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Of the meta-substituted phenols investigated, only 3-chloro- and 3-methyl-phenol are attacked primarily at the OH group. Their transfer constants are not greatly different from that of phenol and it is probable that inductive effects are not of great importance in this hydrogen-abstraction reaction. 4-Methyl- and 4-chloro-phenol have higher transfer constants than the corresponding meta-substituted phenols, presumably due to weak contributions to the transition state of polar structures in which an electron has been donated by the phenol to the radical (12). Inductive and resonance effects from these single substituents are small but the total effect of the four methyl groups in 2,3,4,6tetramethylphenol is large enough to increase its transfer constant to 1.

The ratios of transfer constants for 2,3,4,6-tetramethylphenol towards polymethyl methacrylate (3), polystyryl (1), and polyvinyl acetate radicals are approximately 0.02:1:18 while those for the hydrocarbon toluene are 4:1:170. The difference in relative reactivities of polystyryl and polymethyl methacrylate radicals towards phenols and toluene is interpreted (3) in terms of contributions to the transition state of polar structures in which an electron has been donated by the radical to the phenol. Such contributions are significant in reactions between polystyryl radicals and phenols but are not important in polymethyl methacrylate reactions because of the electron-withdrawing character of the ester group (13). On this interpretation, polar structures with the polyvinyl acetate radical as donor and 2,3,4,6-tetramethylphenol as acceptor contribute to the transition state of this hydrogen-abstraction reaction but are less important than those involved in the corresponding reaction with polystyryl radicals.

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PREPARATION OF 4,4"-BIS(DIPHENYLAMINES) BY THE CHAPMAN REARRANGEMENT

ROBERT BARCLAY, JR.

Very few applications of 4,4"-bis(diphenylamines) to the synthesis of condensation polymers have been reported. Exploratory studies in this area required the development of a convenient laboratory preparation of the diamines, preferably from the corresponding

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diphenols. The method of choice, involving the Chapman rearrangement (1) in its key step, is a standard synthesis of diarylamines, but has apparently not previously been applied to diphenols.

Imido esters (Table I) are prepared from the phenol and the imidoyl chloride in the presence of an acid-acceptor. While anhydrous conditions are commonly employed (2), it was found at least equally convenient to carry out this reaction under conditions suitable for the preparation of polyphenyl esters by interfacial polycondensation (3). In suitable reaction media, both N-arylimidoyl chlorides (4) and acyl halides (5) undergo solvolysis by mechanisms involving a rate-determining ionization step, the rates being increased by the addition of amines; therefore, the similarity in their reactions with aqueous aryloxide ions was not unexpected. The yields were good, but not quantitative; small amounts of benzanilide and of unchanged diphenol were often recovered. Although the pure imido esters are solids with fairly high melting points, it was often difficult to obtain them in a crystalline form. It was, nevertheless, expedient to purify the imido esters, since pure benzamides could not be isolated from the products of rearrangement of crude intermediates.

Rearrangement was effected by heating the molten imido esters in a nitrogen atmosphere at temperatures in the range 220–280° (Table II). In most cases the reaction could be followed by observation of changes in the infrared spectra, especially in the C—O and C—N stretching region. The imido esters exhibited strong bands in the ranges 1206–1225 and 1266–1271 cm⁻¹, while the amides absorbed at 1326–1339 and 1289–1294 cm⁻¹. As reported by Chapman (6) and others (7), reaction is facilitated by electron-attracting substituents in the aryl groups derived from the original phenol. With the benzimidates I and II, for example, rearrangement was complete within 1 h at 240° and 3 h at 220°, respectively.



The dibenzoyl derivatives were hydrolyzed to the free 4,4"-bis(diphenylamines) (Table III) by treatment with potassium hydroxide in hot aqueous ethanol. Conversion in this step appeared to be essentially quantitative. A sample of 4,4"-methylenebis(diphenylamine) prepared in this way was identical with the diamine obtained (8) by the condensation of diphenylamine with formaldehyde.

The methods described above were extended to the preparation of the polymeric substances IV and V. Since the reduced viscosities of IV and V were 0.15 and 0.12, respectively, it is probable that little change in molecular weight accompanied the rearrangement.

EXPERIMENTAL

Melting points are uncorrected. Infrared spectra (except those of the polymers) were determined on glasses obtained by cooling the molten substance or as Nujol mulls; a Beckman IR5 spectrophotometer was used. Tabulated yields refer to once-recrystallized material. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. Reduced viscosities were measured in methylene chloride at 25° (0.2 g of polymer/100 ml of solution).

