When $\partial \bar{g}_1/\partial N_2$ is tending to attain zero as the first degree of N_2, then at $N_2 = 0$, $\partial \bar{g}_2/\partial N_2$ differs from zero, as it is to be seen from equation (1) (Fig. 1).[2] This is one of the two cases pointed out by Lewis and Randall.

When $\partial \bar{g}_1/\partial N_2$ is tending to attain zero as the higher degree of N_2, then $\partial \bar{g}_2/\partial N_2$ is likewise tending to attain zero, but the left part of the equation (1) has for its limit zero (Fig. 2).

Figures 1 and 2 correspond to such partial molal quantities, as for instance the volume (or heat capacity or heat content). According to Fig. 1 in the infinitely dilute solution only the partial molal volume of the solvent is constant. According to Fig. 2 in the infinitely dilute solution the partial molal volumes both of the solvent and solute remain constant. Hence it is natural to turn to such a case, when this constancy extends into the field of finite concentrations (Fig. 3).

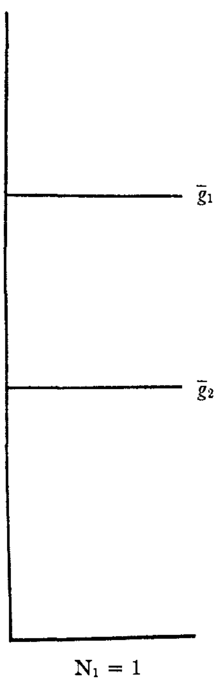

Fig. 3.

As the temperature is rising, *i. e.*, when the abnormality of the solutions is decreasing, it may be expected that the trend will be from Fig. 1 via Fig. 2 to Fig. 3.

The partial molal volumes for the system water–ethyl alcohol[1] (apparently for the temperature 20–25°) calculated by Lewis and Randall correspond to Fig. 1. The calculations made by us of the partial molal volumes for 40° are given in Fig. 2.

With a further rise of temperature it is likely that we shall arrive at Fig. 3.

When $\partial \bar{g}_1/\partial N_2$ is approaching zero as N_2 in a degree below one, then at $N_2 = 0$, $\partial \bar{g}_2/\partial N_2$ is infinite (Fig. 4). The partial molal volumes of the system water–strong electrolyte[3] correspond to this case.

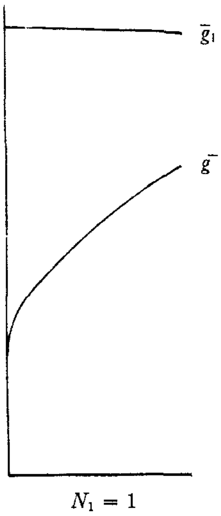

Fig. 4.

The third case when at $N_2 = 0$, $\partial \bar{g}_1/\partial N_2$ and $\partial \bar{g}_2/\partial N_2$ are infinite, is apparently of no practical value.

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[2] Figure 1 corresponds to Fig. 7 of Lewis and Randall.

[3] Redlich and Rosenfeld, *Z. Elektrochem.*, **37**, 705 (1931).

MOSCOW, U. S. S. R. RECEIVED MAY 27, 1935

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

Amides Obtained from Benzenesulfinic Acid

BY L. CHAS. RAIFORD AND STEWART E. HAZLET

A large number of aryl sulfinic acids have been prepared[1] but few of them have been converted into the corresponding acid chlorides, while the behavior of the latter toward amino compounds has received very little attention.

Hilditch and Smiles[2] obtained benzenesulfinyl chloride in rectangular plates that melted at 38°. Braun and Kaiser[3] may have obtained this product as a solid, but they recorded no melting point. Although they used specially purified starting material, Whalen and Jones[4] could not duplicate Hilditch and Smiles' results, and they did not obtain crystals when they followed Braun and Kaiser's directions. Their product was an oil with a boiling range of 85–90° at 3 to 4 mm.

