Recrystallization of the solid from ethanol gave II as white crystals, m.p. 77–79°, in 51% over-all yield.

2-Phenyl-5-(2′-pyridyl)-pentanol-2 (VIII).—To 100 ml. of a 2.0 *M* ethereal solution of phenylmagnesium bromide there was added dropwise with stirring a solution of 14.4 g. of 1-(2′-pyridyl)-4-pentanone[4] in 100 ml. of dry ether. The mixture was boiled under reflux for one hour and was then decomposed by addition of an aqueous ammonium chloride solution. The ether layer was removed, dried and concentrated. The resulting residual oil crystallized after standing for a month. Recrystallization of this solid from pentane gave 11.0 g. (50%) of II as white crystals, m.p. 70–72°. The same product was obtained when the addition of methylmagnesium iodide to phenyl γ-(2-pyridyl)-propyl ketone[3] was carried out in a similar manner.

5-(2′-Pyridyl)-pentanol-2, VII.—To 25 ml. of a 0.8 *M* ethereal solution of lithium aluminum hydride there was added dropwise with stirring a solution of 7.0 g. of 1-(2′-pyridyl)-pentanone-4 in 50 ml. of dry ether. After the solution had been boiled under reflux for fifteen minutes, moist ether was added and the precipitate of metallic hydroxides was removed. The ethereal solution was dried, concentrated and the residual oil was distilled yielding 5.0 g. (71%) of a colorless oil.

1-Phenyl-4-(2′-piperidyl)-butanol-1, IX.—A solution of 8.0 g. of 1-phenyl-4-(2′-pyridyl)-butanol-1,[3] 0.1 g. of platinum oxide, 30 ml. of ethanol and 60 ml. of 1.7 *N* hydrochloric acid was subjected to hydrogenation at room temperature and 3 atm. pressure of hydrogen. The absorption of three molar equivalents of hydrogen was complete in three and one-half hours. The catalyst and part of the solvent were then removed, the aqueous solution was made basic, and the oil which separated was taken up in benzene. After removal of the benzene, the residue was distilled to yield 5.2 g. (63%) of a colorless viscous oil.

DEPARTMENT OF CHEMISTRY
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RECEIVED DECEMBER 4, 1950

The Synthesis of 2-Sulfanilamido-5-aminopyrimidine

BY WILLIAM T. CALDWELL

Although there are many substituted sulfanilamides and, indeed, many substituted sulfanilamidopyrimidines, there has been no record of the preparation of 2-sulfanilamido-5-aminopyrimidine. One reason for this is the fact that various devices for obtaining the compound by conventional or direct procedures all fail. From these may be singled out for mention the vain attempts to convert 2-amino-5-nitropyrimidine into a sulfonamide by the action of either *p*-nitrobenzenesulfonyl chloride or acetylsulfonyl chloride in pyridine, quinoline or other solvents, in the hot or cold, in spite of the fact that 2-acetamido-5-nitropyrimidine was easily obtained by warming with acetic anhydride. Other instances of a similar refractory behavior have been observed.[1] This paper describes the somewhat circuitous path by which the desired product was synthesized.

The author is grateful to Eli Lilly and Company for carrying out pharmacological tests, reports on which will appear elsewhere.

Experimental

2-Acetamido-5-benzamidopyrimidine.—The brownish solid residue obtained (after removing the solvent under diminished pressure without access of air) by catalytic reduction with platinum oxide instead of palladium on charcoal[2] of 30.7 g. of 2-acetamido-5-nitropyrimidine was treated in the cold with an excess (30 cc.) of benzoyl chloride followed by 310 cc. of 1.2 *N* aqueous potassium hydroxide, making sure that the mixture had an alkaline reaction. The buff or khaki-colored precipitate stood overnight in this alkaline medium and then was filtered off in a sintered glass funnel and washed well with cold water. A small sample was recrystallized from alcohol, using Darco, and yielded colorless to very pale yellow needles, that melted at 281–284° (uncor.) to a brown liquid; yield of crude product, 39.2 g. or 90%.

