alkaline solution. The ethyl acetate solution yielded 1.3 g. (71% calculated on the basis of recovered material) of crystalline phenol ether. After sublimation in a high vacuum (oil-bath, 120–150°) and two recrystallizations from 96% ethanol, the m.p. of the short colorless prisms was 204–205°.

Anal. Calc'd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.21; H, 6.74; N, 6.20.

1-Amido-5-n-hexoxynaphthalene (IV). (*a*) *Hydrochloride.* A mixture of 1 g. (*m*/285) of II, 2 ml. of conc'd hydrochloric acid, and 7.5 ml. of 96% ethanol was refluxed for 2 hours on a steam-bath. The hydrochloride crystallized from the mixture and was washed on the funnel with dry ether; yield, 950 mg. (97%) of long fine needles. An analytical sample was recrystallized from acetone-water which contained a trace of 2 *N* HCl; m.p. 190–196° (with decomposition in a sealed capillary).

Anal. Calc'd for $C_{16}H_{22}ClNO$: C, 68.68; H, 7.93; N, 5.01; Cl, 12.67. Found: C, 68.64; H, 7.81; N, 5.21; Cl, 12.60.

(*b*). *Free amine.* The mother liquors from the recrystallizations of the hydrochloride were combined and the acetone was removed under reduced pressure. Solid sodium carbonate was added until the solution was basic to phenolphthalein. A black oil precipitated which was slightly soluble in ether. The oil was extracted with ethyl acetate and was washed with water until it was neutral. The solution was dried with magnesium sulfate and concentrated under reduced pressure. The resulting dark oil could not be crystallized. This unstable oil was distilled twice at a pressure of 0.02 mm. in an oil-bath at 90–100°.

Anal. Calc'd for $C_{16}H_{21}NO$: C, 78.97; H, 8.70; N, 5.76. Found: C, 79.40; H, 8.44; N, 6.18.

1-Carbethoxyamido-5-n-hexoxynaphthalene (V). A mixture of 600 mg. (*m*/466) of the hydrochloride of IV, 600 mg. (*m*/233) of potassium carbonate powder, 500 mg. (excess) ethyl chloroformate, 40 ml. of acetone, and 0.5 ml. of water was stirred violently for 2.5 hours at room temperature. After filtering from the salts, the solution was concentrated under reduced pressure and 620 mg. (92%) of stout prisms were obtained. An analytical sample was prepared by recrystallization from methanol (Norit), m.p. 84–85°.

Anal. Calc'd for $C_{19}H_{25}NO_3$: C, 72.35; H, 7.99; N, 4.44. Found: C, 72.41; H, 8.07; N, 4.53.

1-Carbethoxyoxy-5-carbethoxyamidonaphthalene (VII). A mixture of 2 g. (*m*/80) of 5-hydroxy-1-naphthylamine (VI), 2.5 g. (excess) of powdered potassium carbonate, 50 ml. of acetone, and 2 ml. of water was prepared. Then 3.2 g. (more than *m*/40) of ethyl chloroformate in 10 ml. of acetone was added with stirring to this mixture. After an additional 4 hours stirring at room temperature, the inorganic material was removed and the solvent was evaporated under reduced pressure. The violet-colored residue was dissolved in ethyl acetate, washed with ice-cold 2 *N* HCl, washed with ice-water until neutral, and then was dried with magnesium sulfate. The solvent was removed under reduced pressure, and after the resulting residue was recrystallized from 96% ethanol, 2.5 g. (66%) of the diacyl product was obtained. An analytical sample was recrystallized from ethanol (Norit); m.p. 173–174° (tetragonal platelets).

Anal. Calc'd for $C_{16}H_{17}NO_5$: C, 63.36; H, 5.65; N, 4.62. Found: C, 63.12; H, 5.50; N, 4.67.

