Repetition of the potassium metallation experiments with *N*-phenyl-1-naphthylamine at higher temperatures (refluxing xylene and decalin) led only to unworkable tars.

N-Methyl-N-phenyl-2-naphthylamine was obtained by procedure (a) in 33% yield, m.p. 88–90° (lit.[8] 52–52°).

Anal. Calcd. for $C_{17}H_{15}N$: N, 6.01; Found: N, 6.35.

Higher temperature experiments gave only unworkable tars.

N,N-Dimethyl-1-naphthylammonium picrate. A mixture of *N*-methyl-1-naphthylamine (3.1 g., 0.02 mol.), potassium (1.6 g., 0.04 mol.) and xylene (10 ml.) was refluxed and stirred for 4 hr. in a continuous stream of purified dry nitrogen to give a suspension of a greenish yellow solid. The reaction mixture was cooled and treated overnight with methyl iodide (11.4 g., 0.08 mol.) at room temperature the mixture was warmed, filtered, and the precipitate washed with hot benzene (10 ml.). The filtrate and washings were combined and concentrated. The concentrate was treated with an excess of a saturated solution of picric acid in ethanol. A yellow crystalline solid was obtained melting at 144–145° (lit.[16] m.p. 145°); yield, 4.2 g. (53%).

Anal. Calcd. for $C_{18}H_{16}N_4O_7$: N, 14.00. Found: N, 14.04.

After chromatography of the combined filtrates and washings, and development of the bands, fluorescent examinations show bands identical with those produced by an authentic specimen[3] of *sym*-dimethyl-di(1-naphthyl)hydrazine.

N-Methyl-N-ethyl-1-naphthylammonium picrate. By the same procedure as described above, 3.4 g. (0.02 mol.) of *N*-ethyl-1-naphthylamine gave 4.15 g. (50%) of a picrate melting at 146°.

Anal. Calcd. for $C_{19}H_{18}N_4O_7$: N, 13.53. Found: N, 13.50.

Chromatographic banding and fluorescent examination gave bands suggestive of a tetrasubstituted hydrazine.

Repetition of the same procedure on the ethylation of *N*-methyl-1-naphthylamine gave a 46% yield of a picrate, m.p., 146°, shown by mixed melting point to be identical with *N-methyl-N-ethyl-1-naphthylammonium picrate.*

N-Benzyl-diphenylamine. A mixture of diphenylamine (3.4 g., 0.02 mol.), potassium (0.8 g., 0.02 mol.) and xylene (20 ml.) was refluxed and stirred in a continuous stream of purified dry nitrogen for 4 hr. when a suspension of a pale yellow solid was obtained. The reaction mixture was cooled and allowed to react with benzyl chloride (2.6 g., 0.02 mol.) at room temperature overnight, warmed, and filtered. The filtrate was concentrated to a small volume (6 ml.). On dilution with petroleum ether, 2 g. (44%) of a crystalline solid melting at 84–86° was obtained. Recrystallization from ethanol gave needles, m.p., 88° (lit.[7] 88–88.5°).

Anal. Calcd. for $C_{19}H_{17}N$: N, 5.41; Found: N, 5.63.

Repeated experiments and exhaustive chromatographic separations in attempts to find evidence for the formation of *tetraphenylhydrazine* were negative.

CHICAGO 14, ILL.

(16) H. H. Hodgson and J. H. Crook, *J. Chem. Soc.*, 1500 (1936).

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, UNION CARBIDE CHEMICALS CO., SOUTH CHARLESTON, W. VA.]

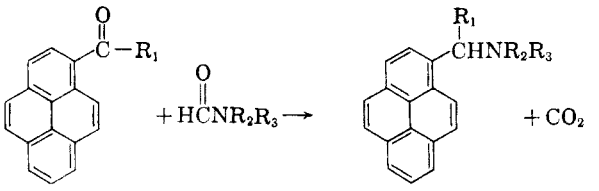
(Aminoalkyl)pyrenes

E. MARCUS AND J. T. FITZPATRICK

Received August 12, 1959

The synthesis of a variety of 1-pyrenemethylamines is described. Most of the compounds were prepared by the Leuckart reaction from the corresponding carbonyl derivative of pyrene and a formamide in the presence of formic acid. Some others were made by catalytic reduction of the imines obtained from 1-pyrenecarboxaldehyde and a primary amine. 1-Pyrenemethylamine was obtained best by reduction of the oxime.

