3-(p-Chlorobenzoyl)dibenzofuran. The ketone was purified by recrystallization from glacial acetic acid or alcohol to give a product with mp 153°, M 306 (by mass spectrometry), and R_f 0.51. IR spectrum: 1665 (C=O) and 845 cm^{-1} (1,4-disubstituted ring) (according to the data in [9], the ketone has mp 152°).

3,6-Dibenzoyldibenzofuran. The ketone was purified by recrystallization from acetic acid or alcohol to give a product with mp 165°, M 376 (by mass spectrometry), and R_f 0.80. IR spectrum: 1664 (C=O) and 705 cm^{-1} (monosubstituted benzene ring) (according to the data in [1, 2], the ketone has mp 167-168°).

LITERATURE CITED

1. W. Borsche and W. Bothe, Ber., 41, 1940 (1908).
2. R. G. Johnson, H. B. Willis, and H. Gilman, J. Amer. Chem. Soc., 76, 6407 (1954).
3. H. Gilman and A. L. Lacogy, J. Org. Chem., 3, 108 (1938).
4. A. Burger and H. W. Brayant, J. Org. Chem., 4, 119 (1939).
5. Kh. Yu. Yuldashev, N. G. Sidorova, and A. G. Khaitbaeva, Deposited Paper (All-Union Institute of Scientific and Technical Information) No. 5848-73; Ref. Zh. Khim., 19, Zh252 (1973).
6. Kh. Yu. Yuldashev, N. G. Sidorova, K. D. Agzamova, A. R. Abdurasuleva, Kh. S. Tadzhimukhamedov, I. A. Stempnevskaya, S. I. Tabachkova, and A. G. Khaitbaeva, USSR Author's Certificate No. 405,850; Byul. Izobr., No. 45, 90 (1973).
7. I. A. Stempnevskaya and N. G. Sidorova, Nauchnye Trudy Tashkent. Gosudarstsv. Univ., Voprosy Khim., No. 419, 152 (1972).
8. Takashi Keumi and Yuzo Maegawa, J. Chem. Soc. Japan, 73, 2417 (1970); Ref. Zh. Khim., 12, Zh278 (1971).
9. J. H. Cornell, U.S. Patent No. 3,341,552 (1967); Ref. Zh. Khim., 3N618P (1970).

DI- AND TRI(2-PYRON-6-YL)ARENES

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Condensation of di- and triacetylarenes with 1,1,1,3-tetrachloro-3-alkoxypropanes or β,β-dichloroacrolein in acidic media gave a number of (dichloropentadienyl)- and tris(dichloropentadienyl)-substituted aryl ketones, which, in the case of acetic acid in the presence of phosphoric acid, are converted to the corresponding di- and tri(2-pyron-6-yl)arenes. It was observed that nitric acid has an oxidation effect on 2-pyrones.

In a continuation of our earlier research [1] in the pyrone series we synthesized systems with two and three α-pyrone rings separated by benzene rings and studied some of their reactions. We accomplished the synthesis of 1,4-di(2-pyron-6-yl)benzene (X), 1,4-(2-pyron-6-yl)diphenyl (XI), and sym-tri(2-pyron-6-yl)benzene (XIII) from p-diacetylbenzene (I), 1,4-diacetyldiphenyl (II), and sym-triacetylbenzene (III), respectively, by the method in [2], which has been previously used for the synthesis of monopyrones.

