Table V. The accuracy of the determination was checked by adding the individual normalities of the acids and comparing the result with a total normality determined by titration with standard base. Agreement was within 3%.

The ratio of starting material to final product indicates that the reaction goes virtually to completion. The difference in the rate and extent of reaction between benzenesulfonic acid, on the one hand, and nitrobenzene and benzoic acid, on the other, as well as the marked difference in the isomer ratios obtained, may well indicate a different mechanism of attack.

OSSINING, N. Y.

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF JOHNS HOPKINS UNIVERSITY AND THE PATHOLOGY DEPARTMENT OF GEORGETOWN UNIVERSITY]

Some N-Alkylsaccharin Derivatives[1]

BY E. EMMET REID, LEONARD M. RICE AND CHARLES H. GROGAN

RECEIVED NOVEMBER 4, 1954

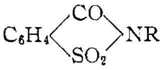
The series of N-alkylsaccharins has been extended to eicosyl. Along with these five ω-cyano and two ω-hydroxy derivatives have been made. Polymethylene-bis-saccharins from methylene to decamethylene have been prepared and characterized. Three N-alkylsulfamic acids have been obtained by opening the rings of N-alkylsaccharins with alkali.

In a recent paper[2] we reported the preparation of a number of N-alkylsaccharins, using dimethyl formamide as a solvent. Since then the use of this solvent and the preparation of several of the same compounds have been reported by Rice and Pettit.[3] We have extended the series of substituted saccharins up to eicosyl and added five cyanoalkyl and two hydroxyalkyl derivatives. In addition we have prepared the polymethylene-bis-saccharins up to the decamethylene and several in which the polymethylene chain is interrupted by oxygen or sulfur atoms.

The preparation of N-alkylsaccharins has been recommended by Merrit, Levy and Cutter[4] for the identification of alkyl halides. They used Carbitol as a solvent. Dimethylformamide is more convenient. If it is desired to identify the halogen as well as the alkyl, the sodium halide may be filtered off from the hot reaction mixture before it is poured into water.

The melting points and analyses of the mono-N-alkylsaccharins are in Table I and the melting points are plotted in Fig. 1. The melting points from hexyl to dodecyl are from our previous paper[2] and those of the lower members from the literature. The melting point pattern is of interest as it characterizes the series. It is important since its regularity is a far more rigid criterion of the purity of the compounds than analyses. This series is unusual in that the swing of the alternation increases from the nonyl up. There is a reversal of phase at the nonyl.

TABLE I

N-ALKYLSACCHARINS 
$C_6H_4\langle{}^{CO}_{SO_2}\rangle NR$

R	Formula	M.p., °C.	Carbon, %		Hydrogen, %		Nitrogen, %	
			Calcd.	Found	Calcd.	Found	Calcd.	Found
Tridecyl	$C_{20}H_{31}O_3NS$	44.8	65.71	65.69	8.55	8.53	...	...
Tetradecyl[a]	$C_{21}H_{33}O_3NS$	60	66.45	66.66	8.76	8.75	...	...
Pentadecyl	$C_{22}H_{35}O_3NS$	53.5	67.13	67.31	8.96	9.36	...	...
Cetyl[a]	$C_{23}H_{37}O_3NS$	67	67.77	68.00	9.15	9.32	...	...
Heptadecyl	$C_{24}H_{39}O_3NS$	60.5	68.36	68.51	9.32	9.59	...	...
Octadecyl[a]	$C_{25}H_{41}O_3NS$	73	68.92	69.28	9.51	9.27	...	...
Nonadecyl	$C_{26}H_{43}O_3NS$	65	69.44	69.68	9.64	9.69	...	...
Eicosyl	$C_{27}H_{45}O_3NS$	76.5	69.94	70.27	9.79	9.97	...	...
$-CH_2CN$	$C_9H_6O_3N_2S$	144	...	...	..	..	12.61	12.81
$-(CH_2)_2CN$	$C_{10}H_8O_3N_2S$	148	...	...	..	..	11.86	11.89
$-(CH_2)_3CN$	$C_{11}H_{10}O_3N_2S$	105	...	...	..	..	11.19	10.87
$-(CH_2)_4CN$	$C_{12}H_{12}O_3N_2S$	98	...	...	..	..	10.60	10.21
$-(CH_2)_5CN$	$C_{13}H_{14}O_3N_2S$	50	...	...	..	..	10.07	10.33
$-(CH_2)_2OH$	$C_9H_9O_4NS$	108	47.57	47.70	3.99	4.29	6.16	5.93
$-(CH_2)_3OH$	$C_{10}H_{11}O_4NS$	74	49.78	50.02	4.60	4.66	...	...