During our study of derivatives of polycyclic hydrocarbons we became interested in the synthesis of 1-pyrenemethylamines. A convenient method for the preparation of such compounds appeared to be the Leuckart reaction.[1]



In the reaction of pyrenecarboxaldehyde with dialkylformamides good yields were obtained when the nitrogen of the dialkylamine part was attached to two methyl or ethyl groups, or when it was part of a heterocyclic system; with higher alkyl groups lower yields were realized. With monoalkylformamides or unsubstituted formamide and pyrenecarboxaldehyde the desired products could also be obtained, but only in low yields; the reaction proceeded further to give large amounts of bis- and tris(pyrenemethyl)amines. The monosubstituted pyrenemethylamines could be made more easily by catalytic hydrogenation of the imines derived from the aldehyde and the corresponding amines. The unsubstituted pyrenemethylamine was prepared best by catalytic reduction of the oxime.

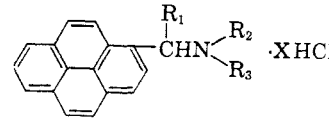
With acetylpyrene and dialkylformamides (we investigated the reaction with dimethylformamide in the presence of formic acid as well as magnesium chloride) the desired reaction did not occur at all. Acetylpyrene reacted fairly well with a monosubstituted formamide and very well with formamide itself; formation of bis- and tris(α-methyl-1-pyrenemethyl)amines was of no importance.

In benzoylpyrene the steric hindrance around the carbonyl group is apparently significant enough, that the reaction even with unsubstituted formamide proceeds only very slowly.

(1) E. Marcus and J. T. Fitzpatrick, *J. Org. Chem.*, **24**, 1031 (1959).

TABLE I

SUBSTITUENTS, MELTING POINTS, AND YIELDS OF PYRENEMETHYLAMINES



Compound No.	R_1	Substituents NR_2R_3	X	M.P.[a,b]	Yield,[b] %	Method
1	H	NH_2	1	244–250[c]	55[c,e]	C[d]
2	H	$NHCH_3$	1	245–253[c]	75[c,e]	B[d]
3	H	$N(CH_3)_2$	1	270–277	72	A
4	H	$N(C_2H_5)_2$	1	238–243[f]	78	A
5	H	$NH(n\text{-}C_4H_9)$	0	88–94[e]	58[c,e]	B
6	H	$NH(n\text{-}C_4H_9)$	1	225–235	54[e]	B
7	H	$N(n\text{-}C_4H_9)_2$	1	149–153[g]	35[g]	A
8	H	$N(n\text{-}C_6H_{13})_2$	1	134–136[g]	42[g]	A
9	H	$N(CH_2)_4$	1	250–260	87	A
10	H	$N(CH_2)_5$	1	256–259	91	A
11	H	$N(CH_2CH_2)_2O$	0	90–93[c]	93[c]	A
12	H	$N(CH_2CH_2)_2O$	1	256–263	95	A
13	H	$N(CH_2CH_2)_2NCH_3$	2	250–260[h]	86	A
14	H	$N[CH_2(1\text{-pyrenyl})]_2$	1	240–255[i]	50[i]	A
15	H	NHC_6H_5	0	143–145[c]	44[c,e]	B
16	H	$NH(\alpha\text{-pyridyl})$	0	165–167[c]	49[c,e]	B
17	CH_3	NH_2	1	230–250	79	A
18	CH_3	$NHCH_3$	1	237–242[j]	48	A
19	CH_3	$NH(n\text{-}C_6H_{13})$	1	220–225[j]	31	A
20	C_6H_5	NH_2	1	240–250[k]	25[l]	A

A. Leuckart reaction. B. Reduction of imines. C. Reduction of oximes. [a] Most of the higher melting compounds melted with decomposition. [b] Crude product unless otherwise indicated. [c] State of purity described in the Experimental section. [d] Compound was also obtained in very low yield by Method A. [e] Overall yield from the aldehyde. [f] After recrystallization from methanol. [g] After recrystallization from acetone. [h] After recrystallization from concentrated hydrochloric acid. [i] From formamide and pyrenecarboxaldehyde; after the mixture of amines had been extracted exhaustively with ether, the insoluble portion was converted to the hydrochloride by refluxing it with a mixture of butanol and concentrated hydrochloric acid. [j] After recrystallization from water. [k] Purified by dissolving the material in a large amount of hot water, filtering, and adding hydrochloric acid to the filtrate. [l] The remainder was largely unchanged starting material.

