SYNTHESIS AND PROPERTIES OF SOME KETOARYLENES
AND THEIR DERIVATIVES

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UDC 542.91:547.572

Aromatic compounds with bridge functional groups represent interest for modeling the chains of heat-resistant polymers [1]. When additional reactive groups are inserted, the corresponding aromatic compounds are monomers with a high molecular weight, which are capable of forming crosslinked polymers [2].

In the present communication are described synthesis methods, some physical properties, and data on the resistance to thermooxidative degradation (TOD) of a number of ketoarylenes and their derivatives with terminal acetylene and nitrile groups.

The synthesis of the ketoarylenes was based on the Friedel—Crafts acylation of diphenyl ether and biphenyl with the acid chlorides of mono- and dibasic aromatic acids. It was established by the PMR spectroscopy method that the p isomers are formed mainly in this case [1, 3]; in the benzoylated and acetylated biphenyl and diphenyl ether the p isomers constitute at least 90-95% [4-7].

The resistance of the synthesized ketoarylenes to TOD is characterized in Table 1. To estimate it a method was developed in [8], which is based on the destructive oxidation of low-molecular-weight organic compounds and polymers to CO and CO_2 in an O_2 medium, in which connection less than 5-10 mole % of the carbon, taken as the ketoarylene, undergoes oxidation.

It may be assumed that for low conversions ($0 < \Delta C \leqslant \sim 0.03 \, C_0$, where C_0 is the starting carbon concentration in mole/liter) the first approximation is

$$-dC/C_0 \, dt \sim k_{ox}$$

TABLE 1. Melting Points and Temperatures for Oxidation* of Aromatic Ketones and Their Acetyl and Cyano Derivatives

Compound	m.p. °C	Amount of oxidized carbon, mole%			
		0.5	1	2	3
		oxidation temperature,* °C			
$C_6H_5OC_6H_4COC_6H_5$ (I)	66—67	371	390	405	414
$(C_6H_5COC_6H_4)_2O$ (II)	163—165	385	401	411	417
$1,4-(C_6H_5OC_6H_4CO)_2C_6H_4$ (III)	216—218	391	398	409	418
$1,4-(C_6H_5C_6H_4CO)_2C_6H_4$ (IV)	294,5—295,5	395	402	418	424
$(C_6H_5OC_6H_4COC_6H_4)_2O$ (V)	237—238	400	411	424	431
$1,4-(C_6H_5COC_6H_4OC_6H_4CO)_2C_6H_4$ (VI)	270—273	397	408	424	435
$(C_6H_5COC_6H_4OC_6H_4COC_6H_4)_2O$ (VII)	285—286	392	405	424	436
$1,4-(C_6H_5SC_6H_4CO)_2C_6H_4$ (VIII)	217—219	357	364	374	382
$(C_6H_5SC_6H_4COC_6H_4)_2O$ (IX)	203—205	—	—	340	362
$1,4-(H_3COCC_6H_4OC_6H_4CO)_2C_6H_4$ (X)	273—274	—	—	—	—
$1,4-(H_3COCC_6H_4C_6H_4CO)_2C_6H_4$ (XI)	358—359	—	—	—	—
$(H_3COCC_6H_4OC_6H_4COC_6H_4)_2O$ (XII)	283,5—285	287	302	327	346
$(NCC_6H_4COC_6H_4OC_6H_4COC_6H_4)_2O$ (XIII)	276—279	346	363	424	434
$NCC_6H_4COC_6H_4OC_6H_5$ (XIV)	99,5—103	380	385	389	395
$NCC_6H_4COC_6H_4OC_6H_4COCH_3$ (XV)	153—154	300	310	324	343

*Temperature of oxidizing the carbon in the ketoarylene to CO and CO_2 in 1 h.

