aromatic amines by this method. The results are presented in Tables I and II in a format that parallels the tabulation in ref. *3*.

EXPERIMENTAL

The amines employed in this study were obtained through commercial sources and were used without further purification, except for *N*,*N*-dimethyl-*p*-phenylenediamine which was redistilled: bp 99.5–100°C (2 mm). Melting points were determined on a modified Hershberg apparatus which matched Anschutz thermometers. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

The 3,5-dinitrobenzanilides were prepared in the following manner: In a 25-ml, round-bottomed flask fitted with a reflux condenser, a solution of the aryl amine (0.5 gram) and 3,5-dinitrobenzoyl chloride (1.3 grams) in dry pyridine (10 ml) was refluxed 30 min. The cooled solution was poured into 100 ml of 5% hydrochloric acid and the solid was collected by suction filtration. The solid was triturated with 50 ml of 5% sodium carbonate solution, collected by suction filtration, washed twice with water, and dried in a vacuum oven. The crude product was recrystallized from 95% ethanol or glacial acetic acid and decolorized with carbon.

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N,*N*′-Diaryl- and *N*,*N*′-Dialkyl-*N*,*N*′-diarylterephthalamides

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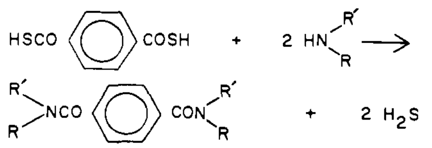
Twelve *N*,*N*′-diarylterephthalamides and two *N*,*N*′-dialkyl-*N*,*N*′-diarylterephthalamides were prepared by the action of dithioterephthalic acid on aromatic amines. The melting behavior and infrared absorption spectra of these compounds were examined.

In the course of a series of studies dealing with the physical properties of phthalamides (*6*), a method for preparing *N*,*N*′-diaryl- and *N*,*N*′-dialkyl-*N*,*N*′-diarylterephthalamides was developed, which would easily and reproducibly yield these compounds in a good state of purity. A survey of the literature indicated that only one preparation route had been used previously, namely the acylation of amines by terephthaloyl chloride, with a variety of solvents and other reaction conditions. In those few cases for which there was more than one report for a given compound, the lack of agreement between reports in respect to both yields and melting points raised a question concerning the reproducibility of this method.

The commercial availability of dithioterephthalic acid suggested the use of this compound as an acylating agent in place of terephthaloyl chloride. Although the use of thiolacids as acylating agents for amines is not novel, its application is rare, and the preparation of the subject terephthalamides by this method has not been reported previously.

Dithioterephthalic acid reacted readily with a two-fold excess of amines to form the desired products, when mixed in an appropriate solvent, and heated:



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The choice of solvent was determined by the degree of *N*-substitution sought. The preparation of *N*,*N*′-diarylterephthalamides from primary aromatic amines gave the best results in *N*,*N*-dimethylformamide. Because of the much higher solu-

Table I. Preparations of *N*,*N*′-Diaryl- and *N*,*N*′-Dialkyl-*N*,*N*′-diarylterephthalamides, *p*-$(ArRNCO)_2C_6H_4$

Ar	R	Recrystallization solvent	Yield, %
C_6H_5	H	1:10 *N*,*N*-Dimethylformamide–water	76
C_6H_5	CH_3	Toluene	66
C_6H_5	*n*-C_4H_9	Methanol	65
o-$CH_3C_6H_4$	H	Absolute ethanol	71
m-$CH_3C_6H_4$	H	Xylene	40
p-$CH_3C_6H_4$	H	1:10 *N*,*N*-Dimethylformamide–water	57
o-$CH_3OC_6H_4$	H	1:10 *N*,*N*-Dimethylformamide–water	38
m-$CH_3OC_6H_4$	H	...[a]	89
p-$CH_3OC_6H_4$	H	*N*,*N*-Dimethylformamide	50
o-$C_2H_5OC_6H_4$	H	95% Ethanol	58
m-$C_2H_5OC_6H_4$	H	1:1 Acetone–dioxane	83
p-$C_2H_5OC_6H_4$	H	...[b]	51
α-$C_{10}H_7$	H	1:2 *N*,*N*-Dimethylformamide–water	46
β-$C_{10}H_7$	H	*N*,*N*-Dimethylformamide	36

[a] Washed with hot 1:1 methanol–dioxane. [b] Washed with hot *N*,*N*-dimethylformamide.

