isopropoxide in isopropyl alcohol was added 0.63 g (2.5 mmol) of *N*-(*tert*-butylsulfinyl)phthalimide. After 0.5 hr of stirring at room temperature, the isopropyl alcohol was evaporated *in vacuo*. The resulting solid foam was taken up in 40 ml of pentane and precipitation of a white solid occurred on cooling. Filtration gave 0.75 g (90%) of the sodium salt **29**, mp 159° dec.

A portion of this material (0.33 g, 1 mmol) was then dissolved in 5 ml of water and acidified to Congo Red end point with hydrochloric acid. The resulting precipitate was filtered and washed with water to furnish 0.25 g (80% of theoretical yield based on the sodium salt **29**) of the amide **30**, mp 115–116°. The product was recrystallized from chloroform–petroleum ether to provide an analytical sample of unchanged melting point.

Acknowledgment.—We thank the National Research Council of Canada and the Defense Research Board of Canada (Grant No. 9530-97) for financial support of this work.

Registry No.—**2** (R = $C_6H_5CH_2$), 14204-26-3; **2** (R = CH_3), 40167-20-2; **2** (R = C_2H_5), 17796-70-2; **2** (R = *i*-C_3H_7), 17796-72-4; **2** (R = *n*-C_4H_9), 17796-73-5; **2** (R = *t*-C_4H_9), 17796-75-7; **2** (R = C_6H_5), 14204-27-4; **2** (R = *p*-$CH_3C_6H_4$), 15199-26-5; **2** (R = $CH_3O_2CCH_2$), 42300-49-2; **2** (R = *i*-C_3H_7S), 33704-40-4; **4**, 40167-14-4; **5**, 40167-13-3; **6**, 40167-12-2; **7**, 40739-92-2; **8**, 40318-14-7; **9**, 40167-16-6; **10**, 40167-15-5; **11**, 42300-58-3; **12**, 42300-59-4; **13**, 42300-60-7; **15**, 42300-61-8; **16**, 921-77-7; **17**, 42300-63-0; **18**, 35810-04-9; **19**, 40167-17-7; **20**, 42300-66-3; **21**, 42300-67-4; **23**, 673-80-3; **24**, 1859-03-6; **25**, 22598-57-8; **26**, 670-98-4; **27**, 42300-72-1; **28**, 42300-73-2; **29**, 42300-74-3; **30**, 42300-75-4; piperidine, 110-89-4; diethylamine, 109-89-7; *N*-methylbutylamine, 110-68-9; cyclohexylamine, 108-91-8; morpholine, 110-91-8; piperazine, 110-85-0.

Reaction of 4-Substituted Pyridines with Sulfenyl Chlorides[1]

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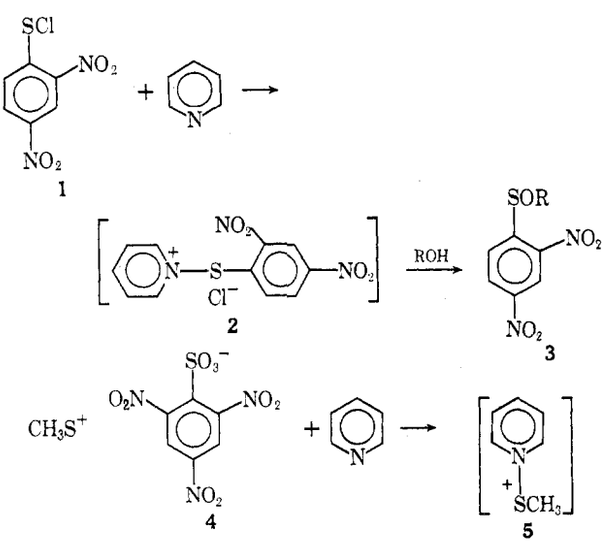
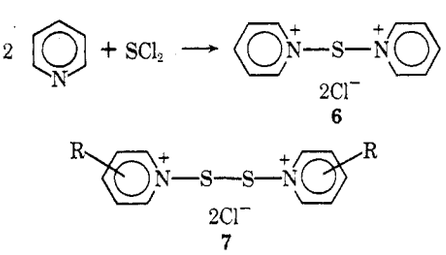
The reaction of 4-alkylpyridines with two substituents on the side-chain α carbon and arylsulfenyl chlorides gave α,α-disubstituted 4-pyridylmethyl aryl sulfides in 48–95% yield. When trichloromethanesulfenyl chloride and 4-benzhydryl- or 4-isopropylpyridine were allowed to react, diphenyl-4-pyridylmethyl or 2-(4-pyridyl)-2-propyl chloride were formed in 99 and 95% yield, respectively, while reaction of these 4-alkylpyridines with sulfur monochloride gave diphenyl-4-pyridylmethyl disulfide (~66%) or 2-(4-pyridyl)-2-propyl disulfide (82%). Analogous 3-alkyl- and 2-alkylpyridines failed to react with any of the above sulfenyl chlorides. A proposed rationalization of these reaction products entails formation of thiopyridinium ions and follows a pathway similar to the rearrangement of 4-alkylpyridine *N*-oxides and acid anhydrides.

The formation of *N*-arylthiopyridinium salts has been proposed by Kharasch[3] to explain pyridine catalysis in the conversion of 2,4-dinitrobenzenesulfenyl chloride (**1**) and alcohols to sulfenate esters **3**; however, attempts to isolate **2** were unsuccessful. More recently,



Helmkamp and coworkers[4] implied the formation of the *N*-methylthiopyridinium cation (**5**) when pyridine was added to a solution of **4** in nitrobenzene or nitromethane. The nmr upfield shift of the SCH_3 resonance supported structure **5** but no salt was isolated. However, crystalline *N*-thiopyridinium salts of structure **6** and **7** have been obtained from the reaction of pyridine



and sulfur dichloride[5] or sulfur monochloride.[6,7] In expanding our interest from *N*-oxypyridinium salts[8,9] to *N*-thiopyridinium salts we have investigated the reaction of various sulfenyl chlorides with a number of alkylpyridines and describe the results in this paper.