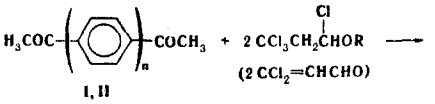

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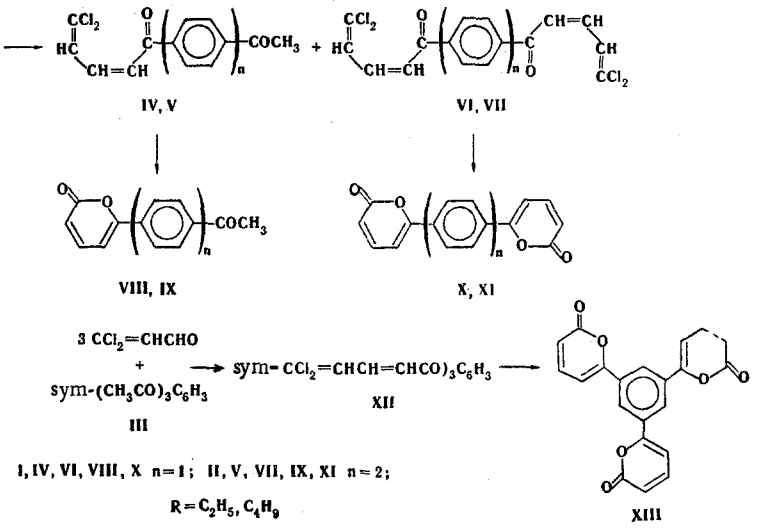
TABLE 1. Characteristics of the Compounds Obtained

Compound	mp, °C	IR spectra, cm^{-1}	Found, %* C	Found, %* H	Empirical formula	Calc., % C	Calc., % H	Yield, %
IV	122—124	1570, 1660, 3030	58,4	3,5	$C_{13}H_{10}Cl_2O_2$	58,0	3,7	22
V	136—137	1580, 1670, 3040	62,5	3,8	$C_{19}H_{14}Cl_2O_2$	62,7	4,0	56
VI	179,5—180 (dec.)	1590, 1650, 3040	51,0	2,8	$C_{16}H_{10}Cl_4O_2$	51,1	2,7	93
VII	180—181 (dec.)	1590, 1610, 1685, 3050	58,3	3,4	$C_{22}H_{14}Cl_4O_2$	58,4	3,1	61
VIII	134—135	1550, 1640, 1730, 3070	72,8	4,8	$C_{13}H_{10}O_3$	72,9	4,7	51
IX	191—192,5	1540, 1650, 1720, 3060	78,6	4,9	$C_{19}H_{14}O_3$	78,6	4,8	57
X	180—181 (dec.)	1550, 1630, 1720, 3080	42,0	3,8	$C_{16}H_{10}O_4$	72,1	3,7	93
XI	280,5—282 (dec.)	1555, 1630, 1730, 3090	77,4	3,8	$C_{22}H_{14}O_4$	77,2	4,0	84
XII	119—120	1590, 1660, 3040	48,2	2,4	$C_{21}H_{12}Cl_6O_3$	48,0	2,3	58
XIII	400 (dec.)	1540, 1630, 1720, 3080	70,0	3,6	$C_{21}H_{12}O_6$	70,1	3,3	60

* The compositions of IV-VII and XII were also confirmed by determination of the chlorine content.



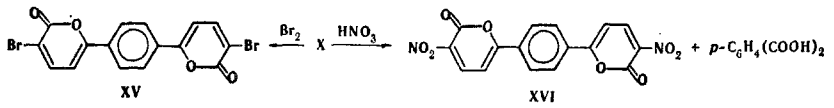
The first step in the synthesis – the preparation of bis(dichloropentadienyl)- and tris(dichloropentadienyl)-substituted aryl ketones (VI, VII, and XII) – was carried out by condensation of acetylarenes I-III with β,β-dichloroacrolein and its bisulfite derivative and 1,1,1,3-tetrachloro-3-alkoxypropanes. The condensation of I with tetrachloroalkoxypropanes proceeds readily at room temperature to give bis(dichloropentadienyl) ketones (VI). The use of dichloroacrolein and its bisulfite derivative leads to the preparation of both bis(dichloropentadienyl)- and mono(dichloropentadienyl)-substituted ketones (IV, VI) in 60-80% overall yields. Diacetyldiphenyl (II) reacts with dichloroacrolein and tetrachloroethoxypropane only on heating (60-80°C), and both acetyl groups are involved in the reaction. A difficult-to-separate mixture of mono-, bis-, and tris(dichloropentadienyl) ketones is formed in the condensation of sym-triacetylbenzene (III) with tetrachloroethoxypropane, whereas XII is isolated in ~60% yield with dichloroacrolein.