[a] Made by Rice and Pettit who give the melting points 52.5–54.5°, 63–65 and 68–71°.

For comparison the melting points of the O-alkylsaccharin derivatives[5] are plotted along with the N-alkyl in Fig. 1. When the oxygen atom is considered a member of the alkyl chain the melting point patterns are remarkably similar from the nonyl on.

Two hydroxy compounds, N-β-hydroxyethyl and N-γ-hydroxypropyl, were prepared from the corre-

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[1] Supported in part by the Geschickter Fund for Medical Research.

[2] L. M. Rice, C. H. Grogan and E. Emmet Reid, THIS JOURNAL, **75**, 4304 (1953).

[3] H. L. Rice and G. R. Pettit, *ibid.*, **76**, 302 (1954).

[4] L. L. Merritt, Jr., Stanley Levey and H. B. Cutter, *ibid.*, **61**, 15 (1939).

[5] J. R. Meadow and E. Emmet Reid, *ibid.*, **65**, 457 (1943).

sponding bromohydrins. The first of these was supposed by Eckenroth and Koerppen[6] to have been formed by the alkaline hydrolysis of N-β-bromoethylsaccharin. Their compound melted at 183° and must have resulted from the opening of the ring by the alkali. As is shown below, this takes place readily. The structure of our compound, m.p. 108°, was confirmed by treating it with phosphorus tribromide which converted it to the N-β-bromoethyl, identified by comparison with an authentic specimen.

We also have obtained the polymethylene-bis-saccharins in practically quantitative yields under the same conditions employed for the monoalkyl. The dihalides used were methylene to decamethylene and octadecylene dibromides and several in which the chain was interrupted by oxygen or sulfur atoms.

The first member of the series had been made by Eckenroth and Koerppen[6] by treating saccharin with formaldehyde and 70% sulfuric acid. They made the second by boiling an alcohol solution of sodium saccharin and ethylene bromide several days. Merritt, Levy and Cutter[4] used boiling Carbitol as a solvent. The third and fourth of our series were obtained by von Braun and Lemke[7] by heating alcoholic solutions of the reactants in sealed tubes at 170–180°.

TABLE II

$$C_6H_4\begin{matrix}CO\\SO_2\end{matrix}NRN\begin{matrix}CO\\SO_2\end{matrix}C_6H_4$$

	R	Formula	M.p., °C.	Nitrogen, % Calcd.	Nitrogen, % Found
1	$-CH_2-$	$C_{15}H_{10}O_6N_2S_2$	>300[a]	7.41	7.39
2	$-(CH_2)_2-$	$C_{16}H_{12}O_6N_2S_2$	259[b]	7.14	7.29
3	$-(CH_2)_3-$	$C_{17}H_{14}O_6N_2S_2$	218[c]	6.89	6.81
4	$-(CH_2)_4-$	$C_{18}H_{16}O_6N_2S_2$	208[c]	6.62	6.92
5	$-(CH_2)_5-$	$C_{19}H_{18}O_6N_2S_2$	145.5	6.45	6.58
6	$-(CH_2)_6-$	$C_{20}H_{20}O_6N_2S_2$	183	6.25	6.54
7	$-(CH_2)_7-$	$C_{21}H_{22}O_6N_2S_2$	131	6.06	5.96
8	$-(CH_2)_8-$	$C_{22}H_{24}O_6N_2S_2$	178	5.88	5.70
9	$-(CH_2)_9-$	$C_{23}H_{26}O_6N_2S_2$	111	5.71	5.83
10	$-(CH_2)_{10}-$	$C_{24}H_{28}O_6N_2S_2$	112	5.55	5.86
11	$-(CH_2)_{18}-$	$C_{32}H_{44}O_6N_2S_2$	90	4.54	4.70
12	$-CH_2C_6H_4CH_2-$	$C_{22}H_{16}O_6N_2S_2$	>310	5.98	5.98
13	$-CH_2OCH_2$	$C_{16}H_{12}O_7N_2S_2$[d]	219	6.86	7.07
14	$-(CH_2)_2O(CH_2)_2-$	$C_{18}H_{16}O_7N_2S_2$	185	6.42	6.46
15	$-(CH_2)_3O(CH_2)_3-$	$C_{20}H_{20}O_7N_2S_2$	119	6.03	6.13
16	$-(CH_2)_4O(CH_2)_4-$	$C_{22}H_{24}O_7N_2S_2$	95	5.69	5.48
17	$-(CH_2)_2OCH_2O(CH_2)_2-$	$C_{19}H_{18}O_8N_2S_2$	67	6.01	5.69
18	$-(CH_2)_2S(CH_2)_2-$	$C_{18}H_{16}O_6N_2S_3$	91	6.19	6.20