In the present work, the purpose of which was to test further the action of benzenesulfinyl chloride on amino compounds, the "crude" acid chloride was obtained in nearly quantitative yield by treatment of benzenesulfinic acid[5] with thionyl chloride at room temperature. Distillation, when successful, gave about 83% of a yellow oil at 80–85° and 2 mm. Often rapid and violent decomposition of material took place. Comparison of products obtained by the action of "crude" chlo-

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[1] Gattermann, *Ber.*, **32**, 1136 (1899); Knoevenagel and Kenner, *ibid.*, **41**, 3315 (1908); Claasz, *Ann.*, **380**, 303 (1911).

[2] Hilditch and Smiles, *Ber.*, **41**, 4115 (1908); *J. Chem. Soc.*, **97**, 2585 (1910).

[3] Braun and Kaiser, *Ber.*, **56**, 552 (1923).

[4] Whalen and Jones, THIS JOURNAL, **47**, 1355 (1925).

[5] Prepared as directed by Gattermann, "Praxis des organischen Chemikers," 18th Auflage, Walter de Gruyter, Berlin, 1923, p. 268.

ride and distilled material showed that little purification was accomplished by distillation.

With the exceptions noted below the sulfinamides listed were obtained by treatment of two molecular proportions of the required amine, dissolved in about three volumes of dry ether, with 1.25 proportions of "crude" benzenesulfinyl chloride in two volumes of ether, with continuous agitation at 0°. The solid that separated was shaken with water to remove amine salt, the residue, if any, was mixed with the ether filtrate and from this the amide was isolated. Analytical

TABLE I

AMIDES FROM BENZENESULFINIC ACID

Starting material	Yield,[a] %	Crystal form[d]	M. p., °C.	Formula	Analyses, % nitrogen Calcd.	Found
o-Chloroaniline[b]	76[c]		107–108	$C_{12}H_{10}ONClS$	5.58	5.40
m-Chloroaniline[b]	Very poor	Tan	106	$C_{12}H_{10}ONClS$	5.58	5.85
p-Chloroaniline	78	Plates[e]	155.5	$C_{12}H_{10}ONClS$	5.58	5.53
o-Bromoaniline[b]	20[c]	Lavendar	108–110	$C_{12}H_{10}ONBrS$	4.73	4.45
m-Bromoaniline	19	Pink[e]	112–114	$C_{12}H_{10}ONBrS$	4.73	4.68
p-Bromoaniline	47	Lavendar[e]	150.5	$C_{12}H_{10}ONBrS$	4.73	4.67
o-Toluidine	29	Pink[e]	124–125	$C_{13}H_{13}ONS$	6.06	5.99
m-Toluidine	44	Needles[e]	102–103	$C_{13}H_{13}ONS$	6.06	5.96
p-Toluidine[b]	56[c]	Yellow plates	100–101	$C_{13}H_{13}ONS$	6.06	5.94
o-Anisidine[b]	Very poor	Purple	113 shrinks 108–113	$C_{13}H_{13}O_2NS$	5.67	5.63
m-Anisidine[b]	Poor	Cubes[e]	133–134	$C_{13}H_{13}O_2NS$	5.67	5.57
p-Anisidine	89	Purple[e]	131	$C_{13}H_{13}O_2NS$	5.67	5.60
p-Aminobenzoic ethyl ester	29		114–115	$C_{15}H_{15}O_3NS$	4.84	4.85
2-Methyl-5-nitroaniline	26	Yellow	133	$C_{13}H_{12}O_3N_2S$	10.14	10.38
β-Naphthylamine	Very poor[g]	Tan rods[e]	143–144	$C_{16}H_{13}ONS$	5.25	5.14
Benzylamine	26	Rods[e]	100–104	$C_{13}H_{13}ONS$	6.06	5.79
4-Aminodiphenyl	High[h]	[f]	165.5	$C_{18}H_{15}ONS$	4.78	4.72
2-Amino-4′-chlorodiphenyl[i]	Very poor[j]	Yellow plates	206	$C_{18}H_{14}ONClS$	4.28	3.89
4-Amino-4′-chlorodiphenyl[i]	Very poor[k]	Pink	165–166	$C_{18}H_{14}ONClS$	4.28	4.05