TABLE 2. Oxidation Temperature* of Aromatic Compounds

Compound	Carbon concentration,† $C_0 \cdot 10^2$, mole/liter	Amount of oxidized carbon, mole %		
		1	3	5
		oxidation temperature,* °C		
Benzene	3,5	392	408	412
	7,0	385	401	406
Biphenyl	3,55	386	403	408
	7,1	385	402	410
p-Terphenyl	4,75	380	401	411
	7,1	372	395	408
p-Quaterphenyl	7,1	381	406	414
	14,2	382	—	—

*Temperature at which the carbon, contained in the sample of the compound, is oxidized to CO and CO_2 in 1 h.
†The carbon concentration in the system was calculated using the equation: $C_0 = an/MV$, where a is the weight of the hydrocarbon sample in g; M and n are respectively the molecular weight of the hydrocarbon and number of carbon atoms in its molecule, and V is the volume of the ampul in liters.
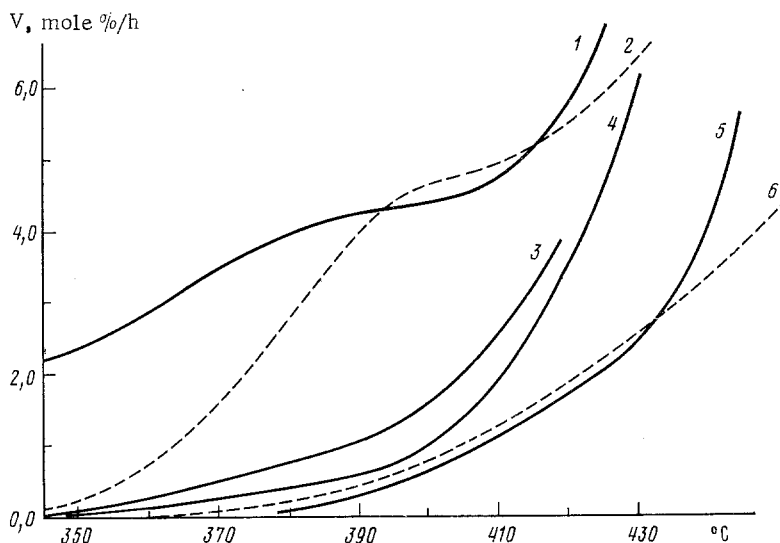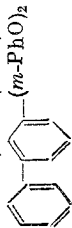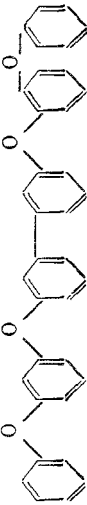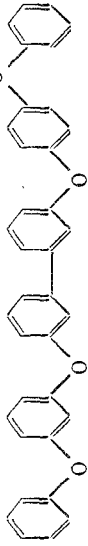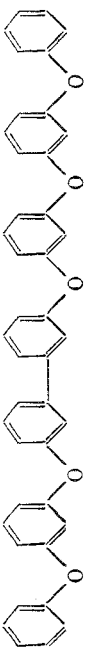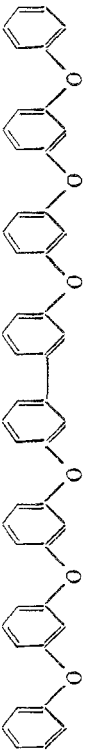

Fig. 1. Initial formation rate of CO and CO_2 as a function of temperature during the thermooxidative degradation in oxygen of the compounds: 1) (IX); 2) (VIII); 3) 4-phenoxybenzophenone; 4) (II); 5) (VI); 6) (VII).

where k_{ox} is the constant of the overall rate of the oxidation reactions. The curves plotted in Figs. 1 and 2, which express the initial oxidation rate $\Delta C/C_0 \Delta t$ as a function of temperature, characterize the resistance of the ketoarylenes to TOD and bear some similarity to the curves for the dynamic thermogravimetric analysis of polymers. The initial oxidation rate (at $C_0 \approx$ const) is expressed in mole % of the oxidized carbon in 1 h (relative to the amount of carbon taken for oxidation). As a comparative analysis of the curves obtained for various aromatic compounds shows [8], their qualitative relationship to the structure of the studied compounds is unequivocal. However, establishing quantitative relationships is frequently made difficult due to the inability of strictly maintaining the homogeneity of the oxidation process. Together with this, the discussed ketoarylenes are comparatively high-melting (see Table 1) and high-boiling compounds, so that differences in the concentration factor are apparently not significant for them. In addition, a noticeable change in the

