Esters and Amides of 2,2′-Diphenic Acid

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Preparation and physical properties of seventeen esters and ten amides of 2,2′-diphenic acid are described. Of these compounds, twelve of the esters and nine of the amides are new. The boiling point, specific gravity, and refractive index is given for each liquid, and the melting point for each solid.

In a study of the use of derivatives of diphenic acid as high boiling solvents, a search of the literature revealed that only a few of the diesters had been prepared, and their characterization was incomplete. This search also revealed that only two diamides had been described. The purpose of the present work was to prepare more of the esters and amides so that complete characterizations could be made of these series. Underwood and Kochmann (*3*) prepared 2,2′-diphenamide and the methyl and ethyl diesters of 2,2′-diphenic acid; Dean and co-workers (*1*) also prepared these esters and the *n*-propyl, *n*-butyl, and *n*-decyl diesters. Roberts and Johnson (*2*) prepared diphenyl-2,2′-diphenamide.

In the present study, 12 new esters, eight new amides, and a few previously prepared esters and amides were prepared and characterized. All attempts to prepare the *tert*-amyl ester failed. Our data on the previously prepared compounds agreed in some cases with published data. Where they disagreed, our data seemed to fit better into the general pattern of the physical constants. This can be seen by a study of the data in Table I. Physical properties and analyses of all compounds prepared are given in Tables I and II.

EXPERIMENTAL

Preparation of Esters. The esters were prepared by one of three general methods. All of the esters were prepared by Method 1, with the exception of the cyclopentyl and the cyclohexyl, which were prepared by Method 2, and the *tert*-butyl which was prepared by Method 3.

METHOD 1. 2,2′-Diphenic acid (0.10 mole) was refluxed for 20 hours with 2.0 moles of alcohol in the presence of 2 ml. of concentrated H_2SO_4. The refluxed mixture was

Table I. Diesters of 2,2′-Diphenic Acid

						Calculated			Found		
R	M.P.[a](° C.)	B.P.[a](° C.)	D_4^{20}	n_D^{25}	Yield, %	C, %	H, %	Sapon. Equiv.	C, %	H, %	Sapon. Equiv.
Methyl[b]	72–73	...	...	...	91	71.11	5.22	...	70.94	5.28	...
Methyl[c]	74	...	...	...	89	...	...	...	...	...	..
Ethyl[b]	41.5–42	...	...	...	76	72.47	6.08	...	72.19	6.09	...
Ethyl[c]	43–44	...	...	...	91	...	...	...	...	...	...
n-Propyl[b]	...	201–202 4 mm.	1.118	1.5441	35	73.60	6.80	...	73.36	7.06	...
n-Propyl[c]	...	...	1.108	1.543	80	73.60	6.80	...	73.57	6.78	...
Isopropyl	74.0–74.5	...	...	...	15	73.60	6.80	163	73.83	7.07	163
n-Butyl[b]	...	192–193 1.5 mm.	1.082	1.5339	40	74.54	7.39	...	74.60	7.23	...
n-Butyl[c]	...	...	1.082	1.507	80	74.54	7.39	...	74.52	7.32	...
Isobutyl	...	191–192 2 mm.	1.085	1.535	49	74.54	7.39	177	74.65	7.62	177
sec-Butyl	81–82	...	...	...	11	74.54	7.39	177	74.62	7.76	176
tert-Butyl	132–133	...	...	...	41	74.54	7.39	177	74.33	7.34	177
n-Pentyl	...	201.5–202.5 1 mm.	1.064	1.529	59	75.36	7.91	191	75.47	7.94	189
Isopentyl	...	229.5–230.5 9 mm.	1.063	1.529	89	75.35	7.91	191	75.04	7.87	194
sec-Pentyl	74.5–75.5	...	...	...	8	75.35	7.91	...	75.35	7.69	...
n-Hexyl	44.5–45.5	...	...	...	25	76.07	8.35	205	76.15	8.52	213
n-Heptyl	...	248–249 5 mm.	1.018	1.5184	97	76.67	8.73	219	76.33	9.02	219
n-Octyl	...	246–247.5 1 mm.	1.015	1.5143	97	77.21	9.07	233	77.54	9.07	242
n-Decyl[b]	...	272–273 1.5 mm.	1.013	1.5093	50	78.11	9.63	...	78.28	9.19	...
n-Decyl[c]	...	...	1.003	1.507	80	78.11	9.63	...	78.03	9.74	...
Cyclopentyl	121–121.5	...	...	...	49	76.15	6.90	189	75.92	6.82	190
Cyclohexyl	51–52	...	...	...	77	76.82	7.44	203	76.70	7.33	203

[a] Corrected.
[b] Previously described in literature (*1, 3*), but these data obtained in this laboratory.
[c] Data from Dean, White, McNeal (*1*).

