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Ion Radicals. XXXIII. Reactions of 10-Methyl- and 10-Phenylphenothiazine Cation Radicals with Ammonia and Amines. Preparation and Reactions of 5-(*N*-Alkyl)sulfilimines and 5-(*N,N*-Dialkylamino)sulfonium Salts[1]

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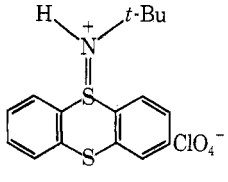
10-Phenyl- (7) and 10-methylphenothiazine cation radical perchlorate (8) reacted readily with primary alkyl amines in acetonitrile solution to form N-protonated *N*-alkylsulfilimine perchlorates, and the parent heterocycle was also formed. Reaction of 7 and 8 with dialkylamines gave *N,N*-dialkylsulfilimine perchlorates. Tertiary amines led to reduction of the cation radicals; with ammonia, dimeric products were formed. 5-(*tert*-Butylimino)-5,5-dihydro-10-methylphenothiazine perchlorate with perchloric acid gave 10-methylphenothiazine cation radical; with HCl, formation of the cation radical was followed by reduction and chlorination.

Although *N*-arylsulfilimines have been known since 1968,[4-10] *N*-alkylsulfilimines were unknown until very recently. Franz and Martin reported in 1973 that the reaction of diphenyl(1,1,1,3,3,3-hexafluoro-2-phenyl-2-propoxy)sulfurane [**1**, R_F = $C(CF_3)_2Ph$] with primary amides gave *N*-aryl- and *N*-alkylidiphenylsulfilimines (**2**, eq 1).[8] Subsequently, Shine and Kim[11] reported that the cation radicals of thianthrene and 10-phenylphenothiazine reacted with *tert*-butylamine to give the perchlorates **3** and **4**, respectively, which were easily deprotonated to give the corresponding *N*-*tert*-butylsulfilimines. Also, dimethylamine reacted with thianthrene cation radical perchlorate to give **5**. At that time the curious reaction was also discovered in which not only ammonia but also methyl-, ethyl-, propyl-, and cyclohexylamine reacted with thianthrene cation radical perchlorate to give the dimeric product **6a**. It appeared at that time, therefore, that the preparation of *N*-alkylsulfilimines by reaction of organosulfur cation radicals with alkylamines would not be a viable reaction. We now show that this is not so. Most recently, Franz and Martin have reported that sulfuranes such as **1** react with primary aryl- and alkylamines to give *N*-aryl- and *N*-alkylsulfilimines (**2**).[12]

$$Ph_2S(OR_F)_2 + PhCONHR \longrightarrow \underset{1}{} \quad \underset{2}{Ph_2S{=}NR} + PhCO_2R_F + R_FOH \quad (1)$$



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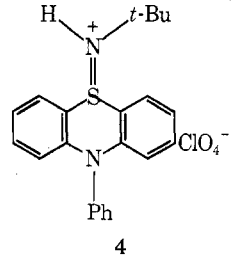

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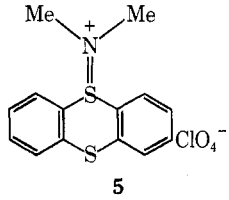

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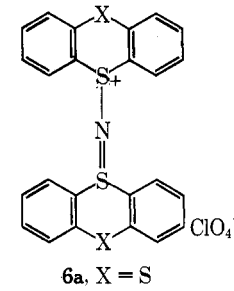


6a, X = S
b, X = *N*-Ph
c, X = *N*-Me

Results and Discussion

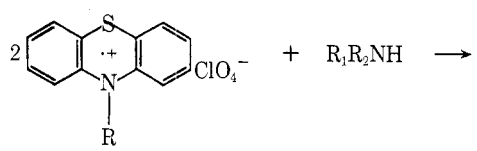
Preparation of Sulfilimines. We have found that, in contrast with thianthrene cation radical perchlorate, 10-phenyl- (**7**) and 10-methylphenothiazine cation radical perchlorate (**8**) react with a variety of simple primary alkylamines to give *N*-alkylsulfilimines. Reaction with dialkylamines gives products corresponding with **5**, i.e., *N,N*-dialkylaminosulfonium salts, while reaction with tertiary amines causes reduction to the parent compounds. Reaction with primary and secondary amines was carried out in acetonitrile solution and was rapid. Not only was the sulfilimine-

Table I
Yields[a] of Products of Reactions of 7 and 8 with Amines According to Equation 2

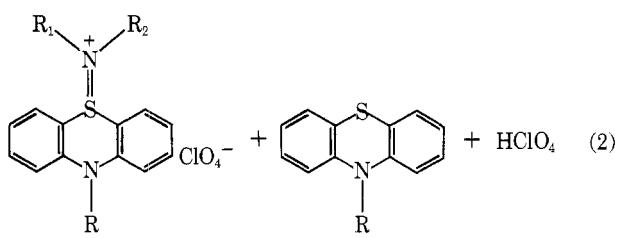
Code	R_1	R_2	% 9	% 11	Mp of 9, °C	% 10	% 12	Mp of 10, °C
a	H	Me	30[b]	52	148–150	29	58	134–136
b	H	Et	25[c]	53	140–141			
c	H	Pr	38[b]	60	153–154	22	65	143–145
d	H	*t*-Bu	*d*	*d*		11	80	163–165
e	H	C_6H_{11}	32[c]	55	167–169	*f*	62	*f*
f	H	$C_6H_5CH_2$	43[b]	52	148–149	25	60	127–129
g	Me	Me	36[b]	66	145–146	23	63	139–140
h	Et	Et	14[c]	78	150–151	0	89	
i	*i*-Pr	*i*-Pr	28[b,e]	65	*e*	18	72	150–151
j	$C_6H_5CH_2$	$C_6H_5CH_2$	27[b]	60	160	*g*		
k	$-(CH_2)_3-$		39[c]	57	155–160	39	61	136–137
l	$-(CH_2)_4-$		28[b]	67	139–140	24	77	139–140
m	$-(CH_2)_5-$		40[c]	50	157–158	28	65	146–147

