[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ANTIOCH COLLEGE]

The Preparation of Substituted Hydrazines. IV. Arylhydrazines *via* Conventional Methods[1]

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The properties and preparation by conventional methods of salts of 28 substituted phenylhydrazines, 3 substituted naphthylhydrazines, 2-hydrazinofluorene, 9-phenanthrylhydrazine, 3-hydrazinopyrene, and 6-quinolylhydrazine are described. Only low yields of the polycyclic arylhydrazines were obtained. Hydrazines whose hydrochloride salts appeared unstable were converted usually to the more stable hydrogen oxalate, which sometimes changed to the neutral oxalate during recrystallization.

In this laboratory during the past four years about 120 hydrazine derivatives of diverse types were screened at a variety of concentrations in D-19 developer for ability to increase the speed of Eastman Kodak Aerographic Tri-X film.[3] Many of these hydrazines, a large majority of which were monosubstituted derivatives ($RNHNH_2$), were prepared in this laboratory. Previous papers in this series[4–7] reported the preparation of certain of these monosubstituted hydrazines *via* the sydnone process. This paper reports the preparation of salts of 35 substituted arylhydrazines and 1 heteroarylhydrazine by conventional reduction of the diazonium salt of the corresponding amine. Of the substituted phenylhydrazines whose salts are reported 22 are monosubstituted (Table I), 5 disubstituted (Table II), and 1 trisubstituted (Table II). In addition, salts of 3 monosubstituted naphthylhydrazines, 2-hydrazinofluorene, 9-phenanthrylhydrazine, 3-hydrazinopyrene, and 6-quinolylhydrazine (all in Table III) are described.

In virtually all cases stannous chloride was used to reduce the diazonium salt. This method is considerably more convenient than the sulfite reduction and is successful in the presence of a large variety of substituent groups on the aromatic ring. In some cases the hydrazine hydrochloride formed as the reduction product, but in most cases the double salt of the hydrazine with hydrochloric acid and tin chloride was obtained. In going from one amine to another the nature of the reduction product could not be predicted even when the proportion of reagents was kept constant. In most cases it was both impractical and unnecessary to determine which salt had formed, because it was filtered from the reduction mixture, treated with excess alkali, and the free base was extracted into ether and converted to a salt of either hydrochloric or oxalic acid. An oxalic acid salt usually was prepared only when the hydrochloride appeared unstable, or at least unstable when not entirely pure. Generally the hydrogen oxalate was obtained, presumably because of the use of an amount of oxalic acid equivalent in moles to the starting amine. However, the neutral oxalate of *o*-tolylhydrazine was obtained apparently because of the use of only half of the usual amount of oxalic acid. In some cases the hydrogen oxalate changed entirely to, or else equilibrated with, the neutral oxalate during attempted recrystallization. Nevertheless, one of the oxalic acid salts formed readily, and either one proved eminently stable on storage. The purity of the hydrazine salt was checked only by neutral equivalent determination if the salt had been reported earlier. Combustion analysis for nitrogen also was performed if the salt had not been reported earlier. Although we prepared salts of many more hydrazines than appear in Tables I, II, and III, a salt appears in the Tables only if it is a new compound or if an earlier description lacked physical constants such as m.p., neutral equivalent, and combustion analysis. Our general procedure (*cf.* Experimental) for preparing arylhydrazines is a variation of Meyer's original method[8] which we found eminently satisfactory in a large number of cases. Departures from this method are given in the footnotes to the Tables.

Most of the hydrazines in Tables I and II showed the expected properties and require no further comment. However, very few hydrazino derivatives of polycyclic aromatic hydrocarbons have been reported. We have now prepared for the first time salts of 9-phenanthrylhydrazine and of 3-hydrazinopyrene. These compounds were obtained in rather

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(3) Results of the sensitometric testing will be published separately.

(4) Tien and Hunsberger, *Chemistry & Industry*, 119 (1955).

(5) Fugger, Tien, and Hunsberger, *J. Am. Chem. Soc.*, **77**, 1843 (1955).

(6) Tien and Hunsberger, *J. Am. Chem. Soc.*, **77**, 6604 (1955).

(7) Tien and Hunsberger, *J. Am. Chem. Soc.*, **77**, 6696 (1955).

(8) Meyer and Lecco, *Ber.*, **16**, 2976 (1883).

low yield because of difficulty in diazotizing the amines, formation of side-products, and instability of the hydrazine bases. It seems certain that the sydnone process[4-7] would give much better results, but no polycyclic arylamine has yet been transformed to a sydnone.

Reduction of diazotized[9] 9-phenanthrylamine with stannous chloride in hydrochloric acid produced very low yields (8.6% and 5.0%) of the hydrazine hydrochloride. The heavy red oil which formed in considerable amount during precipitation of the hydrochloride probably was impure hydrochloride, but we were unable to obtain it in crystalline condition. That considerable deamination accompanied the above reduction was proved by the isolation of phenanthrene in higher yield than the hydrazine hydrochloride. Material presumed to be 9-phenanthrylamine also was isolated.