[a] Unless otherwise noted, yields represent purified material. [b] The amide was ether soluble, and was obtained from the filtrate after removal of the amine hydrochloride by filtration. [c] Represents crude product. [d] When no crystal form is specified, the substance is amorphous; no entry indicates colorless. [e] Crystallized from dilute alcohol. When not designated, a chloroform-ligroin (60–80°) mixture was used. [f] Crystallized from methanol. [g] Largely hydrolyzed during recrystallization. [h] Amide was separated from amine salt by shaking with a mixture of chloroform and water. Treatment of chloroform solution with ligroin precipitated the amide. [i] Prepared in pyridine solution. [j] Reaction mixture stood overnight before being worked up. [k] Reaction seemed complete in half an hour.

TABLE II

ANILIDES OF BENZENESULFONIC ACID

Starting material	Yield, %	Crystal form	M. p., °C.	Formula	Analyses, % nitrogen Calcd.	Found
o-Bromoaniline	72[e]	Needles[a]	130–131	$C_{12}H_{10}O_2NBrS$	4.48	4.47
m-Bromoaniline	69[e]	Plates	117.5–118.5	$C_{11}H_{10}O_2NBrS$	4.48	4.51
o-Toluidine	97[e]	Laven. plates	122–123	$C_{13}H_{13}O_2NS$[g]	..	..
m-Anisidine	Nearly quant.[e]	Needles	82.5–83.5	$C_{13}H_{13}O_3NS$	5.32	5.26
p-Aminobenzoic ethyl ester	Nearly quant.[e]	Plates	183.5–184	$C_{15}H_{15}O_4NS$	4.59	4.46
2-Methyl-5-nitroaniline	88[f]	Cubes	175–176[c]	$C_{13}H_{12}O_4N_2S$	9.61	9.51[d]
4-Aminodiphenyl	67[f]	Needles	147–148	$C_{18}H_{15}O_2NS$	4.53	4.52
2-Amino-4′-chlorodiphenyl	74[f]	Prisms	136–138	$C_{18}H_{14}O_2NClS$	4.07	3.97
4-Amino-4′-chlorodiphenyl	Nearly quant.[f]	Powder[b]	145–145.5	$C_{18}H_{14}O_2NClS$	4.07	4.04

[a] Crystallized from alcohol; in other cases dilute alcohol was used. [b] Chloroform-ligroin (60–80°). [c] Morgan and Micklethwait [*J. Chem. Soc.*, **89**, 1294 (1906)] found 172° and satisfactory analysis for a product obtained by boiling a toluene solution of the amine and acid chloride for three hours, evaporating the mixture to dryness, extracting the residue with sodium carbonate solution and precipitating the amide by acid. No yield was given. In the present work heating ether solution of the reactants, followed by standing, gave no change. Pyridine was then used as a solvent. [d] Determination made by semimicro Dumas method. [e] Reaction carried out in ether solution. [f] The reaction carried out in pyridine. [g] Previously obtained and analyzed by Hinsberg [*Ann.*, **265**, 184 (1891)] who recorded no yield. It was prepared in the present work for comparison with the sulfinamide of the same base, m. p. 124–125°. A mixture of the two melted at 85–95°.

data for these products are given in Table I.

For purposes of comparison of physical properties a number of corresponding sulfonamides were prepared. Data for them are given in Table II.