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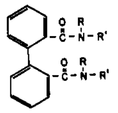
Table II. Properties and Analyses of Amides of 2,2′-Diphenic Acid



R	*R′*	M.P.[a], ° C.	Yield, %	N, %	
				Calcd.	Found
Hydrogen[b]	Hydrogen	209–211	41	...	...
Methyl	Hydrogen	116–116.5	90	10.44	10.40
Ethyl	Ethyl	140–141.5	55	7.90	7.93
n-Propyl	Hydrogen	122.5–123	83	8.63	8.68
n-Propyl	*n*-Propyl	93.5–94	75	6.87	6.84
n-Butyl	Hydrogen	76–77	33	7.94	7.94
Isobutyl	Hydrogen	112.5–113	93	7.94	8.09
tert-Butyl	Hydrogen	200–201	79	7.94	8.10
Phenyl[b]	Hydrogen	231–232	72	...	...
p-Tolyl	Hydrogen	175.5–176.5	71	6.66	6.59

[a] Corrected.

[b] Previously described in literature (*2*, *3*), but these date were obtained in this laboratory.

neutralized by the addition of solid Na_2CO_3. The alcohol was removed by distillation, the residue dissolved in ether and dried over anhydrous Na_2SO_4. Further purification was either by vacuum distillation or recrystallization from petroleum ether.

METHOD 3. Silver 2,2′-diphenate 0.04 mole), prepared by reacting the sodium salt with silver nitrate, was 0.3 mole of pyridine. The pyridine hydrochloride was precipitated by the addition of ether and the ether and alcohol removed by distillation. The residue was dissolved in ether and dried over anhydrous Na_2SO_4. The esters were recrystallized from petroleum ether.

METHOD 3. Silver 2,2′-diphenate (0.14 mole), prepared by reacting the sodium salt with silver nitrate, was suspended in 200 ml. of absolute ether. The alkyl chloride (0.45 mole) was added and refluxed for 24 hours. The mixture was filtered and the ether removed by evaporation. The crude product was recrystallized from petroleum ether.

Preparation of Amides. All of the amides were prepared by refluxing a mixture of 50 ml. of benzene, 0.04 mole of 2,2′-diphenoyl chloride and 0.10 mole of the amine for 15 minutes.

The benzene solution was washed successively with 5 ml. of water, 5 ml. of 5% HCl, 5 ml. of 5% aqueous NaOH, and again with 5 ml. of water. The benzene solution was evaporated cautiously over a water bath. The residue was dissolved in 5 ml. of hot ethanol, decolorized with Norit, and filtered. The amide was recrystallized from an ethanol-water solution until a constant melting point was reached.

LITERATURE CITED

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Solubility of Benzamide in *m*-Xylene

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THE SOLUBILITY of benzamide in *m*-xylene has been determined, with the results shown in Table I.

Table I. Solubilities of Benzamide in *m*-Xylene

Benzamide, Wt. % of Total Solution	Temp., ° C.
0.5	57
1.0	68
5.0	95
10	105
20	108
40	110
50	112

EXPERIMENTAL

Benzamide was purified from Eastman benzamide by crystallizing from water after adjusting to pH8 with ammonia to dissolve acidic substances and decolorizing with active carbon. The purified benzamide had an acid number less than 0.05 and melted at 125–127° C.

m-Xylene from Oronite Division of California Chemical Co. contained 96% *m*-xylene. The impurities were primarily isomeric xylenes, with a trace of ethylbenzene.

Solubilities were determined by sealing weighed amounts of *m*-xylene and benzamide in glass ampoules and determining the temperatures at which complete solution occurred. Solution temperatures were repeatedly determined during both heating and cooling cycles.

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