When a 2:1 molar solution of 4-benzhydrylpyridine (**15**) and 2,4-dinitrobenzenesulfenyl chloride (**1**), respectively, in dry ethylene chloride was stirred at room temperature for 1 hr, the reaction mixture gave a 48% yield of diphenyl-4-pyridylmethyl 2,4-dinitrophenyl sulfide (**16**) and a 38% yield of 2,4-dinitrophenyl disulfide (**9**). This reaction had been extended to other

(1) Presented in part before the Organic Division at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971.

(2) Abstracted from a portion of the Ph.D. Dissertation submitted by J. N. R. in April 1973 at West Virginia University.

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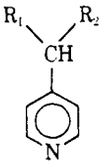
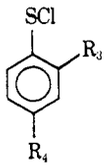
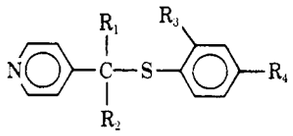
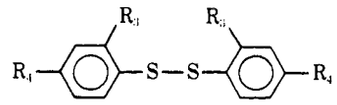
TABLE I

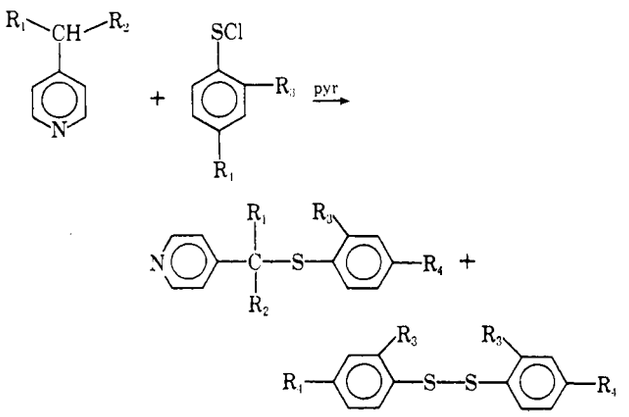
REACTIONS OF 4-ALKYLPYRIDINES WITH ARYLSULFENYL HALIDES

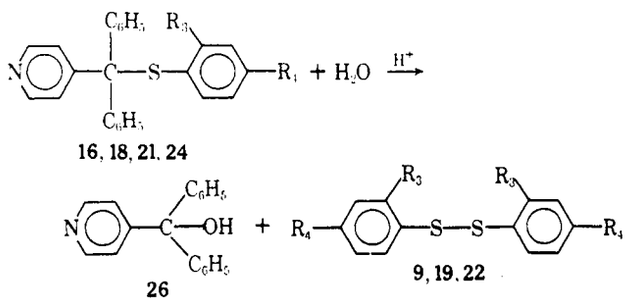
Compd	R_1	R_2	Compd	R_3	R_4	Compd	Yield, %	Compd	Yield, %
8	H	H	1	NO_2	NO_2			9	70
10	C_6H_5	H	1	NO_2	NO_2			9	67
11	CH_3	CH_3	1	NO_2	NO_2	12	95		
13	C_6H_5	CH_3	1	NO_2	NO_2	14	77	9	14
15	C_6H_5	C_6H_5	1	NO_2	NO_2	16	48	9	38
15	C_6H_5	C_6H_5	17	NO_2	H	18	88	19	12
15	C_6H_5	C_6H_5	20	H	NO_2	21	60	22	37
15	C_6H_5	C_6H_5	23	H	H	24	75[a]	25	

[a] In addition to sulfide **24**, diphenyl-4-pyridylcarbinol (24% yield) was also isolated and proposed as a hydrolysis product of **24** during work-up. Thus the projected yield of **24** would approach 99%.

4-alkylpyridines with various arylsulfenyl chlorides as illustrated in the general equation below and summarized in Table I. Pyridine aids the overall reaction but is not essential, since the 4-alkylpyridine could serve as the base.

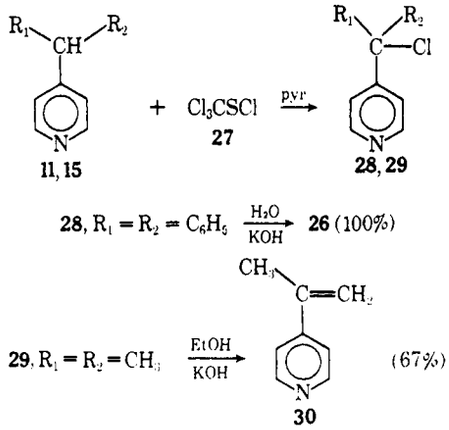


The disulfides **9**, **19**, and **22** are known compounds and were identified *via* melting points and spectral data. Structural assignments for the sulfide products **12**, **14**, **16**, **18**, **21**, and **24** were supported by elemental analysis and characteristic nmr and ir spectra. In addition **16**, **18**, **21**, and **24** were readily hydrolyzed to diphenyl-4-pyridylcarbinol (**26**) and the corresponding disulfide,



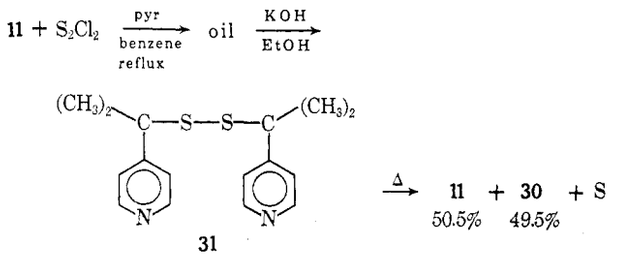
which probably arose by air oxidation of the corresponding arylthiol. The hydrolysis of diphenyl-4-pyridylmethyl phenyl sulfide (**24**) was particularly rapid and appears to be the source of diphenyl-4-pyridylcarbinol isolated in the reaction of 4-benzhydrylpyridine and benzenesulfenyl chloride (Table I). In contrast, sulfides **12** and **14** did not undergo hydrolysis to the corresponding carbinols even under more vigorous conditions.

The reaction of 4-benzhydrylpyridine (**15**) or 4-isopropylpyridine (**11**) with trichloromethanesulfenyl chloride (**27**) was mildly exothermic and formed a black hygroscopic precipitate and the reaction solution gave near-quantitative yields of diphenyl-4-pyridylmethyl chloride (**28**) or 2-(4-pyridyl)-2-chloropropane (**29**). Structural assignments for **28** and **29** were supported by elemental analysis, consistent nmr and ir spectra, the rapid, quantitative hydrolysis of **28** to carbinol **26**, and the base-catalyzed elimination of **29** to 4-isopropenylpyridine (**30**). The black, hygroscopic solid reacted



vigorously with water to produce hydrogen sulfide and colored solutions. A suggested structural possibility for the black solid involves a 2:1 complex of pyridine and thiophosgene.

