concentrated to yield a pale yellow oil that distilled at 144° (0.05 mm.). This oil crystallized from cold ether to give platelets of **4-hydroxy-3,5,5-trimethyl-Δ¹-pyrazoline 2-oxide** (**VII**), m.p. 92–93°.

Anal. Calcd. for $C_6H_{12}N_2O_2$: C, 49.98; H, 8.39; N, 19.43. Found: C, 49.85; H, 8.31; N, 19.75.

The n.m.r. spectrum of VII showed signals at 8.68 τ and 8.60 τ [$(CH_3)_2C$], at 8.40 τ (doublet, J = 6 c.p.s.; CH_3C—H), and a complicated band centering at 5.63 τ which showed a sharp band (*OH*) in the middle of a broad band (*H*C—OH, *H*—C—CH_3). The relative areas of the methyl bands and this unresolved band were 3:1.

B. When the preceding reduction was carried out in the same manner except that the mixture was heated under reflux for 3 hr. instead of stirring at room temperature, the only product obtained was a white solid, m.p. 73–75°, which proved to be identical to 3,5,5-trimethylisopyrazole 2-oxide,[5b] m.p. 77–79°. This same material could also be obtained from VII by heating the latter in ethanolic base for 15 min.

C. Treatment of VII with chromic acid in acetone[16] caused immediate oxidation at room temperature and IIc was isolated by ether extraction of the mixture and identified by infrared analysis and mixed melting point.

(16) A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 2548 (1953).

Aminonitriles. IV.[1] Preparation and Rearrangement of 3-Substituted 4-Imino-5,5-dimethylimidazolidine-2-thiones

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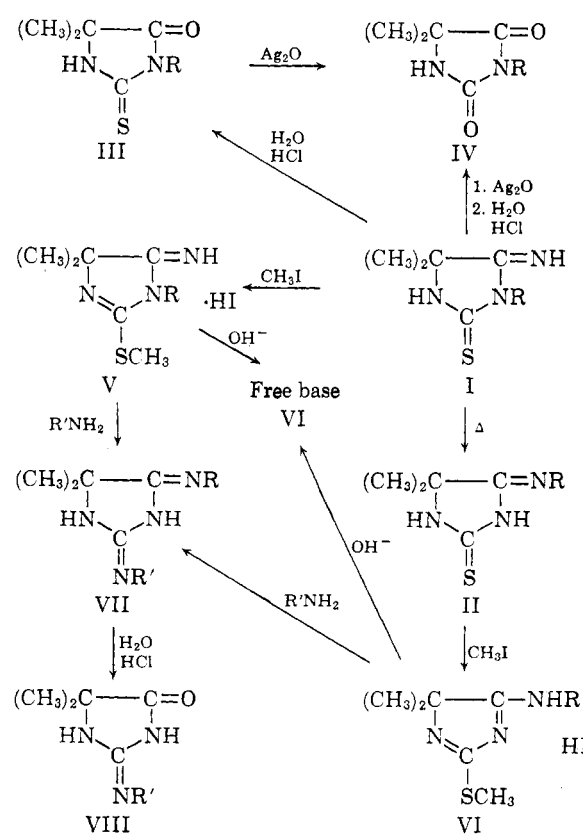
3-Substituted 4-imino-5,5-dimethylimidazolidine-2-thiones, which were prepared by the addition of isothiocyanates to α-aminoisobutyronitrile, rearranged to 4-substituted imino-5,5-dimethylimidazolidine-2-thiones on heating. Methylation of the 3-substituted 4-imino-5,5-dimethylimidazolidine-2-thiones gave the corresponding stable 2-methylmercapto-3-substituted-4-imino 5,5-dimethyl-2-imidazolinium salts. These salts in the presence of base rearranged to 2-methylmercapto-4-substituted amino-5,5-dimethylimidazoles. The 2-methylmercapto-4-substituted amino-5,5-dimethylimidazoles also were obtained directly by the methylation of 4-substituted imino-5,5-dimethylimidazolidine-2-thiones. The positional isomers (V and VI) of the 2-methylmercapto derivatives gave identical 2-substituted imino-4-substituted imino-5,5-dimethylimidazolidines on heating with primary amines.