[a] According to the stoichiometry of eq 2, quantitative conversion of 7 would give 50% of 9 and 50% of 11. A yield of 11 larger than 50% means that some reduction of 7 occurred. The same applies to the conversion of 8 into 10 and 12. [b] Work-up procedure A. [c] Work-up procedure B. [d] See ref 5. [e] Product could not be crystallized and was identified spectroscopically. [f] Product could not be crystallized. [g] Separation of products could not be achieved.

type product formed, but the parent heterocycle, too. The generalized stoichiometry is given in eq 2, although the



7, R = Ph
8, R = Me



9, R = Ph
10, R = Me

11, R = Ph
12, R = Me

(2)

yield of parent heterocycle (i.e., **11** or **12**) obtained showed that in some cases reduction of the cation radical was a competing reaction. This is particularly noticeable in reactions with dialkylamines. For example, with diethylamine in the preparation of **9h** (see Table I), 78% of the cation radical **7** was converted into 10-phenylphenothiazine. Similarly, none of **10h** was obtained from reaction of **8** with diethylamine, the cation radical being reduced almost entirely (89%) to 10-methylphenothiazine.

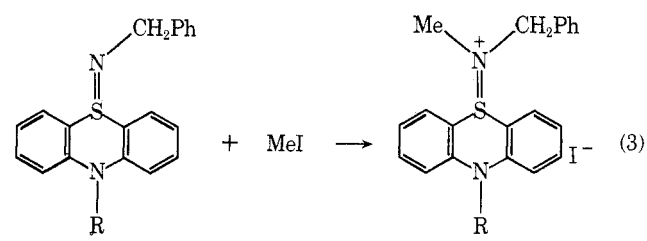
All of the sulfilimines listed in Table I were isolated as perchlorates. Properties of these products are given in Table II (supplementary material). Elemental analyses agreed with anticipated values and are given in Table III (supplementary material). Insofar as those compounds in which R_1 = H are concerned, their isolation indicates that the parent *N*-alkylsulfilimines are readily formed and are reasonably strong bases. All perchlorates were readily isolable and crystallizable except **9i** (from **7** and diisopropylamine), **10e** (from **8** and cyclohexylamine), and **10j** (from **8** and dibenzylamine). Reaction of **8** with ethylamine was not attempted. It should be noted that the maximum conversion of cation radicals into compounds **9** and **10**, according to eq 2, would be 50%, so that the data given in Table I show yields of 22–86% of theory. Yields of **9** were better than those of **10**.

Reaction of trimethylamine and triethylamine with **7** caused respectively 92 and 79% reduction to 10-phenylphenothiazine, while reaction of trimethylamine with **8** caused 85% to be reduced to 10-methylphenothiazine. Search for the products of oxidation of the amines was not made.

Reactions of **7** and **8** with ammonia were also carried out and gave **6b** (X = *N*-Ph, mp 192–193°, 76% yield) and **6c** (X = *N*-Me, mp 153–154°, 82% yield).

Reactions of Compounds 9 and 10 with Sodium Hydroxide. The protonated sulfilimines, i.e., **9a–f** and **10a–f,** were easily deprotonated by treatment with aqueous sodium hydroxide in methanol, giving parent *N*-alkylsulfilimines. Thus **9f** gave 88% of 5-(benzyliminio)-5,5-dihydro-10-phenylphenothiazine (**13**), mp 142–143°. The deprotonation of **9d** was reported earlier.[5] The 10-methyl analog (**14**) of **13** was prepared similarly (but not isolated) for methylation (see later). In contrast with deprotonation of *N*-alkylsulfilimine salts, *N,N*-dialkyl salts, i.e., **9g–m** and **10g–m,** were hydrolyzed by sodium hydroxide, giving respectively 10-phenyl- and 10-methylphenothiazine 5-oxide. Thus, **9m** gave 98% of the former, and **10m** gave 91% of the latter.

Methylation of *N*-Alkylsulfilimines. Addition of methyl iodide to a solution of **13** in ether gave immediately a precipitate of 5-(benzylmethyliminio)-5,5-dihydro-10-phenylphenothiazine iodide (**15**) in 96% yield (eq 3). Meth-



13, R = Ph
14, R = Me

15, R = Ph
16, R = Me

(3)

ylation of **14** in methylene chloride gave 77% of the 10-methyl analog (**16**). Thus, this type of reaction allows the conversion of *N*-alkylsulfilimines into unsymmetrical *N,N*-dialkylaminosulfonium salts. Similar reactions were reported by Franz and Martin with *N*-alkyldiphenyl sulfilimines.[12] By exchange of anions a large variety of both symmetrical and unsymmetrical salts can be made, as illustrated below.