A third product variation occurred in the reaction of 4-isopropylpyridine (**11**) and 4-benzhydrylpyridine (**15**) with sulfur monochloride, which produced, after alkaline treatment, 2-(4-pyridyl)-2-propyl disulfide (**31**) in 82% yield and diphenyl-4-pyridylcarbinol (**26**) in 66% yield, respectively. In the latter case an impure solid, which may be diphenyl-4-pyridylmethyl disulfide, was the precursor to **26** *via* acid or basic hydrolysis. Disulfide **31** had the proper analysis and spectral data for the assigned structure and upon thermal decomposition **31** formed sulfur along with equal amounts of 4-isopropylpyridine (**12**) and 4-iso-

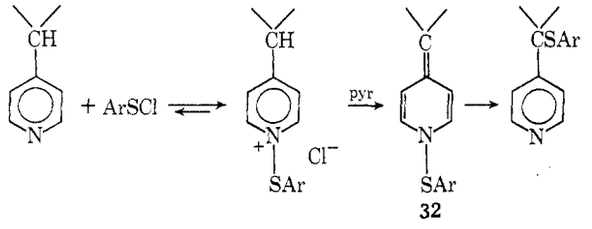


propenylpyridine (**30**). This fragmentation provides another avenue for the decomposition of aliphatic disulfides.[10]

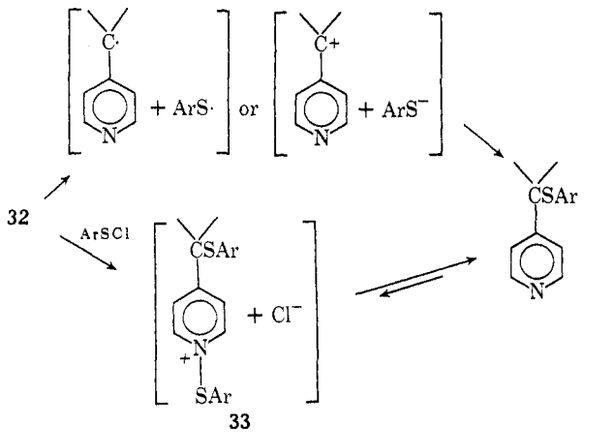
Attempts to extend these reactions to 2-alkyl- and 3-alkylpyridines were unsuccessful. Exposure to 2 benzhydryl- or 3-benzhydrylpyridine to 2,4-dinitrobenzenesulfenyl chloride, trichloromethanesulfenyl chloride, or sulfur monochloride, even under conditions more vigorous than those above, led to >90% recovery of unreacted alkylpyridines. Also no reaction occurred between triphenylmethane and 2,4-dinitrobenzenesulfenyl chloride. These observations exclude any direct attack of the sulfenyl chloride on the side-chain α carbon with substitution for the methine hydrogen and raise the question of involvement of the pyridine nitrogen.

A search for nitrogen–sulfur interaction was conducted *via* nmr measurements on equimolar solutions of pyridine and 2,4-dinitrobenzenesulfenyl chloride or trichloromethanesulfenyl chloride in deuteriochloroform. The expected downfield shift of the pyridine α hydrogens, resulting from salt formation, was absent and the position of the spectral peaks was unaffected by varying concentration. However, these observations do not preclude a low concentration (below nmr detection limits) of the *N*-arylthiopyridinium cation in equilibrium with the reactants. With this latter assumption one can explain the 4-alkylpyridine–sulfenyl halide reaction products *via* a pathway analogous to the rearrangement of 4-alkylpyridine *N*-oxide with acid anhydrides.[9]

The general reaction scheme proposed below proceeds through the key anhydro base intermediate **32**, which

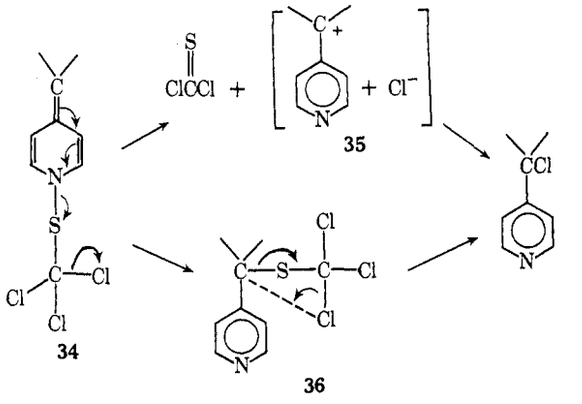


may undergo an intramolecular rearrangement or an intermolecular reaction to form the sulfide product. Fragmentation of **32** may entail homolytic cleavage of the N–S bond to form radical pairs or heterolytic cleavage to an ion pair in which either set may recombine to sulfide products. This intramolecular pathway requires a tight ion or radical pair. The intermolecular process would involve attack of **32** at the side-chain carbon by unreacted sulfenyl chloride to generate **33**, which is in favorable equilibrium with the product. Addition of arylsulfenyl chloride to anhydro



bases[11] or the structurally similar enamines[12,13] has been reported in the literature.

In the reaction of 4-alkylpyridines with sulfur monochloride the disulfide product can be rationalized by the above scheme except that two rearrangements or reactions (one in each pyridine ring) are required. Also support for the initial salt formation is available from isolation of some of these salts (**7**).[6,7] However the generation of diphenyl-4-pyridylmethyl chloride (**28**) or 2-(4-pyridyl)-2-chloropropane (**29**) from reactions using trichloromethanesulfenyl chloride requires some additional mechanistic features. The anhydro base **34** may undergo a concerted fragmentation to ion pair **35**, which recombines to give the chloro product. Alternatively, **34** may lead to **36** by the pathway outlined



above. Further decomposition of **36** analogous to the Sni decomposition of alkyl chlorosulfites or chlorocarbonates[14] should generate the chloro product and thiophosgene.