Previously Cook, *et al.*,[2–4] demonstrated that isothiocyanates combine with α-aminonitriles to give 5-aminothiazoles. They found that the 2-substituted amino-5-aminothiazoles rearranged in the presence of base to 4-substituted 2-mercaptoimidazoles. The isomeric 3-substituted 4-amino-2-mercaptoimidazoles were presumed to be intermediates in this rearrangement. When 2-methylamino-5-aminothiazole was treated with sodium carbonate solution, the rearrangement stopped at this intermediate stage to give 3-methyl-4-amino-2-mercaptoimidazole.[4]

A recent investigation of the reactions of phenyl, benzyl, and 3,4-dichlorobenzyl isothiocyanates with α-aminoisobutyronitrile indicated that the resultart compounds were not the expected thiazoline derivatives. Their infrared spectra showed the presence of one rather than two —C=N— groups. Phenyl isothiocyanate and α-aminoisobutyronitrile in ether at room temperature or in refluxing ether for six hours gave the same compound. This compound was recovered unchanged after refluxing in ethanolic sodium ethoxide solution for one hour. It was hydrolyzed in aqueous hydrochloric acid



(1) Aminonitriles. III. M.-E. Kreling and A. F. McKay, *Can. J. Chem.*, **40**, 143 (1962).

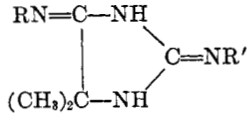
(2) A. H. Cook, J. D. Downer, and I. Heilbron, *J. Chem. Soc.*, 1262 (1948).

(3) C. W. Capp, A. H. Cook, J. D. Downer, and I. Heilbron, *ibid.*, 1340 (1948).

(4) A. H. Cook, J. D. Downer, and I. Heilbron, *ibid.*, 2028 (1948).

TABLE I

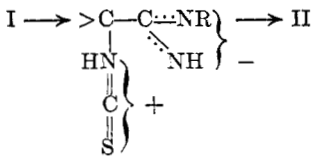
2,4-DI(SUBSTITUTED IMINO)-5,5-DIMETHYLIMIDAZOLIDINES



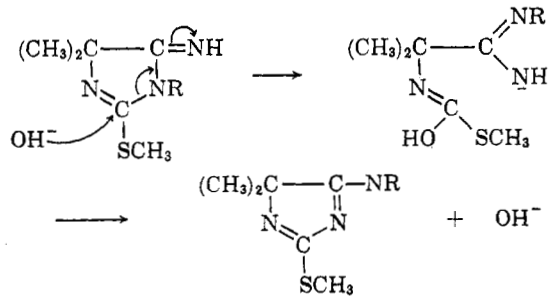
R′	R	M.p., °C.	Yield, %	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Halogen, % Calcd.	Halogen, % Found
Benzyl	Phenyl	132 and 163[a]	86	$C_{18}H_{20}N_4$	73.95	73.75	6.89	6.72	19.16	18.86		
		212[b]	83.4	$C_{18}H_{21}IN_4$	51.43	51.48	5.04	5.12	13.33	13.03	30.20	30.00
		212[c]		$C_{24}H_{23}N_7O_7$	55.31	55.20	4.45	4.43	18.81	18.91		
Phenyl	Benzyl	210[a]	46.6	$C_{18}H_{20}N_4$	73.95	73.90	6.89	6.77	19.16	18.64		
		205[c]		$C_{24}H_{23}N_7O_7$	55.31	55.34	4.45	4.53	18.81	18.81		
2-Cyano-ethyl	Phenyl	221.4[b]	87.3	$C_{14}H_{18}IN_5$	43.88	43.95	4.73	4.96	18.28	18.29	33.12	33.22
		233.4–234[c]	99.6	$C_{20}H_{20}N_8O_7$	49.59	49.57	4.16	4.34	23.13	23.24		
Benzyl	3,4-Dichloro-benzyl	182.5–183.5[b]	72.8	$C_{19}H_{21}ICl_2N_4$	45.34	45.26	4.21	4.09	11.14	10.86	39.31	39.14
		228[c]	100	$C_{25}H_{23}Cl_2N_7O_7$	49.68	49.62	3.84	3.90	16.23	15.85	11.73	11.95
Phenyl	3,4-Dichloro-benzyl	188–188.5[b]	100	$C_{18}H_{19}ICl_2N_4$	44.19	44.52	3.92	4.13	11.45	11.38	40.43	40.66
		216–217[c]	95.1	$C_{24}H_{21}Cl_2N_7O_7$	48.82	48.62	3.59	3.75	16.61	16.82	12.01	12.21
3,4-Di-chloro-benzyl	Phenyl	117–178[b]	80.7	$C_{18}H_{19}ICl_2N_4$	44.19	44.29	3.92	3.94	11.45	11.43	25.94	26.15
		211.5–212.5[c]	100	$C_{24}H_{21}Cl_2N_7O_7$	48.82	48.90	3.59	3.75	16.61	16.66	12.01	11.87
3,4-Di-chloro-benzyl	3,4-Di-chloro-benzyl	168–169[b]	77.5	$C_{19}H_{19}ICl_4N_4$	39.88	39.87	3.35	3.35	9.79	9.67	46.98	47.00
		207.5–208[c]	76	$C_{25}H_{21}Cl_4N_7O_7$	44.60	44.67	3.14	3.34	14.56	14.75	21.07	20.85

