Anal. Calcd for $C_{14}H_8N_4O_{12}$: C, 39.63; H, 1.90; N, 13.21. Found: C, 39.46; H, 2.05, N, 13.09.

ACKNOWLEDGMENT

The authors wish to express their appreciation to Professor Nathan Kornblum of Purdue University for reading and suggesting improvements of the manuscript. Grateful thanks are extended to B. Artman and R. Blanco for the elemental analyses and to W. Arnheim for measurements of spectral data.

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Received for review July 6, 1971. Accepted November 15, 1971.

3,5-Dinitrobenzanilides

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3,5-Dinitrobenzanilides were prepared from 52 primary aromatic amines as the derivative of choice for characterization; 43 of these derivatives are new compounds.

In organic qualitative analysis, amides are the derivatives of choice for amines. Primary and secondary amines can be converted to carboxamides and sulfonamides by standard procedures (*3*). Despite the variety of choice, however, only the 3,5-dinitrobenzamide derivative combines the desirable characteristics of high melting points and easy recrystallizations throughout the range of aromatic amines. Although this derivative has been reported on occasion in the literature (*1*, *2*, *4*), no systematic compilation has been available. We have, therefore, characterized an extensive series of liquid and solid primary

Table I. 3,5-Dinitrobenzanilides of Liquid Primary Amines

Amine	Amine, bp, °C	Deriv. mp, °C[a]
Aniline	183	238.0–8.5[b]
3-Aminobenzotrifluoride	187	169.5–70.5
o-Toluidine	199	247.5–8.0[c]
m-Toluidine	203	263.0–3.5
o-Chloroaniline	207	208.0–8.5
2,4-Dimethylaniline	212	240.5–1.3
o-Ethylaniline	216	187.5–8.0[d]
p-Ethylaniline	216	223.5–4.2
2-Isopropylaniline	223	174.0–5.0
o-Anisidine	225	191.8–2.0
o-Bromoaniline	229	223.0–3.5
o-Phenetidine	229	162.0–2.5
m-Chloroaniline	230	228.5–9.0
m-Phenetidine	248	150.2–0.5
m-Anisidine	251	191.2–1.6
m-Bromoaniline	251	219.5–20.0
p-Phenetidine	254	230.5–1.0
2,6-Diisopropylaniline	257	276.0–7.0
Methyl anthranilate	260	154.0–6.0
Ethyl *m*-aminobenzoate	294	164.0–4.8

[a] Elemental analyses (C, H, N) in agreement with theoretical values were obtained and submitted for review. [b] Lit. mp 239°C; ref. *4*. [c] Lit. mp 241°C; ref. *1*. [d] Lit. mp 186°C; ref. *2*.

Table II. 3,5-Dinitrobenzanilides of Solid Primary Amine

Amine	Amine, mp, °C	Deriv. mp, °C[a]
m-Iodoaniline	27	226.5–7.5
2-Chloro-5-methylaniline	29	207.0–7.5
p-Toluidine	45	284.5–5.0[b]
2-Aminobiphenyl	45	182.5–3.2
3,4-Dimethylaniline	47	261.3–1.5
2,5-Dichloroaniline	50	190.0–0.5
α-Naphthylamine	50	274.0–4.5[c]
2,5-Dibromoaniline	51	205.5–6.5
m-Aminobenzonitrile	53	234.0–4.4
4-Aminobiphenyl	53	264.0–4.3
N,*N*-Dimethyl-*p*-phenylenediamine	53	282.5–3.5
o-Iodoaniline	56	244.5–5.0
p-Anisidine	57	244.0–4.5
p-Iodoaniline	62	253.0–4.0
2,4-Dichloroaniline	63	170.0–0.3
p-Bromoaniline	66	250.0–1.0[d]
p-Chloroaniline	70	236.0–6.7[e]
o-Nitroaniline	71	196.3–7.2
2,4,6-Trichloroaniline	77	232.0–3.0
2,4-Dibromoaniline	79	197.0–8.0
2,6-Dibromoaniline	83	314.5–5.5
p-Aminobenzonitrile	86	275.0–6.0
m-Aminobenzophenone	87	191.0–3.0
Ethyl *p*-aminobenzoate	89	190.2–0.8
o-Aminobenzophenone	105	226.0–6.8
p-Aminoacetophenone	106	205.0–6.0
β-Naphthylamine	112	340.0–1.0
m-Nitroaniline	114	209.0–10.0
p-Aminobenzophenone	124	245.5–6.3
p-Aminoazobenzene	126	244.0–5.0
p-Nitroaniline	147	282.0–2.5[f]
2,4-Dinitroaniline	180	213.5–14.0[g]

[a] Elemental analyses (C, H, N) in agreement with theoretical values were obtained and submitted for review. [b] Lit. mp 284°C; ref. *4*. [c] Lit. mp 268°C; ref. *1*. [d] Lit. mp 251°C; ref. *4*. [e] Lit. mp 237°C; ref. *4*. [f] Lit. mp 280°C; ref. *4*. [g] Lit. mp 213°C; ref. *4*.

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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.

ACKNOWLEDGMENT

Gifts of 2-isopropylaniline and 2,6-diisopropylaniline from the Ethyl Corp. and of 3,4-xylidine from Hoffmann-La Roche, Inc., are gratefully acknowledged.

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RECEIVED for review July 8, 1971. Accepted November 18, 1971. This work was supported in part by funds from a grant to Williams College from the Alfred P. Sloan Foundation.

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

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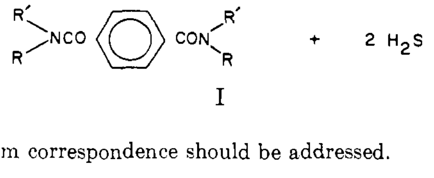
Twelve *N*,*N*′-diarylterephthalamides and two *N*,*N*′-dialkyl-*N*,*N*′-diarylterephthalamides were prepared by the action of dithioterephthalic acid on aromatic amines. The melting behavior and infrared absorption spectra of these compounds were examined.

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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