tassium carbonate solution which was separated and extracted with methylene chloride. The combined organic extracts were dried and the solvent was removed. The residue crystallized from ether in long colorless needles: 0.80 g. (39.4% yield); m.p. 126–126.5°; and infrared absorption, 3160 (NH stretching) and 1635 cm.$^{-1}$ (C=N stretching in nonresonating systems).

Anal. Calcd. for $C_8H_{15}N_3O$: C, 56.78; H, 8.93; N, 24.84. Found: C, 56.98; H, 9.24; N, 24.63.

2,2,6-Triethyl-4-methoxy-1,2-dihydro-*s*-triazine (I, $R_1 = R_2 = C_2H_5$).—A mixture of 1.38 g. of isopropyl propionimidate, 2.94 g. of O-methylisourea *p*-toluenesulfonate, 5 ml. of diethyl ketone, and 15 ml. of benzene was heated under reflux and stirred for 8 hr. Work-up in the manner described above yielded 1.93 g. of recovered O-methylisourea salt and, after crystallization from ether, 0.065 g. (2.7%) of I ($R_1 = R_2 = C_2H_5$) in long colorless prisms, m.p. 142–143.5°. This was shown through comparison of infrared spectra and mixture melting point to be identical with a sample, m.p. 143–145°, obtained by a different route.[1a]

2,6-Diethyl-4-methoxy-2-methyl-1,2-dihydro-*s*-triazine (I, $R_1 = CH_3$; $R_2 = C_2H_5$).—A mixture of 1.38 g. of isopropyl propionimidate and 2.94 g. of O-methylisourea *p*-toluenesulfonate in 5 ml. of methyl ethyl ketone and 10 ml. of 2-propanol became homogeneous at reflux. After heating under reflux for 2.5 hr. and work-up in the manner described above, 1.24 g. of O-methylisourea salt was recovered. Evaporation of the methylene chloride extract gave 1.27 g. of crude product, which on crystallization from pentane afforded 0.74 g. (33.7%) of I ($R_1 = CH_3$; $R_2 = C_2H_5$) in needles and hexagonal prisms: m.p. 121–122°; infrared absorption, 3120 and 1635 cm.$^{-1}$.

Anal. Calcd. for $C_9H_{17}N_3O$: C, 58.98; H, 9.35; N, 22.93. Found: C, 59.12; H, 9.14; N, 22.40.

The Preparation of Hydrazidines and *as*-Triazines Related to Substituted 2-Cyanopyridines[1]

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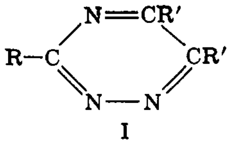
Received October 19, 1964

The preparation of hydrazidines of the formula RC(=NH)NHNH$_2$ has previously been accomplished by the action of hydrazine on the corresponding thioamide[2] or imido ether.[3,4] Less commonly (as in the case of cyanothiazole[4]) they have been prepared by direct action of hydrazine on the nitrile.

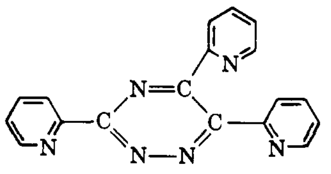
In this laboratory the latter procedure has been applied successfully to 2-cyanopyridine and several of its substitution products as well as 2-cyanoquinoline, 2-cyanopyrimidine, and 2-cyano-1,10-phenanthroline. (The preparation of the last-mentioned compound as well as that of 5-cyano-1,10-phenanthroline is described in the Experimental section.) The resulting hydrazidines, which contain the "ferroin" group, =N—C=C—N=, give a deep red color with Fe(II).

It has further been found that the above hydrazidines with the exception of that from 2-cyanopyrimidine condense readily with benzil and pyridil to form 3,5,6-trisubstituted *as*-triazines of formula I.



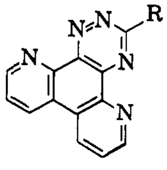
I

Thus, II, resulting from the action of the hydrazidine from 2-cyanopyridine and pyridil, containing three ferroin groups, gives a very sensitive test for Fe(II).



