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ARYL- AND ARYLOXYFURANS AS COMPONENTS OF THE DIENE SYNTHESIS WITH DIMETHYL ACETYLENEDICARBOXYLATE

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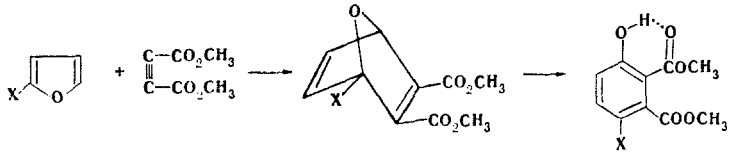
The diene synthesis of 2-aryl- and 2-aryloxyfurans with dimethyl acetylenedicarboxylate gives adducts, the aromatizatio of which under the influence of acetic acid leads to esters of 3-aryl- and 3-aryloxy-6-hydroxyphthalic acids.

The high reactivity of furan and its homologs as diene components in the Diels—Alder reaction is widely known. The behavior of arylfurans in this reaction has been studied in individual cases [1], whereas the behavior of aryloxyfurans in this reaction has not been studied at all.

We have shown that the reaction of aryl- and aryloxyfurans with dimethyl acetylenedicarboxylate give dimethyl 3,6-endoxo-3,6-dihydrophthalates (I), which are converted to methyl 6-hydroxyphthalates (II) as a result of aromatization under the influence of acetic



Ia-g IIa-g

I, II a $X=C_6H_4NHCOCH_3$; b $X=C_6H_4CH_3$-*p*; c $X=C_6H_4OH$-*p*; d $X=C_6H_4OC_4H_9$-*p*; e $X=C_6H_4Cl$-*p*; f $X=OC_6H_4CH_3$-*p*; g $X=OC_6H_5$

acid. Adduct Ia was isolated in quantitative yield; adducts Ib,c were obtained in the form of oils, which we were able to crystallize only partially. In this connection, adducts Ib-g were subjected to aromatization without prior purification.

The presence of the signal of a hydroxy group at 10.77-10.92 ppm and two singlets of ester groups at 3.59-3.92 ppm is characteristic of the PMR spectra of substituted hydroxydiphenyls II. As a rule, the signals of the protons in the 4 and 5 positions and the protons of the substituent in the 3 position are overlapped and form a complex multiplet (Table 1).

Two bands of stretching vibrations of the CO group of the carbomethoxy substituents (high-frequency band at 1733-1744 cm^{-1} and low-frequency band at 1679-1685 cm^{-1} in CCl_4) and ν_{OH} bands of a phenolic hydroxy group (3430-3440 and 3125-3165 cm^{-1} in CCl_4, Table 2) are observed in the IR spectra of crystalline II and solutions of II.

It is apparent from the results (Table 2) that the yields of the adducts of arylfurans with dimethyl acetylenedicarboxylate, which subsequently undergo conversion to hydroxyphthalic acids, depend on the character of the substituent in the benzene ring of the arylfurans;

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TABLE 1. PMR Spectra of IIa-g

Compound	δ, ppm			
	OCH_3	OH	substituent in the X group	aromatic protons
IIa	3,61; 3,86	10,87	2.04 ($COCH_3$); 7.76 (NH)	6,94—7,52
IIb	3,61; 3,89	10,92	2.35	7,00—7,44
IIc	3,62; 3,87	10,91	6,09	6,76—7,44
IId	3,57; 3,84	10,86	0,5 2,0; 3,92	6,76—7,44
IIe	3.59; 3,87	10,91	—	7,00—7,30
IIf	3,84; 3,92	10,77	2,29 (CH_3)	6,72—7,05
IIg	3,71; 3,81	10,54	—	6,71 7,37

TABLE 2. Dimethyl 3-Aryl(aryloxy)-6-hydroxyphthalates (II)