Anal.[3] Calcd. for $C_{13}H_{12}N_4O_2$: N, 21.85. Found: N, 21.31.

2-Amino-5-benzamidopyrimidine.—The residue of 2-acetamido-5-benzamidopyrimidine (39 g.) was boiled for exactly 30 minutes with 170 cc. of 1.1 *N* aqueous potassium hydroxide. During this boiling, the character of the crystals changed in appearance; after cooling thoroughly, filtering through sintered glass and washing well with ice-water, 22 g. (air-dried) of olive colored crystals were obtained. This material was boiled with 900 cc. of water (with Darco); upon filtering and cooling, lustrous white crystals of 2-amino-5-benzamidopyrimidine (IV) separated; m.p. 214–217° (uncor.).

Anal. Calcd. for $C_{11}H_{10}N_4O$: N, 26.12. Found: N, 26.13.

2-Acetylsulfanilamido-5-benzamidopyrimidine.—A solution of 17 g. of acetylsulfanilyl chloride in 35 cc. of dry pyridine was added slowly to a solution of 15.3 g. of 2-amino-5-benzamidopyrimidine in 50 cc. of dry pyridine in an ice-bath. After standing overnight at 45–50° there was a deposit of chunky crystals beneath a reddish-brown liquid. This cake of crystals was broken up with a stirring rod, shaken well and, after another four hours at 50°, had set to a thick porridge of crystals. The material was then heated for one hour on a steam-bath whereupon it became lighter in color, turning a canary yellow. After filtering off the solid and washing well with cold water, the creamy white product melted, after drying overnight at 110°, at 286–293° (uncor.); yield 68.2%. In several other runs, procedures and conditions were varied but yields remained at 68–69%.

Anal. Calcd. for $C_{19}H_{17}N_5O_4S$: N, 17.01. Found: N, 16.85.

2-Sulfanilamido-5-aminopyrimidine.—Although hydrolysis of 2-acetylsulfanilamido-5-benzamidopyrimidine to the final product proceeded satisfactorily with small amounts (5–10 g.) when refluxed overnight with twice the theoretical amount of 1.1 *N* 50% aqueous methanolic potassium hydroxide, it proved desirable to reflux a larger amount (38.9 g.) somewhat longer with 2.2 *N* 50% aqueous methanolic potassium hydroxide. After neutralizing with acetic acid, the product upon recrystallizing from water in which it is, surprisingly enough, even less soluble than "sulfadiazine" in the cold, was obtained as white needles; m.p. 256–259° (uncor.); yields 70–80%.

Anal. Calcd. for $C_{10}H_{11}N_5O_2S$: C, 45.28; H, 4.18; N, 26.40. Found: C, 45.19; H, 4.05; N, 26.58.

DEPARTMENT OF CHEMISTRY
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PHILADELPHIA 22, PENNA.
RECEIVED JANUARY 6, 1951

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[1] English, Clark, Shepherd, Marson, Krapcho and Roblin, THIS JOURNAL, **68**, 1041 (1946).

[2] Roblin, Winnek and English, *ibid.*, **64**, 569 (1942).

[3] All analyses by Clark Microanalytical Laboratory, Urbana, Illinois.

Rhodanine Derivatives[1]

BY FRANCES C. BROWN, CHARLES K. BRADSHER, SARA M. BOND AND MARNY POTTER

The compounds listed in Table I were prepared by the condensation of rhodanine or 3-substituted rhodanines with the appropriate aldehyde or ketone. The reactions, except as noted, were effected in an ethanol–ammonium hydroxide mix-

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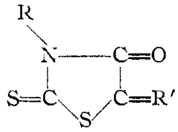
[1] The compounds were prepared under a contract with the Medical Division, Chemical Corps, U. S. Army.