The cyclization of dichloropentadienyl ketones IV-VII and XII proceeds smoothly in glacial acetic acid in the presence of phosphoric acid to give mono-, di-, and tripyronyl compounds VIII-XI and XIII. Data on the compounds obtained are presented in Table 1.

Dipyronyl compounds X and XI can be considered to be heteroaromatic analogs of terphenyl and quaterphenyl, whereas XIII can be considered to be an analog of sym-triphenylbenzene. However, in contrast to the colorless polyphenyls, X and XI are intensely yellow like conjugated polyenes. In conformity with the polarization of the bonds of α-pyrone rings [3], one should expect that the attack of electrophilic reagents will be directed to the carbon atoms in the 3 and 5 positions of the α-pyrone ring, as in the case of the electrophilic reactions of 6-phenyl-2-pyrone (XIV). Thus we obtained 1,4-bis(3-bromo-2-pyron-6-yl)benzene (XV) in the bromination of X. However, the bromination of X proceeds considerably more slowly than the bromination of XIV.

Interesting results were obtained in the reaction of nitric acid with di- and tripyronyl compounds X, XI, and XIII. It is known [4] that the only product in the reaction of nitric acid (sp.gr. 1.40) with XIV is 3-nitro-6-

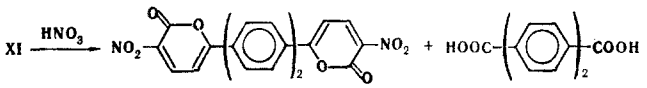
phenyl-2-pyrone. We found that terephthalic acid is formed as a side product along with dinitro compound XVI in the case of nitration of X under the same conditions:



XV XVI

Only oxidation occurs in the case of reactions with nitric acid (sp.gr. 1.35) in glacial acetic acid solutions, during which terephthalic acid is formed in quantitative yield. Similarly, trimesic acid is formed in 80% yield by the action of HNO_3 in glacial acetic acid on tripyronyl compound XIII.

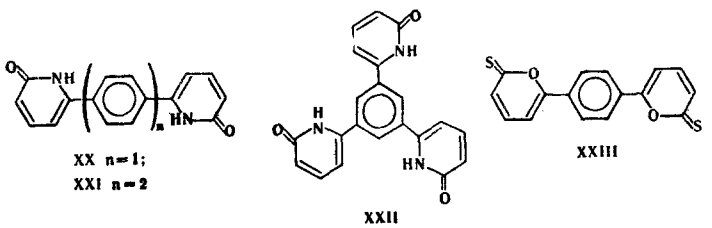
Compound XI reacts with nitric acid in glacial acetic acid and in its absence to give dinitro derivatives XVII and diphenyl-4,4'-dicarboxylic acid:



XVII

This facile oxidation of polypyronyl compounds with nitric acid in glacial acetic acid was a surprise. We therefore carried out the same reaction for XIV. In this case also the only reaction product was benzoic acid. In contrast to XIV, the reaction of 6-(p-nitrophenyl)-2-pyrone (XVIII) proceeds in two directions to give 3-nitro-6-(p-nitrophenyl)-2-pyrone (XIX) and 4-nitrobenzoic acid. The oxidation of XIX with potassium dichromate in sulfuric acid leads to 4-nitrobenzoic acid in 84% yield.