Compound	mp, °C[a]	R_f (in chloroform)	IR spectrum, ν, cm⁻¹				UV spectrum, λ_{max}, nm (log ε)	Found, %		Empirical formula	Calc., %		Yield, %[b]
			in mineral oil		in CCl_4 (0,02%)			C	H		C	H	
			C=O	OH	C=O	OH							
IIa	172—174	0,33	1706 s, 1693s, 1665 s	3352	1733 s, 1701 s 1679s	3130 m br 3430 s	265 (4,42), 320 (3,63)	63,2	5,1	$C_{18}H_{17}NO_6$[c]	63,0	5,0	75
IIb	112—113	0,25[d]	1737 s, 1674s	3040 m	1740 s, 1681 s	3130 m br 3430 vw	230 (4,41) 318 (3,63)	67,8	5,4	$C_{17}H_{16}O_5$	68,0	5,4	39
IIc	145—146	0,15	1729s, 1710s	3350 s, 3420 s	1737 s, 1680s	3125 m br 3430 w, 3590 s	235 (4,33), 322 (3,58)	64,1	4,5	$C_{16}H_{14}O_6$	63,6	4,7	33
IId	92—93	0,5	1737, 1672 s	3070 m br	1740 s, 1682s	3135 m br 3430 vw	236 (4,33), 320 (3,56)	67,2	6,4	$C_{20}H_{22}O_6$	67,1	6,1	94
IIe	84—86[d]	0,30	1745 s, 1682s	3060 m br	1738 s, 1681s	3130 m br 3425 vw	232 (4,35), 316 (3,59)	59,9	4,1	$C_{16}H_{13}ClO_5$[e]	59,9	4,1	3
IIf	88—89	0,5	1749 s, 1686 s	3210 m br	1744 s, 1685 s	3165 m br 3440 vw	280 (3,34)	64,2	5,3	$C_{17}H_{16}O_6$	64,6	5,1	75
IIg	72—74	0,33	1742 s, 1675 s	3200 m br	1741 s, 1683 s	3165 m br 3440 vw	222 (4,39), 326 (3,63)	63,5	4,8	$C_{16}H_{14}O_6$	63,6	4,7	62

a) The compounds were crystallized: IIa,b,d from alcohol, IIc from benzene, IIe from heptane, and IIf,g from hexane. b) Based on the starting aryl(aryloxy)furans. c) Found: N 4.1%. Calculated: N 4.1%. d) In benzene. e) Found: Cl 11.2%. Calculated: Cl 11.1%.

this is in agreement with the available data on the transmission of the effect of a substituent in the benzene ring on the reactivities of arylfurans [2].

The position of the ν_{OH} absorption bands and the low-frequency ν_{CO} band is virtually independent of the concentrations of the solutions for all of the investigated compounds. Thus the ν_{OH} bands and the low-frequency ν_{CO} band in the spectra of a 0.02% solution in CCl_4 (e.g., for IIb ν_{OH} 3430 and ν_{CO} 1681 cm^{-1}) and of a 1% solution in $CHCl_3$ (3430 and 1681 cm^{-1}, respectively) have identical frequencies. In addition, the high-frequency band is shifted from 1733 cm^{-1} (1% solution in $CHCl_3$) to 1740 cm^{-1} (0.02% solution in CCl_4) when the solution is diluted.

A band of a free hydroxy group at 3590 cm^{-1}, which is due to ν_{OH} of the p-hydroxyphenyl substituent, is observed in addition to the bands of stretching vibrations of a bonded hydroxy group (3125 and 3430 cm^{-1}) in the spectrum of IIc, which has a secondary hydroxy group, in a dilute solution in CCl_4. The absence in the IR spectra of bands of stretching vibrations of free hydroxy groups, the low frequency of one of the ν_{CO} bands, and the independence of the position of these frequencies on the concentration of the solutions constitute evidence for the existence in the investigated compounds of an intramolecular hydrogen bond. The indicated hydrogen bond is confirmed in the PMR spectra by the presence of a weak-field signal of a hydroxy group (δ 10.8-10.9 ppm). One should also note that the low-frequency band at 1680-1685 cm^{-1} in the IR spectra of the investigated compounds is due to the stretching vibrations of the CO bond of the carbomethoxy group in the 1 position and that the high-frequency band at 1740 cm^{-1} is associated with ν_{CO} of the carbomethoxy group in the 2 position.