Pure 9-phenanthrylhydrazine hydrochloride turned only slightly pink during several days in an evacuated desiccator, but in air it became pink in a few hours. In view of the nature of 9-phenanthrol and of 9-phenanthrylamine this behavior is not surprising. Since this hydrochloride neither melts sharply nor keeps well, its purity was determined only by neutral equivalent determinations on freshly-prepared samples. However, it was characterized by formation of the *p*-nitrobenzaldehyde 9-phenanthrylhydrazone. Also, the hydrazine was observed to behave like other arylhydrazines when added in small quantities to D-19 developer.[3] Although this latter characterization is unusual from a chemical standpoint, its efficacy for detecting an —NHNH$_2$ group attached to an aromatic ring leaves little to be desired.[10]

9-Phenanthrylhydrazine hydrogen oxalate, which was much more stable than the hydrochloride, was isolated in yields of 23 and 28%. This hydrogen oxalate was only very slightly soluble in the common solvents, and in ethanol solution it appeared to equilibrate with the neutral oxalate. Hence, the hydrogen oxalate was not recrystallized, but merely washed with 1:3 ethanol-ether, prior to analysis. The picrate of 9-phenanthrylhydrazine also was prepared and analyzed to complete the identification.

After much experimentation 3-aminopyrene was converted in 23% yield to the corresponding hydrazine hydrogen oxalate by a process similar to that used for 9-phenanthrylhydrazine. An attempt to repeat this preparation inexplicably produced, as the only product isolated, a small amount of 3-aminopyrene. Furthermore, earlier attempts to prepare 3-hydrazinopyrene by our general procedure, by the sulfite process used for *p*-fluorophenylhydrazine,[11] and by the method used for phenylhydrazine[12] all proved unsuccessful, 3-aminopyrene being the only product identified.

Repeated attempts to prepare 5-hydrazinoacenaphthene gave inconclusive results. Some deamination either accompanied or followed the diazotization.

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EXPERIMENTAL[13]

Starting materials. Most of the liquid amines used as starting materials were freshly distilled from zinc dust. All starting amines were Eastman Kodak White Label products except as noted below. Thus, *o*-ethylaniline, 5-chloro-2-methoxyaniline, and 3-chloro-2-methylaniline were Eastman Practical grade products, while 2,3-dichloroaniline was purchased from Sapon Laboratories, Long Island, N. Y. The following nitro compounds (Eastman Kodak White Label unless designated otherwise) were reduced to amines: *p*-fluoro-, *o*-iodo-, and *m*-iodonitrobenzene, *m*-nitroanisole, *o*- and *p*-nitrodiphenyl ether, *m*-nitrocinnamic acid, 3,4-dichloronitrobenzene, nitromesitylene, 2-nitrofluorene, 5-nitroacenaphthene, 6-nitroquinoline, 3-nitropyrene (Sapon Laboratories), and *o*-, *m*-, and *p*-*tert*-butylnitrobenzene [prepared by nitration[14] of Eastman Kodak White Label *tert*-butylbenzene]. If literature directions were not used in the reductions, the preparations are given briefly later. Three amines were prepared according to literature directions but not from the corresponding nitro compounds, namely 1-chloro-2-naphthylamine,[15] 4-bromo-1-naphthylamine,[16] and 9-phenanthrylamine.[9] In a few cases melting points are reported (see below) for amine hydrochlorides or hydrogen oxalates which were not thus characterized earlier.

General method for preparing arylhydrazines. A stirred slurry of 0.20 mole of the amine in 80 ml. of concentrated hydrochloric acid was treated dropwise at 0° or below with 0.20 mole of sodium nitrite in 70 ml. of cold water.[17] The mixture was stirred for 0.5 hour at about 0°, filtered (if necessary), and in a few cases added to 100 g. of chopped ice before proceeding with the reduction. Dropwise addition (stirring) at about 0° of 0.60 mole of stannous chloride dihydrate in 140 ml. of cold concentrated hydrochloric acid then produced a slurry of the tin double salt of the hydrazine (or in a few cases of the hydrazine hydrochloride). This slurry was refrigerated overnight, filtered, and the precipitate was

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[9] Goldberg, Ordas, and Carsh, *J. Am. Chem. Soc.*, **69**, 260 (1947).

[10] An elaborate experimental justification and amplification of this statement will be published later.

[11] Schiemann and Winkelmüller, *Ber.*, **66**, 727 (1933).

[12] Coleman, *Org. Syntheses*, Coll. Vol. I, 2nd ed., 442 (1943).

[13] All m.p.s are uncorrected and all compounds melted with decomposition unless specified otherwise. Combustion analyses were performed by Clark Microanalytical Laboratory, Urbana, Ill. and/or by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Unless specified otherwise all neutral equivalent determinations were performed by visual titration in water, aqueous alcohol, or alcohol using Cresol Red-Thymol Blue mixed indicator (Chicago Apparatus Co.), whose *pH* range is 7.5–9.5 on the alkaline side.

[14] Nelson and Brown, *J. Am. Chem. Soc.*, **73**, 5605 (1951).

[15] Cleve, *Ber.*, **20**, 1989 (1887).

[16] Morgan, Micklethwait, and Winfield, *J. Chem. Soc.*, **85**, 736 (1904).

[17] If the amine hydrochloride was used as starting material, the proportion of hydrochloric acid was reduced correspondingly. In some cases the slurry of the amine hydrochloride was poured into 100 g. of cracked ice before adding the sodium nitrite.