TABLE 3. Molecular Refractions and Exaltations of Model Aromatic Compounds and PhO and PhCO Groups

Compound	Molecular refraction, cm³/mole		Exaltation, cm³/mole		
	R^{20}_{obs}*	R_{add}[9]	ΔR_{obs}	ΔR_{PhO}	ΔR_{PhCO}
PhOPh	52,82 [10]	51,26	1,56	1,13	—
PhCOPh	56,7 [5]	54,54	2,2	—	1,8
m-(m-C₆H₅OC₆H₄O)₂C₆H₄(PPE)	132,95	127,72	5,2	1,2	—
(m-PhO)₂—————(m-PhO)₂	162,4 [11]	151,44	11,0?	2,0?	—
	160,8 [11]	151,44	9,3	1,6	—
	160,6 [11]	151,44	9,2	1,6	—
	184,2 [11]	176,93	7,3	0,9	—
	211,8 [11]	202,41	9,4	1,1	—

*The refractions were calculated from the literature data.

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TABLE 4. Molecular Refractions and Exaltations of Ketoarylenes

Ketoarylenes	Solution concentration of ketoarylene in PPE, wt%	n_D^{10}	d_4^{10}	Refraction, cm³/mole		Exaltation, cm³/mole			
				R_{obs}^{20}	R_{add} [9]	ΔR_{obs}	ΔR_{add}^*	$\Delta\Delta R$	$\Delta\Delta R/\Delta R_{obs}$
PhOPhCOPhOPhCOPhOPh	4,1	1,6383	1,206	175,1	159,76	15,3	7,6	7,7	0,50
PhOPhCOPhCOPhOPh	5,33 12,31	1,6377 1,6401	1,2056 1,2068	143,9 144,0	134,27	9,7	6,4	3,3	0 34
PhCOPhOPhCOPh	9,30 9,31 16,9	1,6393 1,6392 1,6418	1,2074 1,2067 1,2088	114,9 115,6 115,3	108,78	6,5	5,2	1,3	0,20
(PhCOPhOPhCOPh)₂O	2.83	1,6392	1,2091	233,1	217,28	15,8	11,2	4,6	0,29

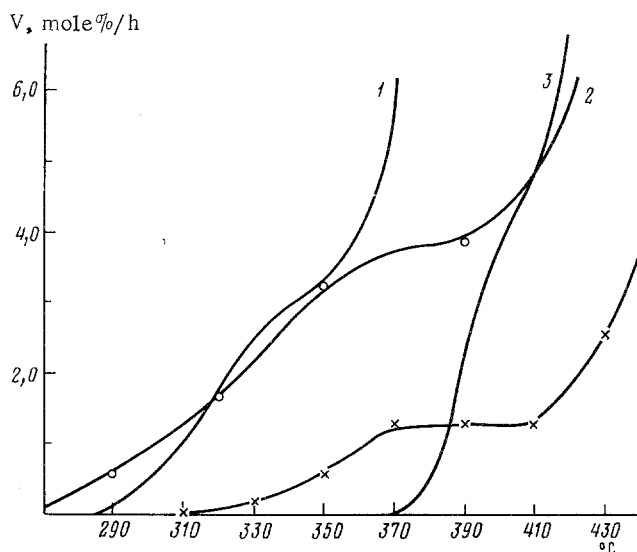*ΔR_{add} was calculated using the equation given in [9].