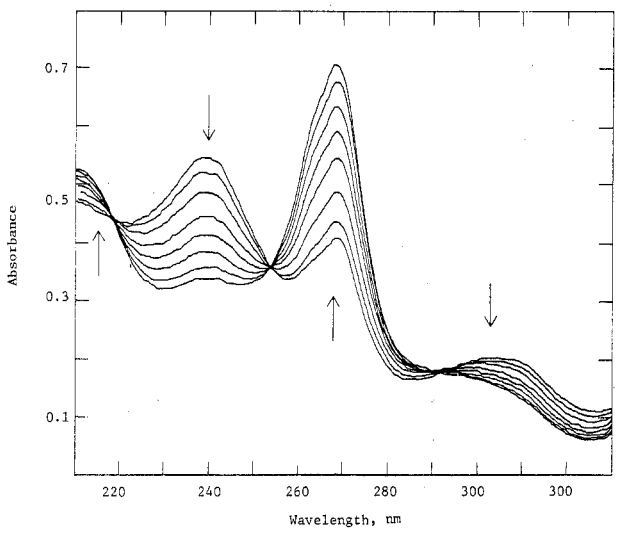
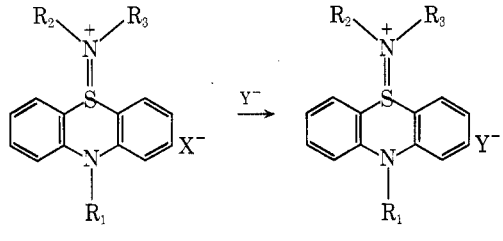


Figure 1. Changes in the spectrum of a 1.58×10^{-5} *M* solution of 5-(diisopropyliminio)-5,5-dihydro-10-methylphenothiazine perchlorate (**10i**) in acetonitrile which was 4.9×10^{-2} *M* in perchloric acid. The eight tracings were recorded at 1, 3, 10, 17, 23, 30, 37, and 44 min after adding the acid, and show the disappearance of protonated **10i** at 240 nm and the appearance of the 10-methylphenothiazine cation radical at 269 nm. Isosbestic points occur at 219, 254, and 292 nm.

Table IV
Exchange of Anions According to Equation 4

Compd	X	R_1	R_2	R_3	Y	Compd
9m	ClO_4	Ph	H	$C_6H_5CH_2$	I	**17**
10m	ClO_4	Me	$-(CH_2)_5-$		I	**18**
16	I	Me	Me	$C_6H_5CH_2$	ClO_4	**10n**
16	I	Me	Me	$C_6H_5CH_2$	NO_3	**20**

Exchange of Anions in Sulfilimine Salts. Reaction of **9m** and **10m** with excess of potassium iodide in methanol solution gave the corresponding iodides **17** (94%) and **18** (86%). Conversion of an iodide into a perchlorate (**16** into **10n**) was carried out with silver perchlorate, while treatment of **16** with silver nitrate gave the corresponding nitrate (**20**) (eq 4 and Table IV).



(4)

Reactions of Compounds 9 and 10 with Acids. Kim and Shine found that addition of a small amount of concentrated hydrochloric acid to a solution of **3** in acetonitrile led to the quantitative formation of thianthrene.[11] Recently, Franz and Martin applied this reaction to *N*-alkyldiphenyl sulfilimines and observed the formation of diphenyl sulfide and chlorodiphenyl sulfides.[12] Reactions of acids with *N*-alkyl- and *N,N*-dialkylsulfilimines in the phenothiazine series is not as straightforward as the previous findings might lead us to believe, however. We have isolated the products of reaction of **9f** and **10d** with hydrochloric acid, and of **9f** and **10m** with hydriodic acid, and we have followed spectroscopically the reactions of some of these compounds with hydrochloric acid (**9c, 10d, 10i,** and **10m**) and perchloric acid (**10i**). Illustrations of spectroscopic changes which occur are given for **10i** with perchloric acid (Figure 1) and for **10d** with hydrochloric acid (Figure 2).

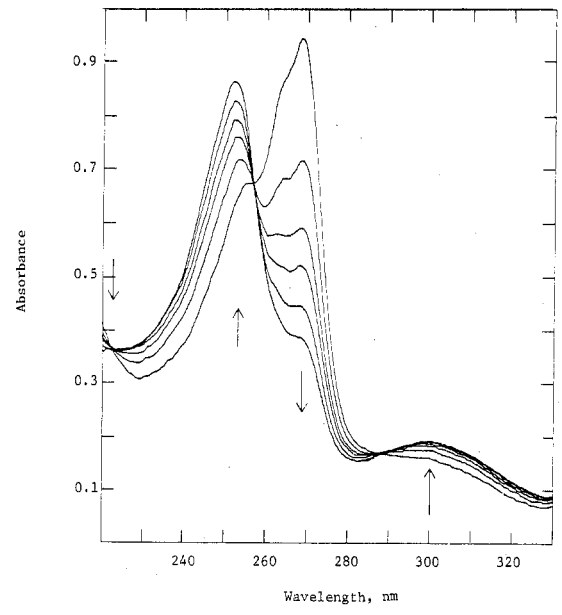
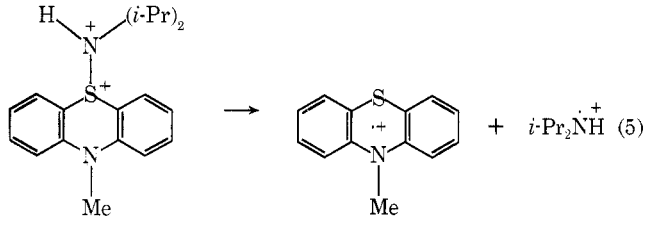


Figure 2. Changes in the spectrum of a 2.5×10^{-5} *M* solution of 5-(*tert*-butyliminio)-5,5-dihydro-10-methylphenothiazine perchlorate in acetonitrile which was 2.8×10^{-2} *M* in hydrochloric acid. The six tracings were recorded at 1, 3.5, 6.5, 10, 15, and 28 min after adding the acid, and show the disappearance of the 10-methylphenothiazine cation radical (formed immediately on adding the acid) at 269 nm and the appearance of a product peak at 252 nm. Isosbestic points occur at 223, 257, and 287 nm.

All reactions with acids were carried out in acetonitrile solution.