[a] Free base. [b] Iodide salts. [c] Picrates.

solution to 3-phenyl-5,5-dimethyl-2-thiohydantoin (III, R = C_6H_5). When it was treated first with silver oxide and then hydrolyzed, it gave 3-phenyl-5,5-dimethylhydantoin (IV, R = C_6H_5). These observations show that the original compound from the reaction of phenyl isothiocyanate with α-aminoisobutyronitrile was 3-phenyl-4-imino-5,5-dimethylimidazolidine-2-thione (I, R = C_6H_5). Compound I (R = C_6H_5) on heating rearranged to 4-phenylimino-5,5-dimethylimidazolidine-2-thione (II, R = C_6H_5). The structure of the latter compound was confirmed by hydrolysis to the known 5,5-dimethyl-2-thiohydantoin.[5] This rearrangement can be considered as an example of intramolecular anionotropy[6] in which an intermediate open chain zwitterion is involved in the rearrangement as follows



Methylation of compound I (R = C_6H_5) with methyl iodide gave 2-methylmercapto-3-phenyl-4-imino-5,5-dimethyl-2-imidazolinium iodide (V, R = C_6H_5). The isomeric 2-methylmercapto-4-phenylamino-5,5-dimethylimidazolium iodide (VI, R = C_6H_5) was obtained by treating 4-phenylimino-5,5-dimethylimidazolidine-2-thione with methyl iodide. Both of these isomers were converted into the same free base 2-methylmercapto-4-phenylamino-5,5-dimethylimidazole on treatment with alkali. The rearrangement of 2-methylmercapto-3-phenyl-4-imino-5,5-dimethylimidazole on treatment with base is undoubtedly initiated by nucleophilic attack of the OH^- at C-2 as follows:



The isomeric methylmercapto hydroiodides (V, R = C_6H_5 and VI, R = C_6H_5) also gave the same 2-substituted imino-4-phenylimino-5,5-dimethylimidazolidines on treatment with primary amines. Imidazolidine derivatives prepared in this manner are described in Table I.

2-Benzylimino-4-phenylimino-5,5-dimethylimidazolidine (VII, R = C_6H_5, R′ = $C_6H_5CH_2$) was hydrolyzed to 2-benzylimino-5,5-dimethyl-4-imidazolidone (VIII, R′ = $C_6H_5CH_2$) and 2-phenylimino-4-benzylimino-5,5-dimethylimidazolidine (VII, R = $C_6H_5CH_2$, R′ C_6H_5) was hydrolyzed to 2-phenylimino-5,5-dimethyl-4-imidazolidone (VIII, R′ = C_6H_5).

When 3-phenyl-4-imino-5,5-dimethylimidazolidine-2-thione (I, R = C_6H_5) was pyrolyzed in the presence of 3,4-dichlorobenzylamine, hydrogen

(5) H. C. Harrington, *J. Chem. Soc.*, 684 (1947).

(6) M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, p. 87.

Table II

Infrared Absorption Band (cm.$^{-1}$) Assignments[a]

Compound	Stretching modes N—H	Stretching modes C=N[b]	Bending modes N—H[c]
3-Phenyl-4-imino-5,5-dimethylimidazolidine-2-thione	3320, 3230	1702, 1672	1604, 1518
3-Benzyl-4-imino-5,5-dimethylimidazolidine-2-thione	3270, 3190	1670	1554, 1516
3-(3,4-Dichlorobenzyl)-4-imino-5,5-dimethylimidazolidine-2-thione	3305, 3200	1669	1568, 1526
4-Phenylimino-5,5-dimethylimidazolidine-2-thione	3190	1692, 1678	1598 (aryl), 1545, 1539
4-Benzylimino-5,5-dimethylimidazolidine-2-thione	3230, 3158	1625	1535, 1510
4-(3,4-Dichlorobenzylimino)-5,5-dimethylimidazolidine-2-thione	3245	1645	1612
2-Methylmercapto-3-phenyl-4-imino-5,5-dimethyl-2-imidazolinium iodide	3125	1688, 1617	1612, 1608, 1594 (aryl)
2-Methylmercapto-3-(3,4-dichlorobenzyl)-4-imino-5,5-dimethyl-2-imidazolinium iodide	3180	1687, 1611	1588 (aryl)
2-Methylmercapto-4-phenylamino-5,5-dimethylimidazolium iodide		1630	1582, 1536, 1512
2-Methylmercapto-4-benzylamino-5,5-dimethylimidazole	3370, 3210	1621	1602 (aryl), 1557, 1540
2-Methylmercapto-4-(3,4-dichlorobenzylamino)-5,5-dimethylimidazolium iodide	3180	1632	1515
2-Phenylimino-4-benzylimino-5,5-dimethylimidazolidine	3425	1680, 1615	1585, 1562
2-Benzylimino-4-phenylimino-5,5-dimethylimidazolidinium iodide	3380, 3150	1671, 1611	1580, 1560, 1532
2-Benzylimino-4-(3,4-dichlorobenzylimino)-5,5-dimethylimidazolidinium iodide	3351, 3110	1672, 1616	1537
2,4-Di(3,4-dichlorobenzylimino)-5,5-dimethylimidazolidinium iodide	3380, 3320, 3200, 3125	1676, 1620	1538
5,5-Dimethyl-2-thiohydantoin	3250, 3130	1748 (C=O)	
3-Phenyl-5,5-dimethyl-2-thiohydantoin	3315	1725 (C=O)	1602 (aryl), 1510
3-Phenyl-5,5-dimethylhydantoin	3210, 3095	1774 (C=O), 1723 (C=O)	1598 (aryl), 1640
2-Benzylimino-5,5-dimethyl-4-imidazolidone	3180	1642, 1695 (C=O)	1606 (aryl), 1570, 1520
2-Phenylimino-5,5-dimethyl-4-imidazolidone	3150, 3080	1655, 1692 (C=O)	1598 (aryl), 1572, 1526, 1507

