replacement of the carbonyl group in the organometallic fragment by a triphenylphosphine ligand with the formation of compounds (III) and (IV) proved to be possible.

It is known that the oxidative dehydrogenation of 4H-pyrans to pyrylium salts does not always take place unambiguously [8] and is not infrequently accompanied by the undesirable cleavage of the C–C bond between the pyran fragment and the substituent in position 4, which leads to the formation of the initial pyrylium salt unsubstituted in the γ-position. The choice of dehydrogenating agent is decisive in such cases. In actual fact, after the action of acetyl perchlorate on the pyrans (I-IV) we isolated only the initial 2,6-disubstituted pyrylium salts, while the dehydrogenation of compounds (I-IV) with trityl perchlorate in acetonitrile gave the manganese-containing pyrylium cations (V-VIII) in practically quantitative yield. Similarly, starting from 2,6-disubstituted pyrylium salts and the lithium derivatives of cyclopentadienylrheniumtricarbonyl and benzenechromiumtricarbonyl we obtained the corresponding 4H-pyrans, which, without additional purification, were converted into pyrylium cations containing residues of the organometallic groups mentioned (IX-XII).

The complexes synthesized (V-XII) (Table 1) consisted of crystalline substances stable in air and having intense colorations. Their IR spectra contained strong bands of the stretching vibrations of carbonyl groups in the 1800-2030 cm^{-1} region, bands in the 1610-1640 cm^{-1} region characteristic for the stretching vibrations of a pyrylium ring, and also a broad band at 1100 cm^{-1} due to absorption by the ClO_4^- anion. The presence of the triphenylphosphine ligand in compounds (III) and (IV) was revealed in the IR spectra by a shift in the absorption band of the CO group by 60-80 cm^{-1} in the long-wave direction as compared with derivatives (I) and (II); in addition, intense bands at 1680-1700 cm^{-1} (stretching vibrations of C=C bonds of the pyran fragment) were characteristic for the 4H-pyrans (I-IV).



IX,X XI,XII

IX, XI R=$(CH_3)_3C$; X, XII R=C_6H_5

TABLE 1. Characteristics of Compounds (I-XVII)

Compound	mp,* °C	IR spectrum, cm^{-1}				Found				Empirical formula	Calculated				Yield, %
		C=O	C=C	ClO_4	other absorption bands†	C, %	H, %	Cl (N)	M		C, %	H, %	Cl (N)	M	
I	49—50	2010, 1925	1700	—	3130, 840, 850	63,6	6,3	—	13,7	$C_{21}H_{25}MnO_4$	63,6	6,3	—	13,9	87
II	119—120	2010, 1920	1690	—	3135, 835, 850	68,9	4,2	—	11,9	$C_{25}H_{17}MnO_4$	68,8	4,1	—	12,6	86
III	186—187	1930, 1860	1700	—	3130, 835, 850	72,5	6,4	—	8,4	$C_{38}H_{40}MnO_3P$	72,4	6,4	—	8,3	64
IV	173—174	1925, 1860	1685	—	3120, 835, 850	75,4	4,6	—	8,0	$C_{42}H_{42}MnO_3P$	75,2	4,8	—	8,2	53
V	205—206	2030, 1960	1620	1110	3140, 840, 855	51,2	5,2	7,1	10,8	$C_{21}H_{24}ClMnO_8$	50,9	4,9	7,2	11,1	98
VI	297—298	1955, 1890	2625	1100	3130, 840, 855	55,9	2,7	6,7	10,2	$C_{25}H_{16}ClMnO_8$	56,1	2,9	6,6	10,3	96
VII	258—259	2020, 1940	1610, 1580	1100	3130, 840, 850	62,3	5,2	4,6	7,2	$C_{38}H_{39}ClMnO_7P$	62,6	5,4	4,9	7,6	93
VIII	263—265	1950, 1895	1625, 1580	1105	3120, 835, 850	65,3	3,9	4,4	7,1	$C_{42}H_{31}ClMnO_7P$	65,6	4,0	4,6	7,2	97
IX	175—176	2030, 1965	1620	1100	3125, 835, 845	40,2	4,0	5,5	29,6	$C_{21}H_{24}ClO_8Re$	40,3	3,8	5,7	29,8	75
X	201—202	2020, 1950	1615, 1580	1100	3130, 840, 855	45,2	3,3	5,1	27,6	$C_{25}H_{16}ClO_8Re$	45,1	3,6	5,3	27,9	78
XI	193—195	2000, 1945	1615	1100	—	52,1	5,1	6,9	10,0	$C_{22}H_{25}ClCrO_8$	52,3	4,9	7,0	10,3	72
XII	213—215	1990, 1935	1610, 1560	1100	—	59,9	3,1	6,4	9,1	$C_{26}H_{17}ClCrO_8$	59,5	3,2	6,8	9,7	70
XIII	104—105	2020, 1935	1600, 1560	—	3130, 840, 855	64,4	5,9	(3,4)	13,8	$C_{21}H_{24}MnNO_3$	64,1	6,1	(3,6)	13,9	97
XIV	151—152	1925, 1865	1605, 1560	—	3125, 840, 850	72,7	6,1	(2,3)	8,6	$C_{38}H_{39}MnNO_2P$	72,7	6,2	(2,2)	8,8	98
XV	148—149	2015, 1925	1615, 1565	—	3135, 835, 850	69,0	3,8	(3,2)	12,6	$C_{25}H_{16}MnNO_3$	69,3	3,7	(3,2)	12,5	95
XVI	239—240	2030, 1950	1600, 1590	1100	3130, 840, 855	54,5	2,8	6,3	9,8	$C_{25}H_{16}ClMnO_7S$	54,5	2,9	6,5	9,9	98
XVII	267—268	2030, 1935	1630, 1560	1110	3130, 840, 855	60,9	3,4	5,5 (2,1)	9,1	$C_{31}H_{21}ClMnNO_7$	61,0	3,5	5,8 (2,3)	9,0	68