Reaction of **9f** with hydrochloric acid gave 19% of 10-phenylphenothiazine, 55% of 3-chloro-10-phenylphenothiazine, and a small amount (11%) of 3,7-dichloro-10-phenylphenothiazine. Reaction of **10d** with hydrochloric acid gave 23% of 10-methylphenothiazine, 65% of 3-chloro-10-methylphenothiazine, and also a small amount (not determined) of the 3,7-dichloro compound. Separation of the products was troublesome and was achieved only with TLC, for which purpose a large number of plates, each streaked with about 4 mg of product mixture, was used.

The complexity of the reactions with acids was revealed when they were followed spectroscopically. Reaction with perchloric acid is illustrated with **10i** in acetonitrile which was 4.9×10^{-2} *M* in acid (Figure 1). Here one sees the disappearance of protonated **10i** at 240 nm and the appearance of the 10-methylphenothiazine cation radical at 269 nm. Three isosbestic points are to be seen, indicating that a simple transformation is occurring. The behavior of **10i** is very much like the behavior of 10-methylphenothiazine 5-oxide and analogous 5-oxides in acid solutions,[13,14] and suggests that protonated **10i** is undergoing homolytic cleavage (eq 5). We do not have, as yet, confirming evidence for

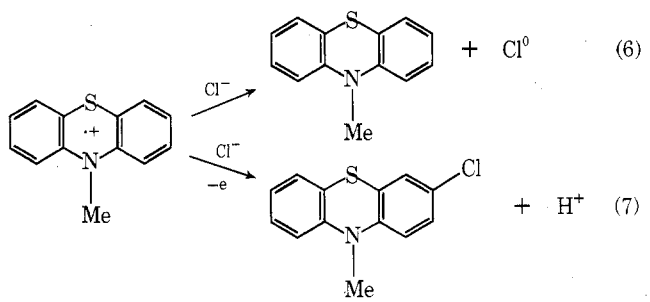


(5)

the formation of the second cation radical, that of diisopropylamine.

Reaction with hydrochloric acid in concentrations near 10^{-2} *M*, in each of the four cases investigated so far (**9c, 10d, 10i, 10m**), led first, rapidly, to the appearance of the parent cation radical. This was followed by the slower dis-

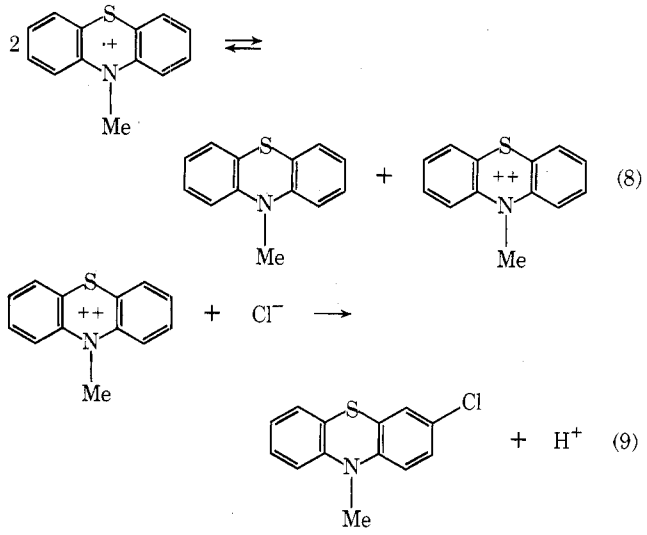
appearance of the cation radical. By adjustment of acid concentration it was possible in some instances to record the rapid rise in concentration of the cation radical before its slower fall. An example of the disappearance of the cation radical, once it had been formed, is given in Figure 2 for the reaction of **10d** in acetonitrile which was 2.8×10^{-2} *M* in acid. Here one sees the disappearance of the 10-methylphenothiazine cation radical at 269 nm and the appearance of a peak at a wavelength approaching 252 nm. (The maximum moves from 254 nm to 252 nm over the run, reflecting the influence of the cation radical's absorbance at 256 nm.) Again, isosbestic points are observed (at 223, 257, and 287 nm), indicating that the transformation of the cation radical into product(s) is direct. This presents a problem at the present time which will require further experimental analysis. That is, the two major products of reaction of **10d** with hydrochloric acid were 10-methyl- and 3-chloro-10-methylphenothiazine. These have very similar absorption spectra, i.e., respectively λ_{max} ($10^{-4}\epsilon$) 250 (3.83), 302 (0.533) and 253 (3.92), 306 (0.529). These data and the changes in Figure 2 suggest that both 10-methyl- and 3-chloro-10-methylphenothiazine are being formed directly from the cation radical, as illustrated in eq 6 and 7. A problem with this interpretation is that some 3,7-dichloro-10-methylphenothiazine was also obtained from **10d**, and some 3,7-dichloro-10-phenylphenothiazine was obtained from **9f**. In contrast, reaction of 10-methylphenothiazine cation radical directly with hydrochloric acid in acetonitrile gave only 10-methyl- and 3-chloro-10-methylphenothiazine. None of the 3,7-dichloro compound was detectable by TLC. Similar results were obtained with 10-phenylphenothiazine cation radical.



(6)

(7)

It is possible, therefore, that eq 6 and 7 do not represent correctly the reaction of the cation radicals with chloride ion, but that this involves disproportionation (eq 8 and 9).



(8)

(9)

To satisfy Figure 2, the disproportionation equilibrium would have to be very small and rapidly reached. The difference in reactions of, say, **10d** and 10-methylphenothiazine cation radical with hydrochloric acid (that is, formation of 3,7-dichloro-10-methylphenothiazine from **10d**) might then lie in the involvement of the alkylamine cation radical (t-$BuNH_2{\cdot}^+$, which may be formed from **10d**) with chloride ion (eq 10).

$$RNH_2{\cdot}^+ + Cl^- \rightarrow RNH_2 + Cl^0 \quad (10)$$

Chlorine so formed would be available to chlorinate 10-methyl- and 3-chloro-10-methylphenothiazine.