[a] Infrared spectra were determined on Nujol mulls of the crystalline compounds. [b] C=N assignments except where indicated otherwise by group noted in brackets. [c] N—H bending assignments with exceptions noted in brackets. In some cases the differentiation between aryl and N—H bending bands is uncertain.

sulfide was evolved and a small yield of 2,4-di(3,4-dichlorobenzylimino) - 5,5 - dimethylimidazolidine was formed. 2,4-Di(α-naphthylmethylimino)-5,5-dimethylimidazolidine was prepared in a similar manner. This reaction is still under investigation.

Infrared Spectra.—The infrared absorption band assignments in Table II show that with the exception of the 2-methylmercapto derivatives all the double bonds of the imidazolidine derivatives are exocyclic. In the 2-methylmercapto-3-substituted 4-imino-5,5-dimethyl-2-imidazolinium iodides, one double bond is endocyclic while in the 2-methylmercapto-4-substituted amino-5,5-dimethylimidazolium iodides both double bonds are endocyclic.

Experimental[7]

α-Aminoisobutyronitrile [b.p. 62° (28 mm.)] was prepared in 64.4% yield by the method of Jacobson.[8]

3-Phenyl-4-imino-5,5-dimethylimidazolidine-2-thione.—Phenyl isothiocyanate (13.5 g., 0.1 mole) and α-aminoisobutyronitrile (8.4 g., 0.1 mole) in absolute ether (25 ml.) were heated under reflux for 6 hr. The crystalline product (m.p. 160–166°) was removed by filtration, yield 16.5 g. (75.3%). Three crystallizations from ethyl acetate raised the melting point to 163–163.5° with resolidification and remelting at 226–227°.

Anal. Calcd. for $C_{11}H_{13}N_3S$: C, 60.24; H, 5.97; N, 19.17; S, 14.62. Found: C, 60.17; H, 5.92; N, 19.10; S, 15.03.

The picrate (m.p. 203–205° dec.) was prepared in 53.3% yield in the usual manner from aqueous solution.

Anal. Calcd. for $C_{17}H_{16}N_6O_7S$: C, 45.53; H, 3.60; N, 18.74; S, 7.15. Found: C, 45.65; H, 3.83; N, 18.79; S, 7.03.

3-Phenyl-4-imino-5,5-dimethylimidazolidine-2-thione was recovered unchanged after refluxing for 1 hr. in alcoholic sodium ethoxide. In some cases a new crystalline modification melting at 173° was obtained. This higher melting form did not depress the melting point of a sample of the original 3-phenyl-4-imino-5,5-dimethylimidazoline-2-thione and the infrared spectra of the two forms were identical.

When phenyl isothiocyanate was added to α-aminoisobutyronitrile in ether at room temperature, the same product, 3-phenyl-4 - imino - 5,5-dimethylimidazolidine-2-thione, was obtained.

3-Benzyl-4-imino-5,5-dimethylimidazolidine-2-thione.—Equivalent molar quantities of benzyl isothiocyanate and α-aminoisobutyronitrile were heated under reflux in absolute ether for 10 hr. After standing at room temperature for 48 hr., the crystals were recovered by filtration, yield 62.5%. The product had a constant melting point of 148–149° after three crystallizations from aqueous methanol.

