Substituted Sulfonamides, Ureas, and Alkyl-3-Nitrophthalimides as Identification Derivatives of Pentyl-, Hexyl-, Heptyl-, Octyl-, and Decylamines[1]

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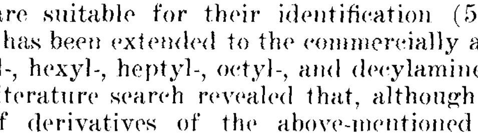
THIS PAPER is a continuation of our systematic study of derivatives of long-chain amines which are suitable for their identification (5). This study has been extended to the commercially available pentyl-, hexyl-, heptyl-, octyl-, and decylamines.

A literature search revealed that, although a number of derivatives of the above-mentioned amines which are suitable identification derivatives has been prepared, nevertheless the information is scattered and incomplete (1, 2, 4, 7).

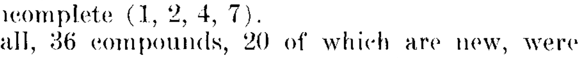
In all, 36 compounds, 20 of which are new, were prepared and evaluated as identification derivatives. These compounds include substituted sulfonamides, substituted ureas, and alkyl 3-nitrophthalimides.

The sulfonamides were prepared according to the Hinsberg method (6).



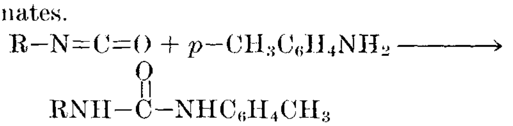
$$RNH_2 + R'SO_2Cl \xrightarrow{NaOH} R'SO_2\underset{\displaystyle Na}{\underset{|}{N}}{-}R \xrightarrow{HCl} R'SO_2NHR$$

The substituted ureas were prepared by the reaction of the amines with aromatic isocyanates.



$$RNH_2 + R'N{=}C{=}O \longrightarrow RNH{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}NH{-}R'$$

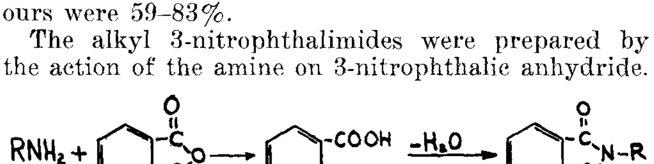
It is interesting to note that Robinson (3) prepared p-tolylureas by the reaction of p-toluidine on alkyl isocyanates.



$$R{-}N{=}C{=}O + p{-}CH_3C_6H_4NH_2 \longrightarrow RNH{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}NHC_6H_4CH_3$$

Our yields of the p-tolyl derivatives however were much higher. Robinson's yields were 3–10% whereas ours were 59–83%.

The alkyl 3-nitrophthalimides were prepared by the action of the amine on 3-nitrophthalic anhydride.



Amyl-3-nitrophthalimide was previously reported with a melting point of 93–94° (4). Our sample of this compound melted at 70.5°. We believe that our melting point more closely represents the true melting point of amyl-3-nitrophthalimide than the one reported in the literature, because of its relationship to the melting points of other members of this series (Table I).

The higher melting point reported by Sah and Ma might be caused by incomplete dehydration of the amido acid; thus the compound would have a free carboxyl group. The infrared spectra of our sample showed no absorption bands typical of carboxylic acids. We therefore think that dehydration of our sample was complete.

Experimental

All melting points are corrected and were determined by the capillary tube method. The analyses, yields of pure products obtained, melting points, and mixed melting points of the amine derivatives are summarized in Table I. The pentyl- ($n^{25/D}$ 1.4111), hexyl- ($n^{25/D}$ 1.4219), and heptylamine ($n^{25/D}$ 1.4239) were obtained from Eastman. The octyl- ($n^{25/D}$ 1.4298) and decylamine ($n^{25/D}$ 1.4364) were obtained from the Aldrich Chemical Company. Analyses were performed by the Midwest Micro Laboratory.

General Procedure for the Preparation of the p-Bromobenzenesulfonamides, p-Toluenesulfonamides, m-Nitrobenzenesulfonamides, and p-Nitrobenzenesulfonamides (6). To 0.02 mole of the appropriate amine in 20 ml. of 10% sodium hydroxide solution was added 0.025 mole of the corresponding sulfonyl chloride, and the mixture was shaken vigorously for a period of 5 min. At the end of this time the mixture was acidified with 3 M hydrochloric acid solution, and the resulting solid was separated by filtration. The derivatives were crystallized repeatedly until there was no increase in melting point. The p-bromobenzene- and p-toluenesulfonamides were crystallized from petroleum ether. The p-nitro and m-nitrobenzenesulfonamides were crystallized from ethanol-water.

General Procedure for the Preparation of the p-Tolylureas and α-Naphthylureas. To 0.02 mole of the appropriate amine in a test tube was added 0.02 mole of p-tolyl or α-naphthylisocyanate, and the mixture was shaken for a period of 5 min. The mixture was then cooled in a beaker of ice until the mass was solidified. The solid was powdered and washed with petroleum ether to remove any unchanged reactants. The product was crystallized from ethanol until there was no increase in melting point.

General Procedure for the Preparation of the Alkyl-3-Nitrophthalimides. To 0.02 mole of the appropriate amine in a test tube was added 0.022 mole of 3-nitrophthalic anhydride, and the mixture was heated to 170° and maintained at that temperature for 5 min. The solid which formed on cooling was crystallized from ethanol until there was no increase in the melting point.

Discussion

A satisfactory identification derivative should be an easily prepared crystalline solid with a narrow melting range. Its melting point moreover should

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[1] Taken from senior theses submitted by Francis A. Carey and Charles M. Paulson.

