PHENYL DERIVATIVES OF 2-PYRONE. IV.* SYNTHESIS OF A NUMBER OF DI- AND TRIALKOXYPHENYL-2-PYRONES

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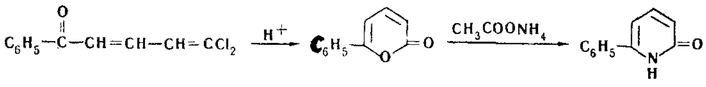
Several phenyl dichloropentadienyl ketones containing a hydroxy or methoxy group in the benzene ring as well as a number of 2-pyrones based on them were synthesized. The possibility of the conversion of the latter to the corresponding 2-pyridones on heating them with ammonium salts is demonstrated.

Dichloropentadienyl phenyl ketones with hydroxy and methoxy groups in the benzene ring (I-V) are obtained by the condensation of 1,1,1,3-tetrachloro-3-ethoxypropane (TCEP) or β,β-dichloroacrolein (DCA) with substituted acetophenones [1, 2]. Like its monosubstituted analog, viz., 1,1-dichloro-5-(2'-methoxyphenyl)-1,3-pentadien-5-one, described in [1], 1,1-dichloro-5-(2',6'-dimethoxyphenyl)-1,3-pentadien-5-one (I) could not be isolated in analytically pure form. (It was characterized by its 2,4-dinitrophenylhydrazone.) Even after chromatographic purification, both ketones are very viscous, uncrystallizable masses. On the other hand, unsaturated ketones containing methoxy groups in other positions as well as all of the hydroxyphenyl dichloropentadienyl ketones are satisfactorily crystallizable substances.

The unsaturated ketones are converted to 2-pyrones (VI-IX) by cyclization in acidic media



I–V VI–IX X–XIII

We note that in contrast to the other analogs, I does not form a pyrone under these conditions, which is apparently due to shielding of the carbonyl group by the o-methoxy groups. The yields of pyrones in the other cases exceed 70%.

The reaction of 6-phenyl- and 6-(3',4'-dimethoxyphenyl)-2-pyrones with ammonium acetate yielded the corresponding 2-pyridones. The reaction proceeds with difficulty and requires prolonged heating.

The structures of the synthesized compounds were confirmed by their IR spectra (Tables 1 and 2).†

EXPERIMENTAL

1,1-Dichloro-5-(3',4'-dimethoxyphenyl)-1,3-pentadien-5-one (III). This was obtained by holding a mixture of 4 g (22 mmole) of 3,4-dimethoxyacetophenone, 5.6 g (25 mmole) of TCEP, and 35 ml of acetic acid for 11 days at room temperature to give 4 g of III with mp 125-126° (benzene–heptane).

Compounds I, II, IV, and V were similarly obtained (Table 1). The yield of V increases if the condensation is carried out with DCA, as described below.

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*See [2] for communication III.

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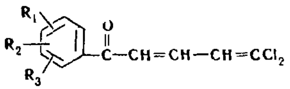
TABLE 1.



Compound	Substituents and positions	React. time, days	mp	IR spectrum* $\nu_{C=O}$, cm^{-1}	Empirical formula	Found, %				Calculated, %				Yield, %
						C	H	Cl	N	C	H	Cl	N	
II	—	4	74,5—75,5†	—	$C_{11}H_8Cl_2O$	—	—	31,21	—	—	—	31,23	—	84
I	2.6-$(OCH_3)_2$	13	—	—	$C_{13}H_{12}Cl_2O_3$	—	—	—	—	—	—	—	—	54,3
	DNP of I ‡	—	236—237	—	$C_{19}H_{16}Cl_2N_4O_6$	—	—	—	11,83	—	—	—	11,99	—
III	3.4-$(OCH_3)_2$	11	125—126	1654	$C_{13}H_{12}Cl_2O_3$	54,16	4,00	24,61	—	54,37	4,21	24,70	—	60,1
	DNP of III‡	—	172,5—173,5	—	$C_{19}H_{16}Cl_2N_4O_6$	—	—	—	12,00	—	—	—	11,99	—
IV	3.4-$(OH)_2$**	30	190,5—191 (dec.)	1644	$C_{11}H_8Cl_2O_3$	51,04	3,16	27,24	—	50,99	3,11	27,37	—	57,9
	Acet. of IV	—	88—88,5	—	$C_{15}H_{12}Cl_2O_5$	52,70	3,48	20,66	—	52,50	3,53	20,66	—	—
V	3,4,5-$(OCH_3)_3$	11	94—95	1669	$C_{14}H_{14}Cl_2O_4$	53,01	4,61	22,30	—	53,01	4,45	22,36	—	4,3
	DNP of V‡	—	160—160,5	—	$C_{20}H_{18}Cl_2N_4O_7$	—	—	—	11,28	—	—	—	11,27	—

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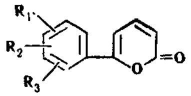
* The spectra of mineral oil pastes were obtained with a UR-10 spectrometer.

