Some Derivatives of Ethylbenzene and Tetralin

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IN SOME PREVIOUS WORK it was shown that a disulfonimide of acenaphthene rearranged to a disulfonamide of acenaphthylene (*1*). In an attempt to extend the scope of this prototropic shift a number of amides of ethylbenzene and tetralin were prepared and which we wish to record. Pure diimides were not obtained by oxidation of the diamide with lead tetraacetate.

EXPERIMENTAL

The derivatives of ethylbenzene (Table I) described were all prepared from *p*-nitroethylbenzene (*2*). The other amides were prepared from 1,2-dinitro-5,6,7,8-tetrahydronaphthalene (*3*).

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(3) Bamberger, E., Schieffelin, W.J., *Ber.* **22**, 1374 (1889).

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Table I. Derivatives of Ethylbenzene and Tetralin

Name	M.P.	Analysis	
p-Benzenesulfonamidoethylbenzene	82–83° from methanol	Calcd. for $C_{14}H_{15}NO_2S$: C, 64.36; H, 5.79; N, 5.36	Found: C, 64.50; H, 5.98; N, 5.54
3-Nitro-4-benzenesulfonamidoethylbenzene	77–78° from acetic acid	Calcd. for $C_{14}H_{14}N_2O_4S$: C, 54.90; H, 4.61; N, 9.15	Found: C, 54.85; H, 4.57; N, 8.89
3-Amino-4-benzenesulfonamidoethylbenzene hydrochloride	181–183° (darkens at 165°)	Calcd. for $C_{14}H_{17}N_2O_2SCl$: Neut. equiv. 312.75	Found: Neut. equiv. 311.3
3-Amino-4-benzenesulfonamidoethylbenzene	113–114° from methanol-water	Calcd. for $C_{14}H_{16}N_2O_2S$: C, 60.86; H, 5.84; N, 10.14	Found: C, 60.91; H, 5.69; N, 10.73
3,4-Dibenzenesulfoamidoethylbenzene	158.5–159.5 from aqueous methanol	Calcd. for $C_{20}H_{20}N_2O_4S_2$: C, 57.69; H, 4.84; N, 6.73 ν_{max}^{KBr} as cm.$^{-1}$: 3220 (NH), 1580, 1500, 1450, 1390, 1330 (SO_2), 1163 (SO_2), 1090, 945, 885, 755, 725, 688	Found: C, 57.84; H, 4.91; N, 6.77
1,2-Dibenzamido-5,6,7,8-tetrahydronaphthalene	254–255° dec. from isopropanol	Calcd. for $C_{24}H_{22}N_2O_2$: C, 77.81; H, 5.99; N, 7.56	Found: C, 77.69; H, 6.20; N, 7.68
1,2-Dibenzenesulfoamido-5,6,6,8-tetrahydronaphthalene	203° dec. from isopropanol	Calcd. for $C_{22}H_{22}N_2O_4S$: C, 59.72; H, 5.01; N, 6.33 ν_{max}^{KBr} as cm.$^{-1}$: 3500, 3400 (NH), 2870, 1620, 1491, 1450, 1370, 1355 (shoulder), 1340, 1165 (SO_2), 943, 896, 807, 754, 746, 719, 685, 647	Found: C, 59.85; H, 5.02; N, 6.27

The Synthesis of Some Heterocyclic Quaternary Amine Iodides

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PRELIMINARY WORK on the analysis of the infrared spectra of cyanine and merocyanine dyes indicated the necessity of first obtaining and analyzing the infrared spectra of the precursors of the dyes, namely, the heterocyclic quaternary amine iodides. This paper deals with the synthesis of the heterocyclic quaternary amine iodides; the infrared spectra of these compounds are discussed in another paper (*1*).

There are discrepancies in the literature with respect to the purity and melting points of some of the heterocyclic quaternary amine iodides. For example, some of these compounds were first synthesized many years ago and no analytical data were given. In other cases, two or more different melting points have been reported for the same compound. In this paper, a few of the quaternary salts reported have been synthesized for the first time. As a

