7-ARYL-6,7-DIHYDRO-8H-INDENO[1',2':2,3]PYRANO-[5,6-c]BENZO[c]PYRAN-6,8-DIONES AND THEIR THIO ANALOGS

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The ability of $3-[\alpha-(1,3-dioxo-2-indany1)benzy1]-4-hydroxy-substituted 2H-benzo[b]pyran-2-ones and benzo[b]thiopyran-2-ones to undergo dehydration under the influence of dehydrating agents to give 7-ary1-6,7-dihydro-8H-indeno[1',2':-2,3]pyrano[5,6-c]benzo[c]pyran-6,8-diones and their thio analogs was demonstrated.$

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 $3-[\alpha-(1,3-\text{Dioxo}-2-\text{indanyl})\text{benzyl}]-2\text{H-benzo}[b]\text{pyran}-2-\text{ones I can exist in chain and ring forms in solutions [1]. It is known that intramolecular addition reactions are followed in many cases by splitting out of water, hydrogen chloride, etc., which leads to stable heterocycles [2]. In this connection, in order to investigate the chemical properties of I and their thio analogs II it was of interest to attempt to split out a molecule of water from them to give the corresponding pyran derivatives III and IV, as described in [3-5] for geminal diindandione derivatives.$



I, III X=0; II, IV X=S; I-IV a R=2-OCH₃; b R=3-NO₂; c R=4-Br

We have accomplished the dehydration of some compounds of the I type and their thio analogs II by heating on a boiling-water bath with acetic anhydride in the presence of catalytic amounts of concentrated sulfuric acid.

The IR spectra of the compounds obtained (Table 1) do not contain the bands of stretching and deformation vibrations of a hydroxy group at 3340-3400 and 1286-1298 cm⁻¹ that are characteristic for starting reagents I and II. At the same time, new intense bands of stretching vibrations of a conjugated C=C bond in the indene ring at $\sim 1660-1662$ cm⁻¹ and of C=O bonds in the pyran ring at 1338-1358 cm⁻¹ appear in the spectra. The remaining parts of the IR spectra of the reaction products and the starting compounds are similar, although the positions of some absorption bands change slightly.

EXPERIMENTAL

Confirmation of the individuality of the compounds and monitoring of the course of the reactions were realized by thin-layer chromatography (TLC) on Silufol UV-254 plates with a fixed layer of silica gel in a benzene-ethyl acetate system (3:1) with development by iodine vapors. The IR spectra of KBr pellets of the compounds were obtained with a Perkin-Elmer spectrometer.

7-Ary1-6,7-dihydro-8H-indeno[1',2':2,3]pyrano[3,5-c]benzo[c]pyran-6,8-diones IIIa-c and 7-Ary1-6,7-dihydro-8H-indeno[1',2':3]pyrano[3,5-c]benzo[c]thiopyran-6,8-diones IVa,b. A 2-mmole sample of Ia-c or IIa,b was mixed with 6 ml of acetic anhydride, one to two drops of concentrated sulfuric acid were added, and the reaction mixture was shaken and then

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TABLE 1. 7-Ary1-6,7-dihydro-8H-indeno[1',2':2.3]pyrano[3,5c]benzo[c]pyran-6,8-diones IIIa-c and Their Thio Analogs IVa.b

Com-	mp,°C	IR spectrum, cm ⁻¹		Found, %			Empirical	Calculated, %			d, %
pound		С—О	C=C	с	н	S[N](Br)	formula	с	н	S[N](Br)	Yiel
IIIa IIIb IIIc IVa IVb	283—284 293—294 296 268—269 270—271	1025—1358 1048—1350 1040—1355 1018—1338 1060—1343	1660 1660 1662 1661 1660	76,4 70,8 65,6 73,5 68,3	3,9 3,0 2,6 3,7 2,9	[3,2] (17,4) 7,4 7,2 [3,1]	$\begin{array}{c} C_{26}H_{16}O_5\\ C_{25}H_{13}NO_6\\ C_{25}H_{13}BrO_4\\ C_{26}H_{16}O_4S\\ C_{25}H_{13}NO_5S\end{array}$	76,4 70,9 65,6 73,6 68,3	3,9 3,1 2,8 3,8 3,0	[3,3] (17,5) 7,5 7,3 [3,2]	46 94 77 42 89

heated on a boiling-water bath. At the end of the reaction (monitoring by TLC), the contents of the flask were cooled, and the solid phase was removed by filtration and washed successively with acetic anhydride and methanol. All of the IIIa-c and IVa, b obtained were yellow and dissolved when they were heated in benzene, chloroform, and acetone.

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SYNTHESIS, HALOGENATION, AND NITRATION OF 6-METHYL-

3-PHENYL-2-PYRONE DERIVATIVES

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Simple methods for the synthesis of 3-ary1-6-methy1-2-pyrones and 3-ary1-5carbalkoxy-6-methyl-2-pyrones by the reaction of ethyl α -formylarylacetates with acetone and acetoacetic acid esters, respectively, are proposed. Some electrophilic substitution reactions of 6-methy1-3-pheny1-2-pyrone and 5-carbethoxy-6-methy1-3-pheny1-2-pyrone were studied.

2-Pyrones are quasi-aromatic compounds with a complex set of chemical properties. The relative activities of pyrone and phenyl rings in electrophilic substitution reactions of derivatives of 4-phenyl-2-pyrone, 5-phenyl-2-pyrone, and 6-phenyl-2-pyrone have been previously studied [1-4]. It was established that, depending on the nature of the electrophilic agent, the structure of the pyrone, and the reaction conditions, substitution may occur in the 3 and 5 positions of the pyrone ring or in the para and meta positions of the phenyl ring.

Electrophilic substitution in 3-pheny1-2-pyrone derivatives has not been studied; this is apparently due to the difficulty in obtaining these compounds. Only the four-step synthesis of 3-phenyl-6-methyl-2-pyrone from phenylacetonitrile and methyl vinyl ketone in 10% overall yield is known [5]. In this connection, we have developed two rather simple methods for the synthesis of 3-ary1-6-methy1-2-pyrones and 3-ary1-5-carbalkoxy-6-methy1-2pyrones and studied their behavior in electrophilic substitution reactions.

The corresponding 3-ary1-6-methy1-2-pyrones IIa-c were synthesized in 20-23% overall yields by condensation of ethyl α -formylarylacetates Ia-c with acetone in the presence of

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