TABLE I

PROPERTIES OF RHODANINE DERIVATIVES



R	R'	M.p., °C.	Yield,[a] %	Formula	Carbon, %[b] Calcd.	Carbon, %[b] Found	Hydrogen, %[b] Calcd.	Hydrogen, %[b] Found
H	*o*-Methylbenzylidene	196	59	$C_{11}H_9NOS_2$	56.14	56.06	3.86	3.94
H	*m*-Methylbenzylidene	182–185	29[c]	$C_{11}H_9NOS_2$	56.14	56.13	3.86	3.69
H	*p*-Methylbenzylidene	219–220	42	$C_{11}H_9NOS_2$	56.14	56.03	3.86	3.81[d]
H	*o*-Fluorobenzylidene[i]	201–203	71	$C_{10}H_6FNOS_2$	50.19	50.61	2.53	2.44
H	*m*-Fluorobenzylidene[i]	201	59	$C_{10}H_6FNOS_2$	50.19	50.35	2.53	2.57
H	*p*-Fluorobenzylidene[i]	226–227	75	$C_{10}H_6FNOS_2$	50.19	50.37	2.53	2.54
H	2,4-Dichlorobenzylidene	231.5–232.5	47	$C_{10}H_5Cl_2NOS_2$	41.39	41.30	1.74	1.60
H	3,4-Dichlorobenzylidene	231–232	87[e]	$C_{10}H_5Cl_2NOS_2$	41.39	41.34	1.74	1.67
H	2-Hydroxy-5-chlorobenzylidene	222–223 d.	36	$C_{10}H_6ClNO_2S_2$	44.20	44.56	2.23	2.47
H	2-Hydroxy-3-methoxybenzylidene	239–240	67	$C_{11}H_9NO_3S_2$	49.42	49.43	3.39	3.40[d]
H	4-Hydroxy-3-ethoxybenzylidene	216	91[e]	$C_{12}H_{11}NO_3S_2$	51.23	51.54	3.94	3.98[d]
H	3,4-Diethoxybenzylidene	196	55	$C_{14}H_{15}NO_3S_2$	54.35	54.47	4.89	5.00[d]
H	3-(2-Furyl)-acrylidene	251 dec.	82	$C_{10}H_7NO_2S_2$	50.62	50.91	2.97	3.07[d]
H	2-Ethyl-3-propylacrylidene[j]	109.5–110.5	76[e]	$C_{11}H_{15}NOS_2$	54.74	54.63	6.27	6.28
H	*α*-Amylcinnamylidene	145–148	62	$C_{17}H_{19}NOS_2$	64.32	64.22	6.03	6.13
H	*o*-Nitrocinnamylidene	250	48	$C_{12}H_8N_2O_3S_2$	49.30	49.65	2.76	2.75
H	2-Ethylbutylidene[j]	104–106	55	$C_9H_{13}NOS_2$	50.20	49.96	6.08	6.21
H	2-Ethylhexylidene[j]	66–68	69	$C_{11}H_{17}NOS_2$	54.28	54.51	7.04	6.78
H	Citrylidene	146–147	17[f]	$C_{13}H_{17}NOS_2$	58.39	58.69	6.41	6.35[d]
H	Decylidene[k]	76–76.5	32	$C_{13}H_{21}NOS_2$	57.52	57.66	7.80	7.62
Methyl	*m*-Methylbenzylidene	164–167	93[e]	$C_{12}H_{11}NOS_2$	57.83	57.87	4.45	4.31
Methyl	*p*-Methylbenzylidene	169.5–170	62	$C_{12}H_{11}NOS_2$	57.83	57.48	4.45	4.48
Methyl	*p*-Isopropylbenzylidene	137–138	58	$C_{14}H_{15}NOS_2$	60.62	60.70	5.45	5.39
Methyl	*p*-Chlorobenzylidene[g,l]	198–200	58	$C_{11}H_8ClNOS_2$	48.97	49.18	2.99	3.01
Methyl	2-Thenylidene[h]	170–170.5	81[c]	$C_9H_7NOS_3$	44.79	44.89	2.92	2.89
Methyl	Cyclopentylidene	108–108.5	45	$C_9H_{11}NOS_2$	50.67	50.90	5.20	5.21
Methyl	Cyclohexylidene	111–112	48	$C_{10}H_{13}NOS_2$	52.83	52.62	5.76	5.68
Methyl	*p*-Methylcyclohexylidene	106	97	$C_{11}H_{15}NOS_2$	54.74	54.78	6.27	6.14
Allyl	*p*-Methylbenzylidene[g]	125–126	48	$C_{14}H_{13}NOS_2$	61.06	61.15	4.76	4.53
Allyl	*p*-Isopropylbenzylidene[g]	48–49	43[f]	$C_{16}H_{17}NOS_2$	63.33	63.08	5.65	5.43
Allyl	*p*-Chlorobenzylidene[g,l]	137–138	76[e]	$C_{13}H_{10}ClNOS_2$	52.78	52.84	3.41	3.25
Allyl	2-Thenylidene[h]	148–149	86[c]	$C_{11}H_9NOS_3$	49.41	49.47	3.39	3.56
Allyl	2-Furfurylidene[g]	102.5–103.5	59	$C_{11}H_9NO_2S_2$	52.57	52.94	3.61	3.80
Allyl	Cyclohexylidene[g]	63–64	66	$C_{12}H_{15}NOS_2$	56.88	56.96	5.97	5.77
Allyl	*p*-Methylcyclohexylidene[g]	49–51	73	$C_{13}H_{17}NOS_2$	58.39	58.30	6.41	6.67
Phenyl	2-Thenylidene[h]	198–200	67[e]	$C_{14}H_9NOS_3$	55.42	55.71	2.99	3.13
Phenyl	Cyclohexylidene[g]	127–128	36	$C_{15}H_{15}NOS_2$	62.25	62.30	5.23	5.27
Phenyl	*p*-Methylcyclohexylidene[g]	119	51	$C_{16}H_{17}NOS_2$	63.33	63.46	5.65	5.95
Phenyl	Propylidene[k]	104–104.5	55	$C_{12}H_{11}NOS_2$	57.80	58.10	4.45	4.42
Phenyl	Isopropylidene	136–137	56	$C_{12}H_{11}NOS_2$	57.80	57.55	4.45	4.30
Phenyl	1-Methylhexylidene[g]	99	58[e]	$C_{15}H_{19}NOS_2$	62.91	62.84	6.27	6.25

