Dimethyl 3-(p-Tolyl)-6-hydroxyphthalate (IIb). A solution of 2.2 g (14 mmole) of 2-(p-tolyl)furan [1] and 4 g (28 mmole) of dimethyl acetylenedicarboxylate in 20 ml of benzene was refluxed for 5 h, after which the benzene was removed by vacuum distillation,* and the residue was diluted with 25 ml of 90% acetic acid and heated for 20 min on a boiling-water bath. The acetic acid was removed by vacuum distillation, and the residue was neutralized with a saturated solution of sodium carbonate to pH 6-7. The resulting precipitate was removed by filtration. Compounds IIc-g (Table 2) were similarly obtained.

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*The oil remaining after removal of the benzene by distillation [adduct Ib with mp 57-60°C and R_f 0.7 (chloroform). Found: C 67.5; H 5.3%. $C_{17}H_{16}O_5$. Calculated: C 68.0; H 5.4%] partially crystallized. A similar procedure was used to obtain adduct Ic [mp 143-144°C and R_f 0.73 (chloroform). Found: C 63.6; H 4.7%. $C_{16}H_{14}O_6$. Calculated: C 63.6; H 4.7%].

PYRYLIUM, PYRIDINE, AND N-PHENYLPYRIDINIUM DERIVATIVES OF CYCLOPENTADIENYLTRICARBONYLMANGANESE

V. V. Krasnikov and G. N. Dorofeenko

UDC 547.81'82'257.1/514.72

2,4,6-Trisubstituted pyrylium salts containing a cymantrenyl substituent in the 6 position were synthesized by condensation of acetylcymantrene with chalcones. As compared with the corresponding pyrylium derivatives of ferrocene, the pyrylium salts obtained exchange a heteroatom more readily and are more stable. The pyrylium derivatives of cymantrene were converted to the corresponding pyridines by the action of ammonium acetate in glacial acetic acid or an aqueous solution of ammonia and to the corresponding N-phenylpyridinium salts by the action of aniline in acetic acid or alcohol.

We have previously reported [1] the synthesis and some properties of γ-unsubstituted pyrylium derivatives of cyclopentadienyltricarbonylmanganese (cymantrene). It seemed of interest to us to synthesize 2,4,6-trisubstituted pyrylium salts containing a cymantrenyl substituent and to compare their properties with the properties of the corresponding ferrocenylpyrylium salts.

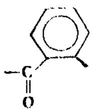
We obtained 2,4-diphenyl-6-cymantrenylpyrylium perchlorate in 9% yield by reaction of acetylcymantrene with benzalacetophenone in ether at room temperature in the presence of anhydrous $HClO_4$. We were unable to increase the yield of the desired product when we carried out the same reaction in refluxing glacial acetic acid in the presence of trityl perchlorate. We found that the best conditions for the reaction are brief (20-40 min) refluxing of equimolar amounts of chalcone, acetylcymantrene, and anhydrous $HClO_4$ in glacial acetic acid. (see scheme on the following page.)

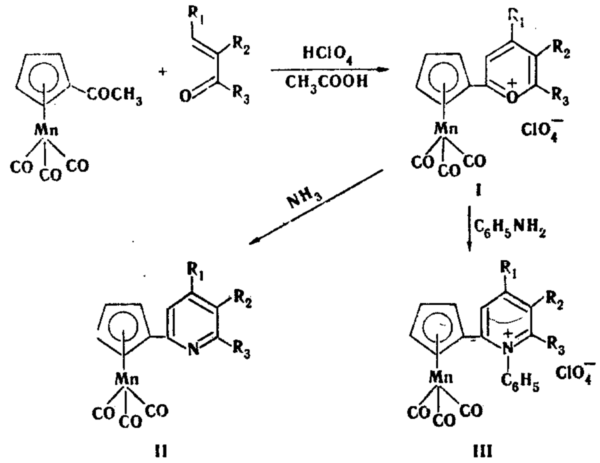
Pyrylium salts I (Table 1) are high-melting red crystalline substances that are stable in air. The IR spectra of salts I contain three absorption bands of carbonyl groups with an absorption maximum at 1930-2025 cm^{-1}, as well as absorption bands of a pyrylium cation at 1612-1615 cm^{-1} and the ClO_4 anion (1090-1100 cm^{-1}). The IR spectrum of salt Id contains the absorption band of a β-carbonyl group at 1728 cm^{-1}.

Scientific-Research Institute of Physical and Organic Chemistry, Rostov-on-Don 344006.
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 21-24, January, 1979. Original article submitted February 14, 1978.

