[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, TEXAS TECHNOLOGICAL COLLEGE, LUBBOCK, TEX., AND VARIAN ASSOCIATES, INSTRUMENT DIVISION, PALO ALTO, CALIF.]

Ion-radicals. The Reaction of Thioaromatic Compounds with Acids. II. Diphenyl Disulfide, Thianthrene and Thianthrene Oxides[1,2]

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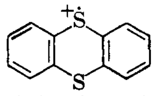
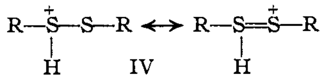
It has not been found possible to recover diphenyl disulfide (I) from solution in 100% sulfuric acid as reported elsewhere.[4] When 100% sulfuric acid is poured through a bed of I and immediately received onto ice the I is recoverable. In this case the acid solution is pale green rather than purple. Solutions of thianthrene (III), its monoxide V and *cis*-dioxide VI in 96%, 97%, 100% and fuming sulfuric acid have been investigated. Ultraviolet, visible, near infrared and e.s.r. spectra have been recorded. Products have been isolated quantitatively. Some observations on III in trifluoroacetic acid are made and the work of Fava, Sogo and Calvin[5] is discussed. Solutions of III in 96–97% sulfuric acid are paramagnetic. It is proposed that the species present is the positive ion-radical . The transformation of V to this species in 96–97% acid is shown in the visible and ultraviolet region and the absorption spectra changes are related to the growth of the spin signal in e.s.r. spectroscopy. The products isolated from III in 96–97% acid are III and V. From III in 100% acid and fuming sulfuric acid the product is mostly V. From solutions of V in 96% acid that have been kept some time the major product is III. It is tentatively proposed that an additional product from these solutions, not yet identified, results from some V behaving as an acceptor during the conversion of V to the ion-radical. Proposals are made to account for the one-electron oxidation of III to the ion-radical. The ion-radical has been detected also in solutions of III in benzene and chloroform to which aluminum chloride was added.

Our interest in the benzidine rearrangement led us some years ago to investigate whether or not diphenyl disulfide (I) would undergo a similar rearrangement to give 4,4'-dimercaptobiphenyl (II). It had already been shown[3] some fifty years earlier that I on treatment with 100% sulfuric acid was converted to water-soluble products and a small amount of thianthrene (III), and our interest lay in further examining the way in which the thianthrene was formed and in the nature of the soluble products.

It developed, from publications that appeared in due course, that somewhat similar investigations to ours were proceeding independently in two other laboratories.[4,5] It developed further that the results obtained in the three laboratories and their interpretations[1,4,5] were not in accord with each other. Thus, Szmant and Lapinsky were able to recover I almost quantitatively from 100% sulfuric acid, while Shine and Bear[1] and Fries and Volk[3] obtained from this solvent only a small amount of III other than products soluble in aqueous sulfuric acid. Further, whereas Shine and Bear obtained from 96% sulfuric acid products which appeared to be derived from polymeric II, Fava, Sogo and Calvin[5] with 98% sulfuric acid interpreted their results on the basis of the conversion of I to III.

In order to unravel these apparent discrepancies we have continued our investigation and are now able to comment briefly on the behavior of I in sulfuric acid and, more importantly, in more detail on the chemistry of III.

Diphenyl Disulfide in Sulfuric Acid.—The discrepancies here seem to result from differences in the strength of the acid, the time of contact and the concentration of I in solution. Szmant and Lapinsky[4] reported that compound I was recoverable from concentrated (5 g./50 ml.) solutions prepared in cold 100% acid and kept subsequently at ice temperature for 30 minutes. The purple color of the solution was attributed to the monoprotonated species IV.



$$R-\underset{H}{\overset{+}{S}}-S-R \longleftrightarrow R-S{=}\underset{H}{\overset{+}{S}}-R$$

IV

The recovery of I was attributed[4] to the fact that diprotonation of I was impossible, because of charge distribution in IV, and, therefore, that the benzidine type rearrangement[6] could not take place.