TABLE I

MONOSUBSTITUTED PHENYLHYDRAZINES[a]

Substituent	Type of Salt[b]	M.p., (°C.)	Yield[c] (%)	Elemental Formula	Neut. Equiv. Calc'd	Neut. Equiv. Found
p-F[d]	HC	216[e]	—	$C_6H_8ClFN_2$	163	160
	NO	167.5–169	50[f]	$C_{14}H_{16}F_2N_4O_4$[g]	171	176
o-Br	HC	186–187	47	$C_6H_8BrClN_2$	223	221
m-Br	HC	228–230	53	$C_6H_8BrClN_2$	223	222
o-I	HC[h]	157–159	47	$C_6H_8ClIN_2$	270	270
m-I	HC	176–177.3	49	$C_6H_8IN_2$	270	270
o-CH_3[i]	HC	193.5–195.5	30[j]	$C_7H_{11}ClN_2$	159	158, 157
	NO	163–165		$C_{16}H_{22}N_4O_4$[k]	167	167, 165
m-CH_3	HC[l]	190–193	75[f]	$C_7H_{11}ClN_2$	159	157
p-CH_3	HC[m]	222–235	14	$C_7H_{11}ClN_2$	159	158
o-C_2H_5	HC[m]	177–181	75[f]	$C_8H_{13}ClN_2$	173	171, 171
o-$(CH_3)_3C$[n,o]	HC	205–209	24	$C_{10}H_{17}ClN_2$	201	190
m-$(CH_3)_3C$[n,o]	HC	207–209	35	$C_{10}H_{17}ClN_2$	201	199
p-$(CH_3)_3C$[n,o]	HC	221–222.5	59[p]	$C_{10}H_{17}ClN_2$	201	202
p-$CH_3CHCH_2CH_2CH_3$[n,o]	HC	176–180	38[q]	$C_{11}H_{19}ClN_2$	215	215
m-CH_3O[r]	HO[h]	143–144	54	$C_9H_{12}N_2O_5$	114	120
	NO[s]	154.4–155	—	$C_{16}H_{22}N_4O_6$[t]	183	181, 186
p-CH_3O[u]	HO[v]	151–153	25	$C_9H_{12}N_2O_5$	114	109, 110
	NO[w]	174–175	—	$C_{16}H_{22}N_4O_6$	183	178
o-C_2H_5O[x]	HO[y]	139–141	56[z]	$C_{10}H_{14}N_2O_5$[aa]	121	122
m-C_2H_5O[x]	HO[bb]	145.5–148	21[z]	$C_{10}H_{14}N_2O_5$[cc]	121	123
o-C_6H_5O[n,dd]	HC	179–181	15[f]	$C_{12}H_{13}ClN_2O$[ee]	237	233
p-C_6H_5O[dd,ff]	HC	185–187	58[f]	$C_{12}H_{13}ClN_2O$[gg]	237	235
p-CH_2COOH[n,hh]	HC	228–229	84[ii]	$C_8H_{11}ClN_2O_2$[jj]	101	102, 101
m-$CH{=}CHCOOH$[h,n,o]	—	194–195	42	$C_9H_{10}N_2O_2$	—	—
	HC	265	—	$C_9H_{11}ClN_2O_2$	107	108, 106
p-AsO_3H_2[kk]	—	188[ll]	43	$C_6H_9AsN_2O_3$	232	231[mm]