Replacement of the oxygen atoms of the pyrone rings of X, XI, and XIII by nitrogen takes place only under severe conditions (prolonged refluxing with excess ammonium acetate in propionic acid) and leads to di- and tri(2-pyridon-6-yl)arenes (XX-XXII). Dithione XXIII is formed in the reaction of X with phosphorus pentasulfide



XX n=1;
XXI n=2

XXII

XXIII

EXPERIMENTAL

1,4-Bis(5,5-dichloro-1-oxo-2,4-pentadienyl)benzene (VI) and 1-Acetyl-4-(5,5-dichloro-1-oxo-2,4-pentadienyl)benzene (IV). A) A solution of 15 g (60 mmole) of tetrachloroethoxypropane [5] in 10 ml of glacial acetic acid was added with stirring to 4.86 g (30 mmole) of p-diacetylbenzene I in 10 ml of glacial acetic acid, and the mixture was allowed to stand at room temperature for 2 days. The resulting precipitate was removed by filtration to give 10.95 g (93%) of yellow crystals of VI, which were crystallized from chloroform.

B) A solution of 6.3 g (26 mmole) of tetrachlorobutoxypropane [5] in 10 ml of glacial acetic acid was added with stirring to a solution of 2 g (12 mmole) of I in 20 ml of glacial acetic acid, and the mixture was allowed to stand at room temperature for 7 days. Workup gave 4.06 g (87%) of VI.

C) A solution of 1.5 g (9.5 mmole) of I in 5 ml of methylene chloride was cooled to +5°, and a solution of 3.1 g (19 mmole) of dichloroacrolein [5] in 5 ml of methylene chloride was added with stirring. Dry hydrogen chloride was bubbled through the mixture for 2 h. After 15 h, the precipitated crystals were removed by filtration and washed with cold methylene chloride to give 1.9 g (53%) of VI. The filtrate was vacuum evaporated, and the residue was purified by chromatography on activity II aluminum oxide (elution with benzene) to give 0.8 g (22%) of yellow crystals of ketone IV.

D) A solution of 2.85 g (12 mmole) of the bisulfite derivative of dichloroacrolein in 20 ml of glacial acetic acid was added to a solution of 1 g (6 mmole) of I in 20 ml of glacial acetic acid, and dry hydrogen chloride was bubbled through the mixture for 8 h. After 20 h, the precipitated crystals were removed by filtration, and the reaction products were separated by chromatography as indicated in method C to give 1.1 g (48%) of VI and 0.3 g (18%) of IV.

E) A solution of 0.5 g (2.3 mmole) of tetrachloroethoxypropane in 5 ml of glacial acetic acid was added to

TABLE 2. Action of Nitric Acid on 2-Pyrones

Charge			Reaction time, h	Yield, %	
pyrone, g (mmole)	HNO_3, ml	CH_3COOH, ml		nitro compound	arylcarboxylic acid
X, 1,45 (5)	35	—	6	XVI, 60	13
X, 1,45 (5)	25	15	0,5	—	97
XI, 0,68 (2)	15	—	8	XVII, 42	21
XI, 0,68 (2)	15	10	10	XVII, 37	56
XIII, 0,9 (2,5)	25	10	20	—	80
XIV, 1,5 (8,8)	15	10	6	—	87
XVIII, 1,8 (8,8)	20	15	6	XIX, 10	62

a solution of 0.5 g (1.9 mmole) of IV in 10 ml of glacial acetic acid, and the mixture was allowed to stand at 35-40° for 40 h. The precipitated crystals were removed by filtration to give 0.66 g (94%) of VI, which was crystallized from chloroform.

4,4'-Bis(5,5-dichloro-1-oxo-2,4-pentadienyl)diphenyl (VII) and 4-Acetyl-4'-(5,5-dichloro-1-oxo-2,4-pentadienyl)diphenyl (V). A) A solution of 4.76 g (20 mmole) of 4,4'-diacetyldiphenyl II in 20 ml of chloroform was added with stirring to a solution of 13.5 g (60 mmole) of tetrachloroethoxypropane in 10 ml of glacial acetic acid, and the mixture was heated at 80° for 60 h. The precipitated crystals were removed by filtration to give 4.86 g (61%) of yellow crystals of VII, which were crystallized from chloroform. The filtrate was vacuum evaporated, and the residue was passed through a column filled with activity II aluminum oxide [elution with benzene–chloroform (1 : 1)]. The solvent was removed from the eluate by distillation to give 2.25 g (32%) of V.