II

By condensing the hydrazidines with 4,7-phenanthroline-5,6-dione,[5] a number of 3-substituted *as*-triazino[5,6-*f*][4,7]phenanthrolines (III) were prepared.

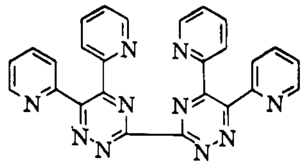


III

Most of these formed with Fe(II) very deep blue complexes.

Previously 5,6-diphenyl-3(3- and 4-pyridyl)-*as*-triazines have been prepared by the action of the corresponding acylhydrazine with benzil and ammonia.[6,7]

We have also prepared tetrakis(2-pyridyl)-3,3′-bi(*as*-triazine) (IV) by the action of oxamide dihydrazone, $H_2N\text{-}N{=}C(NH_2)(NH_2)C{=}N{-}NH_2$, on pyridyl. The corresponding tetraphenyl derivative has previously been reported.[8]



IV

For the preparation of oxamide dihydrazone the action of 95% hydrazine in ethanol on dithiooxamide was found simpler than the previous method (cyanogen and hydrazine[8]).

Experimental

Preparation of Hydrazidines.—A mixture of 0.05 mole of nitrile, 9 ml. of ethanol, and 15 ml. of 95% hydrazine was stirred at room temperature for 2 hr. It was then diluted with an equal volume of water, extracted with ether, and dried over anhydrous sodium sulfate. After removal of ether, the residue was crystallized from the solvent indicated in Table I. The hydrazidines from 2-cyano-4-phenylpyridine, 2-cyanoquinoline, and 2-cyano-1-10-phenanthroline precipitated out on addition of water, and no ether extraction was necessary. In the case of the last-mentioned compound, the proportions of nitrile, 95% hydrazine, and ethanol were 0.008 mole, 5 ml., and 5 ml., respectively. The hydrazine from 2-cyanothiazole was prepared according to the directions of Libman and Slack.[4]

Preparation of 3-Substituted 5,6-Diphenyl-*as*-triazines.—Mixtures of 0.02 *M* quantities of hydrazidine and benzil in 25 ml.

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[1] This work was supported by a grant (G 9645) from the National Science Foundation.

[2] W. Van der Burg, *Rec. trav. chim.*, **74**, 257 (1955).

[3] A. Pinner, *Ber.*, **27**, 985 (1894); *Ann.*, **297**, 221 (1897).

[4] D. Libman and R. Slack, *J. Chem. Soc.*, 2253 (1956).

[5] J. Druey and P. Schmidt, *Helv. Chim. Acta*, **33**, 1085 (1950).

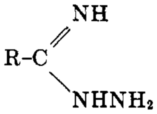
[6] P. Laakso, R. Robinson, and H. Vandrewala, *Tetrahedron*, **1**, 103 (1957).

[7] C. Atkinson and H. Cossey, *J. Chem. Soc.*, 1805 (1962).

[8] G. Dedichen, *Avhandl. Norske Videnskaps-Akad. Oslo*, **5**, 42 (1936); *Chem. Abstr.*, **31**, 4985^3 (1937).

TABLE I

HYDRAZIDINES

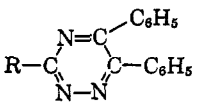


R	Yield, %	M.p., °C.	Crystn. solvent	Formula	Calcd., % C	Calcd., % H	Found, % C	Found, % H
2-Pyridyl	66.7	95–96[a]	Benzene	$C_6H_8N_4$				
4-Methyl-2-pyridyl	72.4[b]	100–101	Benzene	$C_7H_{10}N_4$	56.00	6.67	56.36	6.28
4-Ethyl-2-pyridyl	69.0	66–67	Petr. ether	$C_8H_{12}N_4$	58.54	7.32	58.57	7.25
4-Phenyl-2-pyridyl	84.4	126–127	Benzene	$C_{12}H_{12}N_4$	67.92	5.66	68.39	5.64
2-Quinolyl	90.3	191–192	Ethanol	$C_{10}H_{10}N_4$	64.47	5.42	64.74	5.67
2-Pyrimidyl	5.7	109–110	Benzene	$C_5H_7N_5$	43.80	5.11	43.75	5.36[c]
2-(1-10-Phenanthrolyl)	66.7[d]	192–193 dec.	Water	$C_{13}H_{11}N_5 \cdot 2H_2O$	57.14	5.54	57.56	5.52[e]