We have been repeatedly unable to reproduce this work. Even with the most careful control, beginning with the acid just above its melting point and allowing only 30 minutes contact between the I and the magnetically stirred acid, cooled in ice, the only I recoverable was the I that had not dissolved in the 100% sulfuric acid. We are unable to account for the results reported[4] except for our observation that if the cold sulfuric acid is rapidly filtered through a bed of I and the filtrate is received immediately onto ice the I is recoverable. In this case, however, the resulting solution is not purple before it reaches the ice. Instead it is pale green. Thus, if I is kept in solution long enough to give the characteristic intense purple color it is not recoverable. Now, while our results demonstrate that compound I can be recovered, but not by Szmant and Lapinsky's procedure, they raise another question of whether the purple color is due to IV. From work by Fava, Sogo and Calvin[5] and our results to be described below it appears that the

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[1] For part I see H. J. Shine and J. L. Bear, *Chemistry & Industry*, 565 (1957).

[2] Presented in part at (a) the Southwest Regional Meeting of the American Chemical Society, Baton Rouge, La., December, 1959; and (b) the 18th International Congress of Pure and Applied Chemistry, Montreal, Can., 1961.

[3] K. Fries and W. Volk, *Ber.*, **42**, 1172 (1909).

[4] H. H. Szmant and R. L. Lapinsky, *J. Org. Chem.*, **21**, 847 (1956).

[5] (a) A. Fava, P. B. Sogo and M. Calvin, University of California Radiation Laboratory, Berkeley, Calif., Report UCRL 3531, November 1, 1956. Available from the Office of Technical Services, U. S. Department of Commerce, Washington 25, D. C.; (b) A. Fava, P. B. Sogo and M. Calvin, *J. Am. Chem. Soc.*, **79**, 1078 (1957).

[6] G. S. Hammond and H. J. Shine, *ibid.*, **72**, 220 (1950).

color is not due to IV. It is possible that the fleeting green color is due to the protonated species IV. It is interesting that a similar rapid color change has been observed with perylene[7]; in that case the color change is attributable to protonated species going to the purple solution of the positive ion-radical.

The second discrepancy, that between Shine and Bear using 96% sulfuric acid and Fava, Sogo and Calvin using 98% acid, may be due to no more than the concentration of I used. Results very similar to those of Shine and Bear were obtained by Hilditch[8] working with thiophenol and with benzenesulfinic acid in concentrated sulfuric acid. Hilditch interpreted his results as the formation of *p*-phenylene disulfide, an interpretation that seems to us to be in error because of the great difference between the properties of III and the so-called, somewhat analogous, *p*-phenylene disulfide. The fact that Hilditch and Shine and Bear used high concentrations of solute points to the possible reason for the difference from the interpretation of Fava, *et al.*[5] That is, in the dilute solutions used[5] intramolecular condensation leading to III may occur, while in the highly concentrated solutions[1,8] intermolecular condensation may occur.

Thianthrene and Thianthrene Monoxide.—Fava, Sogo and Calvin found[5] that the near infrared and visible spectra of I and III in 98% sulfuric acid are almost identical. Further, as had been reported in part by others,[9,10] the electron spin resonance spectra of the two solutions are similar. It was concluded[5] that all of these spectra were attributable to a derivative of III; that is, that I was converted to III and then III gave the species responsible for the spectra.[11] In investigating the nature of this species Fava, Sogo and Calvin confined their attention to III and its oxides. These authors, furthermore, obtained most of their quantitative data from solutions in trifluoroacetic acid rather than in sulfuric acid. They found that III and its oxides dissolve in trifluoroacetic acid to give pink solutions exhibiting the same spectral characteristics of the sulfuric acid solutions.