The failure of 3-benzhydrylpyridine to react with sulfenyl chlorides may be attributed to the exclusion of anhydro base formation; however, 2-benzhydryl- or 2-isopropylpyridine are capable of proceeding *via* anhydro bases according to the above pathway and thus the absence of products in these cases was surprising. Perhaps steric factors are inhibiting initial salt and/or anhydro base formation. Another puzzling point is the lack of the expected products in the reactions of 4-benzylpyridine and 4-picoline with sulfenyl

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(14) J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure," McGraw-Hill, New York, N. Y., 1968, p 268.

chlorides. These matters and the overall mechanistic scheme are under further consideration.

In conclusion, the reaction of 4-alkylpyridines which contain two substituents on the side-chain α carbon react readily with a variety of sulfenyl halides to produce high yields of sulfides, disulfides, or chlorides.

Experimental Section[15]

Alkylpyridines.—The following alkylpyridines were commercially available: 4-picoline,[16] 4-isopropylpyridine,[16] 4-benzylpyridine,[16] 4-benzhydrylpyridine,[16] 3-benzhydylpyridine, 2-benzhydrylpyridine, and 2-isopropylpyridine. The liquids were distilled prior to use and stored over KOH while the solid alkylpyridines were recrystallized from benzene or ethanol.

4-(1-Phenylethyl)pyridine.—The procedure of Villani, King, and Papa[17] was employed for the conversion of 4-benzoylpyridine (74 g, 0.39 mol) and methylmagnesium chloride (200 ml, 3 *M*, 0.60 mol) into 56 g (76%) of 1-phenyl-1-(4-pyridyl)ethanol: mp 145–146° (lit.[17] mp 146–147°); nmr ($CDCl_3$) δ 8.56–8.27 (m, 2, pyr C_2 H, C_6 H), 7.53–7.27 (m, 7, pyr C_3 H, C_5 H, and $-C_6H_5$), 4.48 (br s, 1, –OH), and 1.92 (s, 3, $-CH_3$).

To a mixture of 1-phenyl-1-(4-pyridyl)ethanol (25.9 g, 0.132 mol), zinc powder (70 g), and acetic acid (100 ml) at 110° was added with stirring concentrated HCl (90 ml) over a 10-min period followed by more concentrated HCl (60 ml) 30 min later. The reaction mixture was maintained at 110° for 2.5 hr, the residual zinc was filtered, and the filtrate was concentrated, neutralized (Na_2CO_3), and extracted with $CHCl_3$. After the extract was dried and the solvent was removed, distillation of the residue gave 5 g (21%) of 4-(1-phenylethyl)pyridine: bp 128–135° (0.1 Torr); ir (neat) 3040 (w), 2980 (w), and 1595 cm^{-1} (s); nmr ($CDCl_3$) δ 8.60–8.44 (m, 2, pyr C_2 H, C_6 H), 7.40 6.95 (m, 7, pyr C_3 H, C_5 H, and $-C_6H_5$), 4.05 [q, 1, J = 7.5 Hz, $>CH(CH_3)C_6H_5$], and 1.53 (d, 3, J = 7.5 Hz, $-CH_3$).

Benzenesulfenyl Chloride.—The reaction of phenyl disulfide (78.9 g, 0.36 mol) in CCl_4 (200 ml) and Cl_2, as described in the literature,[18] gave 57.6 g (55%) of the deep red benzenesulfenyl chloride: bp 44° (1.1 Torr) [lit.[18] bp 58° (3 Torr)]; nmr ($CDCl_3$) δ 7.70–7.54 (m, 2, C_2 H and C_6 H), 7.36–7.25 (m, 3, C_3, C_4, C_5 H's).

4-Nitrobenzenesulfenyl Chloride.—Using the above procedure,[19] 4-nitrophenyl disulfide (25.8 g, 0.084 mol) in CCl_4 (150 ml) and Cl_2 provided a quantitative conversion (31.8 g) to 4-nitrobenzenesulfenyl chloride: mp 48–49° (lit.[19] mp 52°); nmr ($CDCl_3$) δ 8.37–8.07 (m, 2, C_3 H, C_5 H), 7.57–7.23 (m, 2, C_2 H, C_6 H).

Reaction of 2,4-Dinitrobenzenesulfenyl Chloride with Various Alkylpyridines. 1. 4-Benzhydrylpyridine. Method A.—A solution of 2,4-dinitrobenzenesulfenyl chloride (5.0 g 0.021 mol) in CH_2Cl_2 (30 ml) was added to a stirred solution of 4-benzhydrylpyridine (**15**, 10.4 g, 0.0425 mol) in CH_2Cl_2 (50 ml) under N_2. The reaction mixture was stirred for 2 hr and filtered and gave 0.5 g of 2,4-dinitrophenyl disulfide (**9**), mp 310° dec (lit.[20] mp 290–300°). After CH_2Cl_2 was removed from the filtrate, the residue was treated with acetone, from which an additional 1.1 g (38% combined yield) of 2,4-dinitrophenyl disulfide was isolated. The acetone solution was diluted with water and gave 4.5 g (48%) of yellow, crystalline diphenyl-4-pyridylmethyl 2,4-dinitrophenyl sulfide (**16**), mp 160–163°. Several recrystallizations of the crude product from ethanol gave an analytical sample: mp 167–168°; ir (KBr) 3075 (w), 3040 (w), 1590 (s) 1525 (s, NO_2), and 1340 cm^{-1} (s, NO_2); nmr ($CDCl_3$) δ 8.81 (d, 1, J = 2.5 Hz, dinitrobenzene C_3 H), 8.70–8.46 (m, 2, pyr C_2 H, C_6 H), 7.82 (dd, 1, J = 9, 2.5 Hz, dinitrobenzene C_5 H), 7.33 (m, 12, pyr C_3 H, C_5 H, and C_6H_5), and 7.15 (d, 1, J = 9 Hz, dinitrobenzene C_6 H).

Anal. Calcd for $C_{24}H_{17}N_3O_4S$: C, 65.00; H, 3.86; N, 9.47. Found: C, 64.87; H, 4.13; N, 9.23.