The reaction of hydrochloric acid with *N*-alkyldiphenyl sulfilimines is represented by Franz and Martin[12] as involving the stepwise formation of diphenyl sulfide dichloride, which dissociates into diphenyl sulfide and chlorine. The chlorine then is available to cause nuclear chlorinations of the diphenyl sulfide (eq 11–13). Analogous proposals are to be found in the literature for the reactions of sulfoxides with hydrogen chloride (e.g., in the racemization of optically active sulfoxides[15]). Our present results show that the reactions of sulfilimines with HCl must follow other paths besides this, and that common features are to be seen[13,14] in the reactions of sulfilimines and sulfoxides with acids.

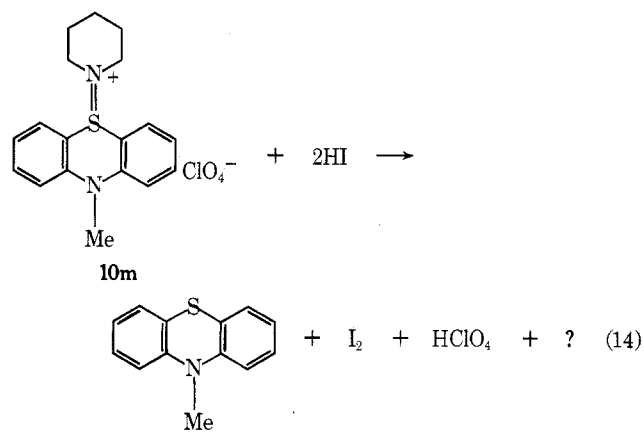
$$Ph_2S{=}NR + HCl \rightarrow \rightarrow Ph_2SCl_2 + RN^+H_3Cl \quad (11)$$

$$Ph_2SCl_2 \rightleftarrows Ph_2S + Cl_2 \quad (12)$$

$$Ph_2S + Cl_2 \rightarrow ClC_6H_4SPh + HCl \quad (13)$$

Certainly, the reactions of sulfilimines in the phenothiazine and related series with acids have unanticipated complexities and merit further study. Our results are reported here in a preliminary way to give some measure of the scope of these reactions which is not apparent from the earlier reports.[11,12]

It is not surprising that hydriodic acid reduces the sulfilimines. Reaction with **10m** gave 93% of 10-methylphenothiazine and 95% of iodine based on the stoichiometry of eq 14. The fate of the piperidine group was not pursued. Reaction of iodide ion alone (as potassium iodide) with **10m** did not cause reduction, but gave 88% of **18**. Similarly, **9f** with hydriodic acid gave 99% of 10-phenylphenothiazine, and **9m** with potassium iodide gave only the iodide salt of **17** in 94% yield. The data can be accommodated with homolytic cleavage of protonated salt (e.g., protonated **10m**) followed by reduction of the two cation radicals (e.g., of 10-methylphenothiazine and piperidine) by iodide ion.



10m

(14)

We recognize also, though, that reduction by hydrogen iodide could take place as in eq 11–13. Dimethyl sulfilimine,[16] its *N*-arylsulfonyl derivatives, and the *N*-arylsulfonyl derivatives of diethyl sulfilimine[17] have been reduced with sodium iodide in aqueous perchloric acid, and the kinetics of reduction have been explained[17] by steps analogous to those in these equations. At the same time, these

dialkyl sulfilimines were stable toward perchloric acid alone and were not reduced by sodium chloride and bromide in perchloric acid.[17] Thus, the behavior of our sulfilimines is different from that of the dialkyl ones in these respects, so that reduction of ours by hydrogen iodide may indeed follow the unusual, cation radical pathway.

Analogously, reaction of some of our sulfilimine perchlorate salts with hydrobromic acid led immediately to the formation of bromine, but we have not given further attention to these reactions yet. We hope to do so, and to report on these hydrogen halide reactions in more detail later.

Experimental Section

10-Phenyl- and 10-methylphenothiazine were commercial samples and were recrystallized before use. 10-Phenylphenothiazine cation radical perchlorate (**7**) was prepared as follows. To a stirred solution of 1.65 g (6 mmol) of *N*-phenylphenothiazine and 1.26 g (5.8 mmol) of $AgClO_4$ in 8 ml of dry MeCN and 25 ml of dry CH_2Cl_2 was added 1.02 g (8 mmol) of solid I_2. The mixture was filtered after being stirred for 1 hr, and **7** was obtained by adding dry ether to the filtrate. The precipitate of **7** (2.1 g, 5.6 mmol, 93%) was filtered on glass-fiber paper and washed with ether. Its purity was determined by reaction with KI and potentiometric titration of the liberated I_2. Routinely, assays of 96–98% cation radical were obtained. 10-Methylphenothiazine cation radical perchlorate (**8**) was prepared by reaction of 3.45 g (15 mmol) of 10-methylphenothiazine 5-oxide and 3.21 g (15 mmol) of 10-methylphenothiazine in 35 ml of 70% $HClO_4$. After 5 min 150 ml of dry acetone and 500 ml of dry ether were added in sequence. The precipitate of 8.27 g (26.4 mmol, 88%) of **8** was filtered on glass-fiber paper and washed with dry ethyl acetate. Iodimetric analysis gave an assay of 92% cation radical. The preparation of **8** by oxidizing 10-methylphenothiazine with I_2–$AgClO_4$ in ethanol has been reported recently,[18] and analysis of the product indicated that it was a monohydrate. If the **8** isolated by us is the hydrate, its cation radical content would be 97%. All yields of products of reactions of **8**, however, were calculated on the basis of 92% cation radical content.