† According to [4], this compound has mp 76-77°.

‡ DNP indicates dinitrophenylhydrazones. They were purified chromatographically on aluminum oxide with subsequent recrystallization from benzene–heptane.

** ν_{OH}: 3490 and 3260 cm^{-1}.

TABLE 2.



Compound	Substituents and positions	Heating time, h	mp	IR spectrum, $\nu_{C=O}$, cm^{-1}	Empirical formula	Found, %		Calculated, %		Yield, %
						C	H	C	H	
VI	—	19	66—67^{1}*	—	$C_{11}H_8O_2$	76,76	4,80	76,73	4,68	98
VII	3,4-$(OH)_2$†	22	214—215	1676, 1539	$C_{11}H_8O_4$	64,91	3,98	64,70	3,95	82
	Ацетат VII	—	113,5—114,5	—	$C_{15}H_{12}O_6$	62,84	4,10	62,50	4,20	77,2
VIII	3,4-$(OCH_3)_2$	35	96—97	1736, 1548	$C_{13}H_{12}O_4$	67,39	4,89	67,23	5,21	76,7
IX	3,4,5-$(OCH_3)_3$	18	121—122	1721, 1548	$C_{14}H_{14}O_5$	64,36	5,27	64,11	5,38	89,5

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* According to [5], the compound melts at 68°.

† ν_{OH}: 3334 and 3240 cm^{-1}.

1,1-Dichloro-5-(3',4',5'-trimethoxyphenyl)-1,3-pentadien-5-one (V). A solution of 3 g (14.2 mmole) of 3,4,5-trimethoxyacetophenone and 1.8 g (14.4 mmole) of DCA in 30 ml of acetic acid was saturated for 75 min with hydrogen chloride, gradually lowering the temperature to 4-5°. The mixture was held for another 20 h at room temperature, diluted with water, and V was extracted with chloroform. After washing and drying, 1.11 g (24.7%) of yellowish crystals of V with mp 94-95° (heptane) was isolated chromatographically (on Al_2O_3) from the extract.

6-(3',4'-Dihydroxyphenyl)-2-pyrone (VII). A mixture of 2.6 g (10 mmole) of IV, 40 ml of acetic acid, and 1.3 ml of 83.8% phosphoric acid was refluxed for 22 h. The bulk of the acetic acid was distilled from the residue to isolate 1.72 g of VII with mp 214-215° (acetic acid).

Compounds VI, VIII, and IX were similarly obtained (Table 2).

6-Phenyl-2-pyridone (X). A mixture of 1.5 g (8.7 mmole) of VI, 5 g of ammonium acetate, and 2 ml of glacial acetic acid was heated for 35 h at 135-140° to give 0.98 g (65.9%) of X with mp 196-197° (from benzene; mp 197° [3]). Found %: C 77.09; H 5.44; N 8.29. $C_{11}H_9NO$. Calculated %: C 77.17; H 5.30; N 8.18.

N-Methyl-6-phenyl-2-pyridone (XI). A total of 0.86 g (5 mmole) of X was dissolved in 15 ml of water containing 0.8 g of sodium hydroxide, and 2.5 ml of dimethyl sulfate was added with shaking. The mixture was heated for 30 min on a boiling-water bath, diluted with water, and the reaction products were extracted with chloroform. The washed and dried extract was evaporated, and the resulting oil was steam distilled to give 0.62 g (67.7%) of residual XI with mp 90.5-91.5° (benzene–heptane). Found %: C 77.44; H 5.90; N 7.52. $C_{12}H_{11}NO$. Calculated %: C 77.81; H 5.99; N 7.56.

The hydrochloride of XI was obtained by the reaction of dry hydrogen chloride with a solution of XI in absolute benzene to give yellow needles which decomposed on heating. Found %: C 65.23; H 5.66; Cl 15.92. $C_{12}H_{11}NO \cdot HCl$. Calculated %: C 65.01; H 5.46; Cl 15.99.

The colorless, transparent oil, which was volatile with steam, was 2-methoxy-6-phenylpyridine (XII). Repeated steam distillation gave 0.1 g (10.9%) of XII. Found %: C 77.46; H 5.73; N 7.63. $C_{12}H_{11}NO$. Calculated %: C 77.81; H 5.99; N 7.56.

6-(3,4-Dimethoxyphenyl)-2-pyridone (XIII). A mixture of 0.8 g (3.5 mmole) of VIII, 1.6 g of ammonium acetate, and 2.5 ml of glacial acetic acid was refluxed for 6 h to give 0.12 g (15%) of XIII with mp 188-189° (alcohol). IR spectrum: 1650 cm^{-1} ($\nu_{C=O}$); 3160 and 3115 cm^{-1} (ν_{NH}). Found %: C 67.49; H 5.57; N 6.05. $C_{13}H_{13}NO_3$. Calculated %: C 67.52; H 5.66; N 6.06.

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