[a] Lit.[2] m.p. 97–98°. [b] Based on product, m.p. 98–99°. [c] *Anal.* Calcd.: N, 51.09. Found: N, 51.08. [d] Based on product, m.p. 190–191° dec. [e] *Anal.* Calcd.: N, 25.64. Found: N, 25.49.

TABLE II

3-SUBSTITUTED 5,6-DIPHENYL-*as*-TRIAZINES

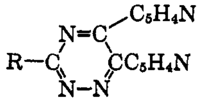


R	Yield, %	M.p., °C.	Crystn. solvent	Formula	Calcd., % C	Calcd., % H	Found, % C	Found, % H
2-Pyridyl	56.7	189–190	Ethanol	$C_{20}H_{14}N_4$	77.42	4.55	77.66	4.59
4-Methyl-2-pyridyl	84.4	169–170	Methyl Cellosolve–water	$C_{21}H_{16}N_4$	77.74	4.98	77.29	5.00
4-Ethyl-2-pyridyl	64.3	150–151	Methyl Cellosolve	$C_{22}H_{18}N_4$	78.06	5.37	78.20	5.40
4-Phenyl-2-pyridyl	69.4	192–193	Ethanol	$C_{26}H_{18}N_4$	80.78	4.70	80.30	4.56
2-Quinolyl	45.9	188–189	Acetone	$C_{24}H_{16}N_4$	79.98	4.48	79.94	4.42
2-Thiazolyl	63.6	229–230	Dimethylformamide	$C_{18}H_{12}N_4S$	68.33	3.82	68.40	3.89[a]

[a] *Anal.* Calcd.: N, 17.73. Found: N, 17.95.

TABLE III

3-SUBSTITUTED 5,6-BIS(2-PYRIDYL)-*as*-TRIAZINES



R	Yield, %	M.p., °C.	Crystn. solvent	Formula	Calcd., % C	Calcd., % H	Found, % C	Found, % H
2-Pyridyl	47.1	186–187	Methyl Cellosolve	$C_{18}H_{12}N_6$	69.23	3.88	69.29	3.84
4-Methyl-2-pyridyl	57.7	204–205	Methyl Cellosolve–water	$C_{19}H_{14}N_6$	69.94	4.29	69.61	4.17
4-Ethyl-2-pyridyl	26.8	169–170	Ethanol–water	$C_{20}H_{16}N_6$	70.59	4.74	70.28	4.88
4-Phenyl-2-pyridyl	75.7	171–172	Methyl Cellosolve–water	$C_{24}H_{16}N_6$	74.23	4.12	74.57	4.37
2-Quinolyl	54.0	176–177	Dimethylformamide–water	$C_{22}H_{14}N_6$	72.93	3.87	72.92	3.89
2-(1-10-Phenanthrolyl)	68.8	215–216	Ethanol	$C_{25}H_{15}N_7 \cdot H_2O$	69.61	3.98	69.51	3.98[a]
2-Thiazolyl	72.7	233–234	Dimethylformamide	$C_{16}H_{10}N_6S$	60.38	3.14	59.58	2.52[b]

[a] *Anal.* Calcd.: N, 22.74. Found: N, 22.67. [b] *Anal.* Calcd.: N, 26.41. Found: N, 26.24.

of ethanol were allowed to stand overnight. The resulting precipitates were removed by filtration and crystallized from the solvents indicated in Table II. In the case of the 2-quinolyltriazine, it was necessary to remove a high-melting impurity.

Preparation of 3-Substituted 5,6-Di(2-pyridyl)-*as*-triazines.—The procedure was similar to that for the diphenyl derivatives. The crystallizing solvents are indicated in Table III.