Acetonitrile was Eastman anhydrous grade (0.01% water) and was stored over molecular sieve in a septum-capped bottle. Thick layer chromatography was performed with Merck silica gel GF254. Commercial amines and ammonia gas were used without further purification.

Reactions of 7 and 8 with Amines and Ammonia. To a solution of **7** or **8** in 5 ml of acetonitrile was added an excess of the reactant. In the case of gaseous amines and ammonia, the gas was bubbled into the acetonitrile solution. Reactions appeared to be over within 1 min, but the reaction mixture was stirred for about 30 min before being worked up.

Work-Up Procedure A. The reaction mixture was extracted with 5 × 50 ml of petroleum ether (bp 30–60°) to remove the 10-substituted phenothiazine and its 5-oxide. The petroleum ether solution was concentrated and chromatographed on silica gel plates with ether as the developer. The acetonitrile solution was diluted with methylene chloride, and this solution was washed with 3 × 100 ml of water, dried, and concentrated to give the crude sulfilimine perchlorate (**9** or **10**) which was crystallized from methylene chloride–pentane.

Work-Up Procedure B. The reaction mixture was streaked on TLC plates and chromatographed using as developer ether for reactions of **7** and carbon tetrachloride for reactions of **8**. The sulfilimine and ammonium perchlorates remained as one band at the origin from which they were removed with methylene chloride and washed with water. The crude sulfilimine perchlorate was crystallized as above.

Reactions of Sulfilimines 9 and 10 with Acids. A. Spectroscopic Changes. Three milliliters of a solution of the sulfilimine (**9c, 10d, 10i, 10m**) of known concentration was placed in a cuvette and to this was added a small amount of acid. A measured volume (0.02–0.05 ml) of standardized aqueous acid was added from a microburet and the final concentration of acid in the acetonitrile solution was calculated. Recording of spectra was begun immediately after the glass-stoppered cuvette was shaken for mixing, and was continued at timed intervals. A Beckman DK-2A spectrophotometer was used.

B. Reaction of 9f with HCl. Products. To a solution of 217 mg (0.519 mmol) of **9f** in 10 ml of acetonitrile was added 1 ml of concentrated HCl. An immediate development of purple-brown color occurred. The mixture was stirred for 4 days, quenched with aqueous Na_2CO_3 solution, dried over K_2CO_3, and evaporated to give 205 mg of solid residue. The residue was separated by TLC, for which purpose about 4 mg at a time was streaked on a plate and developed with CCl_4. Three bands were obtained on each plate, and these were removed and extracted with acetone. The lowest band consisted of 10-phenylphenothiazine (35 mg, 0.127 mmol, 19% of the **9f** used), mp 92° after crystallization from aqueous ethanol. The second band consisted of 3-chloro-10-phenylphenothiazine (89 mg, 0.29 mmol, 55%), mp 82–83° (aqueous ethanol) (lit. mp 76–77°),[19] λ_{max} (MeCN) 255 nm (ϵ 5.04 × 10^4) and 320 (4.30 × 10^3). The uppermost band which overlapped the top of the second band gave 20 mg of a semisolid product which we believe to be 3,7-dichloro-10-phenylphenothiazine, mp 110–112.5° (from ethanol–water), with satisfactory mass spectrum. Yield of crude product was 11%.

C. Reaction of 10d with HCl. Products. A similar procedure was used with 103 mg (0.269 mmol) of **10d**. TLC of the residue (total 70 mg) gave again three bands, the lowest of which gave 13 mg (0.061 mmol, 23% of the **10d** used) of 10-methylphenothiazine, mp 97–99° (from ethanol–water). The second band gave 43.5 mg (0.176 mmol, 65%) of 3-chloro-10-methylphenothiazine, mp 112–113° (from ethanol) (lit. mp 110–112°),[20] λ_{max} (MeCN) 253 nm (ϵ 3.92 × 10^4), 306 (5.29 × 10^3). The uppermost band, which overlapped the top of the second, gave 6 mg of an unidentified product, believed from mass spectrum to be 3,7-dichloro-10-methylphenothiazine.

D. Reaction of 10m with HI. Products. To a solution of 14.2 mg (0.0355 mmol) of **10m** in 15 ml of MeCN was added 4 drops of concentrated HI. The solution immediately turned yellow. Twenty milliliters of water was added, and the iodine in the aqueous solution was titrated potentiometrically with $Na_2S_2O_3$ solution, giving 0.0338 mmol (95%) of I_2.

A second reaction was carried out using 52.9 mg (0.131 mmol) of **10m** in 20 ml of MeCN and 0.5 ml of concentrated HI in 0.2 ml of water. The iodine was reduced with aqueous $Na_2S_2O_3$ and the solution was extracted with petroleum ether, giving, after drying over $MgSO_4$, 26 mg (0.122 mmol, 93%) of 10-methylphenothiazine, mp 98–100°.

E. Reaction of 9f with HI. Product. To a solution of 102 mg 0.212 mmol) of **9f** in 5 ml of MeCN was added 1 ml of concentrated HI. Iodine was formed but not assayed. Work-up (extraction with ether) gave 59 mg (0.212 mmol, 100%) of 10-phenylphenothiazine, mp 93–94°.

Reactions of Sulfilimine Salts with NaOH. A. Formation of 5-(Benzyliminio)-5,5-dihydro-10-phenylphenothiazine (13) from 9f. A solution of 276 mg (0.56 mmol) of **9f** in 20 ml of MeOH was stirred for 2 hr with a few drops of 50% aqueous NaOH. After concentration at room temperature water was added and the precipitated solid was taken up in ether to give 188 mg (0.495 mmol, 88%) of **13**: mp 146–147° (from ether); λ_{max} (MeCN) 207 nm (10^{-4} ϵ 5.19), 254 (1.71), 275 (1.58), 304 (0.86), and 335 (0.77); ^1H NMR ($CDCl_3$) δ 8.5–6.3 (m, 18 H, aromatic) and 3.45 (s, 2 H, $-CH_2-$).

