The heat of adsorption of $LiCl \cdot H_2O$ given by Slonim and Hüttig (5) as 1465 B.t.u. per pound by water, which agreed with the present calculated value of 1490 B.t.u. per pound of water. The heats of adsorption for other salts could not be compared because of the lack of data in the literature. Also the entropy changes for the salts studied could not be compared with the third law entropy changes because of the lack of absolute entropy data.

ACKNOWLEDGMENT

This study was carried out under the auspices of the American Gas Association.

LITERATURE CITED

(1) Appleby, M.P., Crawford, F.H., Gordon, K., *J. Chem. Soc.* 11, 1665 (1934).
(2) Foote, H.W., Foote Mineral Co., Exton, Pa., unpublished data, 1965.
(3) Gokcen, N.A., *J. Am. Chem. Soc.* **73**, 3789 (1951).
(4) Menzies, A., *J. Am. Chem. Soc.* **42**, 1951 (1920).
(5) Slonim, C.H., Hüttig, G.F., *Z. Physik. Chem.* 55 (1929).
(6) Thakker, M.T., M.S. Thesis, Illinois Institute of Technology, Chicago, Ill., 1967.
(7) Wilson, R.E., *J. Am. Chem. Soc.* **43**, 704 (1921).

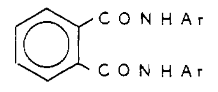
RECEIVED for review April 14, 1967. Resubmitted April 10, 1968. Accepted July 10, 1968.

Some Base-Catalyzed Reactions of Diethyl Phthalate with Aromatic Amines

ROSALIE D. REYNOLDS, M. J. ZEIGLER, D. J. HEUCK, and CARL JOHNSON
Michael Faraday Laboratories, Northern Illinois University, DeKalb, Ill. 60115

The reaction of diethyl phthalate with aromatic amines in the presence of sodium ethoxide has been examined. Several new *N,N'*-diaryldiamides of o-phthalic acid have been synthesized and characterized. Complicating factors have been investigated.

SOME TIME AGO, the authors reported syntheses of the previously unknown di-*o*- and di-*p*-toluides of *o*-phthalic acid (1a and 1b) via reaction of diethyl phthalate with



the appropriate amines in the presence of sodium or sodium ethoxide (7). Extension of this synthetic method to synthesis of other *N,N'*-diaryldiamides of *o*-phthalic acid has met with varying degrees of success.

Diethyl phthalate was treated with each of 15 aromatic amines in ethanolic sodium ethoxide. Amines employed were the *o*, *m*, and *p* isomers of phenylenediamine, anisidine, toluidine, chloroaniline, and nitroaniline. No diamides were isolated from reaction mixtures containing the phenylenediamines or the nitroanilines.

In view of the expected low acidities of the phenylenediamines (*10*), it is not surprising that reaction did not take place under the mild conditions employed. Sufficient concentrations of the sodium salts of the phenylenediamines necessary for the diamide synthesis (7) could, probably, be generated in the presence of a stronger base.

Conversely, the nitroanilines would be expected to be the strongest acids of all the amines used (*10*), and they should react with sodium ethoxide to form comparatively high concentrations of the corresponding sodium salts. However, the lack of concentration of nucleophilicity on the amine nitrogen atom might well render these comparatively stable anions ineffectual in the reactions under consideration. The nitroanilines were recovered unchanged from all reaction mixtures. The failure of this synthetic method in these cases is not particularly serious, inasmuch as the dinitroanilides are among the few *N,N'*-diaryldiamides of *o*-phthalic acid available by other synthetic methods (5, *9*).

Yields and melting points of *N,N'*-diaryldiamides of *o*-phthalic acid which have been successfully prepared via the method under consideration are summarized in Table I.

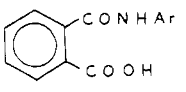
Table I. *N,N'*-Diaryldiamides of o-Phthalic Acid

Compound	Aryl Group	M.P., ° C.	Yield, %
1a	*o*-$CH_3C_6H_4$	209.0–209.5	78
1b	*p*-$CH_3C_6H_4$	181.0–182.0	65
1c	*m*-$CH_3C_6H_4$	200.5–201.2	31
1d	*o*-$CH_3OC_6H_4$	174.5–175.5	28
1e	*p*-$CH_3OC_6H_4$	197.5–199.0	18
1f	*m*-$CH_3OC_6H_4$	169.5–171.0	84
1g	*o*-ClC_6H_4	189.5–191.0	38
1h	*p*-ClC_6H_4	213.0–214.0	28
1i	*m*-ClC_6H_4	213.5–215.0	31
1j	C_6H_5	230.0–231.0[a]	65

[a] Lit., 231–32° C. (*8*).