Anal. Calcd. for $C_{12}H_{15}N_3S$: C, 61.77; H, 6.48; N, 18.01; S, 13.74. Found: C, 61.60; H, 6.46; N, 18.04; S, 13.75.

3-(3,4-Dichlorobenzyl)-4-imino-5,5-dimethylimidazolidine-2-thione.—A solution of 3,4-dichlorobenzyl isothiocyanate[9] (6.5 g., 0.03 mole) and α-aminoisobutyronitrile

(7) All melting points are uncorrected. Microanalyses were performed by Micro-Tech Laboratories, Skokie, Illinois, and Dr. C. Daessle, Montreal, Quebec.

(8) R. A. Jacobson, *J. Am. Chem. Soc.*, **68**, 2628 (1946).

(2.5 g., 0.03 mole) in absolute ether (25 ml.) was heated under reflux for 25 hr. After the solution was evaporated to half volume, petroleum ether (25 ml.) was added. The crystals (m.p. 140–141°) were recovered by filtration, yield 78%. Crystallization from acetone–petroleum ether solution raised the melting point to 145–146°.

Anal. Calcd. for $C_{12}H_{13}Cl_2N_3S$: C, 47.70; H, 4.33; Cl, 23.47; N, 13.91; S, 10.61. Found: C, 47.48; H, 4.18; Cl, 23.89; N, 13.67; S, 10.80.

A picrate (m.p. 206–207°) was prepared in 64.8% yield from aqueous ethanol solution.

Anal. Calcd. for $C_{18}H_{16}Cl_2N_6O_7S$: C, 40.69; H, 3.03; Cl, 13.35; N, 15.82; S, 6.03. Found: C, 40.67; H, 3.07; Cl, 13.06; N, 15.77; S, 5.76.

Thermal Rearrangement of 3-Substituted 4-Imino-5,5-dimethylimidazolidine-2-thiones.—3-Phenyl-4-imino-5,5-dimethylimidazolidine-2-thione was heated at 220° for 2 hr., after which it melted with a single melting point of 226–227°, yield 89%. The melting point was unchanged by crystallization from aqueous ethanol. This product was identified as **4-phenylimino-5,5-dimethylimidazolidine-2-thione** by hydrolysis to the known 5,5-dimethyl-2-thiohydantoin (*vide infra*).

Anal. Calcd. for $C_{11}H_{13}N_3S$: C, 60.24; H, 5.97; N, 19.17; S, 14.62. Found: C, 60.48; H, 6.04; N, 18.70; S, 14.65.

3-(3,4-Dichlorobenzyl)-4-imino-5,5-dimethylimidazolidine-2-thione was rearranged thermally to **4-(3,4-dichlorobenzylimino)-5,5-dimethylimidazolidine-2-thione** (m.p. 235–235.2°) in 97.5% yield by heating at 170° for 1.25 hr. After 50 min. the melt resolidified. The cooled product was crystallized from ethanol (40 ml./g.).

Anal. Calcd. for $C_{12}H_{13}Cl_2N_3S$: C, 47.70; H, 4.33; Cl, 23.47; N, 13.91; S, 10.61. Found: C, 48.02; H, 4.47; Cl, 23.03; N, 13.67; S, 10.71.

4-Benzylimino-5,5-dimethylimidazolidine-2-thione (m.p. 241–242°) was prepared in 72.5% yield by heating 3-benzyl-4-imino-5,5-dimethylimidazolidine-2-thione at 160–200° at 5 mm. pressure for 90 min. The product was purified by crystallizing from methanol.

Anal. Calcd. for $C_{12}H_{15}N_3S$: C, 61.77; H, 6.48; N, 18.01; S, 13.74. Found: C, 61.86; H, 6.48; N, 17.86; S, 13.76.

2-Methylmercapto-4-phenylamino-5,5-dimethylimidazole.—Methyl iodide (0.42 g., 0.003 mole) and 4-phenylimino-5,5-dimethylimidazolidine-2-thione (0.5 g., 0.0023 mole) in methanol (7 ml.) were heated under reflux for 2.5 hr. The solution was diluted with ether until it became turbid. On standing overnight at room temperature, the solution deposited crystals (m.p. 189–197°), yield 0.79 g. (96%). Two crystallizations from methanol–ether solution raised the melting point to 205–206°.

Anal. Calcd. for $C_{12}H_{16}IN_3S$: C, 39.89; H, 4.47; I, 35.13; N, 11.63; S, 8.88. Found: C, 39.75; H, 4.44; I, 35.25; N, 11.32; S, 8.95.

The picrate (m.p. 224°) was prepared in 97% yield from absolute methanol solution.

Anal. Calcd. for $C_{18}H_{18}N_6O_7S$. C, 46.75; H, 3.92; N, 18.18; S, 6.94. Found: C, 46.91; H, 4.13; N, 17.87; S, 6.77.