The formation of the radical by dissolving thianthrene in trifluoroacetic acid appears to be anomalous and was discussed by Fava, Sogo and Calvin. Colored solutions of III reported in the literature have been obtained from III only in oxidizing environments. An exception to this may be the work of Hirshon, Gardner and Fraenkel,[9] who obtained colored solids by heating III and also some other thio compounds with anhydrous aluminum chloride, but in these cases the colored solids showed no paramagnetic absorptions. Recently, the electron acceptor function of aluminum chloride has been proposed by Rooney and Pink[12] who have shown that certain polycyclic hydrocarbons are converted to their positive ion-radicals by aluminum chloride in solution. We have applied this technique to III and have found that with aluminum chloride in both benzene and in chloroform III gives colored solutions which are paramagnetic and which have the same visible and near infrared spectra as the 96% and 97% sulfuric acid solutions. The e.s.r. signals were single broad lines in each of the two solvents. We do not know how aluminum chloride in solution causes radical formation from either the hydrocarbons[12] or thianthrene, but, nevertheless, regardless of how the phenomenon occurs it is one of a one-electron oxidation.[12] Further, MacLean and van der Waals[13] have shown that a solution of thianthrene in hydrofluoric acid is colorless and not paramagnetic. Fava, Sogo and Calvin,[5] in discussing the anomaly of trifluoroacetic acid solutions of III, have attributed the properties of the solutions to the presence of either very strongly absorbed oxygen on the thianthrene or of a transannular peroxide impurity, which undergoes acid-catalyzed scission to lead eventually to the radical species responsible for the observed properties. We have attempted to resolve this question, but without success. We have found that III dissolves easily in trifluoroacetic acid used as purchased and without distillation, and that the solutions are deeply colored. When the acid is distilled the III does not dissolve well, the acid either remains colorless for a while and then becomes faintly colored, or the acid becomes faintly colored immediately and remains so for many days. We have degassed and distilled the acid on a diffusion-pump line onto degassed III. If this is done in apparatus open to the light the III becomes blue at Dry-Ice and liquid nitrogen temperatures and gives a red solution on warming to room temperature. If the apparatus and vacuum lines are wrapped in foil, which is removed only briefly from a small, upper portion of the receiving tube to permit flame-sealing, the solution of III remains colorless at room temperature for over an hour and then slowly on standing, even in wrapped tubes, becomes faintly colored.

We are unable to explain these observations. However, they do appear to be more of a function of the trifluoroacetic acid than of the III. We have observed that the undistilled trifluoroacetic acid liberates iodine from potassium iodide and that addition of 30% hydrogen peroxide solution to distilled trifluoroacetic acid standing colorless over III momentarily gives a strong pink color. It is notable, also, that the extinction coefficient at 546 mμ calculated from the data[5] given for trifluoroacetic acid solutions is approximately 1500, while that obtained by us in 96–97% sulfuric acid is approximately 8800.

The detailed work which we report here refers to solutions in sulfuric acid. Fava, Sogo and Calvin reported[5] that solutions of III in 98% sulfuric acid do not obey Beer's law over the range 10^{-4} to 10^{-3} M in the visible and near infrared, but do obey the Law at about 5×10^{-5} M.

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[7] W. Ij. Aalbersberg, G. J. Hoijtink, E. L. Mackor and W. P. Weijland, *J. Chem. Soc.*, 3049 (1959).

[8] T. P. Hilditch, *ibid.*, 2579 (1910).

[9] J. M. Hirshon, D. M. Gardner and C. R. Fraenkel, *J. Am. Chem. Soc.*, **75**, 4115 (1953).

[10] J. E. Wertz and J. Vivo, *J. Chem. Phys.*, **23**, 2193 (1955).

[11] It should be noted that while the near infrared and visible spectra of I and III in 98% sulfuric acid are almost identical, the ultraviolet spectra are quite different.

[12] J. J. Rooney and R. C. Pink, *Proc. Chem. Soc.*, 142 (1961).

[13] C. MacLean and J. H. van der Waals, *J. Chem. Phys.*, **27**, 827 (1957).