Preparation of 3-Substituted *as*-Triazino[5,6-*f*][4,7]phenanthrolines.—Mixtures of 0.005 *M* quantities of hydrazidine and 4,7-phenanthroline-5,6-dione in 25 ml. of ethanol were heated under reflux for 2 hr. The insoluble material was then removed by filtration and crystallized from dimethylformamide (Table IV).

Tetrakis(2-pyridyl)-3,3′-bi(*as*-triazine).—A mixture of 2.6 g. of dithiooxamide, 12 ml. of ethanol, and 3 ml. of 95% hydrazine was warmed for 5 min. on a steam bath. After copious evolution of hydrogen sulfide, the residue was crystallized from ethanol–water, yielding 1.7 g. of crystals melting over 300° (lit.[8] m.p. over 300°).

A mixture of 1.2 g. of the above oxamide dihydrazone, 4 g. of pyridil, and 25 ml. of ethanol was heated on a steam bath for 3 hr., cooled, and filtered. After crystallization from dimethylformamide, 4.2 g. (87.5%) of pure product was obtained, melting at 278–279°.

Anal. Calcd. for $C_{26}H_{16}N_{10}$: C, 66.67; H, 3.44. Found: C, 66.23; H, 3.63.

2-Cyano-1,10-phenanthroline.—A mixture of 2.5 g. of 2-chlorophenanthroline[9] and 1.5 g. of cuprous cyanide was heated in a

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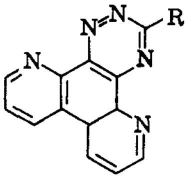
[9] P. Karrer and A. Pletscher, *Helv. Chim. Acta*, **31**, 786 (1948).

TABLE IV

as-TRIAZINO[5,6-*f*][4,7]PHENANTHROLINES



R	Yield, %	M.p., °C.	Crystn. solvent	Formula	Calcd., % C	Calcd., % H	Found, % C	Found, % H
2-Pyridyl	50.0	325	Dimethylformamide	$C_{18}H_{10}N_6$	69.68	3.25	69.58	3.43
4-Methyl-2-pyridyl	61.7	321–322	Dimethylformamide	$C_{19}H_{12}N_6$	70.36	3.63	70.15	3.68
4-Phenyl-2-pyridyl	65.9	358–359	Dimethylformamide	$C_{24}H_{14}N_6$	74.55	3.63	74.24	3.78
2-Thiazolyl	62.5	348–349	Dimethylformamide	$C_{16}H_8N_6S\cdot H_2O$	57.49	2.99	57.65	3.19[a]

[a] *Anal.* Calcd.: N, 25.15. Found: N, 25.33.

test tube at 260° for 5 hr. After cooling, the resulting solid was finely powdered and suspended in 30 ml. of a saturated solution of potassium cyanide. After standing overnight the solid was removed by filtration, dried, and extracted repeatedly with hot benzene. Removal of the benzene and crystallization of the residue from methanol yielded 1.0 g. of material melting at 234° (41.8%). An analytical sample melted at 235–236°.

Anal. Calcd. for $C_{13}H_7N_3$: C, 76.10; H, 3.41. Found: C, 75.85; H, 3.66.

5-Cyano-1,10-phenanthroline.—The procedure was the same as for 2-cyano-1,10-phenanthroline except that the starting product was 5-bromo-1,10-phenanthroline. From 3 g. of the latter compound and 1.5 g. of cuprous cyanide there was obtained 1.2 g. (50.6%) of 5-cyano-1,10-phenanthroline, melting at 212–213° after crystallization from benzene. The analytical sample was dried to constant weight at 100°.

Anal. Calcd. for $C_{13}H_7N_3$: C, 76.10; H, 3.41. Found: C, 76.27; H, 3.64.

Acknowledgment.—The author acknowledges the contribution of Mr. Ben Klodell to the earlier stages of this work.