B) A solution of 1.23 g (9.8 mmole) of dichloroacrolein in 10 ml of glacial acetic acid was added to a refluxing solution of 1 g (4.2 mmole) of II in 15 ml of chloroform, after which dry hydrogen chloride was bubbled through the mixture at 60° for 6 h, and the mixture was allowed to stand at the same temperature for 30 h. The resulting precipitate was separated to give 0.6 g (31.6%) of VII, which was crystallized from chloroform. Work-up of the filtrate gave 0.8 g (56%) of V.

1,3,5-Tris(5,5-dichloro-1-oxo-2,4-pentadienyl)benzene (XII). A solution of 4.1 g (20 mmole) of sym-triacetylbenzene in 60 ml of glacial acetic acid was saturated with dry hydrogen chloride at 45°, after which 8 g (64 mmole) of dichloroacrolein was added, and dry hydrogen chloride was bubbled through the mixture for 13 h. After 15 h, the precipitate (6.1 g) was removed by filtration and crystallized from carbon tetrachloride.

1-Acetyl-4-(2-pyron-6-yl)benzene (VIII). A solution of 1 g (3.5 mmole) of IV in 15 ml of glacial acetic acid and 0.5 ml of phosphoric acid was refluxed for 17 h, after which it was poured into ice water, and the precipitated crystals were removed by filtration to give 0.4 g (51%) of VIII, which was crystallized from chloroform.

4-Acetyl-4'-(2-pyron-6-yl)diphenyl (IX). This compound was similarly obtained and was crystallized from benzene–petroleum ether.

1,4-Di(2-pyron-6-yl)benzene (X). A solution of 4.5 g (17 mmole) of VI in 125 ml of glacial acetic acid and 1 ml of orthophosphoric acid was refluxed for 6 h, and the resulting precipitate was separated and crystallized from dimethylformamide (DMF).

4,4'-Di(2-pyron-6-yl)diphenyl (XI). A solution of 0.5 g (1.1 mmole) of VII in 30 ml of glacial acetic acid and 0.5 ml of orthophosphoric acid was refluxed for 22 h, after which it was worked up to give 0.32 g of yellow acicular crystals of XI, which were crystallized from glacial acetic acid.

1,3,5-Tri(2-pyron-6-yl)benzene (XIII). A solution of 3.3 g (6.3 mmole) of XII in 70 ml of glacial acetic acid and 1 ml of orthophosphoric acid was refluxed for 20.5 h, after which it was worked up to give 2 g of grayish-yellow crystals of XIII, which were crystallized from DMF.

1,4-Bis(3-bromo-2-pyron-6-yl)benzene (XV). A solution of 1.6 g (10 mmole) of bromine in 5 ml of chloroform was added with stirring to a solution of 1.3 g (5 mmole) of X in 20 ml of chloroform, and the mixture was allowed to stand at 60° for 30 h. The resulting precipitate was removed by filtration and washed with chloroform to give 1 g (48%) of shiny yellow plates of XV with mp 360-362° (dec., DMF). Found: C 45.3; H 2.0; Br 37.9%. $C_{16}H_8Br_2O_4$. Calculated: C 45.5; H 1.9; Br 39.7%.

Action of Nitric Acid on 2-Pyrones. Compound X or XI was heated in nitric acid (sp. gr. 1.35) at 60-70°, and the resulting precipitate was separated and washed repeatedly with saturated aqueous sodium carbonate

solution. Nitro compounds XVI and XVII were purified by recrystallization from DMF. Acidification of the sodium carbonate filtrate gave arylcarboxylic acids.