2. 4-(1-Phenylethyl)pyridine. Method B.—After the addition of 2,4-dinitrobenzenesulfenyl chloride (3.60 g, 0.015 mol) in benzene (25 ml) to a stirred solution of 4-(1-phenylethyl)-pyridine (**13**) (2.81 g, 0.015 mol) in pyridine (25 ml) the reaction mixture was refluxed for 2 hr under N_2. The reaction mixture was cooled and filtered to give 0.42 g (14%) of 2,4-dinitrophenyl disulfide. After the filtrate was neutralized (10% Na_2CO_3) and extracted with $CHCl_3$, the $CHCl_3$ was removed and left 4.09 g (77%) of 1-phenyl-1-(4-pyridyl)ethyl 2,4-dinitrophenyl sulfide (**14**): mp 125–127° (from ethanol); ir (KBr) 3080 (w), 1590 (s), 1515 (s, NO_2), and 1350 cm^{-1} (s, NO_2); nmr ($CDCl_3$) δ 8.83 (d, 1, J = 2.5 Hz, dinitrobenzene C_3 H), 8.68 (broad s, 2, pyr C_2 H, C_6 H), 8.07 (dd, 1, J = 9, 2 Hz, dinitrobenzene C_5 H), 7.47 (m, 7, pyr C_3 H, C_5 H, and C_6H_5), 7.25 (d, 1, J = 9 Hz, dinitrobenzene C_6 H), and 2.27 (s, 3, $-CH_3$).

Anal. Calcd for $C_{19}H_{15}N_3O_4S$: C, 59.83; H, 3.96; N, 11.02; S, 8.41. Found: C, 59.56; H, 4.16; N, 10.63; S, 8.42.

3. 4-Isopropylpyridine.—Method B was used in the reaction of 4-isopropylpyridine (**11**, 3.61 g, 0.030 mol) in pyridine (25 ml) and 2,4-dinitrobenzenesulfenyl chloride (7.0 g, 0.030 mol) in benzene (25 ml) with 1 hr reflux and gave 9.03 g (95%) of 2-(4-pyridyl)-2-propyl 2,4-dinitrophenyl sulfide (**12**): mp 167–168° (from ethanol); ir (KBr) 3120 (w), 2960 (w), 1590 (s), 1510 (s, NO_2), and 1335 cm^{-1} (s, NO_2); nmr ($CDCl_3$) δ 8.84 (d, 1, J = 2.6 Hz, dinitrobenzene C_3 H), 8.74–8.50 (m, 2, pyr C_2 H, C_6 H), 8.06 (dd, 1, J = 9, 2 Hz, dinitrobenzene C_5 H), 7.64–7.40 (m, 2, pyr C_3 H and C_5 H), 7.08 (d, 1, J = 9 Hz, dinitrobenzene C_6 H), and 1.87 (s, 6, two $-CH_3$'s).

Anal. Calcd for $C_{14}H_{18}N_3O_4S$: C, 52.66; H, 4.10; N, 13.16; S, 10.06. Found: C, 52.86; H, 4.34; N, 12.78; S, 10.19.

4. Other Alkylpyridines.—4-Picoline, 4-benzylpyridine, 2-benzhydrylpyridine, 2-isopropylpyridine, and 3-benzhydrylpyridine were each trreated with 2,4-dinitrobenzenesulfenyl chloride and refluxed from 1 to 36 hr. Only 2,4-dinitrophenyl disulfide (70–95%) and unreacted alkylpyridines (near-quantitative yield for the last three examples) were recovered.

5. Triphenylmethane.—A solution of 2,4-dinitrobenzenesulfenyl chloride (3.00 g, 0.0128 mol) in benzene (30 ml) and triphenylmethane (3.15 g, 0.0129 mol) in pyridine (30 ml) was refluxed for 18 hr. Work-up *via* method B provided 1.38 g (54% of 2,4-dinitrophenyl disulfide and 2.95 g (95%) of triphenylmethane, identified by melting point (93.5–94°) and the absence of depression in a mixture melting point with authentic material.

Reaction of 4-Benzhydrylpyridine with Various Arylsulfenyl Chlorides. 1. Benzenesulfenyl Chloride.—A solution of 4-benzhydrylpyridine (**15**, 3.4 g, 0.014 mol) in dry pyridine (25 ml) was mixed with benzenesulfenyl chloride (**23**) (2.00 g, 0.0138 mol) in dry benzene (25 ml) in a dark vial. The vial was purged with nitrogen, sealed, shaken at room temperature for 5 min (slight exothermic reaction observed), and kept overnight. The reaction mixture was filtered and gave 0.14 g of diphenyl-4-pyridylcarbinol (**26**), mp 231–235° (lit.[17] mp 238–238.5°).

After the solvent was removed from the filtrate, the oily residue was treated with ether and gave an additional 0.72 g (23.8% total yield) of insoluble diphenyl-4-pyridylcarbinol. The ether was removed and left 3.67 g (75%) of crude diphenyl-4-pyridylmethyl phenyl sulfide (**24**), which upon crystallization from ethanol gave an analytical sample: mp 150.5–151.5°; ir (KBr) 3025–3010 (m), 1585 (s), and 1480 cm^{-1} (s); nmr ($CDCl_3$) δ 8.57–8.30 (m, 2, pyr C_2 H, C_6 H) and 7.33–7.00 (m, 17, pyr C_3 H, C_5 H and three $-C_6H_5$).

Anal. Calcd. for $C_{24}H_{19}NS$: C, 81.55; H, 5.42; N, 3.96; S, 9.07. Found: C, 81.12; H, 5.20; N, 4.06; S, 9.05.

2. 2-Nitrobenzenesulfenyl Chloride.—Using the procedure of method A the reaction mixture of 4-benzhydrylpyridine (2.59 g, 0.0106 mol) in benene (15 ml) and pyridine (15 ml) and 2-nitrobenzenesulfenyl chloride (**17**) (2.00 g, 0.0106 mol) was stirred overnight and processed to give 0.2 g (12%) of 2-nitrophenyl disulfide (**19**), mp 196–197° (lit.[21] mp 192–195°), and 3.68 g (88%) of crude diphenyl-4-pyridylmethyl 2-nitrophenyl sulfide (**18**) as a yellow oil. The oil solidified when treated with ether, and recrystallization from ethanol gave an analytical

(15) All melting points and boiling points are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., or by Clark Microanalytical Laboratory, Urbana, Ill. Infrared spectra were determined on a Beckman IR-8 or a Beckman IR-20A spectrometer and nmr spectra were recorded on a Varian Associates Model HA-60-EL or Model A-60A spectrometer.