The difference in yields of the various products can best be rationalized on the assumption that the reaction is sensitive to changes in the steric requirements of both the formamide and the aldehyde or ketone.

The presence of formic acid was found to be essential to the success of the reaction. From pure dimethylformamide and pyrenecarboxaldehyde no product at all could be isolated, while in the presence of formic acid a 72% yield was obtained.[1] However, some crude dialkylformamides made according to Weilmuenster and Jordan[2] appeared to contain enough residual formic acid to catalyze the reaction, e.g., the addition of formic acid did not raise the already satisfactory yield with crude diethylformamide. On the other hand, crude *N*-formylmorpholine gave only a 19% yield, while additional formic acid improved the yield to 95%.

The effect which some of these (aminoalkyl)pyrenes have on the metabolism of yeast has been described recently.[3]

(2) E. A. Weilmuenster and C. N. Jordan, *J. Am. Chem. Soc.*, **67**, 415 (1937).

(3) J. Fellig and J. W. Brough, *Bacteriol. Proc.*, 130 (1959).

EXPERIMENTAL

All melting points are uncorrected. The neutralization equivalents of the amine hydrochlorides were determined by titration with sodium hydroxide using phenolphthalein as indicator; the values are estimated to be accurate within two or three percent.

The melting points, yields, formulas, and analytical data of the pyrenealkylamines are summarized in Table I and II.

METHOD A. Formamide, methylformamide, and dimethylformamide were obtained from Eastman Kodak Co. The other formamides were made by the method of Weilmuenster and Jordan[2] and used as residue products.

The mixture of about 5 to 7.5 mol. of formamide, 1 mol. of formic acid and 1 mol. of the carbonyl compound was refluxed gently for 4 hr. At the end of the reaction the excess of formamide was removed by distillation. When dialkylformamides were used, the residue was then dissolved in ether and filtered, and dry hydrogen chloride was introduced to precipitate the product. When monoalkylformamides or formamide itself were used, the residue was hydrolyzed with a mixture of butanol and concentrated hydrochloric acid for about 24 hr. The resulting amine hydrochlorides, after distillation of the solvent if necessary, were neutralized, dissolved in ether, and filtered. Introduction of hydrogen chloride precipitated the product.

As an example of the synthesis of the amines by the Leuckart reaction the preparation of *N*-(1-pyrenylmethyl)-morpholine is described.

N-(1-Pyrenylmethyl)morpholine. A mixture of 65.5 g. (0.75 mol.) of morpholine and 38.5 g. (0.75 mol.) of 90% formic