The hydroiodide (m.p. 206°) was dissolved in aqueous methanol, and this solution was made alkaline with aqueous sodium hydroxide. This solution was extracted with chloroform and the chloroform solution of 2-methylmercapto-4-phenylamino-5,5-dimethylimidazole was evaporated to dryness, yield 96%. The crystalline residue, after two crystallizations from ethyl acetate, melted at 230°.

Anal. Calcd. for $C_{12}H_{15}N_3S$: C, 61.77; H, 6.48; N, 18.01; S, 13.74. Found: C, 61.94; H, 6.46; N, 17.92; S, 13.60.

(9) A. F. McKay, D. L. Garmaise, R. Gaudry, H. A. Baker, G. Y. Paris, R. W. Kay, G. E. Just, and R. Schwartz, *J. Am. Chem. Soc.*, **81**, 4328 (1959).

2-Methylmercapto-4-benzylamino-5,5-dimethylimidazole.—A solution of 4-benzylimino-5,5-dimethylimidazolidine-2-thione (1.25 g., 0.005 mole) and methyl iodide (0.9 g., 0.006 mole) in absolute methanol (35 ml.) was heated under reflux for 2 hr. After the solvent was removed *in vacuo*, the oily residue was dissolved in aqueous methanol and made alkaline with aqueous sodium hydroxide solution. This aqueous solution was extracted with chloroform and the chloroform extract was evaporated *in vacuo* to dryness. The solid (1.2 g., 91%) after crystallization from ethyl acetate melted at 166°.

Anal. Calcd. for $C_{13}H_{17}N_3S$: C, 63.13; H, 6.93; N, 16.99; S, 12.95. Found: C, 62.73; H, 6.83; N, 17.23; S, 13.05.

2-Methylmercapto-4-(3,4-dichlorobenzylamino)-5,5-dimethylimidazole.—4-(3,4-Dichlorobenzylimino)-5,5-dimethylimidazolidine-2-thione (2.8 g., 0.009 mole) and methyl iodide (1.71 g., 0.012 mole) in methanol (22 ml.) were heated under reflux for 1 hr. After water was added to the cooled reaction mixture, a crystalline precipitate formed, yield 81%. The melting point was raised from 81–82° to 82–83° by crystallizing from aqueous ethanol.

Anal. Calcd. for $C_{13}H_{16}ICl_2N_3S$: C, 35.15; H, 3.63; Hal., 44.53; N, 9.46; S, 7.22. Found: C, 34.88; H, 3.66; Hal., 44.54; N, 9.10; S, 6.91.

The picrate (m.p. 184.5–186°) was prepared in quantitative yield in the usual manner from aqueous solution. Two crystallizations from absolute ethanol raised the melting point to 187.8–188.2°.

Anal. Calcd. for $C_{19}H_{18}Cl_2N_6O_7S$: C, 41.84; H, 3.33; Cl, 13.00; N, 15.41; S, 5.88. Found: C, 41.68; H, 3.51; Cl, 12.90; N, 15.63; S, 5.85.

Methylation of 3-Phenyl-4-imino-5,5-dimethylimidazolidine-2-thione.—A solution of 3-phenyl-4-imino-5,5-dimethylimidazolidine-2-thione (2.14 g., 0.01 mole) and methyl iodide (1.5 g., 0.01 mole) in absolute methanol (25 ml.) was heated under reflux for 90 min. The cooled reaction mixture was diluted with ether (50 ml.) and allowed to stand overnight. The crystalline reaction product (m.p. 207–213°) was removed by filtration, yield 2.2 g. (61%). Two crystallizations from methanol–ether solution raised the melting point to 212–213°.

Anal. Calcd. for $C_{12}H_{16}IN_3S$: C, 39.89; H, 4.47; I, 35.13; N, 11.63; S, 8.88. Found: C, 40.05; H, 4.36; I, 35.16; N, 11.45; S, 8.87.

The product gave a crystalline picrate (m.p. 196°) in 95.5% yield from aqueous ethanol.

Anal. Calcd. for $C_{18}H_{18}N_6O_7S$: C, 46.75; H, 3.92; N, 18.18; S, 6.94. Found: C, 46.58; H, 3.95; N, 18.00; S, 7.06.

The crystalline hydroiodide of 2-methylmercapto-3-phenyl-4-imino-5,5-dimethyl-2-imidazoline (m.p. 213°) was dissolved in aqueous methanol, and the solution was made alkaline with aqueous sodium hydroxide. The precipitated product was removed by extraction with chloroform and the chloroform solution was evaporated to dryness *in vacuo*, yield 100%. After two crystallizations from ethyl acetate it melted at 230° alone and on admixture with a sample of 2-methylmercapto-4-phenylamino-5,5-dimethylimidazole (230°) prepared from 4-phenylimino-5,5-dimethylimidazolidine-2-thione (*vide supra*).