Certain solid-state infrared absorption peaks of these compounds are summarized in Table II; because of the complexity of the spectra, definite assignments in other regions were not made. However, all spectra are consistent with structural assignments (*2*).

In some cases, another product, the monoamide, 2, was isolated from the reaction mixtures. Yields and melting



2

points of these compounds are summarized in Table III.

The rather poor agreement in values of melting points of these monoamides with previously reported melting points led us to question the structural assignments. However, the acidic nature of these materials, their elemental analyses, and their infrared spectra (Table IV) support the assigned identities. As with the diamides, the complexity of the spectra obtained precluded further assignments of absorption maxima.

That small amounts of water in the reaction mixtures could have resulted in formation of these materials is

Table II. Infrared Absorption Maxima (Cm.$^{-1}$) of Diamides[a]

Compound	Aryl Group	N—H	Amide I CO	CH Out-of-Plane Deformation
1a	o-$CH_3C_6H_4$	3210 (vs)[b] 3190 (m)[c]	1635 (vs)	739–750 (vs)[b]
1b	p-$CH_3C_6H_4$	3200 (vs) 3240 (vs)	1635 (vs)	739 (m)
1c	m-$CH_3C_6H_4$	3300 (vs)[b]	1635 (vs) 1660 (vs)	750 (s)[a] 780,786 (vs)
1d	o-$CH_3OC_6H_4$	3400 (s)[d]	1660 (vs)[d]	745 (vs)[d] 749 (vs)[d]
1e	p-$CH_3OC_6H_4$	3230 (s)	1630 (vs)	753 (m) 817 (vs)[d]
1f	m-$CH_3OC_6H_4$	3240 (s)[b]	1640 (vs)	760–790 (vs)[b] 893 (m)
1g	o-ClC_6H_4	3260 (s)[b]	1640 (vs)[d]	739,747,764 (vs)
1h	p-ClC_6H_4	3250 (s)[d] 3270 (s)[d]	1615 (vs)[d] 1650 (vs)[d]	747 (s)[b] 822 (vs)[b]
1i	m-ClC_6H_4	3270 (s)[d]	1620 (vs)[d] 1650 (vs)[d]	727 (s)[b] 775, 782 (s)[d]
1j	C_6H_5	3190 (vs)[d] 3200 (vs)[d] 3240 (vs)[d]	1620 (vs)[d]	731, 752 (vs)[b]

[a] Relative intensities of absorption maxima indicated by vs, very strong, s, strong, and m, medium. [b] Broad absorption. [c] Shoulder. [d] Very sharp.

Table III. Monoamides of o-Phthalic Acid

Compound	Aryl Group	M.P., ° C.	Yield, %
2c	m-$CH_3C_6H_4$	151.0–53.0 (d)[a]	Very small
2d	o-$CH_3OC_6H_4$	174.5–75.5 (d)[b]	34
2e	p-$CH_3OC_6H_4$	157.0–58.0 (d)[c]	26
2h	p-ClC_6H_4	183.0–84.0 (d)[d]	38
2i	m-ClC_6H_4	170.0–71.5 (d)[e]	65

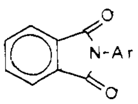
[a] Lit., 159-61° (*11*). [b] Lit., 168-69° (*1*). [c] Lit., 180-85° (*6*). [d] Lit., 187.5° with imide formation (*9*). [e] Lit., 183-84° (*9*).

improbable. When absolute alcohol containing 0.1% water was used as a solvent, hydrolysis of diethyl phthalate with immediate precipitation of sodium phthalate occurred; amines and unreacted diethyl phthalate were recovered unchanged.

Alkyl-oxygen cleavage of an intermediate monoamide-monoester (*5*) could have given the results obtained, since such reactions take place with certain aryl esters (*3*). However, a careful search for ethyl ether in the reaction mixtures via gas chromatographic methods was unsuccessful. Compounds 2c-e, h, and i were probably not initial products of reaction but were formed during treatment of the reaction mixtures.

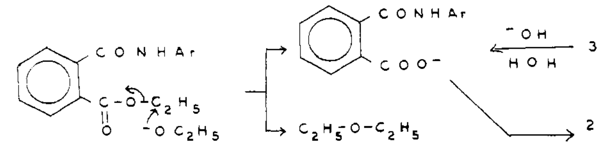
Earlier attempts to prepare N,N'-diaryldiamides of o-phthalic acid often resulted only in formation of the corresponding imides (*3, 7*). Therefore, in certain cases, imides

3



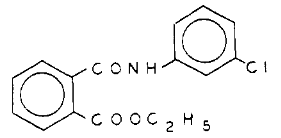
might well be formed under the conditions used in the reactions under investigation. Facile base-catalyzed hydrolysis of the imides during treatment of the reaction mixtures would then account for production of the monoamides. Investigation showed that the imides do react rapidly under conditions used in treatment of reaction mixtures to yield the corresponding monoamides. Further, infrared spectra of crude reaction products from preparation of 1d and 1i indicated the presence of 1d, 3d, 1i, and 3i.