(16) The authors wish to thank Reilly Tar and Chemical Co., Indianapolis, Ind., for a generous supply of these alkylpyridines.

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sample: mp 156–158°; ir (KBr) 3030 (w), 3015 (w), 1585 (s), 1510 (s, NO_2), and 1330 cm^{-1} (s, NO_2); nmr ($CDCl_3$) δ 8.56–8.36 (m, 2, pyr C_2 H, C_6 H) and 7.86–7.00 (m, 16, pyr C_3 H, C_5 H, $-C_6H_5$, and $C_6H_4NO_2$).

Anal. Calcd for $C_{24}H_{18}N_2O_2S$: C, 72.34; H, 4.55; N, 7.03. Found: C, 72.65; H, 4.67; N, 6.97.

3. 4-Nitrobenzenesulfenyl Chloride.—The reaction mixture of 4-nitrobenzenesulfenyl chloride (**20**, 3.0 g, 0.016 mol), 4-benzhydrylpyridine (4.5 g, 0.016 mol), CH_2Cl_2 (50 ml), and pyridine (1 ml) was stirred for 24 hr under nitrogen, and work-up according to method A gave 0.9 g (37%) of 4-nitrophenyl disulfide (**22**), mp 177–178° (lit.[19] mp 181°), and 3.79 g (60%) of diphenyl-4-pyridylmethyl 4-nitrophenyl sulfide (**21**) which was recrystallized from ethanol to give an analytical sample: mp 140–141°; ir (KBr) 3075 (w), 1580 (m), 1510 (s, NO_2), and 1340 cm^{-1} (s, NO_2); nmr ($CDCl_3$) δ 8.60–8.40 (m, 2, pyr C_2 H, C_6 H), 7.81 (d, 2, J = 9 Hz, nitrobenzene C_3 H, C_5 H), 7.40–7.22 (m, 12, pyr C_3 H, C_5 H, and two $-C_6H_5$), and 7.05 (d, 2, J = 9 Hz, nitrobenzene C_2 H, C_5 H).

Anal. Calcd for $C_{24}H_{18}N_2O_2S$: C, 72.34; H, 4.55; N, 7.03. Found: C, 72.25; H, 4.79; N, 6.84.

Hydrolysis of Diphenyl-4-pyridylmethyl Aryl Sulfides. 2,4-Dinitrophenyl Sulfide.—A solution of diphenyl-4-pyridylmethyl 2,4-dinitrophenyl sulfide (**16**) (0.6 g, 0.0014 mol) in 3 N HCl (10 ml) was refluxed for 1 hr and the mixture was filtered to give 0.21 g (81%) of 2,4-dinitrophenyl disulfide (**9**). The filtrate was made basic and gave 0.22 g (62%) of diphenyl-4-pyridylcarbinol (**26**), mp 237–239° (lit.[17] mp 238–238.5°). The ir spectrum was identical with that of an authentic sample.

When 1-phenyl-1-(4-pyridyl)ethyl 2,4-dinitrophenyl sulfide (**14**) or 2-(4-pyridyl)-2-propyl 2,4-dinitrophenyl sulfide (**12**) was refluxed for 1–2 hr in 3 N and 6 N HCl, only unreacted starting sulfides were recovered in near quantitative yield.

Using the preceding procedure hydrolysis of diphenyl-4-pyridylmethyl phenyl sulfide (**24**), diphenyl-4-pyridylmethyl 2-nitrophenyl sulfide (**18**) and diphenyl-4-pyridylmethyl 4-nitrophenyl sulfide (**21**) in 6 N HCl gave diphenyl-4-pyridylcarbinol (**26**) (quantitative, quantitative, and 88% yield, respectively) and the corresponding aryl disulfides 2-nitrophenyl disulfide (**19**) (91%) and 4-nitrophenyl disulfide (**22**) (99%).

Reaction of Trichloromethanesulfenyl Chloride with Alkylpyridines. 1. 4-Benzhydrylpyridine.—To a stirred solution of trichloromethanesulfenyl chloride (3.00 g, 0.016 mol) in dry ethylene chloride (20 ml) was added, at room temperature, a solution of 4-benzhydrylpyridine (3.96 g, 0.016 mol) in dry ethylene chloride (20 ml) and pyridine (20 ml). The reaction became warm and a solid formed while the reaction mixture was stirred at ambient temperature for 1–2 hr under N_2. Filtration of the reaction mixture gave a black, hygroscopic solid which reacted violently with H_2O and formed a purple aqueous solution with the odor of H_2S.

The solvent was distilled from the reaction mixture filtrate and the resulting dark viscous oil was extracted with hexane. After the hexane was removed, the residue was 4.45 g (99%) of diphenyl-4-pyridylmethyl chloride (**28**) as an orange oil which solidified upon scratching the flask. Either sublimation of the solid (130°, 0.05 Torr) or recrystallization from ethanol provided an analytical sample: mp 89.5–90.5°; ir (melt) 3025 (m), 3010 (m) and 1585 cm^{-1} (s); nmr ($CDCl_3$) δ 8.62–8.43 (m, 2, pyr C_2 H, C_6 H), 7.41–7.03 (m, 12, pyr C_3 H, C_5 H, and two $-C_6H_5$).

Anal. Calcd for $C_{18}H_{14}ClN$: C, 77.28; H, 5.04; N, 5.01; S, 12.67. Found: C, 77.15; H, 5.14; N, 5.35; Cl, 12.38.

2. 4-Isopropylpyridine.—The procedure of the preceding experiment was used in the reaction of trichloromethanesulfenyl chloride (6.13 g, 0.033 mol) in CH_2Cl_2 (20 ml) and 4-isopropylpyridine (4.0 g 0.033 mol) in CH_2Cl_2 (10 ml) and pyridine (10 ml) at 0°. The reaction mixture was stirred for 16–18 hr and gave a black, hygroscopic solid similar to that in the preceding experiment and 4.89 g (95%) of 2-(4-pyridyl)-2-chloropropane (**29**). Distillation of the oil provided an analytical sample: bp 44° (0.05 Torr); ir (neat) 3010 (w), 2990 (m), 2960 (w), and 1590 cm^{-1} (s); nmr ($CDCl_3$) δ 8.68–8.52 (m, 2, pyr C_2 H, C_6 H), 7.54–7.38 (m, 2, pyr C_3 H, C_5 H), and 1.93 (, 6, two $-CH_3$).