0009-3122/79/1501-0016$07.50

TABLE 1. Pyrylium Salts I, Pyridines II, and N-Phenylpyridium Salts III

Compound	R_1	R_2	R_3	mp, °C	Found, %					Empirical formula	Calc., %					IR spectrum, cm^{-1}	Yield, %
					C	H	Cl	Mn	N		C	H	Cl	Mn	N		
Ia	C_6H_5	H	C_6H_5	246—248	56,1	3,4	6,7	9,9	—	$C_{25}H_{16}ClMnO_8$	56,1	3,0	6,8	10,3	—	2025, 1940, 1930, 1615, 1585, 1510, 1490, 1093, 770, 675, 650	27—4
Ib	4-$CH_3OC_6H_4$	H	C_6H_5	226—227	55,7	3,7	6,2	9,7	—	$C_{26}H_{18}ClMnO_9$	55,3	3,2	6,3	9,7	—	2020, 1950, 1940, 1612, 1590, 1490, 1250, 1180, 1095, 842, 775, 635	49
Ic	C_6H_5	H	4-$CH_3OC_6H_4$	225—226	54,8	3,6	6,8	9,3	—	$C_{26}H_{18}ClMnO_9$	55,3	3,2	6,3	9,7	—	2020, 1945, 1935, 1612, 1585, 1486, 1246, 1175, 1090, 838, 775, 650	64
Id	C_6H_5			>300	55,1	2,8	5,5	9,3	—	$C_{26}H_{14}ClMnO_9$	55,7	2,5	6,3	9,7	—	2020, 1940, 1728, 1615, 1590, 1500, 1485, 1100, 892, 748, 650	24
IIa	C_6H_5	H	C_6H_5	124—125	69,6	3,8	—	12,3	3,1	$C_{25}H_{16}MnNO_3$	69,3	3,7	—	12,7	3,2	2005, 1925, 1915, 1600, 1551, 785, 700, 663	82
IIb	4-$CH_3OC_6H_4$	H	C_6H_5	139—140	67,5	3,9	—	11,7	2,9	$C_{26}H_{18}MnNO_4$	67,4	3,9	—	11,9	3,0	2012, 1940, 1920, 1589, 1509, 1245, 1179, 1031, 834, 762, 665	80
IIc	C_6H_5	H	4-$CH_3OC_6H_4$	140—141	66,9	3,9	—	11,5	3,2	$C_{26}H_{18}MnNO_4$	67,4	3,9	—	11,9	3,0	2001, 1920, 1900, 1600, 1544, 1511, 1250, 1175, 1048, 835, 760, 660	67
IIIa	C_6H_5	H	C_6H_5	261—262	61,3	3,7	5,3	8,9	2,4	$C_{31}H_{21}ClMnNO_7$	61,0	3,5	5,8	9,0	2,3	2040, 1960, 1933, 1630, 1564, 1100	100
IIIb	4-$CH_3OC_6H_4$	H	C_6H_5	224—225	60,0	3,9	5,5	8,0	2,1	$C_{32}H_{23}ClMnNO_8$	60,0	3,6	5,6	8,6	2,2	2020, 1940, 1925, 1615, 1553, 1510, 1255, 1178, 1089, 1025, 831, 775, 666	76
IIIc	C_6H_5	H	4-$CH_3OC_6H_4$	229—230	59,6	4,0	5,0	8,2	2,4	$C_{31}H_{23}ClMnNO_8$	60,0	3,6	5,6	8,6	2,2	2020, 1945, 1932, 1618, 1550, 1510, 1296, 1254, 1180, 1090, 1030, 834, 777, 660	76



The properties of pyrylium salts I differ markedly from the properties of the corresponding ferrocene derivatives [2]. Thus the α-ferrocenylpyrylium salts are unstable substances in both the solid state and particularly in solutions. Replacement of the heteroatom in the ferrocenylpyrylium salts occurs only under severe conditions and gives the products in low yields; a significant amount of the starting salt undergoes decomposition in the process. We were unable to synthesize N-phenylpyridinium derivatives of ferrocene from α-ferrocenylpyrylium salts.

In contrast to the α-ferrocenylpyrylium salts, the α-cymantrenylpyrylium salts readily exchange a heteroatom under mild conditions — by reaction of pyrylium salts Ia-c with ammonium hydroxide or by brief refluxing with ammonium acetate in glacial acetic acid. The IR spectra of the 2,4-diaryl-6-cymantrenylpyridines II contain three absorption bands of carbonyl groups (1900-2012 cm^{-1}) and absorption bands of aromatic and pyridinium rings (1509-1600 cm^{-1}) (see Table 1).

Brief refluxing of pyrylium salts Ia-c with an equimolar amount of aniline in glacial acetic acid or alcohol leads to the formation of N-phenylpyridinium derivatives III in high yields; in contrast to pyrylium salts I, III are slightly colored cream-yellow compounds. The IR spectra of the pyridinium salts contain three absorption bands of carbonyl groups (1925-2040 cm^{-1}) and absorption bands of a pyridinium cation (1615-1630 cm^{-1}) and a ClO_4 anion (1089-1100 cm^{-1}) (see Table 1).

Thus the pyrylium derivatives of cymantrene are convenient starting compounds for the synthesis of some cymantrenyl-containing heterocycles.

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a Specord-71 IR spectrometer.

