WILGERODT—KINDLER REACTION WITH AROMATIC ALDEHYDES

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The Wilgerodt—Kindler reaction is a convenient method for the synthesis of various thiomorpholides of acids from carbonyl compounds. The most widely used carbonyl compounds are ketones, while aldehydes have received little study [1]. We studied the synthetic aspects of this reaction for aromatic aldehydes [benzaldehyde (I), p-fluoro- (II), p-chloro- (III), p-bromo- (IV), p-nitro- (V), p-dimethylamino- (VI), p-methoxy- (VII), and 2,4-dimethoxybenzaldehyde (VIII)], dialdehydes [(o- (IX), m- (X), and p-phthalaldehyde (XI)], 1,3,5-triformylbenzene (XII), and also for cinnamaldehyde as an example of α,β-unsaturated aldehydes. The best results are obtained by modifying the method previously used for (I), where the reaction was run by heating (I) with sulfur and morpholine in DMF [1]. In essence, the modification was to run the reaction in the presence of catalytic amounts of p-toluenesulfonic acid, the addition of which was recommended in some cases when the reaction was run with ketones in excess morpholine [1]. The reaction course was checked via TLC. Under the modified conditions we were able to obtain good results (Table 1) not only for (I), but also for (II), (III), (VII), and the isomeric (IX)-(XI). Aldehydes, containing strong electron-acceptor or electron-donor groups ((V) and (VI)), or several electron-donor or electron-acceptor substituents ((VIII) and (XII)), tend to form substantial amounts of polymeric products under the reaction conditions, from which only small amounts of the starting aldehydes could be isolated. Cinnamaldehyde was completely polymerized under the reaction conditions to give a powdery amorphous product, which contained nitrogen and sulfur and lacked a definite melting point.

The structure of the obtained thiomorpholides of substituted benzoic acids and dithiomorpholides of phthalic acids was confirmed by the elemental analysis and spectral data (see Table 1). Thiomorpholides (XIII) and (XIV)-(XVI) are characterized by intense absorption in the UV spectra in the 202-207 nm region, while in the case of the dithiomorpholides the maximum absorption is found at 238-240 nm, and only for (XVII) is λ_{max} 204 nm. The IR spectra of all of the compounds have an intense absorption band in the 1480-1500 cm^{-1} region, which is typical for thiomorpholides. Molecular ions M^+ were detected in the mass spectra of compounds (XIII) and (XIV)-(XVI), but in these cases the most intense was the signal with m/e 86, which corresponds to the morpholine fragment $C_4H_8NO^{+\bullet}$. Molecular ions and the ions $(M - 86)^{+\bullet}$ and $(M - 2\cdot 86)^{+\bullet}$, which correspond to the cleavage of either one or two morpholine fragments C_4H_9NO, are also observed in the mass spectra of dithiomorpholides (XVII)-(XIX). In the mass spectrum of (XVII), and in the mass spectra of (XVIII) and (XIX), the $(M - 88)^{+\bullet}$ and $(M - 86)^{+\bullet}$ ions are, respectively, the most intense molecular ion.

EXPERIMENTAL

The TLC was run on Silufol plates in the system: 1:4 hexane—ether, with detection by iodine vapors. The IR spectra were taken as KBr pellets on a UR-20 instrument. The UV spectra were recorded on a Specord instrument using alcohol solutions. The mass spectra were taken on a Varian CH-6 instrument, with direct insertion of the substance into the ion source.

General Procedure for Reacting Aldehydes with Morpholine and Sulfur. A mixture of 0.1 mole of the aldehyde, 0.11 mole of morpholine, 0.15 mole of sulfur (for dialdehydes the amounts of the last two reactants were doubled), and a catalytic amount of p-toluenesulfonic acid was stirred at a definite temperature for a definite time (see Table 1). The mixture was poured on ice, and the precipitate was separated and recrystallized from a suitable solvent. In individual cases additional purification from sulfur was achieved by passing through a silica gel column in the system: benzene—ether. The results are given in Table 1 (the yields are based on the purified products).

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TABLE 1

Starting compound	Reaction product	Yield, %	Conditions		mp., °C	Empirical formula	Found/Calculated, %				
			T., °C	time, h			C	H	S	N	Hal
(I)	(XIII)	98	130	3	133—135	—	—	—	—	—	—
(II)	(XIV)	64,5	60	4	93—96	$C_{11}H_{12}FNOS$	58,50/58,65	5,77/5,37	14,70/14,23	6,10/6,22	8,52/8,43
(III)	(XV)	85	60	3	136—138	$C_{11}H_{12}ClNOS$	54,90/54,90	5,06/5,00	13,19/13,26	5,89/5,82	14,57/14,66
(VII)	(XVI)	78	60	4	106—108	—	—	—	—	—	—
(IX)	(XVII)	62	90	0,5	241—242	$C_{16}H_{20}N_2O_2S_2$	57,28/57,11	5,98/5,99	18,99/19,07	8,39/8,32	
(X)	(XVIII)	79	90	1	148—150	$C_{16}H_{20}N_2O_2S_2$	57,27/57,11	6,21/5,99	18,78/19,07	8,46/8,32	
(XI)	(XIX)	58	20—25	0,4	152—154	$C_{16}H_{20}N_2O_2S_2$	57,00/57,11	5,99/5,99	18,78/19,07	8,54/8,32	

CONCLUSIONS

1. A modified method was proposed for running the Wilgerodt—Kindler reaction for substituted benzaldehydes.

2. We were the first to run the Wilgerodt—Kindler reaction for the o-, m-, and p-phthalaldehydes.

LITERATURE CITED

1. E. Y. Brown, Synthesis, 1975, 358.

OXIDATION—REDUCTION REACTIONS OF PHENOXYL RADICALS

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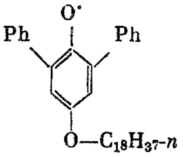
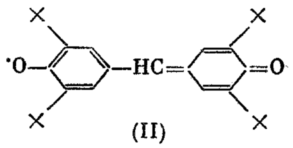
Stable phenoxyl radicals take part in oxidation—reduction reactions with various electron donors and acceptors [1, 2]. In the present paper, using kinetic spectrophotometry and the pulse photolysis method, we studied the reaction of the 2,6-diphenyl-4-stearoxyphenoxyl radical (I) with compounds of the transition metals in propanol. For comparison we studied the analogous reaction of the galvinoxyl radical (II), whose oxidation—reduction properties are known [3, 4]:



(I)



(II)

A study of the reaction of radical (I) with compounds of the transition metals has special interest: the starting phenol is widely used as a highly efficient antioxidant and inhibitor of the degradation of polymers (inhibitor ES-63) [5].

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