Anal. Calcd for $C_8H_{10}ClN$: C, 61.74; H, 6.48; N, 9.00. Found: C, 61.58; H, 6.35; N, 8.97.

3. Other Alkylpyridines.—The above procedure was used for the reaction of equimolar amounts of 2- and 3-benzhydrylpyridine and trichloromethanesulfenyl chloride for 3 and 5 days, respectively, at room temperature and gave 2-benzhydrylpyridine (94% recovery) and 3-benzhydrylpyridine (91% recovery), respectively.

Hydrolysis of Diphenyl-4-pyridylmethyl Chloride.—When 1 N ethanolic KOH (10 ml) was added to a solution of diphenyl-4-pyridylmethyl chloride (**28**, 0.46 g, 1.64 mmol) in ethanol (10 ml), an immediate precipitate formed which dissolved upon the addition of 2–5 ml of H_2O. The reaction mixture was diluted with more H_2O (20–25 ml) and filtered to give 0.43 g (100%) of diphenyl-4-pyridylcarbinol (**26**), mp 238–239°. A mixture melting point with an authentic sample was not depressed and the ir spectra of the two samples were identical.

Reaction of 2-(4-Pyridyl)-2-chloropropane with KOH.—A solution of 2-(4-pyridyl)-2-chloropropane (**29**, 0.57 g, 3.36 mmol) in 1 N ethanolic KOH (25 ml) was refluxed for 1 hr, cooled, and filtered, and the filtrate was diluted with an equal volume of ether. The ether was separated and dried and the solvent was removed to give 0.29 g (67%) of 4-isopropylpyridine (**30**): nmr ($CDCl_3$) δ 8.53–8.33 (m, 2, pyr C_2 H, C_6 H), 7.30–7.13 (m, 2, pyr C_3 H, C_5 H), 5.56 (broad s, 1, =CHH), 5.25–5.20 (m, 1, =CHH), 2.13 (s, 3, $-CH_3$). The ir spectrum was identical with that of a known sample.

Reaction of Alkylpyridines with Sulfur Monochloride. 1. 4-Isopropylpyridine.—A solution of sulfur monochloride (2.5 g, 0.0185 mol) in benzene (20 ml) was added to 4-isopropylpyridine (**11**, 4.49 g, 0.037 mol) in 25 ml of a 1:1 mixture of benzene–pyridine and the mixture was refluxed under N_2 for 30 min. The reaction mixture was filtered and gave 4.12 g (97%) of hygroscopic, white, crystalline pyridine hydrochloride, which had ir and nmr spectra that were identical with those of an authentic sample.

The filtrate from the reaction mixture was concentrated and refluxed for 15 min in 3 N ethanolic KOH (25 ml). The solution was filtered, diluted with H_2O, and extracted with ether. The extract was dried and the solvent was removed to give 4.23 g (82%) of 2-(4-pyridyl)-2-propyl disulfide (**31**). Recrystallization from ethanol provided an analytical sample: mp 70–71°; ir (melt) 3035 (s), 3010 (m), 2980 (m), 2960 (m), 2930 (w), and 1590 cm^{-1} (s); nmr ($CDCl_3$) δ 8.42 (m, 4, 2 pyr C_2 H, C_6 H), 7.15 (m, 4, 2 pyr C_3 H, C_5 H), 1.47 (s, 12, 4 $-CH_3$).

Anal. Calcd for $C_{16}H_{20}N_2S_2$ C, 63.12; H, 6.62; N, 9.20. Found: C, 63.23; H, 6.66; N, 8.94.

2. 4-Benzylhydrylpyridine.—Sulfur monochloride (1.65 g, 0.0122 mol) in benzene was added to 4-benzhydrylpyridine (6.00 g, 0.0245 mol) in 30 ml of a 1:1 mixture of benzene and pyridine and the reaction mixture was stirred overnight at room temperature under N_2. The reaction mixture was filtered and gave 2.5 g (89%) of pyridine hydrochloride.

The solvent was removed from the filtrate, the residue was treated with ether, and the ether solution was filtered. The ether was removed and left 6.54 g (97%) of crude diphenyl-4-pyridylmethyl disulfide as a yellow, sticky solid: mp 50–55°; nmr ($CDCl_3$) δ 8.50–8.44 (m, 4, 2 pyr C_2 H, C_6 H), and 7.21–7.12 (m, 24, 2 pyr C_3 H, C_5 H, and 4 C_6H_5). Attempts to purify the product by crystallization or chromatography were unsuccessful.

A solution of the yellow, sticky solid (0.99 g, 0.0018 mol) in 6 N HCl (15 ml) was refluxed for 1 hr, cooled, made basic with aqueous KOH, and filtered to give 0.62 g (66%) of diphenyl-4-pyridylcarbinol, mp 235–237°. The ir spectrum of this sample was identical with that of the known compound.

3. 2-Benzhydrylpyridine.—A solution of 2-benzhydrylpyridine (3.00 g, 0.0122 mol), sulfur monochloride (0.83 g, 0.0061 mol) in benzene (400 ml), and pyridine (20 ml) was refluxed for 1 hr under N_2, cooled, and quenched with H_2O (25 ml). The organic layer was separated and dried ($MgSO_4$) and the solvent was removed to provide 2.86 g (96%) of 2-benzhydrylpyridine, mp 55–57°. The nmr spectrum was identical with that of an authentic sample.

Thermal Decomposition of 2-(4-Pyridyl)-2-propyl Disulfide.—2-(4-Pyridyl)-2-propyl disulfide (**31**, 0.94 g, 3.09 mol) was placed in a microvacuum distillation apparatus and evacuated to 0.05 Torr and the still pot was heated slowly until, between 175 and 210°, a distillate collected in a receiver immersed in a Dry Ice–acetone bath. The residue (black with some yellow solid) in the distilling flask was extracted with hot CS_2 and from the cooled solution yellow crystalline sulfur, mp 119–120°, was obtained. A mixture melting point with an authentic sample of sulfur gave no depression.