Alkylation of Organic Disulfides[1]

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Received September 18, 1964

The reaction of disulfides with alkyl halides has been demonstrated to proceed with the ultimate formation of trialkylsulfonium salts.[3] The process is slow at room temperature but may be accelerated by the addition of mercuric iodide as catalyst.[4] The process proposed for the formation of the sulfonium salt involves initial alkylation on sulfur followed by decomposition of the resulting salt to the sulfonium halide (eq. 1).[5,6] Evidence for this is found in the isolation of the mercuric iodide double salt of diethylethylthiosulfonium iodide from the reaction of ethyl iodide and diethyl disulfide in the presence of mercuric iodide.[5] Prolonged treatment of the reactants resulted in the corresponding sulfonium salt. It has also been observed that the reactivity of alkyl halides toward sulfides is greater than toward disulfides[7] and that the reaction is first order in disulfide.[8]

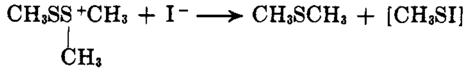
$$RSSR + R'X \longrightarrow RR'S^+SR\ X^- \longrightarrow R'_2RS^+X^- \quad (1)$$

We have recently reported the formation of a stable alkylated disulfide, dimethylmethylthiosulfonium 2,4,6-trinitrobenzenesulfonate (1) from the reaction of methyl disulfide with trimethyloxonium 2,4,6-trinitrobenzenesulfonate.[9] We now wish to establish the extent of the applicability of this rapid and facile means of alkylating disulfides.

When methyl disulfide was treated with trimethyloxonium 2,4,6-trinitrobenzenesulfonate, alkylation occurred on sulfur without subsequent cleavage of the sulfur–sulfur bond (eq. 2). When alkylated disulfide 1 (where R = R′ = CH_3) was dissolved in a solvent containing iodide ion, immediate formation of iodine, methyl sulfide, and methyl disulfide took place (eq. 3 and 4).[9] This suggests that it is the presence of iodide as the counter ion in previous preparations reported in the literature[3] that initiates the decomposition of the alkylated disulfides, probably through a displacement reaction involving attack of iodide ion on sulfur.

$$RSSR + R'_3O^+X^- \longrightarrow \underset{1}{RR'S^+SR\ X^-} \longrightarrow \underset{2}{RR'_2S^+X^-} \quad (2)$$

X = 2,4,6-trinitrobenzenesulfonate



$$CH_3S\underset{\displaystyle CH_3}{\underset{|}{S^+}}CH_3 + I^- \longrightarrow CH_3SCH_3 + [CH_3SI] \quad (3)$$

$$2CH_3SI \longrightarrow CH_3SSCH_3 + I_2 \quad (4)$$

The methylation reaction has been applied to ethyl, *n*-propyl, *sec*-butyl, *n*-butyl, phenyl, *p*-tolyl, and *p*-anisyl disulfides (Table I).

Ethyl disulfide was found to react in the same manner as its methyl analog, yielding only the ethylmethylethylthiosulfonium salt. With higher homologs, or with aryl disulfides, the only pure compound isolated in the alkylation reaction was the sulfonium salt 2, in

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[1] Supported in part by Grant GM 8185 from the National Institutes of Health, U. S. Public Health Service.

[2] Abstracted in part from the Ph.D. Thesis of D. J. Pettitt.

[3] J. Goerdeler in "Methoden der Organischen Chemie" (Houben-Weyl), E. Müller, Ed., Georg Thieme Verlag, Stuttgart, 1955, p. 182.

[4] Hilditch and Smiles[5] report that in the reaction of ethyl iodide with ethyl disulfide no visible change occurs for 2 or 3 months. At the end of 3 years the only product isolated was the triethylsulfonium salt. This compares with a reaction time of 3 days in the presence of mercuric iodide.

[5] T. P. Hilditch and S. Smiles, *J. Chem. Soc.*, **91**, 1394 (1907).

[6] O. Hass and G. Daugherty, *J. Am. Chem. Soc.*, **62**, 1004 (1940).

[7] M. L. Selker and A. R. Kemp, *Ind. Eng. Chem.*, **36**, 16 (1944).

[8] W. Scheele and W. Triebel, *Kautschuk Gummi*, **11**, WT 127 (1958).

[9] D. J. Pettitt and G. K. Helmkamp, *J. Org. Chem.*, **28**, 2932 (1963); **29**, 2702 (1964).