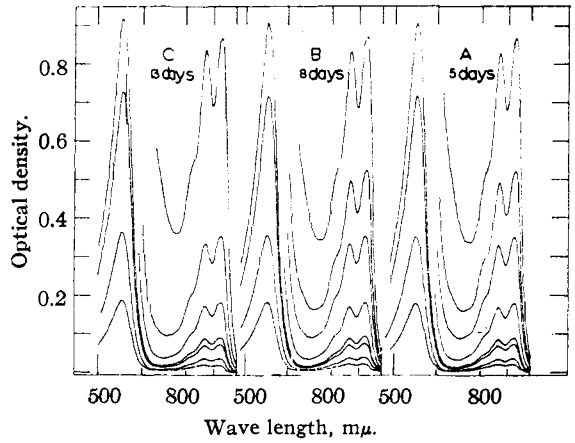


Fig. 1.—Thianthrene in 96% H_2SO_4; 2, 4, 8, 10, 20, 40, 60 and 100 × 10^{-5} *M*. Times begin from time of first contact of III with acid. Spectra show stability of solutions.

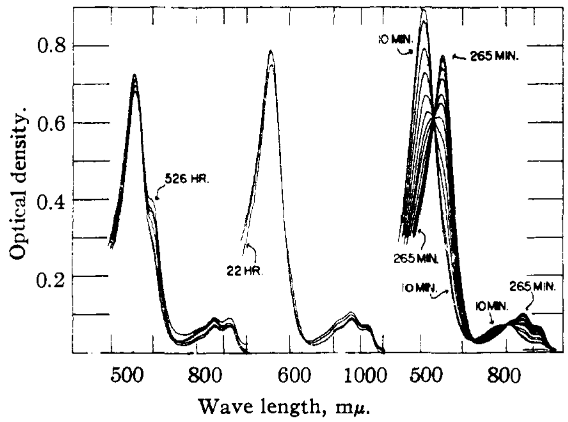


Fig. 2.—Thianthrene monoxide in 96% H_2SO_4; variation with time in the visible and near infrared spectra of an 8 × 10^{-5} *M* solution.

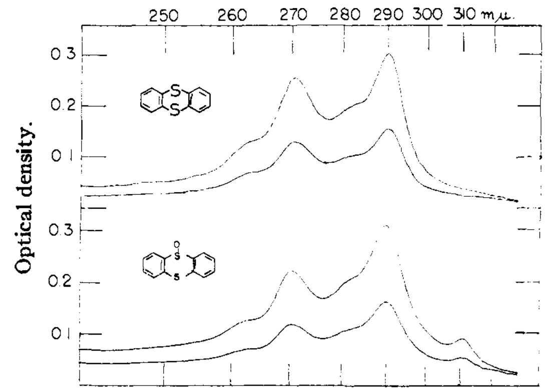


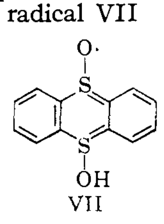
Fig. 3.—Ultraviolet absorption spectra of thianthrene and its monoxide in 96% H_2SO_4. The V solutions were 4 and 8 × 10^{-6} *M* and were 18 days old. The III solutions were 4 and 8 × 10^{-6} *M* and were 5 days old.

In our early work, carried out before the appearance of this[5] report, we found that Beer's law was obeyed over an extensive range in sulfuric acid. In view of the equilibrium system which has been proposed[5] for trifluoroacetic acid solutions, and which, presumably, might apply also to sulfuric acid solutions, we have again made a considerable number of optical density measurements with sulfuric acid solutions. We have worked mostly with III and its monoxide V. Some experiments with the *cis*-dioxide VI were also carried out. We have found that Beer's law is obeyed by solutions of III in 96% sulfuric acid over the range 2 × 10^{-5} to 10^{-3} *M* at the peaks 546, 920 and 1050 mμ, and over the range 4 × 10^{-6} to 4 × 10^{-5} *M* at the peaks 270.5 and 290.5 mμ. The concentration ranges covered were limited by the spectrophotometer and cells available. Solutions of III in 96% acid are stable over long periods of time as shown in Fig. 1.