5



Therefore, the competing reaction to form imide should proceed best in the case of the reaction of diethyl phthalate with m-chloroaniline. On the basis of extrathermodynamic free energy relationships (*4*) one would expect that the intermediate monoamide-monoester (4i) would be the strongest acid of all such intermediates involved in this

4i



investigation. Hence, 4i should rapidly react with base; internal attack to yield imide should proceed readily and compete very favorably with external attack to form the diamide (1i).

EXPERIMENTAL

Melting points were taken on a Büchi melting point apparatus calibrated against standard substances. Infrared spectra were determined in potassium bromide pellets (0.5 mg. of sample per 50 mg. of KBr) on a Beckman IR-8 spectrophotometer. Elemental analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich.

Materials. Aromatic amines and diethyl phthalate were purchased commercially and purified by standard methods immediately prior to use.

***N,N'*-Diaryldiamides of *o*-Phthalic Acid (1).** Diamides were prepared via a modified version of method B (*7*); ethanol was dried immediately prior to use and distilled under nitrogen into the reaction vessel. Reactions were allowed to proceed at room temperature in a closed nitrogen atmosphere for approximately 40 hours. Ethanol was removed via a rotary evaporator with mild heating, and water was added. Suction filtration yielded the diamides, which were purified by recrystallization from acetonitrile.

Analyses. Previously reported for 1a, 1b, and 1j (*7*). Calculated for 1c, $C_{22}H_{20}N_2O_2$: C, 76.74; H, 5.81; N, 8.14. Found: C, 76.86; H, 5.83; N, 8.19.

Calculated for 1d, 1e, 1f, $C_{22}H_{20}N_2O_4$: C, 70.21, H, 5.32; N, 7.45. Found: 1d: C, 70.24; H, 5.32; N, 7.45. 1e: C, 70.12; H, 5.40; N, 7.30. 1f: C, 70.31; H, 5.43; N, 7.39.

Calculated for 1g, 1h, and 1i, $C_{20}H_{14}Cl_2N_2O_2$: C, 62.24; H, 3.66; N, 7.28; Cl, 18.40. Found: 1g: C, 62.39; H, 3.77; N, 7.25; Cl, 18.30. 1h: C, 62.17; H, 3.64; N, 7.27; Cl, 18.32. 1i: C, 62.19; H, 3.69; N, 7.14; Cl, 18.42.

Table IV. Infrared Absorption Maxima (Cm.$^{-1}$) of Monoamides

Compound	Aryl Group	N—H	Carboxyl CO	Amide I CO	CH Out-of-Plane Deformation
2c	m-$CH_3C_6H_4$	3300 (s)	1720 (vs)	1640 (vs)	768 (vs)
2d	o-$CH_3OC_6H_4$	3400 (vs)	1690 (vs)	1625 (vs)	752 (vs)
2e	p-$CH_3OC_6H_4$	3240 (vs)	1666 (vs)	1630 (vs)	820 (vs)
2h	p-ClC_6H_4	3300 (vs)	1700 (vs)	1625 (vs)	756 (vs) 813 (vs)
2i	m-ClC_6H_4	3300 (s)	1710 (vs)	1600 (vs)	768 (vs)

Monoamides of o-Phthalic Acid (2). Acidification of the filtrates from preparation of the diamides sometimes resulted in formation of 2 (see above). Monoamides were recrystallized from acetonitrile. The monoamide (2c) was obtained in a quantity too small for complete characterization. However, identification was established on the basis of its infrared spectrum, which was identical with that of an authentic sample (*11*).

Analyses. Calculated for 2d, and 2e, $C_{15}H_{15}NO_4$: C, 66.42; H, 4.79; N, 5.16. Found: 2d: C, 66.31; H, 4.76; N, 5.19. 2e: C, 66.34; H, 4.74; N, 5.25. Calcd. for 2h and 2i, $C_{14}H_{10}ClNO_3$: C, 61.00; H, 3.63; N, 5.08; Cl, 12.9. Found: 2h: C, 61.10; H, 3.65; N, 4.99; Cl, 12.86. 2i: C, 61.01; H, 3.83; N, 5.38; Cl, 12.85.

Formation of Monoamides (2) from N-Arylphthalimides (3). The *N*-arylphthalimides [3d (*1*) and 3i (*9*)] in ethanolic sodium ethoxide were subjected to treatment described for production of monoamides of *o*-phthalic acid. The monoamides (2d and 2i) were isolated in yields of 70%.