TABLE II

FORMULAS AND ANALYTICAL DATA[a] OF PYRENEMETHYLAMINES

Compound No.	Formula	Carbon, %		Hydrogen, %		Nitrogen, %		Chlorine, %		Neutral Equiv.	
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
1	$C_{17}H_{14}NCl$	76.25	76.02	5.27	5.09	5.23	5.30	—	—	268	272
2	$C_{18}H_{16}NCl$	76.73	77.24	5.72	5.85	4.99	5.05	12.58	12.32	282	283
3	$C_{19}H_{18}NCl$	77.14	77.00	6.13	6.43	4.74	4.70	—	—	296	299
4	$C_{21}H_{22}NCl$	77.88	77.36	6.85	7.18	4.33	4.05	—	—	324	327
5	$C_{21}H_{21}N$	87.76	87.33	7.37	7.41	4.87	5.23	—	—	—	—
6	$C_{21}H_{22}NCl$	77.88	77.65	6.85	6.53	4.33	4.34	10.95	10.85	324	328
7	$C_{25}H_{30}NCl$	79.02	78.40	7.96	7.97	3.69	3.73	—	—	380	383
8	$C_{29}H_{38}NCl$	79.87	79.99	8.78	9.11	3.21	3.53	—	—	436	436
9	$C_{21}H_{20}NCl$	78.41	77.84	6.22	6.36	4.35	4.55	11.02	11.05	322	324
10	$C_{22}H_{22}NCl$	78.66	78.19	6.61	6.86	4.17	4.37	10.56	11.02	331	332
11	$C_{21}H_{19}NO$	83.69	83.81	6.35	6.30	4.65	4.56	—	—	—	—
12	$C_{21}H_{20}NOCl$	74.65	74.74	5.97	6.17	4.15	4.24	—	—	338	347
13	$C_{22}H_{24}N_2Cl_2$	68.21	67.96	6.25	6.25	7.23	7.24	18.26	17.94	194	198
14	$C_{51}H_{34}NCl$	87.97	87.38	4.92	4.88	2.01	1.96	5.09	4.61	696	707
15	$C_{23}H_{17}N$	89.86	89.56	5.58	5.23	4.56	4.85	—	—	—	—
16	$C_{22}H_{16}N_2$	85.69	85.12	5.23	5.53	9.08	9.31	—	—	—	—
17	$C_{18}H_{16}NCl$	76.76	76.33	5.68	5.44	4.98	4.67	12.58	12.49	282	280
18	$C_{19}H_{18}NCl$	77.14	77.32	6.13	6.14	4.74	4.63	—	—	296	292
19	$C_{24}H_{28}NCl$	78.82	78.71	7.65	7.72	3.84	3.99	9.69	9.74	366	373
20	$C_{23}H_{18}NCl$	80.36	80.37	5.24	5.32	4.08	4.16	—	—	344	346

[a] The state of purity of the compounds is described in the footnotes to Table I referring to the M.P. column.

acid was heated slowly up to 200° to remove water and any unchanged amine and acid by distillation. To 82 g. of the residue were added 23.0 g. (0.1 mol.) of 1-pyrenecarboxaldehyde and 5 ml. of 90% formic acid. After refluxing for 4 hr. between 182 and 185° the excess of *N*-formylmorpholine was removed by vacuum distillation. The residual oil was dissolved in ether and filtered. Introduction of dry hydrogen chloride precipitated 32.3 g. (95%) of nearly white *N*-(1-pyrenylmethyl)morpholine hydrochloride, m.p. 256–263° with decomposition.

The hydrochloride (2.0 g.) was treated with a mixture of 100 ml. of ether, 20 ml. of concentrated ammonium hydroxide solution, and 20 ml. of water. The organic layer was separated, washed with water, dried over magnesium sulfate, and filtered. After removal of the ether by distillation, 1.75 g. of a viscous, yellow oil remained which was recrystallized from petroleum ether, b.p. 65–70°, to give an analytical sample of light yellow *N*-(1-pyrenylmethyl)morpholine, m.p. 90–93°.

METHOD B. N-Methyl-1-pyrenemethylamine hydrochloride. A rapid stream of methylamine was bubbled into 450 ml. of refluxing ethanol. Then 23.0 g. of 1-pyrenecarboxaldehyde was added with stirring during a 10 min. period. The solution was refluxed with stirring for another hour; during this time the introduction of methylamine was continued. After removal of solvent the residue was recrystallized from petroleum ether, b.p. 93–111°, to give 17.2 g. of a yellow solid, m.p. 102–104° with softening at 90°. Work-up of the mother-liquor gave an additional 3.0 g., m.p. 99–102° with softening at 90°, combined yield 89%. Two recrystallizations (one with the aid of charcoal) of material from the first crop afforded an analytical sample of *N*-methyl-1-pyrenemethylenimine, m.p. 104–105.5° with softening at 102°.

Anal. Calcd. for $C_{18}H_{13}N$: C, 88.86; H, 5.39; N, 5.76. Found: C, 88.75; H, 5.12; N, 5.81.

A mixture of 14.0 g. of *N*-methyl-1-pyrenemethylenimine, 200 ml. of ethanol, and 0.5 g. of Adams' catalyst was hydrogenated for 1 hr. at room temperature at 3.4 atm. pressure. After filtration and removal of solvent the residual oil was recrystallized from methanol to give 12.5 g. (88%) of a tan solid, m.p. 48–50° with softening at 40°. Introduction of dry hydrogen chloride into an ethereal solution of 8.0 g. of the amine gave 8.9 g. of a white solid whose neutral equivalent was 283 (calcd. 282).