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Table II. Behavior of *N,N'*-Diaryl- and *N,N'*-Dialkyl-*N,N'*-diarylterephthalamides on Heating, p-$(ArRNCO)_2C_6H_4$

		Melting point, °C			Decomposition point, °C		
Ar	R	Found	Reported	Reference	Found[a]	Reported[b]	Reference
C_6H_5	H	345–6	334–7	*(12)*	>500	340	*(13)*
			338–40	*(13)*			
			340–5	*(7)*			
C_6H_5	CH_3	212–13	212–13	*(2)*	394	...	...
C_6H_5	n-C_4H_9	175–6	...	...	...[c]	...	...
o-$CH_3C_6H_4$	H	303–4	297–8	*(13)*	318	300	*(13)*
m-$CH_3C_6H_4$	H	275–6	275–6	*(13)*	309	276	*(13)*
p-$CH_3C_6H_4$	H	350–1	343–5	*(13)*	...[d]	340	*(13)*
o-$CH_3OC_6H_4$	H	245–6	245–6	*(13)*	325	270	*(13)*
m-$CH_3OC_6H_4$	H	248–50	...	...	...[e]	...	...
p-$CH_3OC_6H_4$	H	351–2	246–8	*(11)*	352	...	...
o-$C_2H_5OC_6H_4$	H	192–3	...	...	193	...	...
m-$C_2H_5OC_6H_4$	H	279–80	...	...	280	...	...
p-$C_2H_5OC_6H_4$	H	350–1	...	...	351	300	*(11)*
α-$C_{10}H_7$	H	367–8	334–5	*(12)*	368	335	*(12)*
β-$C_{10}H_7$	H	344–5	...	...	...[e]	...	...

[a] Differential scanning calorimeter. [b] Temperature at which visible discoloration first appears. [c] Sharp transition at 265°C. [d] Sharp transition at 368°C. [e] See experimental section.

Table III. Infrared Spectra of *N,N'*-Diaryl- and *N,N'*-Dialkyl-*N,N'*-diarylterephthalamides, p-$(ArRNCO)_2C_6H_4$

Ar	R	ν_{NH}, cm^{-1}		ν_{CO}, cm^{-1}	ν_{CNH}, cm^{-1}
C_6H_5	H	3302	664	1645	1529
C_6H_5	CH_3	...	...	1631	...
C_6H_5	n-C_4H_9	...	...	1638	...
o-$CH_3C_6H_4$	H	3257	676	1641	1526
m-$CH_3C_6H_4$	H	3274	679	1639	1533
p-$CH_3C_6H_4$	H	3289	683	1639	1525
o-$CH_3OC_6H_4$	H	3427	...	1675	1538
m-$CH_3OC_6H_4$	H	3266	684	1637	1530
p-$CH_3OC_6H_4$	H	3295	673	1637	1526
o-$C_2H_5OC_6H_4$	H	3382	...	1676	1525
m-$C_2H_5OC_6H_4$	H	3295	683	1643	1528
p-$C_2H_5OC_6H_4$	H	3305	685	1643	1521
α-$C_{10}H_7$	H	3168	683	1644	1530
β-$C_{10}H_7$	H	3261	697	1639	1551

bilities of the *N,N,N',N'*-tetrasubstituted terephthalamides, these compounds were more effectively recovered from xylene, a less powerful solvent. Preparative data are summarized in Table I. New compounds, and those compounds whose melting points failed to come within five degrees of published values, were analyzed. Elemental analyses (C, H, N) in agreement with theoretical values were obtained and submitted for review.

The lack of reproducibility among the published values of the melting points for the better known examples of these compounds led to a careful examination of this property. The parent compound of the series, terephthalamide, for example, is variously reported to melt above 250° (*8*), above 260° (*10*), and at 317-24° (*4*), and to decompose at 350°C (*1*). A sample of terephthalamide, also prepared from dithioterephthalic acid, melted at 345-6°C with decomposition after purification by repeated extractions with hot *N,N*-dimethylformamide and washing with water. All of the compounds were purified until reproducible measurements of melting point could be obtained by both visual measurement and by use of a differential scanning calorimeter. The temperatures at which decomposition initiates, which have also been used as identifying properties of the terephthalamides (*13*), were determined with the latter instrument. These measurements were complicated by the tendency of the terephthalamides to sublime. The results of the temperature measurements are compared with previously published values in Table II.

The infrared absorption frequencies, for KBr pellets, characteristic of the amide group, are recorded for the *N,N'*-diarylterephthalamides in Table III. With two exceptions, the frequencies for the secondary amides are characteristic of intermolecularly hydrogen-bonded amides (*3*). These exceptions are *N,N'*-bis(*o*-methoxyphenyl)terephthalamide and *N,N'*-bis(*o*-ethoxyphenyl)terephthalamide whose amide frequencies correspond to those for a dilute solution. Evidently, a sufficiently bulky *ortho*-group on the *N*-substituent sterically prevents hydrogen bonding. This effect is also reflected in the comparatively low melting point of *N,N'*-bis(*o*-ethoxyphenyl)terephthalamide.