Fig. 2. Initial oxidation rate of CO and CO₂ as a function of temperature during the thermooxidative degradation of acetyl- and cyano-substituted ketoarylenes: 1) (XV); 2) (XII); 3) (XIV); 4) (XIII).

starting concentration C_0 of model aromatic compounds (benzene, biphenyl, etc.) exerts a comparatively small effect on the temperature, needed for the same degree of oxidation, and correspondingly on the position of the oxidation curve (Table 2). The greatest resistance to TOD is shown by the ketoarylenes in whose molecular chains the ketophenylene and phenylene oxide groups alternate [1]. Additional examples, confirming this fact, are given in the present paper.

The refractometric method [9] was used to estimate the intramolecular interactions (mesomeric effect) in the ketoarylenes. We determined the refractive indices and the densities of the polyphenyl ether (PPE), m-(m-C₆H₅OC₆H₄O)₂C₆H₄, and of solutions of the ketoarylenes in PPE (Table 3). The refraction [12] and exaltation [9] values of the PPE and ketoarylenes were calculated from these data. On the basis of the literature data we also calculated the exaltations of the simpler aromatic compounds that model the keto-arylene unit (diphenyl ether, polyphenyl ethers, benzophenone, biphenyl). Then on the basis of these models we calculated the exaltations of the phenoxy and ketophenylene groups (see Table 3):

$$\Delta R_{PhO} = (\Delta R_{(PhO)_n Ph} - \Delta R_{Ph})/n \qquad (1)$$

$$\Delta R_{PhO} = (\Delta R_{(PhO)_m PhPh(PhO)_n} - \Delta R_{PhPh})/(m + n) \qquad (2)$$

$$\Delta R_{PhCO} = \Delta R_{(Ph)_2 CO} - \Delta R_{Ph} \qquad (3)$$

Based on the data of Table 3, the average values of ΔR_{PhO} and ΔR_{PhCO} are respectively equal to 1.2 and 1.8 cm³. In harmony with the determination method, the ΔR_{PhO} and ΔR_{PhCO} values are somewhat high, since they contain the contribution to the exaltation, caused by the conjugation of the indicated groups with the aromatic ring to which they are connected. Starting with the concept that the exaltation of compounds in which the conjugation does not extend beyond the limits of the unit is additive [13], we calculated the minimum exaltations ΔR_{add} of hypothetical ketoarylenes with unconjugated units (Table 4):

$$\Delta R_{add} = m\Delta R_{PhO} + n\Delta R_{PhCO} + \Delta R_{Ph} \qquad (4)$$

The contribution to the exaltation of a ketoarylene, related to the conjugation of the units, can be determined using the following equation:

$$\Delta\Delta R = \Delta R_{obs} - \Delta R_{add} \qquad (5)$$

As can be seen from Table 4, this contribution is 20-50% of the total exaltation.

The resistance to TOD decreases noticeably when going from ketophenylene oxides to ketophenylene sulfides (see Fig. 1), and also to the acetyl and cyano derivatives (see Fig. 2). It is noteworthy that among the various reactive groups the greatest resistance to TOD is shown by benzonitrile groups.

The polycyclotrimerization of dicyano aromatic compounds leads to obtaining heat-resistant crosslinked polymers [2]. However, benzonitrile groups react with difficulty and, despite long heating at high temperatures (350-400°) and the use of catalysts, the lack of curing remains substantial [2]. This shows that a benzonitrile group, blocked in a crosslinked polymer, does not belong to the element of its structure that is unstable toward TOD.

EXPERIMENTAL

1-Phenoxybenzophenone (I). With stirring, to 53.7 g (0.315 mole) of diphenyl ether (DE) were gradually added 26.5 g (0.2 mole) of anhydrous $AlCl_3$ and a solution of 7.3 g (0.052 mole) of benzoyl chloride (BC) in 21.5 g (0.126 mole) of DE. Then, with stirring, another 26.5 g (0.2 mole) of anhyd. $AlCl_3$ was added to the reaction mixture, and after the HCl evolution had ceased the mixture was repeatedly treated with ether to remove the excess DE. The adduct of (I) with $AlCl_3$ was decomposed with a mixture of dilute HCl solution and ice. The final product was washed with water and dried to give 1.4 g of (I) with mp 66-67° (from 85% alcohol) (cf. [5]). Found: C 83.27; H 5.22%. $C_{19}H_{14}O_2$. Calculated: C 83.19; H 5.14%. Infrared spectrum (ν, cm^{-1}): 1645 (C=O), 1590, 1490 (aromatic rings), 1252 (COC).