Methylation of 3-(3,4-Dichlorobenzyl)-4-imino-5,5-dimethylimidazolidine-2-thione.—3-(3,4-Dichlorobenzyl)-4-imino-5,5-dimethylimidazolidine-2-thione (3.4 g., 0.01 mole) and methyl iodide (1.6 g., 0.012 mole) in absolute methanol (10 ml.) were heated under reflux for 2 hr. Addition of ether (90 ml.) to the cooled solution gave 2.6 g. (52%) of crystalline product (m.p. 155–158°). Two crystallizations from methanol–ether (1:10) solution raised the melting point to 174–175°.

Anal. Calcd. for $C_{13}H_{16}ICl_2N_3S$: C, 35.15; H, 3.63; Hal., 44.53; N, 9.46; S, 7.22. Found: C, 35.20; H, 3.76; Hal., 44.22; N, 9.50; S, 7.11.

The picrate (m.p. 208–214°) was prepared in 89.7% yield in the usual manner from aqueous methanol. Two crystallizations from aqueous methanol raised the melting point to 216.5–218°.

Anal. Calcd. for $C_{19}H_{18}Cl_2N_6O_7S$: C, 41.84; H, 3.33; Cl, 13.00; N, 15.41; S, 5.88. Found: C, 42.15; H, 3.42; Cl, 12.62; N, 15.17; S, 5.68.

Hydrolysis of 4-Phenylimino-5,5-dimethylimidazolidine-2-thione.—4-Phenylimino-5,5-dimethylimidazolidine-2-thione (0.7 g., 0.0032 mole) in 30% aqueous hydrochloric acid (4 ml.) was heated under reflux for 25 min. The product (m.p. 171–174°) separated from solution on cooling and it was removed by filtration, yield 56.6%. The crude 5,5-dimethyl-2 thiohydantoin was purified by crystallizing from acetone–*n*-hexane solution. The final melting point was 179.6–180° (lit.,[5] 178–179°).

2-Benzylimino-4-phenylimino-5,5-dimethylimidazolidine. Method A.—A solution of 2-methylmercapto-3-phenyl-4-imino-5,5-dimethyl-2-imidazolinium iodide (2.6 g., 0.007 mole) and benzylamine (1.27 g., 0.012 mole) in absolute ethanol (25 ml.) was refluxed for 48 hr. The cooled reaction mixture was diluted with water and made alkaline with aqueous sodium hydroxide. This aqueous solution was extracted with chloroform (three times) and the combined chloroform extracts were taken to dryness *in vacuo*. The crude 2-benzylimino-4-phenylimino-5,5-dimethylimidazolidine was crystallized from ethyl acetate, yield 1.8 g. (86%). The free base had a double melting point of 132 and 163°.

The picrate (m.p. 212°) was prepared in 89.5% yield from aqueous ethanol.

Method B.—2-Methylmercapto-4-phenylamino-5,5-dimethylimidazolium iodide (1.08 g., 0.003 mole) and benzylamine (0.32 g., 0.003 mole) in absolute ethanol were heated under reflux *ca.* 16 hr. Ether was added to the cooled solution and the crystalline precipitate (190°) was removed by filtration, yield 1.05 g., (83.4%). After crystallization from ethanol–ether solution, the melting point was 212°.

This hydroiodide was converted into the free base as described above in method A. The free base, after crystallizing from ethyl acetate melted with a double melting point of 132° and 163°. It did not depress the melting point of 2-benzylimino-4-phenylimino-5,5-dimethylimidazolidine (m.p. 132° and 163°) obtained by method A.

The picrate (m.p. 212°) also did not depress the melting point of the picrate of 2-benzylimino-4-phenylimino-5,5-dimethylimidazolidine (m.p. 212°) obtained in the reaction by method A.

Other imidazolidine derivatives prepared by method B are listed in Table I.

Condensation of Amines with 3-Phenyl-4-imino-5,5-dimethylimidazolidine-2-thione.—An intimate mixture of 3-phenyl-4-imino-5,5-dimethylimidazolidine-2-thione (2.19 g., 0.01 mole) and 3,4-dichlorobenzylamine (2.58 g., 0.0147 mole) was heated at 225° for 50 min. The cooled reaction mixture was extracted with ether (4 × 25 ml.). A residue of gray powder (m.p. 60–63°) remained, yield 0.5 g. (13.3%). The powder in ethanol was treated with an ethanolic solution of picric acid. After the crystalline picrate was crystallized from absolute ethanol it melted at 208°. This picrate did not depress the melting point of the picrate (m.p. 208°) of 2,4-di(3,4-dichlorobenzylimino)-5,5-dimethylimidazolidine prepared by the reaction of 2-methylmercapto-4-(3,4-dichlorobenzylamino)-5,5-dimethylimidazolium iodide with 3,4-dichlorobenzylamine (*cf.* Table I).