N-Butyl-1-pyrenemethylamine hydrochloride. A mixture of 28.7 g. (0.125 mol.) of 1-pyrenecarboxaldehyde, 91.3 g. (1.25 mol.) of *n*-butylamine, and 500 ml. of ethanol was refluxed for 1 hr. After removal of solvent and excess butylamine the residue was recrystallized from petroleum ether, b.p. 65–67°, with the aid of charcoal to give a first crop of 24.5 g., m.p. 64–65.5°, and a second crop of 4.3 g., m.p. 63–65°, combined yield 81%. Another recrystallization from petroleum ether gave an analytical sample of yellow *N*-butyl-1-pyrenemethylenimine, m.p. 65–67°.

Anal. Calcd. for $C_{21}H_{19}N$: C, 88.38; H, 6.71; N, 4.91. Found: C, 88.08; H, 6.41; N, 5.28.

N-Butyl-1-pyrenemethylenimine was hydrogenated for 1 hr. at 3.4 atm. pressure in ethanol. The product was isolated by recrystallization from ethanol in 72% yield and converted to the amine hydrochloride in the usual way.

N-Phenyl-1-pyrenemethylamine. A mixture of 23.0 g. of 1-pyrenecarboxaldehyde, 9.3 g. (0.1 mol.) of aniline, and 100 ml. of ethanol was refluxed for 1 hr. and 40 min. to give 28.69 g. (94%) of a yellow solid, m.p. 126–128°. Another recrystallization from ethanol gave an analytical sample of *N*-phenyl-1-pyrenemethylenimine of the same melting point.

Anal. Calcd. for $C_{23}H_{15}N$: C, 90.46; H, 4.95; N, 4.59. Found: C, 90.99; H, 4.35; N, 4.59.

The imine was hydrogenated in acetic acid for 2 hr. at 3.4 atm. pressure. After neutralization and recrystallization from butanol a 47% yield of a golden-yellow solid, m.p. 141–143.5°, was obtained. Another recrystallization from ethanol gave an analytical sample, m.p. 141–143.5°.

N-(2-Pyridyl)-1-pyrenemethylamine. A mixture of 23.0 g. (0.1 mol.) of 1-pyrenecarboxaldehyde and 9.4 g. (0.1 mol.) of 2-aminopyridine was heated for 40 min. between 167 and 186°. A constant nitrogen stream removed the water formed during the reaction. Recrystallization from benzene gave 19.4 g. (63%) of a yellow solid, m.p. 152–157°. Another recrystallization from benzene afforded an analytical sample of *N*-(2-pyridyl)-1-pyrenemethylenimine, m.p. 158–160°.

Anal. Calcd. for $C_{22}H_{14}N_2$: C, 86.25; H, 4.61; N, 9.15. Found: C, 86.40; H, 4.57; N, 9.17.

The desired material could not be obtained by refluxing a solution of pyrenecarboxaldehyde and aminopyridine in ethanol.

The imine was hydrogenated for 4 hr. at 2.5 atm. pressure in ethanol. Recrystallization from butanol gave a 78% yield of fine ivory-colored needles, m.p. 165–167°. Another recrystallization from ethanol afforded an analytical sample of *N*-(2-pyridyl)-1-pyrenemethylamine of the same melting point.

METHOD C. 1-Pyrenemethylamine hydrochloride. 1-Pyrenecarboxaldehyde oxime was prepared by the pyridine method[4] from 1-pyrenecarboxaldehyde and hydroxylamine hydrochloride in the presence of pyridine using ethanol as a solvent. After recrystallization from butanol a 78% yield of yellow needles was obtained. Another recrystallization from butanol afforded an analytical sample, m.p. 191.5–192.5°.

(4) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Sytematic Identification of Organic Compounds," Wiley, New York, 1956, p. 254.

Anal. Calcd. for $C_{17}H_{11}NO$: C, 83.24; H, 4.52; N, 5.71. Found: C, 82.89, H, 4.32; N, 6.05.