1,1'-Bis(4-benzoylphenyl) ether (II) was obtained by a modification of the method given in [6]. With stirring, to a mixture of 30 ml of CS_2, 48.6 g (0.345 mole) of BC, and 20 g (0.15 mole) of anhyd. $AlCl_3$ was gradually added a solution of 9.7 g (0.057 mole) of DE in 21.85 g (0.155 mole) of BC. At the end of reaction the CS_2 and excess BC were distilled off. The mixture was treated with a mixture of dilute HCl solution and ice, washed with water, and the obtained ether was dried to give 25 g of (II) with mp 162-164° (from toluene and alcohol). Found: C 82.55; H 4.90%. $C_{26}H_{18}O_3$. Calculated: C 82.52; H 4.79%. Infrared spectrum (ν, cm^{-1}): 1642 (C=O), 1595, 1502 (aromatic rings), 1255 (COC).

1,4-Bis(4'-phenoxybenzoyl)benzene (III), 1,4-bis(4'-phenylbenzoyl)benzene (IV), and bis(4'-phenoxy-4-benzoylphenyl) ether (V) were obtained as described in [1, 14].

1,4-Bis(4''-benzoyl-4'-phenoxybenzoyl)benzene (VI). With stirring, to a mixture of 50 ml of CH_2Cl_2, 6 g (0.05 mole) of anhyd. $AlCl_3$, and 5.22 g (0.037 mole) of BC, cooled to 0°, was gradually added 5 g (0.0106 mole) of aromatic diketone (III), and the mixture was stirred for 2 h at 0-3°, kept for 12 h at ∿20°, treated with a mixture of dilute HCl solution and ice, and the obtained product was washed and dried to give 7 g of (VI) with mp 270-273° (from pyridine). Found: C 81.1; H 4.65%. $C_{46}H_{30}O_6$. Calculated: C 81.40; H 4.46%. Infrared spectrum (ν, cm^{-1}): 1646 (C=O), 1590, 1495 (aromatic rings), 1245 (COC).

Bis(4''-benzoyl-4'-phenoxy-4-benzoylphenyl) Ether (VII). With stirring, to a mixture of 25 ml of CH_2Cl_2, 4 g (0.030 mole) of anhyd. $AlCl_3$, and 3.16 g (0.022 mole) of BC, cooled to 0-3°, was gradually added 5 g (0.009 mole) of ketoarylene (V) in 1 h, and then another 3 g (0.0225 mole) of $AlCl_3$, after which the mixture was kept for 12 h at ∿20°, treated with a mixture of dilute HCl solution and ice, filtered, washed with water, and dried to give 6.7 g of ketoarylene (VII) with mp 285-286° (from pyridine). Found: C 80.33; H 4.64%. $C_{52}H_{34}O_7$.

Calculated: C 81.02; H 4.45%. Infrared spectrum (ν, cm^{-1}): 1645 (C=O), 1595, 1505 (aromatic rings), 1255 (COC).

1,4-Bis(4'-phenylthiobenzoyl)benzene (VIII). With stirring, to a mixture of 13.8 g (0.0741 mole) of diphenyl sulfide (DS) and 11 g (0.0825 mole) of AlCl$_3$ was gradually added a solution of 5 g (0.0246 mole) of terephthaloyl dichloride in 9.2 g (0.0494 mole) of DS, after which the mixture was heated for 30 min at 70°, cooled, and repeatedly treated with ether; the precipitate was treated with dilute HCl solution, washed with water, and dried to give 6.5 g of (VIII) with mp 217-219° (from toluene). Found: C 77.0; H 4.61; S 12.9%. C$_{32}$H$_{22}$O$_2$S$_2$. Calculated: C 76.46; H 4.41; S 12.76%. Infrared spectrum (ν, cm^{-1}): 1656 (C=O), 1595, 1486 (aromatic rings).