In contrast to III, solutions of V in 96% sulfuric acid undergo two distinct changes, an early fast change followed by a slow. When V is first dissolved in 96–97% sulfuric acid the solution is amber. On standing, the solution becomes purple. These observations were made long ago by Fries and Vogt.[14] The amber solution has a visible spectrum with a peak at 502 mμ. As the solution changes color this peak disappears and is replaced by one at 546 mμ, the peak characteristic of solutions of III. At the same time the flattened maximum in the region 750–825 mμ for the amber solution is replaced by the two peaks at 920 and 1040 mμ of the purple solution. This change is shown in the first family of curves in Fig. 2. The second, slow change in V solutions is the development of a shoulder at 590 mμ shown in the third family of curves in Fig. 2. We shall refer to this region and its origin later.

Corresponding changes are observable in the ultraviolet. Thus, Fig. 3 shows the ultraviolet spectra of old solutions of III and V in 96% sulfuric acid, while Fig. 4 shows III and V in 100% sulfuric acid. It is evident that the spectra are almost identical in each acid. In Fig. 5 can be seen the change that occurs in the ultraviolet when V is first dissolved in 96% sulfuric acid. The replacement of the peak at 311 mμ by those at 270.5 and 290.5 mμ corresponds with the fast change shown in the visible and near infrared in Fig. 2. It is evident, therefore, that in 96% sulfuric acid V is converted to III or to a derivative of III, which III itself forms in 96% sulfuric acid. Once the fast change has occurred, that is, in solutions of V in 96% acid that are a day or so old, Beer's law is obeyed at 502, 590, 920 and 1040 mμ over the range 2 × 10^{-5} to 10^{-3} *M*, and at 270.5 and 290.5 mμ over the range 4 × 10^{-6} to 4 × 10^{-5} *M*.

Fava, Sogo and Calvin[5] have attributed the electron spin resonance spectra and consequently the absorption spectra, too, of solutions of III, V and VI to the radical VII



VII

and the VII is postulated as arising from equilibria involving V and VI. They have proposed that in

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[14] K. Fries and W. Vogt, *Ann.*, **381**, 312 (1911).

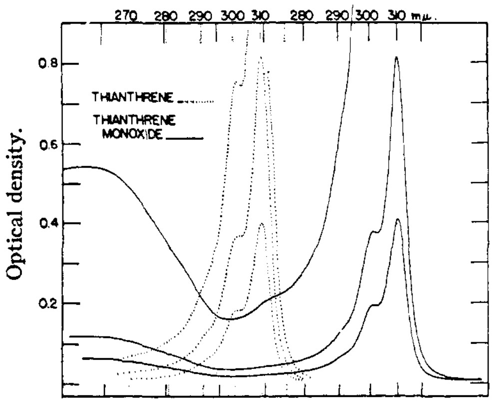

Fig. 4.—Ultraviolet absorption spectra of thianthrene and its monoxide in 100% H_2SO_4. The V solutions were 4, 8 and 40 × 10^{-6} *M*. The III solutions were 4, 8 and 16 × 10^{-6} *M*. All solutions were 2 days old.

trifluoroacetic acid the radical is a tautomeric system, but this proposal does not seem tenable.[15]

It appears that if VII is the responsible species and it arises as shown by Fava, Sogo and Calvin, then, when III is dissolved in 96% sulfuric acid, we might expect it to be first oxidized to V and VI in order to give the observed results. When III, V and VI are dissolved in 30% fuming sulfuric acid they give solutions with identical absorption spectra. The solutions obey Beer's law. The spectra have the characteristic peak at 502 mμ and are stable. At 502 mμ the extinction coefficients are III(14820), V(15320) and VI(4030). (These extinction coefficients were obtained from solutions that had been kept for 3 days. However, the optical densities did not change noticeably during that period.) It appears, here, that III is oxidized to V and no further, and that the spectrum with λ_{max} 502 mμ is probably that of the protonated sulfoxide. If III is oxidized to no further than V in 30% fuming sulfuric acid it is unlikely that it will be oxidized to both V and VI in acids of less than 100% sulfuric acid. Therefore, it does not appear probable that in 96% sulfuric acid the formation of the radical from III occurs by way of an equilibrium system involving V and VI.