Table I. List of Quaternary Salts Synthesized

Compound	Method of Prep., Solv.[a]	Reaction Time[b] (Hrs.)	Exptl. M.P. ° C.[c]	Experimental Analysis, % Composition							
				C		H		I		N	
				Found	Theor.	Found	Theor.	Found	Theor.	Found	Theor.
quinolinemethiodide	II, 1	2	136–7	44.50	44.31	3.84	3.72	46.98	46.81	4.93	5.17
quinoline ethiodide	II, 2	3	160–1	46.50	46.34	4.24	4.24	44.74	44.51		
2-methylquinolinemethiodide	II, 1	2	190–1	46.12	46.33	4.01	4.24	44.41	44.51	5.05	4.91
2-methylquinoline ethiodide	II, 2	3	232–3	47.95	48.18	4.78	4.72	42.35	42.42	4.61	4.68
2-iodoquinoline methiodide	II, 1	72	193–4	30.60	30.26	2.32	2.29	63.77	63.93		
2-iodoquinoline ethiodide	II, 1	288	190–1	32.30	32.14	2.71	2.69	61.21	61.75		
4-methylquinoline methiodide	II, 1	1	175–6	46.17	46.33	4.14	4.24	44.34	44.50	5.02	4.91
4-methylquinoline ethiodide	II, 1	4	143–4	47.99	48.18	4.93	4.72	42.73	42.42	4.42	4.68
benzothiazole methiodide	II, 3	3	207–8	34.40	34.67	2.80	2.91	46.20	45.79		
benzothiazole ethiodide	II, 3	16	136–7	37.32	37.13	3.56	3.46	43.85	43.59		
2-methylbenzothiazole methiodide	II, 3	1	222–3	37.31	37.13	3.39	3.46	43.42	43.59		
2-methylbenzothiazole ethiodide	II, 3	16	193–5	39.52	39.36	4.08	3.96	41.83	41.58		
2-(methylmercapto)benzothiazole methiodide	II, 2	6	136–7	33.68	33.45	3.06	3.12	38.87	39.26		
2,5,6-trimethylbenzothiazole ethiodide	II, 1	9	220–1	43.25	43.25	4.89	4.84	37.84	38.08		
benzoxazole ethiodide	I[d]	3	164–5	39.45	39.30	3.70	3.66	46.26	46.13		
2-methylbenzoxazole ethiodide	II, 1	56	199–200	41.60	41.54	4.17	4.18	44.16	43.89		
2,5,6-trimethylbenzoxazole ethiodide	II, 4	20	233–4	45.33	45.44	4.95	5.09	39.88	40.01		
2-methylbenzoselenazole ethiodide	II, 3	72	206–7	33.83	34.11	3.41	3.44	36.27	36.04		
2,5,6-trimethylbenzoselenazole ethiodide	II, 3	5	199 (sublimes)	37.65	37.92	4.15	4.24	33.31	33.38		
2,3,3-trimethylindolenine ethiodide	II, 1	16	212–3	49.51	49.54	5.79	5.76	40.32	40.26		
1,3-diethyl-2-methylbenzimidazole iodide	I	96	200–1	45.28	45.59	5.68	5.42	40.22	40.14	8.90	8.86
2-methyl-α-naphthoxazole ethiodide	II, 3	7	212–3	49.51	49.57	4.24	4.16	37.45	37.42		
2-methyl-β-naphthothiazole methiodide	III	144	204–5	45.57	45.76	3.55	3.54	37.14	37.19		
2-methyl-β-naphthothiazole ethiodide	III	144	202–3	46.67	47.33	4.26	3.97	35.62	35.72		
2-methylthiazoline ethiodide	II, 1	16	183–5	27.91	28.03	4.70	4.70	49.34	49.35	5.34	5.45
2,4-dimethylthiazole ethiodide	II, 1	3	215–6	31.15	31.24	4.40	4.49	47.58	47.15	5.15	5.20

[a] Solvents are indicated as follows: 1, acetone; 2, ethanol, 3, cyclohexanone; 4, methyl ethyl ketone. [b] In all cases, the reaction time exceeded the precipitation stage to afford a maximum yield. [c] Melting points have been corrected. [d] This compound was not recrystallized but was just washed with acetone. The compound analyzed correctly. All attempts to recrystallize the compound failed as the compound decomposed during this process.

result, the melting points and analytical data are given for all the heterocyclic quaternary salts reported in this paper.

All the tertiary amines were obtained commercially and purified by either distillation or recrystallization before use. These compounds were then converted into quaternary salts in one of the following ways:

Method I. The tertiary amine and methyl iodide (or ethyl iodide) were sealed in a tube and heated to approximately 100° C. In all runs a 20% molar excess of quaternizing agent was employed. The length of time of heating was a function of the particular tertiary amine which was to be quaternized. The quaternary salt was washed with acetone, then washed with ether, and finally recrystallized from absolute alcohol.

Method II. The tertiary amine and methyl iodide (or ethyl iodide) were added to acetone, ethyl alcohol, cyclohexanone or methyl ethyl ketone and refluxed. In all runs a 20% molar excess of quaternizing agent was employed. The solvent was chosen for the desired reflux temperature and for reaction homogeneity. The quaternary salt usually precipitated during the reaction. The solid was washed with acetone, then with ether and finally recrystallized from absolute alcohol.

Method III. The tertiary amine was mixed with methyl-*p*-toluene sulfonate (or ethyl-*p*-toluene sulfonate) and heated for two days at 110° C. In all runs a 20% molar excess of quaternizing agent was employed. The solid mass obtained was washed with actone and then dissolved in methyl alcohol. The solution was heated to 60° C. and a warm methanolic KI solution was added. The quaternary methiodide (or ethiodide) was precipitated and separated from the mother liquor, then washed with water and finally with acetone. The solid was recrystallized from methyl alcohol.

Table I. lists the quaternary salts synthesized.

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