(4'-Phenylthio-4-benzoylphenyl) Ether (IX). To a mixture of 8.9 g (0.0478 mole) of DS and 3.0 g (0.0225 mole) of anhyd. AlCl$_3$ were simultaneously added a solution of 5 g (0.01694 mole) of the dichloride of 4,4'-dicarboxydiphenyl ether in 7.24 g (0.0389 mole) of DS and 6 g (0.045 mole) of anhyd. AlCl$_3$. When the HCl evolution had ceased, the mixture was repeatedly treated with ether, then with dilute HCl solution, washed with water, and the precipitate was washed with water and dried to give 5.9 g of (IX) with mp 203-205° (from toluene). Found: C 77.0; H 4.60; S 10.67%. C$_{38}$H$_{26}$O$_3$S$_2$. Calculated: C 76.74; H 4.41; S 10.78%. Infrared spectrum (ν, cm^{-1}): 1640 (C=O), 1585, 1497, 1400 (aromatic rings).

1,4-Bis(4"-acetyl-4'-phenoxybenzoyl)benzene (X) [15]. With vigorous stirring, to a mixture of 80 ml of CS$_2$* 35 g (0.262 mole) of anhyd. AlCl$_3$, and 25 g (0.318 mole) of acetyl chloride (AC) was added in portions 16.6 g (0.0353 mole) of (III) in 1.5 h. The mixture was heated for 1 h at 35°, and the precipitate was separated, dried in the air, treated with a mixture of dilute HCl solution and ice, washed with water, and dried to give 18.6 g (95%) of (X) with mp 273-274° (from pyridine). Found: C 77.60; H 4.80%. C$_{36}$H$_{26}$O$_6$. Calculated: C 77.96; H 4.72%. Infrared spectrum (ν, cm^{-1}): 1680 (COCH$_3$), 1650 (C=O of benzophenone unit), 1600, 1500, 1450 (aromatic rings), 1245 (COC).

1,4-Bis(4"-acetyl-4'-phenylbenzoyl)benzene (XI) [14]. a) With stirring, to a mixture of 75 g of CS$_2$ and 44 g (0.33 mole) of anhyd. AlCl$_3$ was added 7.8 g (0.018 mole) of (IV) and the mixture was heated for 2 h at 40°. Then the CS$_2$ layer was separated by decantation and the precipitate was dried, treated with a mixture of dilute HCl solution and ice, washed with water, and dried to give 7.9 g (84%) of (XI) with mp 358-359° (from pyridine).

b) With stirring, to a mixture of 20 ml of CS$_2$, 6.5 g (0.09 mole) of anhyd. AlCl$_3$, and 5.5 g (0.028 mole) of 4-acetylbiphenyl was added 2.46 g (0.012 mole) of terephthaloyl dichloride and the mixture was heated for 6 h at 40°. The product was isolated as indicated above to give 1.2 g of (XI) with mp 358.5-360.5°. Found: C 82.1; H 5.16%. C$_{36}$H$_{26}$O$_4$. Calculated: C 82.74; H 5.01%. Infrared spectrum (ν, cm^{-1}): 1675 (COCH$_3$), 1640 (C=O of benzophenone unit), 1600, 1495 (aromatic rings).

Bis(4"-acetyl-4'-phenoxy-4-benzoylphenyl) Ether (XII) [14]. With stirring, to a mixture of 100 g of CS$_2$, 54 g (0.4 mole) of anhyd. AlCl$_3$, and 17.7 g (0.23 mole) of AC was added 28.13 g (0.05 mole) of (V). The product was isolated as indicated above. After a double recrystallization from pyridine the yield of (XII) was 19.4 g (60%), mp 283.5-285°. Found: C 77.63; H 4.74; O 17.63%. C$_{42}$H$_{30}$O$_7$. Calculated: C 78.00; H 4.68; O 17.3%. Infrared spectrum (ν, cm^{-1}): 1678 (COCH$_3$), 1645 (C=O of benzophenone unit), 1595, 1500 (aromatic rings), 1240 (COC).