Diphenol N-phenylbenzimidates.—In a 250-ml, three-necked Morton-type flask with stirrer, dropping funnel, and thermometer were placed 0.04 mole of the diphenol, 0.0816 mole of sodium hydroxide, 3.3 g of

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TABLE I Diphenol N-phenylbenzimidates



						C, %		Н, %			N, %
R ₁	R_2	R ₃	Yield, $\%$	M.p., °C	Formula	Calcd.	Found	Calcd.	Found	Calcd.	Found
$\begin{array}{c} C(CH_3)_2\\ C(CH_3)_2\\ SO_2\\ CH_2 \end{array}$	H Cl H H	H Cl H H	$74 \\ 74 \\ 80 \\ 60$	138-139* 170.5-174* 141.5-144† 124-127‡	$\begin{array}{c} C_{41}H_{34}N_{2}O_{2}\\ C_{41}H_{30}Cl_{4}N_{2}O_{2}\\ C_{38}H_{28}N_{2}O_{4}S\\ C_{39}H_{30}N_{2}O_{2} \end{array}$	$\begin{array}{r} 83.93 \\ 67.97 \\ 74.98 \\ 83.85 \end{array}$	$83.82 \\ 68.05 \\ 74.63 \\ 83.76$	5.844.174.645.41	$5.77 \\ 4.21 \\ 4.77 \\ 5.32$	$4.77 \\ 3.87 \\ 4.60 \\ 5.01$	4.61, 4.53 4.97

*Recrystallized from benzene-ethanol. †Recrystallized from acetone-ethanol. ‡Recrystallized from toluene-heptane.

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R ₁	\mathbb{R}_2	\mathbb{R}_3	Yield, %	M.p., °C	Formula	Calcd.	Found	Calcd.	Found	Calcd.	Found
C(CH ₃) ₂	Н	Н	85	98.5–99.5*·†	$C_{27}H_{26}N_2$		ł	I	ļ	7.40	7.74
C(CH ₃) ₂ SO ₂ CH ₂	ннС	ннC	74 85 80	172-173.5* 221-223§ 121-122*₁¶	$\begin{array}{c} C_{21}H_{22}CI_4N_2t\ C_{24}H_{20}N_2O_2S\ \ C_{25}H_{22}N_2\end{array} \\ C_{25}H_{22}N_2\end{array}$	62.81 71.97	62.86 72.14 —	$\frac{4.30}{5.03}$	$\frac{4.29}{5.24}$	5.43 7.00	5.38 7.01
2,2"-CH2(C ₆ H ₄	NHPh)2		62	121-122*, **	$C_{25}H_{22}N_2$	85.68	$84.79 \\ 84.54$	6.33	$6.10 \\ 5.99$	7.99	7.75
*Recrystallized! +D. Craig (11) rr +D. Craig (11) rr Anal. Calcd.: C Recrystallized! Rear Calci. S D. Craig (8) re **This compoun.	from ethanol. eported m.p. 99-1 1, 27.47. Found: (from acetone-eth 9.01. Found: S, 8 ported m.p. 122-1 d was evidently n	00°. 21, 27.28. anol. 3.27. 123° (higher r 123° to pure. Mixt	melting form). ture melting point w	ith the 4,4″-isomer exi	ibited strong depression.	- -					

TABLE III 4,4"-Bis(diphenylamines)

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sodium chloride, 30 ml of water, and 40 ml of methylene chloride. A solution of 0.08 mole of N-phenylbenzimidoyl chloride (9) in 70 ml of methylene chloride was added with rapid stirring over 2–3 hours at 23–27°. The solution was diluted with 200 ml of water, the layers were separated, and the aqueous phase was extracted with three 100-ml portions of methylene chloride. The combined organic solution was washed with three 100-ml portions of water and dried over anhydrous magnesium sulfate. The methylene chloride was removed by distillation, leaving the crude imido ester as a residue product.

Rearrangement.—The purified imido ester was heated by means of an oil bath in a large test tube with side arm. Dry nitrogen gas was bubbled through the melt. When the reaction was complete, the cooled glassy reaction product was recrystallized from a suitable solvent.

Hydrolysis.—The preparation of 4,4"-isopropylidenebis(diphenylamine) is typical. A mixture of 32.9 g (0.0561 mole) of 4,4"-isopropylidenebis(diphenylbenzamide), 16.5 g (0.25 mole) of potassium hydroxide pellets, 135 ml of ethanol, and 15 ml of water was heated under reflux for 22 hours. The cooled reaction mass was diluted with 500 ml of water and extracted with a total of 500 ml of methylene chloride in three portions. The combined extract was washed with three 150-ml portions of water and dried over magnesium sulfate. Removal of methylene chloride by distillation left as a residue 19.84 g (94%) of crude diamine. Recrystalization from 180 ml of ethanol gave 18.10 g (85%) of 4,4"-isopropylidenebis(diphenylamine), m.p. 98–100°.

4,4''-Methylenebis(diphenylamine).—This compound was prepared via the Chapman rearrangement. However, preparation by the condensation of diphenylamine with formaldehyde (8) is more convenient.