The distillate, which weighed 0.56 g (76%), was analyzed by nmr and shown to contain a mixture of 4-isopropylpyridine (**11**,

50.5%) determined from the signal at δ 1.23 [-CH(CH_3)$_2$] and 4-isopropenylpyridine (**30**, 49.5%) determined from the signal at δ 2.13 [pyr-C(CH_3)=CH_2]. The nmr spectrum of the mixture had the following peaks: nmr ($CDCl_3$) δ 8.67–8.50 (m, 4, pyr C_2 H, C_6 H), 7.31 (m, 2, C_3 H, C_5 H, of 4-isopropenylpyridine), 7.16 (m, 2, C_3 H, C_5 H of 4-isopropylpyridine), 5.57 [s, 1, pyr-C(CH_3)=C**H**], 5.28–5.20 [m, 1, pyr-C(CH_3)=C**H**], 2.87 [septet, 1, pyr-C**H**(CH_3)$_2$], 2.13 [s, 3, pyr-C(CH_3)=CH_2], and 1.23 [d, 6, pyr-CH(CH_3)$_2$].

Registry No.—**11**, 69-30-0; **12**, 42362-46-9; **13**, 42362-47-0; **14**, 42362-48-1; **15**, 3678-72-6; **16**, 42362-50-5; **17**, 7669-54-7; **18**, 42362-51-6; **20**, 937-32-6; **21**, 42362-52-7; **23**, 931-59-9; **24**, 42362-53-8; **28**, 42362-54-9; **29**, 40473-14-1; **30**, 17755-30-5; **31**, 42362-57-2; 1-phenyl-1-(4-pyridyl)ethanol, 19490-94-9; phenyl disulfide, 882-33-7; Cl_2, 7782-50-5; 4-nitrophenyl disulfide, 100-32-3; 2,4-dinitrobenzenesulfenyl chloride, 528-76-7; trichloromethanesulfenyl chloride, 594-42-3; sulfur monochloride, 10025-67-9; diphenyl-4-pyridylmethyl disulfide, 42362-59-4.

Notes

Reaction of Tertiary Aliphatic Amines with 2,4-Dinitrobenzenesulfenyl Chloride

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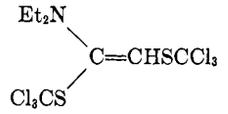
Sulfenyl chlorides react readily with primary and secondary amines to form sulfenamides;[2,3] however, tertiary amines appeared to be inert and useful as bases in the reactions of sulfenyl chlorides.[2] Some years ago Senning[4] observed a reaction between trichloromethanesulfenyl chloride and triethylamine which produced a bis(trichloromethylthio)-*N*,*N*-diethylaminoethene which was assigned structure **1**, although structure **2** could



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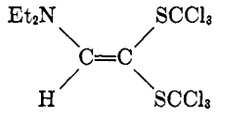

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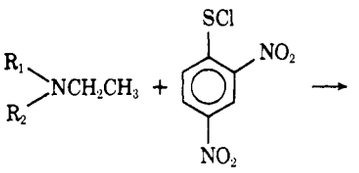
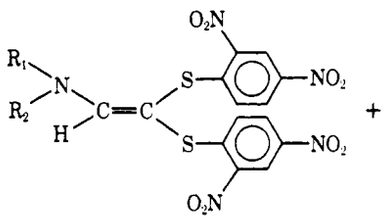
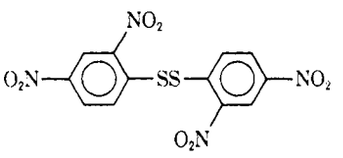
not be ruled out on the basis of spectral and chemical evidence. In a recent report Senning and Kelly[5] changed the assignment to structure **2**, which was supported by an X-ray crystallographic study.[6] In addition they reported[5] that attempts to extend this reaction to several other amines, such as tri-*n*-propylamine, tri-*n*-butylamine, diethylmethylamine, and others, with trichloromethanesulfenyl chloride were unsuccessful and the reaction of triethylamine and *o*-nitrobenzenesulfenyl chloride or 1,2,2,2-tetrachloroethanesulfenyl chloride failed to produce any products.

In our study of the formation of *N*-arylthiopyridinium salts[7] we had occasion to examine the mixture of triethylamine and 2,4-dinitrobenzenesulfenyl chloride and observed that reaction occurred with the formation of 1,1-bis(2,4-dinitrophenylthio)-2-*N*,*N*-diethylaminoethene (**3**). This reaction has been extended with 2,4-dinitrobenzenesulfenyl chloride and *N*,*N*-diethylcyclohexylamine or *N*,*N*-diisopropylethylamine with the formation of **4** and **5**, respectively. However, similar reactions of 2,4-dinitrobenzenesulfenyl chloride with tri-*n*-propylamine, tri-*n*-butylamine, and *N*-methylpiperidine failed to produce the corresponding enamines. The yield for each of the enaminic products **3**, **4**, and **5** was approximately 50%[8] as was the yield of bis(2,4-dinitrophenyl) disulfide (**6**) in each reaction.





3, $R_1 = R_2 = CH_3CH_2$
4, $R_1 = c\text{-}C_6H_{11}$; $R_2 = CH_3CH_2$
5, $R_1 = R_2 = (CH_3)_2CH$



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The accountability for the starting sulfenyl chloride was essentially quantitative in each reaction.

The assignment of structures **3**, **4**, and **5** was based on elemental analysis, on spectral data, and by analogy to compound **2** reported by Senning.[5] The infrared spectra showed the presence of the dinitrobenzene rings and the presence of the enaminic double bond (1585, 1565, 1570, and 1578 cm^{-1} [5] for **3**, **4**, **5**, and **2**, respectively) while the nmr had a characteristic olefinic peak (δ 7.43, 7.62, 7.74, and 7.55[5] for **3**, **4**, **5**, and **2**, respectively). In addition the nmr spectrum for **3** and **5** revealed the presence of two different dinitro-

(1) Abstracted from a portion of the Ph.D. Dissertation submitted by J. N. R. in April 1973 at West Virginia University.
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(8) The yield of the enaminic products was based on 2,4-dinitrobenzenesulfenyl chloride.