Analysis of Crude Reaction Mixtures. Crude reaction mixtures from preparation of 1d and 1i were evaporated to dryness under nitrogen at room temperature. Repeated washing with small amounts of dry ether and dry alcohol yielded white powders which were subjected to infrared analysis. Absorption peaks typical of 1d, 3d, 1i, and 3i were apparent.

LITERATURE CITED

(1) Allegri, C., *Gazz. Chim. Ital.* **40**, I, 533 (1910); *CA* **5**, 1403 (1911).
(2) Bellamy, L.J., "Infrared Spectra of Complex Molecules," pp. 203 ff, Wiley, New York, 1958.
(3) Bunnett, J.F., Robison, M.M., Pennington, F.C., *J. Am. Chem. Soc.* **72**, 2378 (1950).
(4) Leffler, J.E., Grunwald, E., "Rates and Equilibria of Organic Reactions," pp. 171 ff, Wiley, New York, 1963.
(5) Pawlewski, Br., *Ber.* **28**, 1118 (1895).
(6) Piutti, A., Abati, G., *Ibid.*, **36**, 998 (1903).
(7) Reynolds, R.D., Anderson, G.L., *J. Org. Chem.* **28**, 3223 (1963).
(8) Rogow, M., *Ber.* **30**, 1442 (1897).
(9) Sherrill, M.L., Schaeffer, F.L., Shoyer, E.P., *J. Am. Chem. Soc.* **50**, 474 (1928).
(10) Stewart, R., O'Donnell, J.P., *Can. J. Chem.* **42**, 1694 (1964).
(11) Tingle, J.R., Rolker, H.F., *J. Am. Chem. Soc.* **30**, 1882 (1908).

RECEIVED for review August 11, 1967. Accepted May 7, 1968. The National Science Foundation supported part of this research through its program in Research Participation for High School Teachers. M. J. Zeigler was an appointee in that program during the summers of 1965 and 1966.

Synthesis of Perfluoroallyl-Substituted 1,3,5-Triazines

HENRY C. BROWN and MING T. CHENG
Department of Chemical Engineering and Department of Chemistry, University of Florida, Gainesville, Florida 32601

2,4,6-tris(Perfluoroallyl)-1,3,5-triazine and 2,4-bis(perfluoroallyl)-6-perfluoropropyl-1,3,5-triazine were synthesized and their physical properties were determined.

AS AN EXTENSION of a study of the perfluoroalkyl-substituted 1,3,5-triazines (*3*), the authors desired to investigate the properties of a symmetrical triazine with carbon-carbon unsaturation in the substituent fluorinated alkyl groups. Although considerable information was available concerning the chemical characteristics of both the perfluoroalkyl-substituted triazines and fluorinated olefins, no specific conclusions could be drawn concerning the effect of the aromatic, nitrogen-containing ring in an allylic position on the reactivity of the carbon-carbon double bond or, conversely, the influence of the chain unsaturation on the behavior of the perfluoroalkyl-substituted ring system.

A synthesis was designed, therefore, to produce 1,3,5-triazines with perfluoroallyl groups in two or three of the 2, 4, and 6 positions, with perfluoroalkyl groups in the remaining positions as shown in Table I.

The starting material required for this synthesis was 3,4-dichloropentafluorobutyric acid, prepared from the chlorinated dimer, $CF_2ClCFClCF_2CFCl_2$, of chlorotrifluoroethylene by the method of Barnhart and Wade (*1*). This acid was converted to the methyl ester, the ester converted to the amide by treatment with ammonia, and the amide in turn converted to 2,3-dichloropentafluorobutyronitrile by dehydration with phosphorous pentoxide.

3,4-Dichloropentafluorobutyronitrile was converted to the corresponding amidine by treatment with liquid ammonia (*4*); heating this amidine at atmospheric pressure until ammonia evolution ceased produced the corresponding 2,4,6-tris (2,3-dichloropentafluoropropyl)-1,3,5-triazine. The dechlorination of the substituent groups by treatment with zinc in dioxane produced 2,4,6-(perfluoroallyl)-1,3,5-triazine.

For preparation of triazine with both perfluoroallyl and perfluoroalkyl substituent groups, 3,4-dichloropentafluorobutyronitrile was mixed with heptafluorobutyronitrile, the mixture subject to deammonation to produce a mixture of substituted triazines. These compounds were separated by fractional distillation and subsequently dehalogenated to form both 2,4-bis(perfluoroallyl)-6-perfluoropropyl-1,3,5-triazine and 2-perfluoroallyl-4,6-(perfluoropropyl)-1,3,5-triazine. The latter compound was not purified.

Although perfluoroallyl cyanide was prepared from 3,4-dichlorobutyronitrile, the use of this compound to prepare