Anal. Calcd for $C_{25}H_{20}N_2S$: C, 78.9; H, 5.29; N, 7.36. Found: C, 79.0; H, 5.41; N, 7.36.

B. Hydrolysis of 9m to 10-Phenylphenothiazine 5-Oxide. Treatment of 85 mg (0.183 mmol) of **9m** as above gave 52 mg (0.179 mmol, 98%) of 10-phenylphenothiazine 5-oxide, mp 171–172° (lit. mp 172–173°).[21]

C. Hydrolysis of 10m. Formation of 10-Methylphenothiazine 5-Oxide. A solution of 103 mg (0.260 mmol) of **10m** in 25 ml of EtOH and 1 ml of 50% NaOH was boiled for 24 hr. Dilution with water and extraction with CH_2Cl_2 gave 54.2 mg (0.236 mmol, 91%) of 10-methylphenothiazine 5-oxide, mp 192–194° (lit. mp 194–196°).[13]

Methylation of *N*-Benzylsulfilimines. A. Formation of 5-(Benzylmethyliminio)-5,5-dihydro-10-phenylphenothiazine Iodide (15) from 13. To a solution of 300 mg (0.79 mmol) of **13** in 25 ml of dry ether was added several milliliters of MeI. The immediately formed white precipitate was removed and washed with ether, giving 401 mg (0.77 mmol, 96%) of **15**: mp 149–150° (from CH_2Cl_2–ether); λ_{max} (MeCN) 347 nm (10^{-3} ϵ 9.3), 308 (9.7), and 243 (42.7); ^1H NMR ($CDCl_3$) δ 8.4–8.16 (m, 2 H, aromatic), 7.9–7.0 (m, 14 H, aromatic), 6.83–6.6 (m, 2 H, aromatic), 4.4 (s, 2 H, NCH_2-), 2.45 (s, 3 H, *N*-Me).

Anal. Calcd for $C_{26}H_{23}N_2SI$: C, 59.8; H, 4.43; I, 24.3. Found: C, 59.6; H, 4.52; I, 24.1.

B. Formation of 5-(Benzylmethyliminio)-5,5-dihydro-10-methylphenothiazine Iodide (16) from 10f. To a solution of 563 mg (1.34 mmol) of **10f** in 30 ml of MeOH was added 1 ml of 50% NaOH. After adding 30 ml of water the solution was extracted with

CCl_4, and to the dried ($MgSO_4$) CCl_4 solution was added 3 ml of MeI. The solution was evaporated, the residue was taken up in CH_2Cl_2, and ethyl acetate was added to induce crystallization, giving 476 mg (1.03 mmol, 77%) of **16**: mp 128–129°; λ_{max} (MeCN) 355 nm (10^{-3} ϵ 6.7), 302 (7.1), 241 (30.0); ^1H NMR ($CDCl_3$) δ 8.32–7.16 (m, 13 H, aromatic), 4.27 (s, 2 H, NCH_2–), 3.94 (s, 3 H, 10-Me), 2.31 (s, 3 H, *N*-Me).

Anal. Calcd for $C_{21}H_{21}N_2SI$: C, 54.8; H, 4.60; N, 6.08; S, 6.96; I, 27.6. Found: C, 55.0; H, 4.54; N, 5.98; S, 6.75; I, 27.4.

Exchange of Anions in Sulfilimine Salts. A. Formation of 5-(Benzyliminio)-5,5-dihydro-10-phenylphenothiazine Iodide (17) from 9m. To a solution of 125 mg (0.26 mmol) of **9m** in 20 ml of MeOH was added several grams of KI. The mixture was stirred for 2 hr, diluted with 200 ml of water, and extracted with CH_2Cl_2. The dried CH_2Cl_2 solution was evaporated, and the residue was crystallized from CH_2Cl_2–ether, giving 125 mg (0.246 mmol, 94%) of **17**: mp 147–148.5°; λ_{max} (MeCN) 346 nm (10^{-3} ϵ 7.78), 311 (8.35), 271 (13.7), and 243 (38.2).

Anal. Calcd for $C_{25}H_{21}N_2SI$: C, 59.1; H, 4.16; I, 24.9. Found: C, 59.5; H, 4.07; I, 24.7.

B. Formation of 5,5-Dihydro-10-methyl-5-piperidinium-1-ylidenephenothiazine Iodide (18) from 10m. To a solution of 497 mg (1.25 mmol) of **10m** in 75 ml of MeOH was added 5 g of KI in 15 ml of water. After 20 min the solution was extracted with CH_2Cl_2. Drying and evaporation of the CH_2Cl_2 gave 457 mg (1.08 mmol, 86%) of **18**: mp 137–138° (from CH_2Cl_2–ether); λ_{max} (MeCN) 350 nm (10^{-3} ϵ 6.1), 307 (7.0), 267 (14.0), and 242 (29.0); ^1H NMR ($CDCl_3$) δ 8.4–7 (m, 8 H, aromatic), 3.95 (s, 3 H, 10-Me), 2.8 (s, 4 H, 2 $-CH_2-$), and 1.43 (s, 6 H, 3 $-CH_2-$).

Anal. Calcd for $C_{18}H_{21}N_2SI$: C, 50.9; H, 4.99; I, 29.9. Found: C, 50.6; H, 4.95; I, 29.6.

C. Formation of 5-(Dibenzyliminio)-5,5-dihydro-10-phenylphenothiazine Iodide (19) from 9j. The procedure for making **17** was followed, using 106 mg (0.185 mmol) of **9j**, and giving 102 mg (0.171 mmol) of **19**, mp 138.5–140°.