[a] All hydrazines were prepared by our general process unless otherwise noted. Except as noted, the hydrazine bases have been reported previously, but the salts shown have been either not reported previously or else reported without physical constants. [b] HC = hydrochloride; HO = hydrogen oxalate; NO = neutral oxalate. [c] All yields are based on the related amine and correspond to pure products except as noted otherwise. [d] Reduction of the diazonium salt of *p*-fluoroaniline[18] and isolation of the hydrochloride[11] appeared to produce considerable decomposition, but the procedure used to prepare 2,4,6-trimethylphenylhydrazine[19] gave much better results. Treatment of the ether extract of this basified reduction mixture with alcohol saturated with excess oxalic acid dihydrate precipitated the neutral oxalate, which was recrystallized from methanol. The free base, obtained from the oxalate, was converted to the hydrochloride in the usual manner. [e] Bubbled slightly at 216°, then turned dark and sublimed; lit. m.p.'s: 200°,[20] volatilized with decomposition but without melting.[11] [f] Yield before recrystallization. [g] *Anal.* Calc'd: N, 16.37. Found: N, 16.43. [h] Not recrystallized. [i] Prepared according to our general procedure, but part of the hydrazine was converted to the hydrochloride and part to the neutral oxalate. The hydrogen oxalate did not form presumably because of the use of insufficient oxalic acid. [j] Combined yield of the two salts, each of which was recrystallized from ether-ethanol. [k] *Anal.* Calc'd: N, 16.76. Found: N, 18.23, 16.61, 16.99. The high value for nitrogen presumably was caused by drying the sample at too high a temperature just prior to analysis, thus causing decomposition into the free hydrazine and oxalic acid. The checking values were obtained on samples dried at 56°. [l] Recrystallized once from ether-methanol. [m] Recrystallized once from ether-ethanol. [n] Neither the free base nor its salts have been reported previously. [o] Details of the preparation are given separately in the Experimental section. [p] Yield before the last reprecipitation from dilute hydrochloric acid. [q] Yield of distilled hydrazine base. [r] The hydrazine was prepared[21] from *m*-anisidine hydrochloride, m.p. 170–172°, which was obtained in 97% yield by hydrogenation (Parr apparatus) of *m*-nitroanisole in glacial acetic acid over 4% palladium-charcoal catalyst. [s] Obtained by recrystallization of the hydrogen oxalate from water to which ethanol was added. [t] *Anal.* Calc'd: N, 15.29. Found: N, 15.08. [u] This hydrazine was prepared by the method used for the phenethylhydrazines. A strong phenolic odor was noted during reduction of the diazonium salt. [v] Recrystallized once from glacial acetic acid. [w] Obtained by one recrystallization of the hydrogen oxalate from aqueous ethanol. Attempts at further recrystallization led to unidentified material containing only about half as much nitrogen. [x] The hydrazine was prepared essentially according to Stolz' directions for the *p*-isomer,[22] except that the volume of water was kept to the minimum because the product was soluble in water. The hydrochloride salt of the *o*-isomer was unstable when not entirely pure [compare ref. (23).] [y] Recrystallized from methanol and then from ether-ethanol. [z] Yield before the last recrystallization. [aa] *Anal.* Calc'd: N, 11.57. Found: N, 11.29. [bb] Recrystallized from methanol and then from ether-methanol. [cc] *Anal.* Calc'd: N, 11.57. Found: N, 11.51. [dd] Concentration of the ether from which the hydrochloride was precipitated left an oil (presumably diphenyl ether) which was not susceptible to crystallization. [ee] *Anal.* Calc'd: N, 11.79. Found: N, 11.15. [ff] No physical properties have appeared for the hydrazine base or its salts, but the effect of this compound on myeloid mouse leukemia has been reported.[24] [gg] *Anal.* Calc'd: N, 11.79. Found: N, 11.78. [hh] Prepared essentially according to directions for the *o*-isomer[25] except that the hydrazine was isolated as the hydrochloride. The analytical sample was prepared as snow-white crystals by dissolving the crude hydrochloride in water, decolorizing, treating the solution (at 0°) with hydrogen chloride, and then repeating the process but without decolorization. The free base, prepared by dissolving the hydrochloride in 25% sodium carbonate and acidifying with acetic acid, decomposed near 175° with rapid evolution of gas. [ii] Yield before the last two reprecipitations. [jj] *Anal.* Calc'd: N, 13.83; Found: N, 14.02. [kk] Prepared according to Friedheim,[26] who gave no m.p. information. [ll] Decomposed without melting. [mm] Titration was difficult, apparently because of the slow reaction with the added base. The given value resulted from a very slow titration (endpoint, *p*H 8.3).

TABLE II

DI-AND TRI-SUBSTITUTED PHENYLHYDRAZINES^{a}

Substituents	Type of Salt^{b}	M.p., (°C.)	Yield^{c} (%)	Elemental Formula	Neut. Equiv. Calc'd	Neut. Equiv. Found
2,3-diCl^{d,e}	HC^{f}	241–242	65^{g}	$C_6H_7Cl_3N_2$^{h}	214	214
3,4-diCl^{d,e}	HC^{i}	212–217	24^{j}	$C_6H_7Cl_3N_2$^{k}	214	213
2,4-diCH$_3$^{l}	HC^{m}	183–186	33	$C_8H_{13}ClN_2$	173	172, 174
3-Cl-*2*-CH$_3$^{d}	HC	218–220	16	$C_7H_{10}Cl_2N_2$	193	192
5-Cl-*2*-CH$_3$O^{d}	HC	192	43	$C_7H_{10}Cl_2N_2O$	209	208
2,4,6-triCH$_3$^{n}	HO^{o}	185.5–187	29^{j,p}	$C_9H_{15}ClN_2$	187	188

^{a,b,c} Same as corresponding footnotes to Table I. ^{d} Neither the free base nor its salts have been reported previously. ^{e} This hydrazine was prepared by the method used[27] for its isomers. ^{f} The crude hydrochloride was recrystallized from very dilute hydrochloric acid and then from ether-ethanol. ^{g} Yield before the last recrystallization. ^{h} *Anal.* Calc'd: N, 13.12. Found: N, 13.36. ^{i} The crude hydrochloride was recrystallized three times from ether-methanol. ^{j} Yield before recrystallization. ^{k} *Anal.* Calc'd: N, 13.12. Found: N, 13.68, 13.62. ^{l} Prepared essentially according to ref. (28). ^{m} Not recrystallized. ^{n} Mesidine hydrochloride, m.p. 245–247°, was obtained in 85% yield by subjecting nitromesitylene to a four-day hydrogenation (Parr apparatus) over Adams' catalyst. The hydrazine was prepared roughly according to Franzen.[19] ^{o} Recrystallized from ether-ethanol. ^{p} Franzen's[19] low yield (7.5%) probably was occasioned by the considerable decomposition which accompanies precipitation of the hydrazine hydrochloride from an ether solution of the impure free base. Precipitation from hydrochloric acid is preferable.

