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PHENOLIC DERIVATIVES OF 2-PYRONE

II. Transformations of 1,1-Dichloro-5-(2',5'-dimethoxyphenyl)-1,3-pentadien-5-one*

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The cyclization of 1,1-dichloro-5-(2',5'-dimethoxyphenyl)-1,3-pentadien-5-one and the product of its partial demethylation leading to the corresponding derivatives of 2-pyrone and 2-(β,β-dichlorovinyl)-6-methoxy-4-chromanone has been studied. Irradiation causes the dimerization of 1,1-dichloro-5-(2',5'-dimethoxyphenyl)-1,3-pentadien-5-one.

During its formation from 2,5-dimethoxyacetophenone and 1, 1, 1, 3-tetrachloro-3-ethoxypropane, 1, 1-dichloro-5-(2',5'-dimethoxyphenyl)-1,3-pentadien-5-one (I) undergoes partial demethylation to 1,1-dichloro-5-(2'-hydroxy-5'-methoxyphenyl)-1,3-pentadien-5-one (II). The structure of II has been confirmed by independent synthesis and by its conversion into I. Compound II, like 1,1-dichloro-5-(2'-hydroxyphenyl)-1,3-pentadien-5-one [1] can be cyclized in two directions—with the formation of 6-(2'-hydroxy-5'-methoxyphenyl)-2-pyrone (III) and of 2-(β,β-dichlorovinyl)-6-methoxy-4-chromanone (IV). Under the same conditions, I gives only 6-(2',5'-dimethoxyphe-

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*For part I, see [1].

Properties and Analytical Data of the Compounds Synthesized

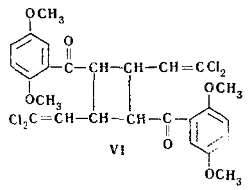
Compound	Mp, °C	UV spectra*		IR spectra**		Empirical formula	Found, %			Calculated, %			Yield, %
		λ_{max}, nm	log ε	$\nu_{C=O}$, cm⁻¹	ν_{OH}, cm⁻¹		C	H	Cl	C	H	Cl	
I	106—107	372; 298,5; 220	3.628; 4.421; 4.162	1646	—	$C_{13}H_{12}Cl_2O_3$^a	54.69	4.00	24.33	54.37	4.21	24.70	90.1
II	108—109	310; 407; 220	4.441; 3.682; 4.104	1575	—b	$C_{12}H_{10}Cl_2O_3$	52.56	3.76	26.27	52.77	3.69	25.96	80.5
V	98—99	—	—	1725	—	$C_{13}H_{12}O_4$	67.03	5.09	—	67.23	5.21	—	95.8
III	161.5—162.5	375; 325; 242; 221	4.100; 3.886; 3.823; 4.328	1702	3210	$C_{12}H_{10}O_4$	65.84	4.55	—	66.05	4.62	—	30.0
IV	86—86.5	350; 256; 225,5	3.582; 3.886; 4.386	1690	—	$C_{12}H_{10}Cl_2O_3$	52.61	3.80	25.86	52.77	3.69	25.96	18.0
VI	142—142.5	338; 252	3.894; 4.130	1666	—	$C_{26}H_{24}Cl_4O_6$^c	54.70	4.20	24.72	54.37	4.21	24.70	100.0

* EPF-3 ultraviolet spectrophotometer, solvent ethanol.

** UR-10 infrared spectrophotometer, in the form of a mull in paraffin oil.

[a] 2,4-Dinitrophenylhydrazone of I—mp 192-193° C. Found, %: N 11.96. Calculated for $C_{19}H_{16}Cl_2N_4O_6$, %: N 11.99. [b] Absent because of a hydrogen bond. [c] Molecular weight, found: 570 (cryoscopically); calculated: 574.

nyl)-2-pyrone (V). It is interesting that under the action of light I undergoes photodimerization being converted into a cyclobutane derivative with the structure VI. The structure of the conversion products has been confirmed by IR and UV spectra (see table).



EXPERIMENTAL

1,1-Dichloro-5-(2',5'-dimethoxyphenyl)-1,3-pentadien-5-one (I) was obtained by method A, described previously, from 2,5-dimethoxyacetophenone [1]. Compound II was obtained from the mother liquors from the recrystallization of I. It was also obtained from 2-hydroxy-5-methoxyacetophenone by method B [1].

6-(2',5'-Dimethoxyphenyl)-2-pyrone (V) was obtained by the cyclization of I [2]. Under the same conditions, compound II forms III and IV.

Dimerization was carried out by irradiating I with sunlight. The properties of the compounds obtained are given in the table.

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SYNTHESIS OF SILACYCLOBUTANES FROM HALOALKYLMETHOXYSILANES

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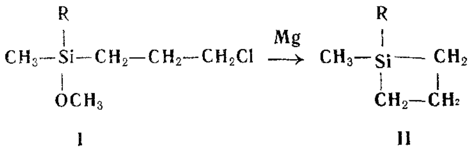
The possibility of synthesizing silacyclobutane derivatives from haloalkylalkoxysilanes has been studied (with γ-chloropropylmethyldimethoxysilane and γ-chloropropyldimethylmethoxysilane as examples). The intramolecular cyclization of these compounds takes place only when polar solvents are used.

Substituted 1-silacyclobutanes are of definite interest not only from the theoretical but also from the practical aspect as initial monomers for the production of silacarbane polymers [1].

The intramolecular organometallic ring closure of γ-chloropropyl derivatives of silicon in a polar solvent is usually used for the synthesis of the silacyclobutanes [2, 3]. We decided to transfer this reaction to γ-chloropropylmethyldimethoxysilane and γ-chloropropyldimethylmethoxysilane, since it appeared possible to carry out the ring-closure reaction in an excess of the initial methoxy derivatives, using them as the polar solvent.



$$\underset{\text{I}}{CH_3-\underset{OCH_3}{\overset{R}{Si}}-CH_2-CH_2-CH_2Cl} \xrightarrow{Mg} \underset{\text{II}}{CH_3-\overset{R}{Si}(CH_2CH_2CH_2)}$$

I II

R=OCH$_3$, CH$_3$

However, it was found that intramolecular cyclization does not take place under these conditions (see table).

Carrying out the reaction in an aromatic solvent (xylene) by the method used for synthesizing organometallic compounds proposed by Ashby [5] gave a very small yield of silacyclobutanes (II).

Only when polar solvents (diethyl and dibutyl ethers) were used were 1,1-dimethylsilacyclobutane and 1-methyl-1-methoxysilacyclobutane, respectively, obtained in satisfactory yields. The latter has not been described in the literature (its structure was confirmed by independent synthesis by the direct methoxylation of 1-chloro-1-methylsilacyclobutane and also by spectral data). The IR spectrum of 1-methyl-1-methoxysilacyclobutane contains bands at 1187, 1123, and 909 cm^{-1}, which are characteristic for all silacyclobutane compounds [4], at 1098 cm^{-1}, which is characteristic for Si—O—C vibrations, and at 1253 and 790 cm^{-1} which are characteristic for the Si—CH$_3$ grouping.

EXPERIMENTAL

γ-Chloropropylmethyldichlorosilane and γ-chloropropyldimethylchlorosilane were synthesized by a published method [6]. γ-Chloropropylmethyldimethoxysilane and γ-chloropropyldimethylmethoxysilane were obtained by the methoxylation of the corresponding chlorosilanes