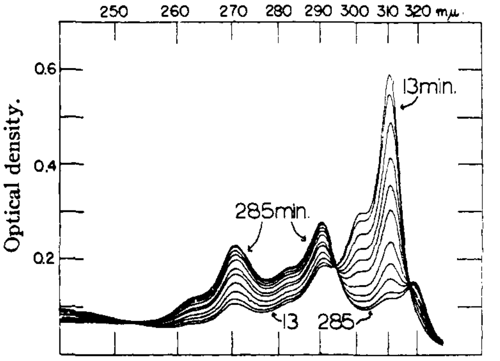

Fig. 5.—Thianthrene monoxide in 96% H_2SO_4; variation with time in the ultraviolet spectrum of an 8 × 10^{-6} *M* solution.

In Table I we have listed the products isolated from sulfuric acid solutions by pouring onto ice.

TABLE I

PRODUCTS OF REACTIONS

Run	Orig. solute[a]	Acid[b]	Time[c]	Yld. V, mole %	Yld. III, mole %	Tan,[d] wt. %	Total yld., %[e]
1	III	95.77	119 hr.	38.1	45.9		84.0
2	III	95.77	120 hr.	30.0	45.7		75.7
4	III	95.77	120 hr.	37.2	43.1		80.3
11	III	96.17	120 hr.	35.9	44.3		80.2
16	III	96.93	31 dy.	39.2	47.0	0.5	86.7
5	III	100.15	48 hr.	78.1	6.7		84.8
7	III	100.15	50 hr.	84.0	5.1		89.1
6	V	100.15	48 hr.	83.1	3.8		86.9
9	V	96.17	1 min.	88.1	3.1		91.2
12	V	96.17	165 min.	31.5	29.3	32.5	93.3
10	V	96.17	121 hr.	14.0	51.9	31.6	97.5
13a	V	96.17	16 dy.	12.2	55.1	28.2	95.5
18	V	96.93	29 dy.	12.8	53.5	30.2	96.2
17	VI	96.93	31 dy.	2.1	3.8	87.9	93.8

[a] All solutions 10^{-2} *M* except run 2 which was 5 × 10^{-3} *M*. [b] The concentration of the acid at the start. [c] From time of first contact with the acid. [d] Material insoluble in cyclohexane. [e] Where the products included tan solid the total yield was calculated as if the tan solid had the same mol. wt. as the original solute.

The product yields were determined spectroscopically. It is seen (run 9) that if V is worked up immediately after dissolving in 96% sulfuric acid it is recovered in good yield. On the other hand, if it remains in solution for some while (runs 10, 13a, 18), a major product is III. These observations were also made long ago by Fries and Vogt.[14] It will be seen that the amount of III obtained is constant after a certain time; we do not know what this time is exactly since we have no data between 2.75 hr. and 121 hr.

A third product from solutions of V is a tan solid. Such a product was obtained from each of the runs 10, 12, 13a and 18, but it does not appear that the solids are all quite the same. They do not have

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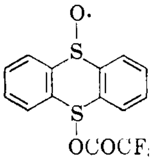
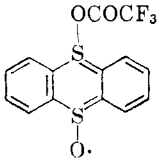
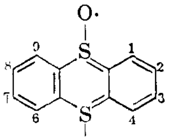
[15] The two trifluoroacetates proposed[5a] are A and B. These radicals are labeled IV and VIII in ref. 5a. In ref. 5b, B (labeled VIII) is drawn incorrectly. The structures A and B are called tautomers.[5]