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*Compounds (V-XII), XVI, and XVII) melted with decomposition.

†The absorption bands characteristic for the C—H and C—C vibrations of the cyclopentadienyl ring are given.

It is known that in carbocations connected with metallocenyl substituents, the positive charge is substantially displaced in the direction of the organometallic fragment, a consequence of which is an increase in the stability of the carbonium ion and a fall in its electrophilic properties [9]. At the same time, in the IR spectra of metallocenyl carbonium ions, the CO frequency is shifted by 40-80 cm^{-1} in the direction of higher wave numbers as compared with the uncharged precursors [10]. In our case, the 4H-pyran—pyrylium cation transition was accompanied by a relatively small change in the CO absorption of ≈10-30 cm^{-1}, which shows only a slight redistribution of the positive charge in the pyrylium ring under the action of the metallocenyl substituent and, consequently, a retention of high reactivity in relation to nucleophilic reagents.

In actual fact, under the action of an alcoholic solution of ammonium acetate the magnesium-containing pyrylium cations (V-VII) were converted readily and with high yields into the corresponding cymantrenyl-substituted pyridines (XIII-XV). The reaction of 2,6-diphenyl-4-cymantrenylpyrylium perchlorate (VIII) with sodium sulfide in aqueous acetone led to the thiopyrylium perchlorate (XVI). The same pyrylium cation, on being boiled with aniline in acetic acid, gave a pyridinium salt containing a cymantrene residue in position 4 (XVII).

Thus, in reactions with nucleophilic reagents, pyrylium salts with metallocarbonyl substituents behave similarly to triaryl-7-substituted pyrylium cations, which opens up broad possibilities for the directed synthesis of π-complexes of heterocyclic compounds.

EXPERIMENTAL

IR spectra were taken in paraffin oil on a UR-20 instrument. Melting points were determined on a Boetius heated stage.

The characteristics of the compounds synthesized are given in Table 1.

4-(Cyclopentadienylmanganesetricarbonyl)-2,6-di-tert-butyl-4H-pyran (I). With vigorous stirring, a suspension of 5.84 g (20 mmole) of 2,6-di-tert-butylpyrylium perchlorate in 50 ml of ether was added to a solution of cymantrenyllithium in 40 ml of THF that had been obtained at −60°C from 4.08 g (20 mmole) of cymantrene and 13.8 ml of a 1.46 N hexane solution of butyllithium. After the pyrylium salt had dissolved, the temperature of the reaction mixture was allowed to rise to 0°C and it was treated with a saturated solution of ammonium chloride. The organic layer was separated off and was washed with water and dried with sodium sulfate. Then solvent was driven off, and the solid residue was chromatographed on Al_2O_3 of activity grade II; compound (I) was eluted with hexane. The yield was 6.8 g (87%). After recrystallization from methanol, the pyran (I) was isolated in the form of colorless acicular crystals.