4-Cyanobenzoic Acid. A mixture of 30 g (0.2288 mole) of 4-cyanobenzaldehyde and 60 g of 35% aqueous NaOH solution was shaken in a separatory funnel for 2-6 min, 300 ml of cold water was added, and the mixture was extracted with ether. The aqueous layer was added to a mixture of dilute HCl solution and ice, and the precipitate was washed with water and dried. The yield of 4-cyanobenzoic acid was 12.3 g (73%), mp 119-120° (from water) (cf. [16]). Found: N 9.62%. C$_8$H$_5$NO$_2$. Calculated: N 9.52%. Infrared spectrum (ν, cm^{-1}) 2245 (C≡N). From the ether layer we obtained 4-cyanobenzyl alcohol, mp 36-39°.

4-Cyanobenzoyl chloride was obtained as described in [16], mp 68-68.5° (from petroleum ether) (cf. [16]).

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*The acetylation was also run in CH$_2$Cl$_2$ at 0-5°. After the reaction had ceased and a part of the CH$_2$Cl$_2$ was removed the reaction mixture was decomposed with a mixture of dilute HCl solution and ice.

Bis(4'''-cyano-4''-benzoyl-4'-phenoxy-4-benzoylphenyl) Ether (XIII). To a mixture of 30 ml of CH_2Cl_2, 4.9 g (0.0296 mole) of 4-cyanobenzoyl chloride, and 6.0 g (0.045 mole) of anhyd. $AlCl_3$ at 0-5° was gradually added 7.5 g (0.0133 mole) of ketoarylene (V) and the mixture was stirred for 21 h in an argon stream, after which another 6.0 g (0.045 mole) of anhyd. $AlCl_3$ was added and the mixture was stirred for 10 h, treated with a mixture of dilute HCl solution and ice, and the precipitate was washed in succession with water, alcohol, and hot toluene. The yield of (XIII) was 10 g, mp 276-279° (from pyridine). Found: C 78.80; H 4.13; N 3.2%. $C_{54}H_{32}N_2O_7$. Calculated: C 79.01; H 3.93; N 3.41%. Infrared spectrum (ν, cm^{-1}): 2240 ($C\equiv N$), 1650 (C=O of benzophenone unit), 1595, 1585, 1497 (aromatic rings), 1247 (COC).

4'-Phenoxy-4-benzoylbenzonitrile (XIV). With stirring, to 13.2 g (0.08 mole) of 4-cyanobenzoyl chloride in 95 g (0.56 mole) of DE was added in portions, at 40°, in an N_2 atmosphere, 21.5 g (0.16 mole) of anhyd. $AlCl_3$, the mixture was stirred for 12 h, another 10 g (0.075 mole) of $AlCl_3$ was added, and the mixture was kept for 48 h at 20°. Ether and a mixture of dilute HCl solution and ice were added to isolate the end product. The ether layer was subjected to fractional distillation in vacuo. After removal of the ether and DE we obtained 18.4 g (77%) of (XIV), mp 99.5-103° (from petroleum ether). Found: C 79.8; H 4.48; N 4.70%. $C_{20}H_{13}NO_2$. Calculated: C 80.25; H 4.38; N 4.68%. Infrared spectrum (ν, cm^{-1}): 2218 ($C\equiv N$), 1650 (C=O), 1600, 1585, 1590 (aromatic rings), 1255 (COC).