When 3-phenyl-4-imino-5,5-dimethylimidazolidine-2-thione (1.27 g., 0.005 mole) and α-naphthylamine (1.7 g., 0.01 mole) were heated in the same manner and the product treated as above 0.6 g. (25.5%) of light gray powder (m.p. 90–95°) was obtained. The powder in ethanol on addition of ethanolic picric acid solution gave a crystalline picrate (m.p. 144–145°). Two crystallizations from absolute ethanol raised the melting point to 205.5–206.5°.

Anal. Calcd. for $C_{33}H_{29}N_7O_7$: C, 62.36; H, 4.60; N, 15.43. Found: C, 62.61; H, 4.82; N, 15.18.

2-Benzylimino-5,5-dimethyl-4-imidazolidone.—2-Benzylimino-4-phenylimino-5,5-dimethylimidazolidine (0.7 g., 0.0024 mole) in 30% aqueous hydrochloric acid solution (7 ml.) was heated under reflux for 30 min. The cooled reaction mixture was made alkaline with aqueous sodium hydroxide and the crystalline precipitate (m.p. 241–243°) was removed by filtration, yield 0.47 g. (90.4%). Crystallization from ethyl acetate raised the melting point to 244–245°.

Anal. Calcd. for $C_{18}H_{19}N_3O$: C, 66.34; H, 6.96; N, 19.34. Found: C, 66.12; H, 6.68; N, 19.26.

2-Phenylimino-5,5-dimethyl-4-imidazolidone.—2-Phenylimino-4-benzylimino-5,5-dimethylimidazolidine (0.7 g., 0.0024 mole) was hydrolyzed to 2-phenylimino-5,5-dimethyl-4-imidazolidone in 88% yield by the method described above for the preparation of 2-benzylimino-5,5-dimethyl-4-imidazolidone. The melting point was raised from 281 to 284° by crystallizing from ethyl acetate–methanol solution.

Anal. Calcd. for $C_{11}H_{13}N_3O$: C, 65.00; H, 6.45; N, 20.68. Found: C, 65.08; H, 6.55; N, 20.79.

Hydrolysis of 3-Phenyl-4-imino-5,5-dimethylimidazolidine 2-thione.—When 3-phenyl-4-imino-5,5-dimethylimidazolidine-2-thione (0.5 g., 0.0023 mole) was hydrolyzed under the conditions described above for the preparation of 2-benzylimino-5,5-dimethyl-4-imidazolidone, 3-phenyl-5,5-dimethyl-2-thiohydantoin was obtained in 95.5% yield. The melting point was raised from 170 to 174–175° by crystallizing from water.

Anal. Calcd. for $C_{11}H_{12}N_2OS$: C, 59.97; H, 5.49; N, 12.73; S, 14.55. Found: C, 59.64; H, 5.50; N, 12.96; S, 14.53.

3-Phenyl-5,5-dimethylhydantoin.—Freshly precipitated moist silver oxide, which was prepared by treating silver nitrate (1 g.) with aqueous sodium hydroxide, was added to 3-phenyl-4-imino-5,5-dimethylimidazolidine-2-thione (0.5 g., 0.0023 mole) in absolute ethanol (15 ml.). After the mixture had been heated under reflux for 90 min., it was filtered through Celite and the filter cake was thoroughly washed with ethanol. The dark brown ethanolic filtrate was refluxed for 1 min. in the presence of charcoal, and the mixture again was filtered through Celite. The filtrate was taken to dryness *in vacuo*, and the residue was dissolved in 30% hydrochloric acid (10 ml.). After the solution was heated under reflux for 15 min., it was taken to dryness *in vacuo*. The product was triturated with absolute ethanol to remove ammonium chloride. The ethanol solution was heated with charcoal and filtered. The filtrate was taken to dryness and the product was crystallized from aqueous methanol. The final melting point was 163–165°, yield 68.8%.

Anal. Calcd. for $C_{11}H_{12}N_2O_2$: C, 64.69; H, 5.93; N, 13.71. Found: C, 64.79; H, 5.67; N, 13.64.

3-Phenyl-5,5-dimethylhydantoin (m.p. 164–165°) was prepared also from 3-phenyl-5,5-dimethyl-2-thiohydantoin by heating with moist silver oxide in ethanol. An admixture of samples of 3-phenyl-5,5-dimethylhydantoin prepared by these two procedures gave no depression in melting point.

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