[a] Ref. 6 gives m.p. 290°. [b] Ref. 4 gives m.p. 254°. [c] Ref. 7 gives m.p. 196 and 206°. [d] *Anal.* Calcd. C, 47.05; H, 2.96. Found: C, 47.21; H, 3.17.

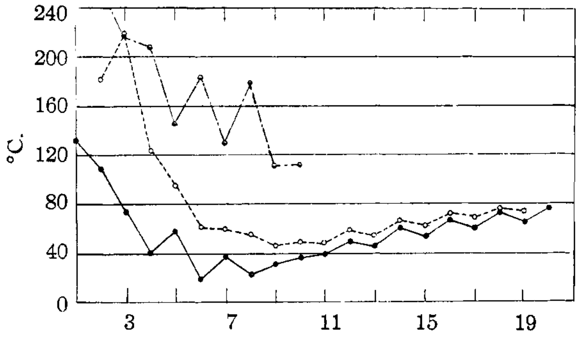


Fig. 1.—Melting points of saccharin derivatives: N-alkyl, —●—●—; O-alkyl, --○---○--; polymethylene-bis, ——⊖——⊖——.

The melting points and analyses are in Table II. The melting points of the polymethylene-bis-saccharins are plotted in the upper left-hand part of Fig. 1. The melting points of the first three members of the series are high, then there is a wide swing in the alternation which appears to change character at the ninth member. The melting points of numbers 3 and 13, in which the connecting chains are $-CH_2CH_2CH_2-$ and $-CH_2OCH_2-$ are close together, as might be expected from isosters.

Three N-alkylsulfamic acids have been prepared by the alkaline hydrolysis of the corresponding N-alkylsaccharins previously described.[2] Their melting points and analytical data are in Table III.

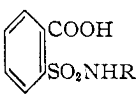
Experimental

For the N-alkylsaccharins, tridecyl to octadecyl, 1.0 cc. of the alkyl bromide was added to a warm solution of 2 g. of sodium saccharin in 5 cc. of dimethylformamide in a test-tube. The mixture was heated in an oil-bath, with occasional shaking, to about 130° for about an hour. The hot mixture was poured into 15 cc. of water. The precipitated compound was filtered off, washed several times with water, dried and recrystallized from ethyl acetate or methanol. The bromides used were those prepared by Meyer and Reid.[8] The yields were practically quantitative. The nonadecyl and eicosyl compounds were made on a smaller scale from 100 and 200 mg., respectively, of the bromides.

The polymethylene-bis-saccharins, from tetramethylene up, were made similarly, using 1.0 cc., or 1.0 g., of the dihalide with 5 g. of sodium saccharin in 10 cc. of the solvent. The ethylene and trimethylene compounds were obtained as by-products in larger scale preparations, in which an excess of the dibromide was used in order to get usable quantities of the intermediate ω-bromoalkylsaccharins. No matter how large this excess was, some of the bis-compound was always present in the product. As these bis-saccharins are only sparingly soluble in boiling alcohol, in which the bromoalkyl compounds are very soluble, they are easily isolated from the mixtures. No intermediate could be obtained with methylene bromide, even when it was used in excess. Up to the pentamethylene the bis-saccharins were recrystallized from benzene, the rest from ethyl acetate.