[a] After one crystallization. [b] Analyses by Clark Microanalytical Laboratory. [c] Yield after four crystallizations. [d] Analysis by University of Pittsburgh Microchemical Laboratory. [e] Yield of crude product. [f] Yield after two crystallizations. [g] Ammonium chloride omitted. [h] Ammonium hydroxide and ammonium chloride omitted. [i] Aldehyde prepared from the corresponding fluorotoluene by the method of Coleman and Honeywell, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 89. [j] Aldehyde obtained through the courtesy of Carbide and Carbon Chemicals Division. [k] Compound prepared by R. J. Grantham by the sodium acetate–acetic acid method; see ref. 7. [l] Aldehyde obtained through the courtesy of Heyden Chemical Corp.

ture, using ammonium chloride as catalyst.[2,3] The physical constants and analytical data are assembled in Table I.

5-(5-Nitrofurfurylidene-2)-rhodanine.—Since sulfuric acid has been used to catalyze both the hydrolysis of the diacetate to the aldehyde,[4] and the condensation of rhodanine with aldehydes,[5] the two steps were carried out in one reaction mixture. A stirred mixture of 0.1 mole rhodanine, 0.1 mole 2-nitro-5-furfural diacetate, 15.2 ml. concentrated sulfuric acid and 82.5 ml. water was refluxed on a steam-bath in a carbon dioxide atmosphere for one hour. After washing with hot water, the red precipitate was recrystallized from acetone (21% yield). The purified product melted at 201–201.5°.

Anal. Calcd. for $C_8H_4N_2O_4S_2$: C, 37.49; H, 1.57. Found: C, 37.59; H, 1.83.