TABLE III

POLYCYCLIC ARYL- AND HETEROARYL-HYDRAZINES^{a}

Hydrazine	Type of Salt^{b}	M.p.,^{c} (°C.)	Yield (%)	Elemental Formula	Neut. Equiv. Calc'd	Neut. Equiv. Found
1-Chloro-2-naphthylhydrazine	HC^{d}	193–199^{e}	63^{f}	$C_{10}H_{10}Cl_2N_2$	229	238
4-Bromo-1-naphthylhydrazine^{g}	HC^{h}	177.5–178^{i}	21	$C_{10}H_{10}BrClN_2$	274	276
1-Naphthylhydrazine-4-sulfonic acid^{j}	—	260–261.5	100^{k}	$C_{10}H_{10}N_2O_3S$	238	254
2-Hydrazinofluorene^{l}	HC^{m}	250–255	64	$C_{13}H_{13}ClN_2$	233	230, 234
	HC	—^{n}	8.6	$C_{14}H_{13}ClN_2$	245	241
			5.0			
9-Phenanthrylhydrazine^{o,p}	HO	172–174	23	$C_{16}H_{14}N_2O_4$	149	154, 151
			28			
	Picrate	172–174	—	$C_{20}H_{15}N_5O_7$	437	440, 430
3-Hydrazinopyrene^{o,p}	HO	182–185	23	$C_{18}H_{14}N_2O_4$	161	168, 162
6-Quinolylhydrazine^{q}	di-HC^{r}	219–220	45	$C_9H_{11}Cl_2N_3$	116	116, 116

^{a,b,c} Same as the corresponding footnotes to Table I. ^{d} Recrystallized from dilute acetic acid saturated with hydrogen chloride. ^{e} Spattered on the side of the capillary just prior to melting. ^{f} Yield before recrystallization. ^{g} Prepared according to ref. (29) except the reduction product was worked up according to our general procedure. ^{h} Recrystallized from hot water containing enough hydrogen chloride to render the hydrochloride insoluble on cooling. ^{i} Sample inserted in a bath preheated to 175°. On a regular m.p. determination the sample turned dark at 175–180° and then slowly decomposed as the temperature was raised. ^{j} This hydrazine, which does not form a hydrochloride, was prepared according to ref. (30) and purified essentially according to ref. (31). However, an entirely ash-free sample never was obtained. Its qualitative identification was established by sensitometric testing in D-19 developer. ^{k} Yield before purification. ^{l} The reduction product was treated with excess 25% sodium hydroxide and the crude free base was obtained by evaporation of an ether extract of this alkaline mixture. Repeated ether extraction was required because of the low solubility of the free base [compare ref. (32)]. ^{m} Obtained as greenish-white crystals (which turned black at about 240°) by dissolving the crude hydrazine in 1:1 acetic acid-water, decolorizing, and reprecipitating with dilute hydrochloric acid. ^{n} Gradually decomposed at 250° and above (see details of preparation). ^{o} Neither the free base nor its salts have been reported previously. ^{p} Details of the preparation are given separately in the Experimental section. ^{q} The hydrazine was prepared essentially according to ref. (33) and (34). On saturating a solution of the free base in dry ether with dry hydrogen chloride the yellow solid (monohydrochloride) which first formed changed to an orange material (dihydrochloride) which became crystalline on aging and cooling. This product was not recrystallized. ^{r} Dihydrochloride.

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(18) Rinkes, *Chem. Weekblad*, **11**, 360, 952 (1914); *Chem. Abstr.*, **10**, 194 (1916).

(19) Franzen, Onsager, and Faerden, *J. prakt. Chem.*, [2] **97**, 336 (1918).

(20) Suschitzky, *J. Chem. Soc.*, 3326 (1953).

(21) Kermack, Perkin, and Robinson, *J. Chem. Soc.*, **119**, 1602 (1921).

(22) Stolz, *Ber.*, **25**, 1663 (1892).

(23) Franzen and Schmidt, *J. prakt. Chem.*, [2] **96**, 1 (1917).

(24) Freedlander and Furst, *Proc. Soc. Exptl. Biol. Med.*, **81**, 638 (1952).

(25) Neber, *Ber.*, **55**, 826 (1922).

(26) Friedheim, U. S. Patent 2,390,529 (Dec. 11, 1945).

(27) Carlin and Fisher, *J. Am. Chem. Soc.*, **70**, 3421 (1948).

(28) Willgerodt and Klein, *J. prakt. Chem.*, [2] **60**, 97 (1899).

(29) Plant and Tomlinson, *J. Chem. Soc.*, 2192 (1932).

(30) Bean and Russell, U. S. Patent 2,604,400 (July 22, 1952).

(31) Johnson, *J. Soc. Chem. Ind.* (*London*), **40**, 176T (1921).

(32) Diels, *Ber.*, **34**, 1758 (1901).

(33) Wieland and Horner, *Ann.*, **536**, 89 (1938).

(34) Knueppel, *Ann.*, **310**, 75 (1900).

(35) Larner and Peters, *J. Chem. Soc.*, 680 (1952).

washed with saturated sodium chloride followed by 2:1 petroleum ether-ether. The filtered solid was treated with excess concentrated sodium hydroxide and the hydrazine was extracted into ether. The ether extract was washed, dried, decolorized (if necessary), and saturated with dry hydrogen chloride (at ice-bath temperatures in most cases). If necessary, the hydrochloride was recrystallized from methanol, ethanol, water, or some mixture of these solvents. In a few cases the hydrochloride was dissolved in hot 1:1 methanol-chloroform and petroleum ether, b.p. 30–65°, was added to turbidity. Unless designated otherwise in the Tables, two recrystallizations sufficed to produce an analytically pure sample.