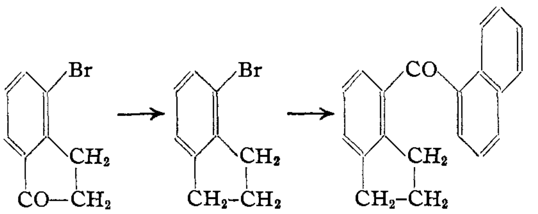
IOWA CITY, IOWA RECEIVED MARCH 23, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Cholanthrene and Related Hydrocarbons

BY LOUIS F. FIESER AND ARNOLD M. SELIGMAN

The synthesis of cholanthrene by three different methods has been reported recently by Cook and his associates.[1] We have found that the modified Elbs synthesis[2] provides still another route to this interesting hydrocarbon. The ketone III was prepared from the known 4-bromohydrindone-1 (I)[3] as indicated, and on pyrolysis there was obtained a hydrocarbon corresponding to the description[1] of cholanthrene, IV. From the ketone resulting from the reaction of the Grignard compound of II with β-naphthoyl chloride, the isomeric hydrocarbon V was obtained.



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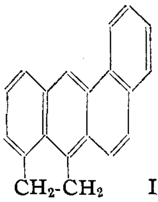
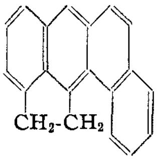


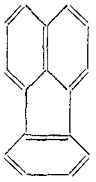
IV



V

Dr. M. J. Shear has observed that crystalline cholanthrene injected subcutaneously in mice produced effects similar to those obtained with methylcholanthrene and in approximately the same time. The hydrocarbon induced ulcerations beginning with the fortieth day and the first tumor, noted on the sixty-second day, took successfully on transplantation. From these preliminary results it appears that a methyl group at C_{20} is of less influence in determining the carcinogenic activity than might have been expected on the basis of the available data.[4]

Another hydrocarbon having the cholanthrene ring system was obtained very easily starting with fluoranthene (VI) from coal tar. By the methods of Fittig and Liepmann,[5] modified in some details, fluorene-1-carboxylic acid can be prepared in any desired quantity by the oxidation of fluoranthene, followed by the reduction of the resulting keto acid VII. 1-(α-Naphthoyl)-fluorene (VIII) was obtained from α-naphthylmagnesium bromide and fluorene-1-carboxylic acid chloride, and on pyrolysis it yielded the hydrocarbon IX.



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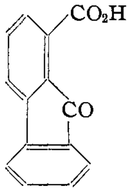

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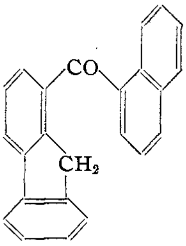

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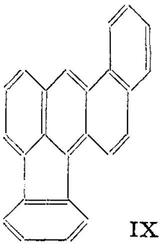

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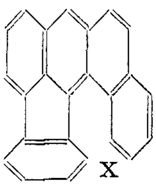

X

To indicate the relationship to the carcinogenically active parent hydrocarbon, this substance may be called 15,16-benzdehydrocholanthrene.[6]

The Friedel and Crafts reaction of the above acid chloride with naphthalene was investigated, with rather unexpected results. The condensation proceeded poorly in carbon bisulfide, probably because of the sparing solubility of the com-

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[1] Cook, Haslewood and Robinson, *J. Chem. Soc.*, 667 (1935); Cook and Haslewood, *ibid.*, 767, 770 (1935).

[2] Fieser and Seligman, THIS JOURNAL, **57**, 942 (1935).

[3] Miersch, *Ber.*, **25**, 2110 (1892); Mayer, Phipps, Ruppert and Schmitt, *ibid.*, **61**, 1966 (1928).

[4] Cook and co-workers, *Proc. Roy. Soc.* (London), **B111**, 455, 484 (1932); **B117**, 318 (1935).

[5] Fittig and Liepmann, *Ann.*, **200**, 1 (1879).

[6] Fieser and Seligman, THIS JOURNAL, **57**, 1377 (1935).