5-(5-Chloro-furfurylidene-2)-rhodanine.—5-Chloro-furfural, prepared by the method of Chute and Wright,[6] and rhodanine reacted in a sodium acetate–acetic acid mixture, following the procedure of Julian and Sturgis.[7] The prod-

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(2) F. C. Brown, C. K. Bradsher, S. G. McCallum and M. Potter, *J. Org. Chem.*, **15**, 174 (1950).

(3) M. Girard, *Ann. chim.*, [11] **16**, 333 (1941).

(4) H. Gilman and G. F. Wright, THIS JOURNAL, **52**, 2550 (1930).

(5) M. Nencki, *Ber.*, **17**, 2277 (1884).

(6) W. J. Chute and G. F. Wright, *J. Org. Chem.*, **10**, 541 (1945).

(7) P. L. Julian and B. M. Sturgis, THIS JOURNAL, **57**, 1126 (1935).

uct, after recrystallization from alcohol (50% yield), melted at 220° with decomposition.

Anal. Calcd. for $C_8H_4ClNO_2S_2$: C, 39.10; H, 1.64; S, 26.10. Found: C, 39.37; H, 2.12; S, 26.48.

DEPARTMENT OF CHEMISTRY
DUKE UNIVERSITY
DURHAM, N. C.

RECEIVED DECEMBER 18, 1950

Synthesis and Properties of Trimethylhydrazine

BY J. B. CLASS AND J. G. ASTON

We have recently performed the first successful synthesis of trimethylhydrazine, the simplest member of the trisubstituted hydrazine series. Previous attempts by Klages and co-workers[1] indicated the impracticability of chloramine coupling and methylation means, so we attempted and succeeded in reducing N,N-dimethyl-N′-methylenehydrazine with $LiAlH_4$.

Identification of the product resulted from equivalent weight determinations by electrometric titration with HCl (equivalent weight: calcd., 74.13; found, 74.53, 74.59). A cryoscopic determination in water gave a molecular weight of 67.2 (calcd. 74.13) indicating one equivalent per molecule. A satisfactory combustion has not yet been obtained due to the compound exploding in the combustion tube.

Trimethylhydrazine is a colorless liquid possessing a strong, fish-like odor. Unlike hydrazine and the other known methylhydrazines, *it is relatively stable to the atmosphere.* The compound fumes on dilution with water, the process of solution being strongly exothermic. The low boiling point of 59°, which is lower than that of the methyl and dimethylhydrazines, indicates that the hydrogen bonding characteristic of hydrazine is further decreased by introducing a third methyl group.

A preliminary determination of its physical constants gave the following: b.p. 59° (740 mm.); d^{18}_4 0.814; n^{18}_D 1.406; MR calcd. 23.60, found 22.39; pK_b 7.0 (determined by electrometric titration using a glass electrode).

[1] F. Klages, G. Nober, F. Kircher and M. Bock, *Ann.*, **547**, 1 (1941).

SCHOOL OF CHEMISTRY AND PHYSICS
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STATE COLLEGE, PENNSYLVANIA

RECEIVED JANUARY 22, 1951

Structure of the Hexachlorocyclohexane Melting at 145°

BY G. CALINGAERT,[1] A. J. KOLKA AND H. D. ORLOFF

A hexachlorocyclohexane melting at 145° has been prepared[2,3] and shown to have zero dipole moment.[3] This material was considered to be a new isomer (ζ) of benzene hexachloride (1,2,3,4,5,6-hexachlorocyclohexane), and a steric structure that would have zero dipole moment was postulated.[3] Subsequently the structure proposed for the "ζ" isomer was assigned to the ε isomer of benzene hexachloride,[4] thus leaving no convincing evidence for or against any particular structure for the hexachlorocyclohexane melting at 145°.

Five steric isomers of benzene hexachloride have been isolated[5,6] and their structure established by X-ray diffraction,[7] electron diffraction,[8] and measurement of their dipole moments.[9] Because only two of the possible steric isomers of benzene hexachloride can have zero dipole moment, and both of these (β and ε) have been identified, the product reported to be the "ζ" isomer of benzene hexachloride must be a hexachlorocyclohexane other than a 1,2,3,4,5,6-positional isomer.