If the crude hydrochloride appeared unstable, *e.g.* if it turned dark red during filtration, the ether solution of the free base was poured into an alcoholic solution containing an amount of oxalic acid equivalent in moles to the starting amine. The resulting hydrogen oxalate usually was recrystallized at least once. Sometimes the hydrogen oxalate changed to the neutral oxalate during recrystallization.

o-, m-, and p-tert-Butylphenylhydrazine hydrochlorides. *tert*-Butylbenzene was nitrated[14] and the product was fractionated in a Todd column to give a 69% yield of the three *nitro-tert-butylbenzenes.* The 15 fractions first collected were combined into 3 fractions as follows: *ortho*, b.p. 110–120° at 5–10 mm., n_D^{27} 1.5178–1.5285; *meta*, b.p. 118–134° at 5–8 mm., n_D^{27} 1.5300–1.5309; *para*, b.p. 136–139° at 10–11 mm., n_D^{27} 1.5319–1.5322. Although each of these 3 fractions probably contained small amounts of undesired isomers, the apparent ratio of *ortho*:*meta*:*para* was 1.37:1:3.58 [compare ref. (14)].

The nitro compounds were hydrogenated separately over Adams' catalyst in 95% ethyl alcohol (*meta* isomer) or in ether (*ortho* and *para* isomers). The *tert*-butylanilines were isolated as the *hydrochlorides: ortho*, 42% yield, m.p. 250–252°; *meta*, 72% yield, m.p. 252–254°; *para*, 85% yield, m.p. 255–260° (lit.[35] m.p. 270–274°). These salts partly sublimed during the m.p. determinations. *m-tert*-Butylaniline was characterized as its *acetyl derivative*, m. p. 93–94.5° (lit. m.p.'s: 101–102°,[14] 99°,[36] and 101°,[37]) unchanged after three recrystallizations from aqueous methanol.

The amines were converted separately to the corresponding hydrazines by use of our general method. About one-half of the reduction product obtained from 11.4 g. (0.0614 mole) of *m-tert*-butylaniline hydrochloride was made basic and extracted with ether. Saturation of this dried and cooled extract with dry hydrogen chloride produced a thick gelatinous precipitate which was bright red on the surface. During filtration, some of the solid turned into a thick red sirup which passed through the filter with the ether washings. The small amount of filtered white solid soon turned red even in an evacuated desiccator. This impure hydrochloride was dissolved in water and reprecipitated by addition of hydrochloric acid to yield light-colored crystals, m.p. 199–202°. The remainder of the above reduction product was dissolved in water at 80–90°, treated with 20 ml. of concentrated hydrochloric acid, and the solution was cooled to yield a white solid, m. p. 204–207°. The two fractions were combined and recrystallized from 50 ml. of methanol (ether added) to afford 4.2 g (35%) of white solid, m.p. 207–209°, presumably the pure *m-tert-butylphenylhydrazine hydrochloride.*

The *o*- and *p-isomers* were prepared in essentially the same way, except that all of the reduction product was precipitated directly from dilute hydrochloric acid and then was recrystallized from methanol. The *p*-isomer was subjected to an additional precipitation from hydrochloric acid. A red substance appeared during diazotization of *o-tert*-butylaniline hydrochloride. This was removed by filtration prior to reduction.

Anal. Calc'd for $C_{10}H_{17}ClN_2$: N, 13.96. Found: N, 14.15 (*p-tert*-butylphenylhydrazine hydrochloride).

p-(1-Methylbutyl)phenylhydrazine hydrochloride. The dough-like slurry of the tin complex salt of the hydrazine, obtained by our general procedure from 22.5 g. (0.138 mole) of freshly-distilled *p-sec*-amylaniline, was filtered as completely as possible while cold to yield a soft solid which became more fluid as it approached room temperature. The contents of the filter funnel were treated with excess 25% sodium hydroxide and the bright yellow mixture was stirred for one hour and extracted with ether. Treatment of the dried extract with dry hydrogen chloride yielded a thick yellowish precipitate containing a top layer of viscous red oil. Filtration removed most of the oil, and the desiccated solid was treated with 50 ml. of 25% sodium hydroxide. An ether extract of this mixture was fractionated to yield 9.4 g. (38%) of the crude hydrazine as a viscous yellow oil, b.p. 106–120° (some distilled up to 135°) at 2 mm. This product was treated in 100 ml. of ether at 0° with dry hydrogen chloride and the resulting solid was reprecipitated by saturating its solution in cold water with hydrogen chloride. In this way 3.2 g. of pink solid, m.p. 175–182°, was obtained. Two additional reprecipitations afforded the colorless analytical sample, m.p. 176–180°, which soon developed a pink tinge.