TABLE III

N-ALKYLSULFAMIC ACIDS



$$C_6H_4(COOH)(SO_2NHR)$$

R	Formula	M.p., °C.	Neut. equiv. Calcd.	Neut. equiv. Found	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
Et	$C_9H_{11}NSO_4$	119	229.2	229.5	47.15	47.28	4.84	4.80	6.11	6.20
Hex	$C_{13}H_{19}NSO_4$	109	285.3	289.5	54.71	54.93	6.71	6.88	4.91	5.24
Oct.	$C_{15}H_{23}NSO_4$	110	311	313	57.48	57.55	7.40	7.47	4.47	4.86

The dihalides containing ether linkages reacted satisfactorily under the standard conditions. Potassium iodide was

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[6] Hugo Eckenroth and Georg Koerppen, *Ber.*, **30**, 1265 (1877).

[7] Julius von Braun and Georg Lemke, *ibid.*, **55**, 3526 (1922).

[8] Jane Dick Meyer and E. Emmet Reid, THIS JOURNAL, **55**, 1574 (1933).

added when the terminal halogens were chlorine. Thus 10 g. of 4,4′-dichlorobutyl ether ($(ClCH_2CH_2CH_2CH_2)_2O$ (0.05 mole) was added to a solution of 30 g. of sodium saccharin and 1 g. of potassium iodide in 55 cc. of dimethylformamide. After heating, the mixture was poured into 150 cc. of water. The yield was 22 g. or 90%. The one sulfur compound was prepared from mustard gas which was added to the cold solution of the sodium saccharin. Dioxane was used for recrystallizing this group.

The cyano alkyl halides reacted regularly under the standard conditions, except when the bromine was in the β-position, as has been mentioned above.

As the β-hydroxyethyl- and γ-hydroxypropylsaccharins are somewhat soluble in water, it was found better to evaporate off the dimethylformamide, after the reaction was judged to be complete, by heating the mixture under vacuum. The desired compound was extracted from the residue by boiling methanol from which it was recrystallized.

N-Alkylsulfamic Acids.—The alkylsaccharin was dissolved in a moderate excess of alcoholic sodium hydroxide. After standing overnight this solution was evaporated to dryness and the residue taken up in water, from which the sulfamic acid was precipitated by hydrochloric acid. The free sulfanic acids were recrystallized from mixtures of ether and petroleum ether.

BALTIMORE, MD.
WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, FACULTY OF SCIENCE, CAIRO UNIVERSITY]

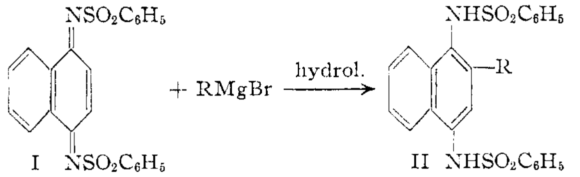
Experiments with Quinone Imides. II. A Novel Synthesis of 1,2-Diphenylnaphthalene

BY AHMED MUSTAFA AND MOHAMED KAMEL

RECEIVED MAY 2, 1955

1,2-Naphthoquinone-1-benzimide (III) reacts with arylmagnesium bromides, *e.g.*, phenylmagnesium bromide, to give the corresponding 1-benzamido-2-hydroxy-1,2-diaryl-1,2-dihydronaphthalene derivatives (IV), *e.g.*, 1-benzamido-2-hydroxy-1,2-diphenyl-1,2-dihydronaphthalene (IVa). When IVa is treated with a mixture of zinc dust, acetic acid and hydrochloric acid, 1,2-diphenylnaphthalene (VII) is obtained in an almost quantitative yield. With ethylmagnesium iodide, III is readily reduced to the corresponding amide derivative, namely, 1-benzamido-2-naphthol (V). The mixture (Mg + MgI_2) and thiophenol effect the reduction of III to V. III undergoes photochemical addition reaction with aromatic aldehydes in sunlight to give the photo-products, namely, 1-benzamido-2-naphthyl esters of aromatic acids (XIVa-c) or (XVa-c) (possibility of ring-chain tautomerism; scheme B).