Anal. Calcd for $C_{32}H_{27}N_2SI$: C, 64.2; H, 4.54; I, 21.2. Found: C, 64.2; H, 4.51; I, 20.9.

D. Formation of 5-(Benzylmethyliminio)-5,5-dihydro-10-methylphenothiazine Perchlorate (10n) from 16. To a solution of 90.3 mg (0.196 mmol) of **16** in 10 ml of MeOH was added 500 mg of $AgClO_4$ in 5 ml of water. AgI precipitated and was filtered. Extraction of the filtrate with CH_2Cl_2 and drying ($MgSO_4$) gave 73 mg (0.168 mmol, 86%) of **10n**: mp 137–138° (from CH_2Cl_2–ether); λ_{max} (MeCN) 355 nm (10^{-3} ϵ 6.9), 308 (7.5), 266 (14.0), and 220 (34.0); ^1H NMR (CD_3CN) δ 8.12–7.12 (m, 13 H, aromatic), 4.08 (s, 2 H, $-CH_2-$), 3.78 (s, 3 H, 10-Me), 2.22 (s, 3 H, *N*-Me).

Anal. Calcd for $C_{21}H_{21}N_2O_4SCl$: C, 58.3; H, 4.89; Cl, 8.19. Found: C, 57.95; H, 5.07; Cl, 7.98.

E. Formation of 5-(Benzylmethyliminio)-5,5-dihydro-10-methylphenothiazine Nitrate (20) from 16. A similar procedure using $AgNO_3$ gave 96% of **20**: mp 129–130° (from CH_2Cl_2–ether); λ_{max} (MeCN) 354 nm (10^{-3} λ 7.0), 308 (7.7), and 266 (15.0); ^1H NMR ($CDCl_3$) δ 8.18–6.91 (m, 13 H, aromatic), 4.15 (s, 2 H, NCH_2–), 3.85 (s, 3 H, 10-Me), and 2.25 (s, 3H, *N*-Me).

Anal. Calcd for $C_{21}H_{21}N_3O_3S$: C, 63.8; H, 5.35; N, 10.6. Found: C, 63.9; H, 5.38; N, 10.5.

Reaction of 8 with HCl. Products. To a solution of 100 mg (0.321 mmol) of **8** in 10 ml of MeCN was added 1 ml of concentrated HCl. The solution was stirred for 4 days, quenched with aqueous $NaHCO_3$, and extracted with CH_2Cl_2. Work-up by TLC (see earlier) gave 34.8 mg (0.163 mmol, 55%) of 10-methylphenothiazine and 25 mg (0.101 mmol, 34%) of 3-chloro-10-methylphenothiazine, mp 112–113° (from ethanol). No 3,7-dichloro-10-methylphenothiazine appeared to have been formed.

Registry No.—**7**, 52156-15-7; **8**, 54014-67-4; **9a**, 55222-71-4; **9b**, 55222-73-6; **9c**, 55267-56-6; **9e**, 55222-75-8; **9f**, 55222-77-0; **9g**, 55222-79-2; **9h**, 55222-81-6; **9i**, 55222-83-8; **9j**, 55222-85-0; **9k**, 55222-87-2; **9l**, 55222-89-4; **9m**, 55222-91-8; **10a**, 55222-93-0; **10c**, 55222-95-2; **10d**, 55222-97-4; **10e**, 55222-99-6; **10f**, 55223-01-3; **10g**, 55223-03-5; **10i**, 55223-05-7; **10k**, 55223-07-9; **10l**, 55223-09-1; **10m**, 55223-11-5; **10n**, 55223-13-7; **11**, 7152-42-3; **12**, 1207-72-3; **13**, 55223-14-8; **15**, 55223-15-9; **16**, 55223-16-0; **17**, 55223-17-1; **18**, 55223-18-2; **19**, 55223-19-3; **20**, 55223-20-6; propylamine, 107-10-8; *tert*-butylamine, 75-64-9; cyclohexylamine, 108-91-8; benzylamine, 100-46-9; dimethylamine, 124-40-3; diethylamine, 109-89-7; diisopropylamine, 108-18-9; dibenzylamine, 103-49-1; azetidine, 503-29-7; pyrrolidine, 123-75-1; piperidine, 110-89-4; methylamine, 74-89-5; ethylamine, 75-04-7; ammonia, 7664-41-7; 10-methylphenothiazine 5-oxide, 2234-09-5; 3-chloro-10-phenylphenothiazine, 16684-59-6; 3,7-dichloro-10-phenylphenothiazine, 16717-05-8; 3-chloro-10-methylphenothiazine, 4048-46-8; 3,7-dichloro-10-methylphenothiazine, 55223-21-7; 10-phenylphenothiazine 5-oxide, 23099-78-7.

Supplementary Material Available.—Tables II and III will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JOC-75-2590.

References and Notes

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(19) I. M. Roushdi and S. Rida, *J. Pharm. Sci. UAR*, **6**, 99 (1965), prepared 3-chloro-10-phenylphenothiazine by treating 10-phenylphenothiazine 5-oxide with concentrated HCl. We have repeated this procedure and find that the separation of the 3-chloro-10-phenyl- and 10-phenylphenothiazine, both of which are formed, by crystallization as described could not be achieved completely. It is our feeling, therefore, that the reported melting point and yield of 3-chloro-10-phenylphenothiazine are in error. Separation was achieved only by TLC, by which technique we also isolated a small amount of 3,7-dichloro-10-phenylphenothiazine: λ_{max} (MeCN) (10^{-4} ϵ) 252 (5.39), 255 (5.04), and 257.5 (4.90), respectively.
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