Anal. Calc'd for $C_{11}H_{19}ClN_2$: N, 13.05. Found: N, 13.09.

m-Hydrazinocinnamic acid. The insolubility of this hydrazine base in ether and the high solubility of the hydrochloride salt in water rendered preparation of this compound by stannous chloride reduction of the diazonium salt very difficult. Hence, the hydrazine was prepared essentially according to the method used for its *o*-isomer.[38] Thus, 18 g. (0.11 mole) of *m*-aminocinnamic acid[39] in 18 ml. (0.22 mole) of concentrated hydrochloric acid was diazotized in an ice-salt bath with 7.6 g. (0.11 mole) of sodium nitrite in 20 ml. of water. A cold sodium sulfite solution[40] was poured with vigorous stirring (Hershberg stirrer) into the diazonium solution. After a few minutes 9.2 ml. (0.11 mole) of concentrated hydrochloric acid and some zinc dust were added to the bright orange mixture. The color changed rapidly to pale yellow, and the zinc was removed by filtration. While on a steam-bath the filtrate was saturated with sodium chloride, cooled overnight, and the precipitation of the sodium sulfonate salt of the hydrazine was completed by adding 26 g. of glacial acetic acid. For 4 hours a stream of moist hydrogen chloride was passed over this filtered solid, which was stirred manually at intervals, but the color change reported for the *o*-isomer[38] was not observed. Hence, the solid was placed in 100 ml. of water. Since solution did not occur and since the liquid was now quite acidic, the suspended solid was removed by filtration and placed in 250 ml. of fresh water. After addition of 7.8 g. of sodium acetate the mixture was stirred for 2 hours and the filtered solid washed twice with water and once with cold ethanol to yield 8.3 g. (42%) of *m*-hydrazinocinnamic acid, m.p. 194–195°. No solvent suitable for recrystallizing this compound could be found. Similar difficulty was reported for the *o*-isomer.[38]

Anal. Calc'd for $C_9H_{10}N_2O_2$: N, 15.72. Found: N, 15.56.

The *hydrochloride*, precipitated from a 5% hydrochloric acid solution, melted with decomposition only when plunged into a bath at above 265°.

Salts of 9-phenanthrylhydrazine. To a vigorously stirred solution of 34 ml. of concentrated hydrochloric acid in 350 ml. of water at 0° a solution of 10 g. (0.052 mole) of pure 9-phenanthrylamine[9] in 37 ml. of dioxane was added in a fine continuous stream, followed immediately (temperature kept below 3°) by 4.1 g. (0.059 mole) of sodium nitrite in

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(36) Shoesmith and Mackie, *J. Chem. Soc.*, 2334 (1928).

(37) Gelzer, *Ber.*, **21**, 2941 (1888).

(38) Fischer and Kuzel, *Ann.*, **221**, 261 (1883).

(39) Blout and Silverman, *J. Am. Chem. Soc.*, **66**, 1442 (1944).

(40) Prepared by passing sulfur dioxide into a cold solution of 22 g. (0.55 mole) of sodium hydroxide in 165 ml. of water for 3 minutes beyond the phenolphthalein endpoint.

18 ml. of ice-cold water. During stirring at 2 to −3° for $1^3/_4$ hours the originally white suspension became orange-brown, then dark red, and finally yellow.[41] Dropwise addition at 0° of 35.3 g. (0.156 mole) of stannous chloride dihydrate in 75 ml. of concentrated hydrochloric acid and 36 ml. of water then produced a salmon-colored suspension of the tin complex salt. This mixture was stirred for 3 hours at below 2°, treated (vigorous stirring) with 650 ml. of 25% sodium hydroxide, and extracted with a total of 600 ml. of ether. The combined extracts were washed with water, filtered to remove 3.5 g. of finely-divided solid (A), dried, shaken 10 minutes with Norit, filtered, and saturated with dry hydrogen chloride. The light brown solid thus obtained was pressed as free as possible of the admixed heavy red oil. The solid (2.07 g.) was dissolved (room temperature) in 25 ml. of methanol, the solution was shaken with Norit, and the light yellow-brown filtrate was diluted to 85 ml. with ether. Cooling afforded 0.057 g. of presumably pure *9-phenanthrylhydrazine hydrochloride* as a white, ash-free solid which darkened at about 250° but did not melt completely even at 340°. Successive dilutions of the above filtrate with ether produced an additional 1.04 g. of fairly pure hydrochloride, the total yield being 8.6%.

(A) was recrystallized from methanol and sublimed twice at 3–4 mm. to yield a pale yellow solid, m.p. 90–98°, which soon turned to a rose color. This material presumably was the low-melting form of *9-phenanthrylamine,* which is reported to melt at 104° when recrystallized from alcohol[42] and to assume a rose color on brief standing in moist air.[43]

In another similar preparation starting from 10 g. of *crude* 9-phenanthrylamine a 5.0% yield of hydrazine hydrochloride was obtained. In this preparation the ether filtrate left after removal of the crude hydrazine hydrochloride was evaporated to dryness, leaving 4.3 g. of halogen-free, dark red solid, m.p. below 105°. Recrystallization (Norit) from aqueous methanol left 1.10 g. of tan solid, m.p. 90–98°. Recrystallization from ethanol yielded 0.58 g. of nitrogen-free tan crystals, m.p. 93–100°, which on sublimation at 90–95° and 3 mm. produced beautiful shiny white crystals of pure *phenanthrene,* m.p. 100.8–101.6° (corr.), whose identity was confirmed by mixture m.p.

9-Phenanthrylhydrazine hydrogen oxalate, m.p. 172–174°, prepared in the usual manner, was pure without recrystallization.