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N-(ω-Bromoalkyl)saccharins and N,N′-Undecamethylenedisaccharin

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Interest has recently been shown in the reaction of sodium saccharin with alkyl halides to yield N-alkylsaccharins[1–4] and with α,ω-dihaloalkanes to yield polymethylenedisaccharins.[4] To these different series we wish to add several N-(ω-bromoalkyl)saccharins (Table I). These compounds were synthesized by the condensation of sodium saccharin with α,ω-dibromoalkanes having two to ten carbon atoms in the normal hydrocarbon chain in the presence of approximately 3% by volume of dimethylformamide. The ω-(bromoalkyl)saccharins are useful as chemical intermediates, but their low melting points and the difficulties encountered in purification make them unsuitable as derivatives. In several compounds it was necessary to pass a solution of the reaction products through a silicic acid chromatographic column to prepare the analytical sample.

In each reaction a higher-melting solid was also obtained which was proved to be the polymethylenedisaccharin by independent synthesis from the same starting materials using an excess of sodium saccharin. The melting points of these compounds agree very closely with those recently reported by Reid, Rice, and Grogen.[3]

We also wish to report the synthesis of the bis-compound containing eleven carbons in the methylene chain.

EXPERIMENTAL[5]

N-(ω-Bromoalkyl)saccharins. In a flask fitted with an efficient reflux condenser were placed 5.5 g. (0.027 mole) of anhydrous sodium saccharin, 3 ml. of dimethylformamide, and the appropriate polymethylene dibromide (0.11 mole). The mixture was heated for three hours at 160–170°. The mixture was filtered, after cooling, to remove the precipitated sodium bromide and the filtrate then was poured into 50 ml. of cold water. The organic phase was extracted with three 50-ml. portions of ether and dried. After stripping off the solvent, the excess dibromide was removed by vacuum distillation. The residue was treated with diethyl ether and the ether-insoluble impurities were removed by filtration. After removal of the ether, the product was recrystallized alternately from petroleum ether and isopropyl alcohol.

N,N′-Undecamethylenedisaccharin. Anhydrous sodium saccharin, 2.25 g. (0.011 mole), dimethylformamide (10 ml.), and 1,11-dibromoundecane, 5.7 g. (0.005 mole), were placed in a flask and refluxed for one hour. The reaction mixture was cooled and filtered to remove sodium bromide. The

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(1) Merritt, Levy, and Cutter, *J. Am. Chem. Soc.*, **61**, 15 (1939).

(2) Rice, Grogan, and Reid, *J. Am. Chem. Soc.*, **75**, 4304 (1953).

(3) Rice and Pettit, *J. Am. Chem. Soc.*, **76**, 302 (1954).

(4) Reid, Rice, and Grogan, *J. Am. Chem. Soc.*, **77**, 5628 (1955).

(5) Analyses by Clark Microanalytical Laboratory, Urbana, Illinois.

TABLE I[a]

N-(ω-BROMOALKYL)SACCHARINS

N-ω-Bromoalkyl Substituent	Yield,[b] %	M.P., °C.	Formula	Carbon Calc'd	Carbon Found	Hydrogen Calc'd	Hydrogen Found
2-Bromoethyl	97	96[c]	$C_9H_8BrNO_3S$				
3-Bromopropyl	61	92.5	$C_{10}H_{10}BrNO_3S$	39.49	39.68	3.31	3.16
4-Bromobutyl	70	71–72	$C_{11}H_{12}BrNO_3S$	41.53	41.81	3.80	3.87
5-Bromopentyl	33	53.5	$C_{12}H_{14}BrNO_3S$	43.38	43.67	4.25	4.58
6-Bromohexyl	46	70.5–71	$C_{13}H_{16}BrNO_3S$	45.11	45.56	4.65	4.86
7-Bromoheptyl	64	47.5–48	$C_{14}H_{18}BrNO_3S$	46.67	47.04	5.04	5.19
8-Bromooctyl	59	54	$C_{15}H_{20}BrNO_3S$	48.13	48.18	5.39	5.54
9-Bromononyl	62	28	$C_{16}H_{22}BrNO_3S$	49.49	49.43	5.71	5.66
10-Bromodecyl	83	43–44	$C_{17}H_{24}BrNO_3S$	50.74	51.02	6.01	5.99

[a] All melting points are corrected. [b] Yield after recrystallization based on sodium saccharin. [c] H. Eckenroth, *Ber.*, **29**, 1951 (1896) reported m.p. 96°.

filtrate then was poured into 50 ml. of water. The product separated as an oil and was recovered by decanting the water layer. The crude material was alternately recrystallized from acetone and ethyl alcohol to a constant melting point of 68°. Yield, 42% (after recrystallization based on the dibromide).