4''-Acetyl-4'-phenoxy-4-benzoylbenzonitrile (XV). With stirring, to a mixture of 25 ml of CH_2Cl_2, 5.5 g (0.0702 mole) of AC, and 17.5 g (0.1312 mole) of anhyd. $AlCl_3$ at 2-5° was added 14 g (0.0468 mole) of (XIII). After reaction had ceased the mixture was treated with 1 liter of a mixture of dilute HCl solution and ice. The product was washed with water and dried. The yield of (XV) was 13 g, mp 153-154° (from toluene). Found: C 77.54; H 4.55; N 4.05%. $C_{22}H_{15}NO_3$. Calculated: C 77.40; H 4.43; N 4.10%. Infrared spectrum (ν, cm^{-1}): 2242 ($C\equiv N$), 1683 ($COCH_3$), 1643 (C=O), 1607, 1592, 1508 (aromatic rings), 1255 (C-O-C). The n_D^t and d_4^t of solutions of the ketoarylenes in PPE (as supercooled liquids [melts]) were determined at low temperature (5-10°). A refractometer of the Abbe type (IPF-22) was used to measure the n_D^t, and a pycnometer to measure the d_4^t.

CONCLUSIONS

1. The synthesis, physical properties, and resistance to thermooxidative degradation of a number of ketoarylenes was described.

2. An increase in the resistance to thermooxidative degradation of ketoarylenes with regularly alternating electron-donor and electron-acceptor groupings in the molecular chain is related to the strong intramolecular interaction (conjugation) of the indicated groupings.

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REACTION OF ACETALS WITH ALIPHATIC NITRO COMPOUNDS

2. EFFECT OF STRUCTURE OF DIETHYL ACETALS

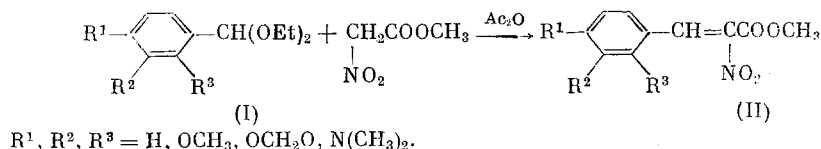OF BENZALDEHYDES ON C- AND O-ALKYLATION

OF NITROACETIC ESTER

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Previously we had shown that the diethyl acetals of benzaldehyde and its derivatives with electron-donor groups when heated in the presence of Ac_2O easily alkylate the esters of nitroacetic acid (NAE) at the α-C atom to give the esters of α-nitrocinnamic acids (II) in high yields [1]:

$$R^1\text{—}\langle\rangle\text{—}CH(OEt)_2 + CH_2COOCH_3 \xrightarrow{Ac_2O} R^1\text{—}\langle\rangle\text{—}CH=CCOOCH_3$$
$$\underset{R^2 \quad R^3}{} \quad \underset{NO_2}{} \quad \underset{R^2 \quad R^3}{} \quad \underset{NO_2}{}$$

(I)   (II)

R^1, R^2, R^3 = H, OCH_3, OCH_2O, $N(CH_3)_2$.

In the present communication we report the results of studying the reaction of the NAE with the diethyl acetals of benzaldehydes with electron-acceptor substituents (Ia-d). We found that in this case, together with the C-alkylation products (II), are formed in variable yield the ethyl esters of the benzoic acids corresponding to the taken acetals (Table 1).

TABLE 1. Reaction of Acetals $R^1\text{—}\langle\rangle\text{—}CH(OEt)_2$ with $\underset{R^2}{}$

$\underset{NO_2}{CH_2COOCH_3}$

Compound	R^1	σ_p	R^2	σ_m	$T.,°C$	Time, h	Yield of (II), %	Yield of (VI), %
(Ia)	OAc	+0,31	OMe	+0,115	120–160	6	95	4*
(Ib)	OAc	+0,31	OAc	+0,39	130–150	15	60(28)†	38(69)†
(Ic)	Br	+0,232	H	0	120–130	10	73(44)	25(54)
(Id)	NO₂	+0,778	H	0	120–140	11	0	96
(Ie)‡	OMe	−0,268	H	0	110–155	8	95	—

*Determined via the PMR spectra (δ, ppm): 1.13 t, 4.57 q, 3.82 s, 2.22 s (OAc), 7.4 m (Ar).
†The values obtained when the reaction is run in the presence of 5 ml of diglyme are given in parentheses.
‡Data from [1].