B) Compound X, XI, XIII, XIV, or XVIII was heated in glacial acetic acid with nitric acid (sp. gr. 1.35) at 85-90°, and the resulting nitro compound (XVI, XVII, or XIX) and arylcarboxylic acids were isolated as in method A. The experimental results are presented in Table 2. The arylcarboxylic acids were identified from their melting points or the melting points of their methyl esters. 1,4-Bis(3-nitro-2-pyron-6-yl)benzene (XVI) had mp 203° and ν_{NO_2} 1540 and 1340 cm^{-1}. Found: N 7.4%. $C_{16}H_8N_2O_8$. Calculated: N 7.9%. 4,4'-Bis(3-nitro-2-pyron-6-yl)diphenyl (XVII) had mp 220° (dec.) and ν_{NO_2} 1530 and 1345 cm^{-1}. Found: N 6.3%. $C_{22}H_{12}N_2O_8$. Calculated: N 6.5%. 3-Nitro-6-(p-nitrophenyl)-2-pyrone (XIX) had mp 173.5-175°. Found: N 10.3%. $C_{11}H_6N_2O_6$. Calculated: N 10.7%.

1,4-Di(2-pyridon-6-yl)benzene (XX). A mixture of 2.66 g (10 mmole) of X, 10.4 g (135 mmole) of ammonium acetate, and 20 ml of propionic acid was refluxed for 60 h, and the precipitated X (0.5 g) was separated. The filtrate was poured into water, and the resulting precipitate was removed by filtration and purified by sublimation to give 1.1 g (55%) of light lemon-colored crystals of XX with mp 386.5-388° (dec.). IR spectrum: 3145, 3056, and 2950 (NH); 1650 cm^{-1} (C=O). Found: C 72.2; H 4.6; N 10.1%. $C_{16}H_{12}N_2O_2$. Calculated: C 72.5; H 4.6; N 10.5%.

4,4'-Di(2-pyridon-6-yl)diphenyl (XXI). This compound was similarly obtained in 42% yield and had mp 381-382° (dec., sublimation). IR spectrum: 3136, 3060 (NH); 1655 cm^{-1} (C=O). Found: N 8.4%. $C_{22}H_{16}N_2O_2$. Calculated: N 8.2%.

1,3,5-Tri(2-pyridon-6-yl)benzene (XXII). The method used to prepare XX gave this compound, with mp 500° (dec.), in 22% yield. IR spectrum: 3140, 3050 (NH); 1665 cm^{-1} (C=O). Found: N 8.4%. $C_{21}H_{15}N_2O_3$. Calculated: N 8.6%.

1,4-Di(2-thiopyron-6-yl)benzene (XXIII). A mixture of 1.33 g (5 mmole) of X, 2.3 g (10 mmole) of phosphorus pentasulfide, and 75 ml of nitromethane was refluxed for 15 h, after which the hot solution was decanted, and the residual solid was washed with two 25-ml portions of hot nitromethane. The nitromethane solutions were combined, and the solvent was removed by vacuum distillation to give 1.1 g (74%) of red acicular crystals of XXIII, which were crystallized from DMF to give a product with mp 270° (dec.). Found: C 63.9; H 3.6; S 21.3%. $C_{16}H_{10}O_2S_2$. Calculated: C 64.0; H 3.3; S 21.3%.

The IR spectra of KBr pellets of the compounds were recorded with a UR-10 spectrometer.

LITERATURE CITED

1. Yu. V. Maevskii, S. V. Sokolovskaya, and I. P. Komkov, Khim. Geterotsikl. Soedin., No. 9, 1160 (1970).
2. L. I. Zakharkin and L. P. Sorokina, Izv. Akad. Nauk SSSR, Ser. Khim., 73 (1964).
3. M. E. Perel'son and A. V. Tutkevich, Teor. Eksp. Khim., 2, 575 (1966).
4. L. I. Zakharkin and L. P. Sorokina, Izv. Akad. Nauk SSSR, Ser. Khim., 870 (1965).
5. A. N. Nesmeyanov, R. Kh. Freidlina, and L. I. Zakharkin, Dokl. Akad. Nauk SSSR, 99, 781 (1954).