Anal. Calc'd for $C_{16}H_{14}N_2O_4$: N, 9.36. Found: N, 9.39.

A sample of *9-phenanthrylamine hydrogen oxalate,* m.p. 205–207°, was prepared for comparison. Recrystallization of the hydrazine hydrogen oxalate from ethanol produced material whose neutral equivalent and nitrogen content indicated it to be a mixture of the hydrogen oxalate and the neutral oxalate.

The *picrate* was prepared by heating[44] a mixture of an alcohol solution of picric acid with an ether solution of the hydrazine base. The light yellow product, m.p. 172–174°, was washed thoroughly with 1:3 ethanol-ether and used directly as an analytical sample since attempts at recrystallization apparently produced serious decomposition.

Anal. Calc'd for $C_{20}H_{15}N_5O_7$: N, 16.02. Found: N, 15.75.

Roughly in accord with a general procedure for preparing hydrazones,[45] 0.18 g. (0.0012 mole) of *p*-nitrobenzaldehyde was added to 0.30 g. (0.0012 mole) of 9-phenanthrylhydrazine hydrochloride in 12 ml. of methanol. A red solid immediately began to separate. Anhydrous sodium acetate (0.10 g., 0.0012 mole) was added, and after 2 hours at room temperature the suspension was diluted with 10 ml. of water to yield 0.27 g. (66%) of crude hydrazone, m.p. 190–215°. That part of this product which was insoluble in 55 ml. of boiling ethanol was recrystallized from 15 ml. of ethyl acetate to yield dark red crystals, m.p. 233–236° (corr.). An additional recrystallization from 10 ml. of ethyl acetate afforded tiny dark brown-red crystals of pure *p-nitrobenzaldehyde 9-phenanthrylhydrazone,* m. p. 235.5–237.5° (corr.).

Anal. Calc'd for $C_{21}H_{15}N_3O_2$: N, 12.31. Found: N, 11.95.

3-Hydrazinopyrene hydrogen oxalate. Commercial 3-nitropyrene was hydrogenated (Parr apparatus) in methanol over W-7 Raney nickel (1 g. of catalyst per 5 g. of nitro compound) and the *amine* was isolated in 82% yield as the *hydrochloride,* m.p. 260–263°.

A solution of 2.5 g. (0.012 mole) of 3-aminopyrene in 10 ml. of dioxane was introduced slowly into a solution of 9 ml. of concentrated hydrochloric acid in 90 ml. of water at 0°. The resulting pink-white suspension was treated rapidly with 0.83 g. (0.012 mole) of sodium nitrite in 5 ml. of water and the dark mixture was stirred for 1.5 hours at 0°. After dropwise addition (stirring) of 8.1 g. (0.036 mole) of stannous chloride dihydrate in 18 ml. of concentrated hydrochloric acid the mixture was stirred for 2 hours and refrigerated overnight. The reddish mixture was layered with ether and rendered alkaline with 170 ml. of 25% sodium hydroxide. The dried ether extract was partially decolorized (if decolorized too much, the hydrazine also is removed) and treated with a solution of 1.1 g. (0.012 mole) of oxalic acid in the minimum of ethyl alcohol. In this way 0.9 g. (23%) of the *hydrazine hydrogen oxalate* was obtained as a pinkish-white solid, m.p. 182–185°, which turned red even in an evacuated desiccator. Qualitative identification of this material as a hydrazine was obtained, as in the case of 9-phenanthrylhydrazine, by sensitometric testing in D-19 developer.

An attempt to repeat this preparation yielded only *3-aminopyrene,* which was isolated as its *hydrochloride* (B). The product from other methods of reduction also was the *amine hydrochloride* (C), m.p. 260–262° after recrystallization from dilute hydrochloric acid. The corresponding free base, m.p. 114–118°, was identified by mixture m.p. with authentic 3-aminopyrene.

Anal. Calc'd for $C_{16}H_{12}ClN$ (aminopyrene hydrochloride): Neut. equiv., 254; N, 5.52. Found: Neut. equiv., 246 (B), 248 (B),[46] 250 ± 5 (C), 255 ± 5[47] (C); N, 5.65 (B).

5-Aminoacenaphthene. Catalytic hydrogenation (Parr apparatus) of 5-nitroacenaphthene in methanol over W-7 Raney nickel is a much better method for preparing 5-aminoacenaphthene than previously reported processes.[48,49] The pure *amine hydrochloride,* m.p. 218.5–220° with prior sublimation, was isolated in 64% yield. The *amine hydrogen oxalate,* m.p. 198–199.5°, also was prepared.

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[41] The diazotized mixture could be refrigerated overnight with no apparent disadvantage.

[42] Schmidt and Heinle, *Ber.,* **44,** 1488 (1911).

[43] Schmidt and Strobel, *Ber.,* **34,** 1461 (1901).

[44] This salt did not form unless heat was used.

[45] Chattaway and Clemo, *J. Chem. Soc.,* **123,** 3041 (1923).

[46] Titration performed with a *p*H meter.

[47] Endpoint of this titration was very difficult to observe.

[48] Fleisher and Schranz, *Ber.,* **55,** 3253 (1922).

[49] Morgan and Stanley, *J. Soc. Chem. Ind. (London),* **43,** 343T (1924).