4-(Cyclopentadienylmanganesetricarbonyl)-2,6-diphenyl-4H-pyran (II) was synthesized under the conditions of the preceding experiment. Straw-colored acicular crystals were obtained.

Replacement of the Carbonyl Ligand in Pyrans (I) and (II) by Triphenylphosphine. An ethereal solution of a mixture of one of the pyrans (I) and (II) and triphenylphosphine (molar ratio 1:1) was irradiated with a DRT-220 lamp for 4.5 h. The solvent was driven off under reduced pressure, and the residue was chromatographed on Al_2O_3 of activity grade II; compound (III) was eluted by the chloroform—hexane (1:4) system (pale yellow plates after recrystallization from ethanol), and compound (IV) by the benzene—hexane (1:4) system (yellow cubic crystals from ethanol).

4-(Cyclopentadienylmanganesetricarbonyl)-2,6-di-tert-butylpyrylium Perchlorate (V). With stirring, 0.70 g (2 mmole) of triphenylmethyl perchlorate was added to a solution of 0.78 g (2 mmole) of the pyran (I) in 20 ml of acetonitrile. After 0.5 h, 100 ml of ether was added to the reaction mixture and the orange crystals were filtered off, washed with ether, and dried. Yield 0.92 g (98%).

The reactions of pyrans (II-IV) with triphenylmethyl perchlorate were performed similarly, giving substances (VI-VIII), respectively, in the form of small dark cherry-red crystals (from acetic acid).

Rhenium- and Chromiumtricarbonyl Derivatives of Pyrylium Salts (IX-XII). With vigorous stirring and cooling to −70°C, a suspension of a 2,6-disubstituted pyrylium salt in 30 ml of ether was added to a solution of 5 mmole of the lithium derivative of cyclopentadienylrheniumtricarbonyl or benzenechromiumtricarbonyl in THF, and the mixture was kept at −70°C for 0.5 h and was then warmed to 0°C. After this it was treated with a saturated solution of ammonium chloride, and the organic layer was separated off, washed with water, and dried with sodium sulfate. The solvent was eliminated in vacuum and the residue was dissolved in 30 ml of acetonitrile and, with stirring, 4 mmole of triphenylmethyl perchlorate was added to the resulting solution. After 45 min, the reaction mixture was diluted with 100 ml of ether. The precipitate was filtered off, and it was washed with a small amount of cold acetonitrile and ether and dried. For purification, the complexes (IX-XII) were reprecipitated from solution in methylene chloride with ether, whereupon compounds (IX) and (X) were obtained in the form of dark green crystals, while compounds (XI) and (XII) had a violet color.

The Pyridines (XIII-XV). A suspension of 1 mmole of one of compounds (I-III) in 10 ml of ethanol was treated with 1 g of ammonium acetate and the mixture was heated in a flask with a reflux condenser until the initial pyrylium salt had dissolved completely. Then the reaction mixture was cooled and was poured into 50 ml of water. The precipitate that deposited was filtered off, washed with water, and recrystallized from ethanol to give the corresponding pyridine (XIII, XIV, or XV) in the form of a yellow crystalline substance.

4-(Cyclopentadienylmanganesetricarbonyl)-2,6-diphenylthiopyrylium Perchlorate (XVI). With stirring, 5 ml of a 10% aqueous solution of sodium sulfide was added to a suspension of 0.53 g (1 mmole) of the pyrylium salt (VI) in 20 ml of acetone. The violet solution formed was acidified with 10 ml of 20% perchloric acid and was then diluted with 50 ml of water. After 1 h, the precipitate was filtered off, washed with water, and dried. The yield was 0.52 g (98%) of dark cherry-red needles after reprecipitation from acetonitrile with ether.

4-(Cyclopentadienylmanganesetricarbonyl)-1,2,6-triphenylpyridinium Perchlorate (XVII). A mixture of 0.53 g (1 mmole) of compound (VI) and 0.09 g (1 mmole) of aniline in 10 ml of glacial acetic acid was boiled for 0.5 h. The yellow solution formed was cooled and diluted with 50 ml of ether. The precipitate was separated off, washed with ether, and dried. The yield was 0.42 g (68%). After recrystallization from acetic acid, compound (XVII) was obtained in the form of yellow cubic crystals.

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