The oxime was reduced catalytically according to a method described by Hartung[5] for the preparation of benzylamine from benzaldoxime. A mixture of 2.0 g. (0.0081 mol.) of 1-pyrenecarboxaldehyde oxime, 150 ml. of ethanol containing 0.0405 mol. of hydrogen chloride, and 2.0 g. of 5% palladium on charcoal was hydrogenated at 3.4 atm. pressure at room temperature for 2 hr. The mixture was brought to boiling and filtered. The filter cake was extracted with more boiling ethanol. After removal of solvent from the combined extracts, the residual solid was dissolved in much boiling water and filtered. Addition of hydrochloric acid to the filtrate and cooling afforded 1.56 g. (72%) of a nearly white solid.

SOUTH CHARLESTON, W. VA.

(5) W. H. Hartung, U. S. Patent 1,989,093, Jan. 29, 1935.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

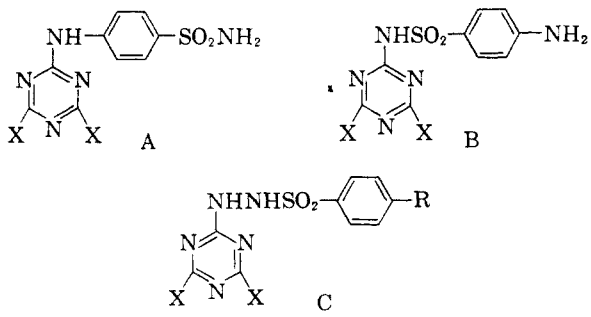
Preparation of Some Sulfonylhydrazide Derivatives of *s*-Triazine[1]

G. F. D'ALELIO AND ROBERT H. BECKER

Received August 14, 1959

Arylsulfonylhydrazides react with cyanuric chloride at 0–10° to replace one chlorine atom; these products react smoothly with secondary amines to produce 2,4-diamino-6-arylsulfonylhydrazido-*s*-triazines. A series of new compounds were prepared by the reaction sequence which is described in this paper.

The preparation of a series of N^4-sulfanilamide derivatives of *s*-triazine (A) was described in a previous paper from this laboratory.[2] It was originally planned to prepare a corresponding series of N^1-sulfanilamide derivatives (B); however all attempts in this direction failed.[3] It was then decided to substitute the sulfonylhydrazido moiety (R–SO_2-NHNH–) for the sulfonamido group (RSO_2NH–) and prepare a series of arylsulfonylhydrazide derivatives (C) to be submitted for pharmacological screening.[4]



(1) Abstracted from a portion of the Ph.D. thesis of Robert H. Becker, University of Notre Dame, 1959.

(2) G. F. D'Alelio and H. J. White, Jr., *J. Org. Chem.*, **24**, 643 (1959).

(3) H. J. White, Jr., Ph.D. Thesis, University of Notre Dame, October, 1957.

(4) Pharmacological testing is being carried out by Merck Sharp and Dohme Research Laboratories, Rahway, New Jersey.

This work shows that cyanuric chloride (III) reacts with one mole of an arylsulfonylhydrazide (II), in the presence of sodium bicarbonate, at 0–10° to form a 2,4-dichloro-6-arylsulfonylhydrazido-*s*-triazine (IV). These compounds are isolated in good yield from aqueous dioxane solution. Because of the reactivity of the remaining chlorine atoms on the triazine nucleus, it is very difficult to effect a good purification of these dichloro-*s*-triazines. However, it was found that the products as obtained from the reaction mixture and washed with water and toluene would work very well in the subsequent reactions, thus eliminating a lengthy purification which involved high loss of material.

Although none of the dichloro intermediates were purified enough to obtain good analyses, they separated from the reaction mixture as dihydrates. When a sample was dried in a vacuum oven at 50° to 100° for varying periods of time, the calculated amount of weight was lost and subsequent reactions utilizing anhydrous material gave yields comparable to those utilizing the dihydrated intermediates.

The arylsulfonylhydrazides (II) used for the preparation of the dichloro-*s*-triazines were prepared from the corresponding arylsulfonyl chlorides (I) using the procedure of Curtius and Stoll[5] with slight variations.

(5) T. Curtius and W. Stoll, *J. prakt. Chem.*, 112, 117 (1926).