TABLE I

Identification Derivatives of Primary Amines

Compound	Yield	M. P.	Mixed m.p. with next higher member [1]	Analyses			
				Carbon		Hydrogen	
				Calc'd	Found	Calc'd	Found
	%	°C.	°C.	%	%	%	%
p-Bromobenzenesulfonamides							
Pentyl[a]	28	60	44–47	43.1	43.2	5.27	5.29
Hexyl[b]	45	54	47–50	45.0	44.9	5.66	5.75
Heptyl[c]	27	63.5–64	54–57	46.7	46.4	6.03	5.99
Octyl	39	64.5–65.5	......	48.4	48.2	6.38	6.52
p-Toluenesulfonamides							
Hexyl[d]	78	61	46–47.5	61.1	61.4	8.29	8.39
Octyl	58	56	46.5–47.5	63.4	63.8	8.89	8.92
Decyl	96	63.5–64	......	65.5	65.7	9.38	9.45
m-Nitrobenzenesulfonamides							
Pentyl[e]	56	58.5–59.5	56–57.5	48.5	48.7	5.93	5.97
Hexyl[f]	62	64.5–65.5	60–64	50.3	50.4	6.35	6.38
Heptyl[g]	64	68–69	66–68	52.0	51.9	6.72	6.78
Octyl	75	74.5–75.5	71–74	53.5	53.5	7.07	7.13
Decyl	78	82–83	......	56.1	56.1	7.65	7.71
p-Nitrobenzenesulfonamides							
Pentyl[h]	47	62–62.5	54–56	48.5	48.4	5.93	5.96
Hexyl[i]	67	70	66.5–68	50.3	50.5	6.35	6.37
Heptyl[j]	71	80.5–81.5	72–73	52.0	51.8	6.72	6.65
Octyl	63	75–75.5	66–67.5	53.5	53.6	7.07	7.11
Decyl	47	84–85	......	56.1	56.0	7.65	7.76
p-Tolylureas							
Hexyl[k]	77	84	79–82	71.8	71.6	9.48	9.32
Heptyl[l]	74	108.5	88–90	72.5	72.2	9.74	9.81
Octyl[m]	59	91.5	87–90	73.2	73.3	9.99	9.97
Decyl[n]	83	98	......	74.4	74.6	10.41	10.44
1-Naphthylureas							
Pentyl	72	149–149.5	137–140	75.0	75.1	7.87	8.01
Hexyl	98	146–146.5	128–130	75.5	75.0	8.20	8.30
Heptyl	92	130	128–129	76.0	75.8	8.45	8.46
Octyl	87	129.5	127–128	76.4	76.4	8.76	8.71
Decyl[o]	61	129	......	77.2	76.9	9.26	9.10
p-Nitrophenylureas							
Pentyl	40	118–119	108–109	57.3	57.0	6.82	6.82
Hexyl	55	110–110.5	106–108	58.8	58.4	7.22	7.13
Heptyl	52	109.5–110	107.5–108.5	60.2	59.9	7.66	7.39
Octyl	75	112–112.5	108.5–109.5	61.4	61.2	7.90	7.76
Decyl	79	116.5	......	63.5	63.5	8.47	8.52
3-Nitrophthalimides							
Pentyl[p]	44	70.5	66.5–69	59.5	59.6	5.39	5.41
Hexyl	70	70	66–67.5	60.9	61.0	5.85	5.79
Heptyl	53	74–74.5	67.5–71	62.0	62.0	6.26	6.24
Octyl	57	71	67–71	63.1	63.0	6.64	6.46
Decyl	84	75	......	65.1	65.1	7.29	7.39

Previously reported to melt at: [a] 55° (2); [b] 55° (2); [c] 65° (2); [d] 62° (2); [e] 59° (1); [f] 67° (1); [g] 71° (1); [h] 63° (1); [i] 71° (1); [j] 83° (1); [k] 86° (3); [l] 108° (3); [m] 92° (3); [n] 98° (3); [o] 129.5° (7); [p] 92–94° (4):

[1] Mixed melting points of octyl derivatives were made with decyl derivatives.

differ from derivatives prepared from similar compounds sufficiently to distinguish between them, and the mixture of the two derivatives should melt below either one.

Among the compounds which were synthesized, the most satisfactory identification derivatives appear to be *m*-nitrobenzenesulfonamides, *p*-nitrobenzenesulfonamides, and *p*-tolylureas (Table I). The equimolar mixtures of the consecutive members melt at a lower temperature than either member.

Summary

p-Bromo-, *m*-nitro-, *p*-nitrobenzenesulfonamides, *p*-toluenesulfonamides, *p*-tolyl-, and *a*-naphthylureas, and 3-nitrophthalimide derivatives of pentyl-, hexyl-, heptyl-, octyl-, and decylamines were prepared. *m*-Nitrobenzenesulfonamides, *p*-nitrobenzenesulfonamides, and *p*-tolylureas appear to be the most satisfactory derivatives for the identification of these amines.

REFERENCES

1. Demeny, L., Rec. Trav. Chim., *48*, 1145 (1929).
2. Demeny, L., *ibid.*, *50*, 51 (1931).
3. Robinson, J. R., Can. J. Chem., *32*, 557 (1954).
4. Sah, P. T., and Ma, T. S., Ber. *65B*, 1630 (1932).
5. Sasin, Richard, Butte, W. A., Borror, A. L., and Sasin, G. S., J. Am. Oil Chemists' Soc., *34*, 358 (1957).
6. Shriner, R. L., Fuson, R. C., and Curtin, D. Y., "The Systematic Identification of Organic Compounds," 4th ed., pp. 103–106, New York, John Wiley and Sons Inc., 1956.
7. Talvities, Y., Ann. Acad. Sci. Fennicae, *26A*, 1 (1927).

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