EXPERIMENTAL

***N,N'*-Diaryl- and *N,N'*-Dialkyl-*N,N'*-diarylterephthalamides.** To a solution of 2.85 grams of dithioterephthalic acid (98% purity; 0.0126 mole) in 50 ml. of *N,N*-dimethylformamide was added 0.05 mole of a primary aromatic amine. The mixture was refluxed with stirring for one hour *in a hood*, cooled, and filtered. The filtrate was diluted with an equal volume of water. The combined precipitate was washed with water, then with 0.1*N* sodium hydroxide, and again with water, then dried, and recrystallized. The data for recrystallizations and yields are presented in Table I.

For preparations involving secondary amines, 50 ml of xylene was used as the solvent, and the product was isolated by chilling the reaction mixture and filtering. Analyses were done by Atlantic Microlab, Inc., Atlanta, Ga., or by Midwest Microlab, Inc., Indianapolis, Ind.

Terephthalamide. A solution of 7.47 grams of dithioterephthalic acid (98% purity; 0.037 mole) in 30 ml. of concentrated ammonium hydroxide was evaporated to dryness. The residue was recrystallized from *N,N*-dimethylformamide, giving 4.0 grams (67%). Further purification was done by repeated alternate washings with 5 ml of hot *N,N*-dimethylformamide and hot water, until a reproducible melting point of 345-6°C, with decomposition, was obtained. The infrared spectrum of terephthalamide has been presented elsewhere (*5*, *9*).

Physical Measurements. Melting points were determined both with an Electrothermal melting-point apparatus (capillary method; air-bath) and with a Perkin-Elmer DSC-1B differential scanning calorimeter, and are corrected (Table II). Decompositions were indicated with the differential scanning calorimeter by a very broad endotherm, for which only the initial temperatures are recorded in Table II.

In a number of attempted measurements of decomposition temperatures, the capsules ruptured violently. Because of this effect, reproducible decomposition temperature measurements could not be obtained for *N*,*N'*-bis(*m*-ethoxyphenyl)-terephthalamide, and for *N*,*N'*-bis(β-naphthyl)terephthalamide.

Infrared absorption spectra were determined with a Beckman IR-5 spectrophotometer, using potassium bromide pellets containing 0.5% by weight of the sample.

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Isothermal Vapor-Liquid Equilibrium Data by Total Pressure Method

SIR:

Equilibrium data for the binary system, acetaldehyde and water, have been determined (*1*) using an isoteniscope. Activity coefficients were calculated by the Redlick-Kister equation using the experimentally determined total pressure at a known liquid composition and temperature.

By use of Equation 1 (*1*) and the Redlich-Kister coefficients for acetaldehyde and water in Table II of the article, the activity coefficient for acetaldehyde at infinite dilution in water were calculated as shown in Table I.

Data in Table I were used to calculate the heat of mixing at infinite dilution (L_1^∞) from the following thermodynamic relationship:

$$\left(\frac{d \ln \gamma_1}{dT}\right)_{P,X_1 \to 0} = \left(\frac{H_1^\circ - \bar{H}_1}{RT^2}\right)_{P,X_1 \to 0} = -\frac{L_1^\infty}{RT^2}$$

At 15°C the heat of solution at infinite dilution for acetaldehyde in water was calculated to be 6.8 kcal/g-mol and to have a positive value which indicates an endothermic heat of solution.

However, data reported in the literature (*2*, *3*) show that the heat of solution for acetaldehyde in water at infinite dilution is exothermic.

Table I. Acetaldehyde Activity Coefficients at Infinite Dilution Decrease with Increasing Temperature

t,°C	γ_1^∞	t,°C	γ_1^∞
10	5.46	25	3.57
15	4.26	30	3.54
20	3.60		

With exothermic heats of solution the activity coefficient of acetaldehyde in water should increase with increasing temperature. However, the data show high endothermic heats of solution especially at the lower temperatures, 10–15°C. Since these data indicate a very large change in the heat of mixing with temperature, it is suggested that a constant error may be present. To determine equilibrium data by the total pressure method is difficult experimentally because small constant errors may lead to substantial ones in the calculated results. For example, if in degassing the samples in sections *A* and *B* residual air remained, the calculated activity coefficient of acetaldehyde in water would be too high, especially at the lower temperatures.

In summary, other literature data indicate that the heat of solution at infinite dilution for acetaldehyde in water is exothermic and that the activity coefficient of acetaldehyde increases with increasing temperature. Consequently, the use of the data obtained by the total pressure method at other temperatures will lead to serious error. Also these data illustrate the experimental difficulties of obtaining equilibrium data by the total pressure method.

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