2,4-Diphenyl-6-cymantrenylpyrylium Perchlorate (Ia). A) A 0.2-ml (0.002 mole) sample of 70% $HClO_4$ and 0.6 ml (0.006 mole) of acetic anhydride were added dropwise successively to a solution of 0.42 g (0.002 mole) of benzalacetophenone in 15 ml of ether. After 2-3 min, 0.5 g (0.002 mole) of acetylcymantrene was added to the reaction mixture, and the resulting mixture was allowed to stand at room temperature for 24 h. The precipitate was removed by filtration and washed with ethyl acetate–ether (1:4) to give 0.1 g (9%) of Ia.

B) A mixture of 0.5 g (0.002 mole) of acetylcymantrene, 0.42 g (0.002 mole) of benzalacetophenone, 1.0 g (0.003 mole) of triphenylmethyl perchlorate, and 10 ml of glacial acetic acid was refluxed for 1 h, after which it was diluted with ether, and the resulting precipitate was removed by filtration to give 0.1 g (9%) of Ia.

General Method for the Synthesis of Pyrylium Salts I by Condensation of Chalcones with Acetylcymantrene. A 0.2-ml (0.002 mole) sample of 70% $HClO_4$ and 0.6 ml (0.006 mole) of acetic anhydride were added successively to a solution of 0.002 mole of the chalcone in 10 ml of glacial acetic acid. After 2-3 h, 0.5 g (0.002 mole) of acetylcymantrene was added to the mixture, and the resulting mixture was refluxed for 20-40 min. It was then allowed to stand at room temperature for 2 h, and the resulting precipitate was removed by filtration (seeding was sometimes necessary to start crystallization). An additional amount of the pyrylium salt was precipitated from the mother liquor by the addition of ether. Data on the yields and properties of pyrylium salts I and the results of analysis are presented in Table 1.

Synthesis of Pyridines II from Pyrylium Salts I. A) Pyrylium salt Ia was suspended in glacial acetic acid, a fivefold excess of ammonium acetate was added, and the mixture was refluxed for 1 h. It was then diluted with water and neutralized with NH_4OH. The aqueous mixture was extracted with benzene, the solvent was removed from the extract by vacuum evaporation to dryness, and the residue was recrystallized from heptane.

B) The pyrylium salt (Ib,c) was suspended in C_2H_5OH, 25% ammonium hydroxide was added, and the mixture was allowed to stand for 2 days. It was then extracted with ether, and the ether was removed from the extract by vacuum evaporation to dryness. The residue was recrystallized from alcohol (Table 1).

Synthesis of N-Phenylpyridium Salts III from Pyrylium Salts I. A mixture of equimolar amounts of aniline and pyrylium salt I was refluxed for 1 h in glacial acetic acid (in the case of Ia) or for 1.5-2 h in C_2H_5OH (in the case of Ib,c), after which the mixture was cooled, and the precipitate was removed by filtration. An additional amount of salt III can be precipitated by means of ether. Pyridinium salt III contained crystallization acetic acid from which it can be freed by drying at 160-190°C. Analytically pure samples of pyridium salts III were obtained by recrystallization from alcohol (Table 1).

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CHEMISTRY OF HETEROANALOGS OF ISOFLAVONES.

7.* SYNTHESIS OF THIAZOLE ANALOGS OF ISOMERIC ISOFLAVONES

V. P. Khilya, V. F. Vakulenko, and I. P. Kupchevskaya

UDC 547.814.1'789.1.07

Thiazole analogs of isomeric isoflavones were synthesized from α-(2,4-dimethyl-5-thiazolyl)-2-hydroxyacetophenones, and their reaction with hydrazine hydrate and alkylating and acylating agents was studied. The reaction of thiazole derivatives of 7-hydroxychromone with hydrazine hydrate proceeds with opening of the pyrone ring and subsequent cyclization of the intermediate to o-hydroxyphenylpyrazole derivatives. The reaction of hydrazine hydrate with thiazole derivatives of 5-hydroxychromone, which proceeds with retention of the pyrone ring, leads to hydrazones. The structures of the new compounds were confirmed by the PMR spectra.

Flavonoids are an interesting and unusual group of natural compounds with a broad spectrum of biological activity [2], owing to which they have found application as medicinals. In addition to the utilization of preparations isolated from natural raw material, synthetic products, particularly modified flavonoids, are becoming increasingly valuable. The phenyl group in their molecules is replaced by other groups, including heterocyclic residues with aromatic character.

In the development of research on the synthesis and study of the chemical and biological properties of heterocyclic derivatives of isoflavone as potential physiologically active substances we obtained new thiazole analogs of isomeric isoflavones I-III, as well as compounds of the IV series, and investigated their reactivities with respect to hydrazine hydrate and alkylating and acylating agents. The starting compounds for the synthesis of these

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*See [1] for communication 6.

T. V. Shevchenko Kiev State University, Kiev 252017. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 25-28, January, 1979. Original article submitted December 23, 1977.

0009-3122/79/1501-0019\$07.50