Depending on the substituent, the yields of 3-aryl(aryloxy)-6-hydroxyphthalic acid esters range from 33 to 94%. Thus the reaction of aryl- and aryloxyfurans with dimethyl acetylenedicarboxylate may be of interest as one of the methods for the synthesis of esters of 3-aryl(or aryloxy)-6-hydroxyphthalic acids. This method has advantages as compared with the existing method for the preparation of compounds of this sort (the Gomberg [3] and Ullmann [4] reactions), since it provides a possibility for the synthesis of inaccessible (by other methods) esters of hydroxyphthalic acids with a similar orientation of the substituents.

EXPERIMENTAL

The IR spectra of mineral oil suspensions and solutions (in CCl_4 and, in some cases, 1% solutions in $CHCl_3$) of the compounds were recorded with UR-10 and Perkin-Elmer 457 spectrometers. The UV spectra of alcohol solutions of the compounds were obtained with an EPS-3 spectrophotometer. The PMR spectra of solutions of the compounds in $CDCl_3$ were recorded with JNM-4H-100 and C-60-HL spectrometers with tetramethylsilane as the internal standard. Thin-layer chromatography (TLC) was carried out on Silufol UV-254 with development in UV light.

2-(p-Acetamidophenyl)furan. A 2.3-g (44 mmole) sample of 2-(p-aminophenyl)furan was heated in 12 ml of acetic anhydride for 1 h on a boiling-water bath, after which the mixture was cooled, and the precipitated crystals were removed by filtration and washed with water to give 2.6 g (85%) of 2-(p-acetamidophenyl)furan with mp 196-198°C (from dichloroethane). Found: C 71.3; H 5.4; N 7.2%. $C_{12}H_{11}NO_2$. Calculated: C 71.6; H 5.6; N 7.0%.

2-(n-Butoxyphenyl)furan. A mixture of 2 g (13 mmole) of 2-(p-hydroxyphenyl)furan [5], 0.8 g of potassium hydroxide, and 30 ml of butyl iodide was heated at 100-110°C for 2.5 h, after which it was cooled and poured into 200 ml of water. The organic layer was separated, and the aqueous layer was extracted with ether. The combined extracts were dried with sodium sulfate and evaporated, and the residue was recrystallized from alcohol to give 1.1 g (43%) of 2-(p-butoxyphenyl)furan with mp 35-37°C. Found: C 77.9; H 7.3%. $C_{14}H_{16}O_2$. Calculated: C 77.8; H 7.6%.

Dimethyl 3-(p-Acetamidophenyl)-6-hydroxyphthalate (IIa, Table 2). A solution of 6 g (42 mmole) of 2-(p-acetamidophenyl)furan and 8.3 g (84 mmole) of dimethyl acetylenedicarboxylate in 60 ml of benzene was heated on a boiling-water bath for 5 h, after which it was cooled, and the resulting precipitate was removed by filtration to give 9.6 g (95%) of adduct Ia with mp 160-161°C (from alcohol) and R_f 0.25 (chloroform). Found: C 62.9; H 5.1; N 3.9%. $C_{18}H_{17}NO_6$. Calculated: C 63.0; H 5.0; N 4.1%. A solution of 9.1 g of adduct Ia in 50 ml of concentrated acetic acid was heated on a boiling-water bath for 1 h, after which it was cooled and neutralized with a saturated solution of sodium carbonate to pH 6-7. The resulting precipitate was removed by filtration.

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

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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}.

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