Anal. Calc'd for $C_{25}H_{30}N_2O_6S_2$: C, 57.90; H, 5.83. Found: C, 57.73; H, 5.61.

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3-*tert*-Butylthianaphthene

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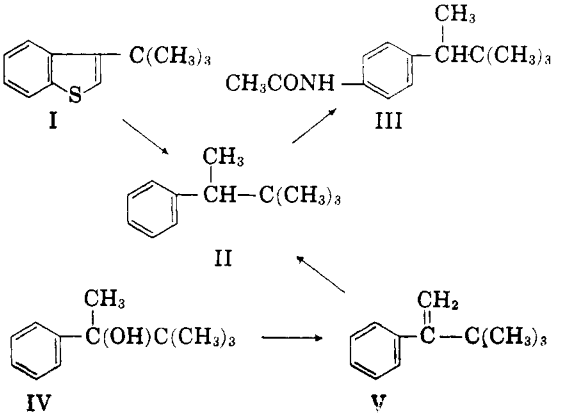
3-*tert*-Butylthianaphthene (I) was prepared in 77% yield by the alkylation of thianaphthene at 125° with isobutylene in the presence of 100% phosphoric acid. Desulfurization of compound I by means of Raney nickel[2] gave hydrocarbon II, whose acetamino derivative (III) was identical with the acetamino derivative of authentic α-*tert*-butylethylbenzene (II), prepared *via* IV and V. In the desulfurization there was a 10% survival of olefin V, although the mole ratio of hydrogen adsorbed on the Raney nickel to 3-*tert*-butylthianaphthene was 9/1. α-*tert*-Butylethylbenzene (II) and its acetamino derivative (III) are new compounds.



EXPERIMENTAL[3]

Purification of thianaphthene. The commercial sample[4] was 99.5 mole-% pure (t_f 31.07 ± 0.01°).[5] It was purified to 99.99 mole-% purity (t_f 31.309° ± 0.005°). The freezing point of pure thianaphthene is estimated to be 31.314° ± 0.07°.[6]

3-tert-Butylthianaphthene (I). Into a stirred mixture of 201 g. (1.5 moles) of thianaphthene and 50 g. of 100% phosphoric acid at 125° was passed 2.4 cu. ft. (3.0 moles) of isobutylene. The organic layer was dissolved in 600 ml. of ether; the solution was washed with aqueous carbonate followed by water, and dried. The ether was evaporated and the residue was fractionated to give 219 g. (75% yield based on thianaphthene) of product; b.p. 149°/20 mm.[7] n^{25}_D 1.5871, d^{25}_4 1.0578. The compound solidified to a glassy material when cooled in Dry Ice-acetone or liquid nitrogen.

Anal. Calc'd for $C_{12}H_{14}S$: C, 75.71; H, 7.41. Found: C, 75.81; H, 7.41.

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(1) Present address: Verona Research Center, Koppers Co., Inc., Verona, Pa.

(2) Mozingo, Wolf, Harris, and Folkers, *J. Am. Chem. Soc.*, **65**, 1013 (1943).

(3) All melting and boiling points are uncorrected; t_f is corrected.

(4) Jefferson Chemical Co., Inc., N. Y. 16, N. Y.

(5) t_f = freezing temperature determined by extrapolation of freezing curve; temperatures measured by platinum resistance thermometer and G-2 Mueller bridge which had been certified by National Bureau of Standards and checked prior to the thianaphthene measurements at the triple point of water and with a National Bureau of Standard benzoic acid cell.

(6) The equilibrium temperature of the 99.99% sample was 0.005° ± 0.002° lower than t_f when half frozen; hence t_{f0} is estimated to be 31.314° ± 0.007°.

(7) Conary and McCleary, U. S. Patent 2,652,405 (1953), reported b.p. 132°/10 mm.