A mixture of 2 249 g (13.29 moles) of diphenylamine, 136 g (1.68 moles) of 37% formaldehyde solution, 9 ml of concentrated hydrochloric acid, and 2.2 l of ethanol was heated under reflux ($80-81^{\circ}$) for 1 h. The solution was cooled and divided into six portions, each of which was added to a mixture of 3 g of sodium hydroxide, 1.65 l of water, and 1.0 kg of crushed ice in a Waring Blendor. The precipitated solids were collected by filtration, washed thoroughly with water, and dried in a vacuum oven at 40°. The unchanged diphenylamine (1700 g) was recovered by distillation to a final pot temperature of 230° (0.2 mm), and a crude product fraction was obtained by heating to a pot temperature of 358° (0.75 mm). The diamine was purified by redistillation, 294.8 g being collected, b.p. $259-286^{\circ}$ (0.25-0.55 mm). Recrystallization from 5.75 l of ethanol gave 207.8 g (36.6%, based on diphenylamine not recovered) of 4,4"-methylenebis(diphenylamine), m.p. $121-123^{\circ}$.

Imidoyl chloride III.—Reaction of 4,4'-methylenedianiline with benzoyl chloride and pyridine in chloroform gave the dibenzoyl derivative, m.p. 250–251.7° (250° (10)). A mixture of 20.4 g (0.0502 mole) of the latter and 22 ml (0.30 mole) of thionyl chloride was heated under reflux for 3.5 h by means of an oil bath kept at 110–113°. Unchanged thionyl chloride was removed by distillation under reduced pressure (bath temperature 125°), giving 22.1 g (99%) of the yellow imidoyl chloride III. After two recrystallizations from toluene-heptane there remained 16.3 g (73%) of nearly pure III, m.p. 140–143°.

Anal. Calcd. for C₂₇H₂₀Cl₂N₂: Cl, 16.0. Found: Cl, 15.7, 15.8.

Poly-(imido ester) IV.—The polymer was prepared from 10.27 g (0.0450 mole) of bisphenol A, 19.95 g (0.0450 mole) of III and 3.72 g (0.091 mole) of sodium hydroxide essentially as described above for the N-phenylbenzimidates. Addition of III required 3 hours, the temperature being maintained at 14–16°. The polymer was precipitated by addition of the water-washed methylene chloride solution to 1.6 l of ethanol in a Waring Blendor and dried overnight in a vacuum oven at 60°. The yield of polymer, reduced viscosity 0.15, was 22.3 g (83%).

The infrared spectrum, measured as a potassium bromide pellet, included typical imido ester bands at 1208 and 1267 cm⁻¹.

Polyamide V.—The polymer IV was heated in a nitrogen atmosphere for 18 h at $265-270^{\circ}$. The resulting polymer, reduced viscosity 0.12, exhibited infrared absorption bands at 1 294 and 1 330 cm⁻¹, typical of N,N-diarylbenzamides.

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THE IONIZATION OF SOME TYPICAL WEAK BASES IN CONCENTRATED PERCHLORIC ACID

KEITH YATES AND HENRY WAI

In connection with a study of the acidity of 0-80% perchloric acid, we have investigated the behavior of nine typical weak organic bases in this medium. These include representatives of the amine, carbonyl, and ether type of base. All these classes have been extensively investigated in sulfuric acid (1) but little is known of their stability, spectral changes, and basicity constants in perchloric acid. We find that the amines and carbonyl compounds are quite stable even at the highest acid concentrations used and although there is some evidence of slow decomposition of phenol and anisole in these solutions, even these compounds are quite stable within the usual time required to measure ultraviolet spectra. This is in contrast to their behavior in sulfuric acid where rapid and irreversible sulfonation of phenols and anisoles occurs at the acidities required to measure their pK values.

Ultraviolet absorption in perchloric acid at 25 °C

Compound	λ_{B}^{*} (m μ)	€B [*]	$\lambda_{BH}^{+\dagger}$ (m μ)	$\epsilon_{ m BH}$ +†
2-Chloro-4,6-dinitroaniline N,N-Dimethyl-2,4,6-trinitroaniline	$350 \\ 385 \\ 222$	$\frac{13\ 000}{13\ 600}$	350 385	390 110
Benzoic acid Benzamide	$230 \\ 225 \\ 250 $	$10\ 300\ 8\ 900\ 11\ 400$	258 240 205	$14\ 100\ 11\ 900\ 10\ 200$
Acetophenone	$\frac{250}{250}$	$11\ 400$ $12\ 000$	$295 \\ 295$	$19\ 200$ 20\ 200

*Measured in acid solutions about $2 H_0$ units greater than pK. †Measured in acid solutions about $2 H_0$ units less than pK.

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