Action of Grignard Reagents.—In part I,[1] Mustafa and Kamel have shown that 1,4-naphthoquinone dibenzenesulfonimide (I) reacts with Grignard reagents to give the corresponding 2-substituted naphthalene-1,4-dibenzenesulfonamide (II) together with naphthalene-1,4-dibenzenesulfonamide (II, R = H), presumably by 1,4-addition followed by rearrangement.



We have now investigated the action of arylmagnesium bromides on *o*-quinonemonoimides, namely, 1,2-naphthoquinone-1-benzimide (III). Thus, when the orange III is treated with an excess of phenylmagnesium bromide, it reacts with two moles of the Grignard reagent to give, after hydrolysis, 1-benzamido-2-hydroxy-1,2-diphenyl-1,2-dihydronaphthalene (IVa).

The formation of the amino-alcohol derivative IV may be paralleled to the formation of glycols by the action of the same reagent on *o*-quinones.[2a,b] Similarly, 1-benzamido-2-hydroxy-1,2-di-(*p*-bromophenyl)-1,2-dihydronaphthalene (IVb) has been obtained by the action of *p*-bromophenylmagnesium bromide on III.

Compounds IVa-b are obviously of analogous structure. The constitution of IVa was established from the following facts: it is colorless and has the correct molecular weight. It does not give the ferric chloride test nor the Platkonskaya test,[3] for highly hindered phenols, is insoluble in aqueous sodium hydroxide solution and is stable toward acetic anhydride in the presence of fused sodium acetate, thus excluding the presence of a phenolic group.

When a solution of IVa in glacial acetic acid is treated with a mixture of zinc dust and concentrated hydrochloric acid in the presence of a few drops of platinum chloride solution, 1,2-diphenylnaphthalene (VII) is obtained in an almost quantitative yield together with benzoic acid and ammonium chloride.

One possible explanation of the formation of VII is the reduction of a tertiary alcoholic group (OH → H)[4] and the replacement of an amino group (formed by the hydrolysis of the benzamido group) attached to a tertiary carbon atom[5] by a hydroxyl group (*cf.* the intermediates VIa and VIb). For the easy dehydration of VIb to VII, reference should be made to the ready formation of 1,2-diphenyl-3,4-dihydronaphthalene when an alcoholic solution of 1-hydroxy-1,2-diphenyl-1,2,3,4-tetrahydronaphthalene is heated with a few drops of concentrated hydrochloric acid.[6]

This hydrocarbon VII has been prepared by Crawford[6] and Bergmann, *et al.*,[7] by long syntheses

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[1] A. Mustafa and M. Kamel, THIS JOURNAL, **75**, 2939 (1953).

[2] (a) A. Werner and A. Grob, *Ber.*, **37**, 2887 (1904); (b) E. Beschke, O. Beitler and S. Strum, *Ann.*, **369**, 184 (1909).

[3] V. M. Platkonskaya and S. G. Vatkina, *J. Appl. Chem.* (*U.S.S.R.*), **10**, 202 (1937); *C. A.*, **31**, 4232 (1937).

[4] *Cf.* D. Y. Curtin and S. Schmukler, THIS JOURNAL, **77**, 1105 (1955).

[5] *Cf.* the ready transformation of triphenylmethylamine to triphenylcarbinol and ammonium chloride by the action of hot dilute hydrochloric acid (K. Elbs, *Ber.*, **17**, 701 (1884)), and the ready cleavage of β-naphtholphenylmethylamine by the action of hot 0.05 *N* hydrochloric acid to benzaldehyde, β-naphthol and ammonium chloride (M. S. Kharasch and L. B. Howard, THIS JOURNAL, **56**, 1370 (1934)).

[6] H. M. Crawford, *ibid.*, **61**, 608 (1939).

[7] F. Bergmann, H. E. Eschinazi and D. Shapiro, *ibid.*, **64**, 557 (1942).