Of the other positional isomers of hexachlorocyclohexane, only two can have steric isomers possessing zero dipole moment. These are 1,1,3,3,5,5-hexachlorocyclohexane, capable of existence in only one steric structure, and the 1,1,2,4,4,5-isomer, which can theoretically have two zero dipole forms out of three possible steric isomers. Dehydrochlorination of 1,1,3,3,5,5- and 1,1,2,4,4,5-hexachlorocyclohexane can yield only 1,3,5- and 1,2,4-trichlorobenzene, respectively.

The preparation of the hexachlorocyclohexane melting at 145° was repeated in this Laboratory, and the purified material was dehydrochlorinated with 10% alcoholic potassium hydroxide solution by the method of Kauer, *et al.*[6] The product was proved to consist of only 1,2,4-trichlorobenzene by examination of its infrared absorption spectrum. It is concluded that the hexachlorocyclohexane melting at 145° is 1,1,2,4,4,5-hexachlorocyclohexane.

[1] Hobart College, Geneva, New York.

[2] Sabatier and Mailhe, *Bull. soc. chim.*, **29**, 977 (1903); *Ann. chim. phys.*, [8] **10**, 534 (1907); Beveridge, British Patent 573,712.

[3] Bastiansen and Hassel, *Acta Chem. Scand.*, **1**, 683 (1947).

[4] Bastiansen, Ellefsen and Hassel, *ibid.*, **3**, 918 (1949).

[5] Van der Linden, *Ber.*, **45**, 231 (1912).

[6] Kauer, DuVall and Alquist, *Ind. Eng. Chem.*, **39**, 1335 (1947).

[7] Dickinson and Bilicke, THIS JOURNAL, **50**, 764 (1928); Bijvoet, *Rec. trav. chim.*, **67**, 777 (1948); van Vloten, Kruissink, Strijk and Bijvoet, *Nature*, **162**, 771 (1948); *Acta Cryst.*, **3**, 139 (1950); van Bommel, Strijk and Bijvoet, *Proc. Koninkl. Nederland Akad. Wetenschap*, **53**, 47 (1950).

[8] Hassel and Ottar, *Acta Chem. Scand.*, **1**, 929 (1947); Bastiansen, Ellefsen and Hassel, *ibid.*, **3**, 918 (1949).

[9] Hetland, *Acta Chem. Scand.*, **2**, 678 (1948); Amble and Hassel, *Research*, **3**, 52 (1950); Lind, Hobbs and Gross, THIS JOURNAL, **72**, 4474 (1950).

RESEARCH LABORATORY ETHYL CORPORATION
DETROIT, MICHIGAN

RECEIVED JANUARY 5, 1951

Synthesis of Cycloheptanone by a Nitromethane Condensation Sequence

BY HYP J. DAUBEN, JR., HOWARD J. RINGOLD,[1] ROBERT H. WADE AND ARTHUR G. ANDERSON, JR.

Large scale preparation of cycloheptanone from cyclohexanone by the diazomethane method[1a] presents the difficulties of preparation and use of large amounts of diazomethane and of fractional distillation of a product mixture of homologous cyclic ketones and epoxides. The alternative method of ring enlargement, diazotization of 1-(aminomethyl)-cyclohexanol (V), produces cycloheptanone conveniently and in moderate yield (60%)[2] but the synthesis of the requisite amino-

[1] Atomic Energy Commission Predoctoral Fellow, 1948–1950.

[1a] E. P. Kohler, M. Tishler, H. Potter and H. T. Thompson, THIS JOURNAL, **61**, 1059 (1939).

[2] (a) M. Tiffeneau, P. Weill and B. Tchoubar, *Compt. rend.*, **205**, 54 (1937); (b) B. Tchoubar, *ibid.*, **212**, 195 (1941); (c) B. Tchoubar, *Bull. soc. chim. France*, 160, 164, 169 (1949).