A



B



C

They are not isoelectronic, however, and a referee has pointed out that the structure A is a typographical error in ref. 5a,b. Although the correct structure intended for A was not suggested by the referee it may be presumed from the equations preceding[5] to be C, the trifluoroacetate of the "parent" radical (VII in the present paper and I in ref. 5a,b). If this presumption is correct the two "tautomers" would be B and C. These structures are identical, and the electron can interact with only four protons, *e.g.*, at positions 2, 4, 6 and 8 in C. Tautomerism (if it existed) between B and C does not change this feature. Hence, the interaction with four protons at a time, referred to in ref. 5a, b, would mean with four protons which are not in similar environments. Instead, these protons are assignable to two sets of two protons, and would not explain well the 5-line e.s.r. spectrum.

There is another error in ref. 5b, which does not occur in 5a, and since 5a may not be as readily available as 5b it may be useful to note the error. In part of 5b the structure B, given the numeral VIII, is referred to as VII. No structure in 5b is labeled VII, but it is apparent in 5b, and is shown in 5a, that VII refers to a radical which, coincidentally, is the one to which we attribute the spin signal, that is, our VIII.

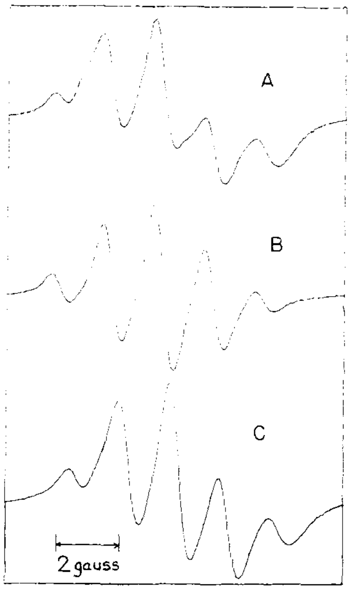


Fig. 6.—E.s.r. spectra of: A, 2 day old 5 × 10^{-4} *M* (assumed) solution of the tan solid from run 18 in 97% H_2SO_4; B, 13 month old 10^{-4} *M* solution of III in 97% H_2SO_4; C, a mixture of equal volumes of A and B.

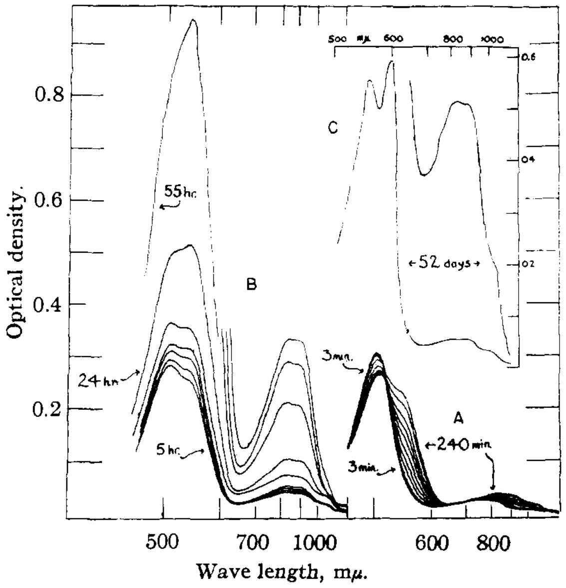


Fig. 7.—Thianthrene dioxide in 96% H_2SO_4; variation with time in the visible and near infrared. Groups A and B show scanning of a 2.5 × 10^{-3} *M* solution. The 55-hr. scan in superimposed and 0.5 should be added to its optical density scale. The group C is superimposed and is from a different run. The two scans are 10^{-4} and 10^{-3} *M*.

sharp melting points and are rather insoluble in organic solvents. Their ultraviolet spectra in 95% ethanol are similar but are different from that of the dioxide VI. Each of the solids dissolved in 96% sulfuric acid. The solids from runs 10, 13a and 18 each gave a blue solution with λ_{max} at 594 to 598 mμ and a shoulder at 560 mμ, while the solid from run 12 gave a wine colored solution with λ_{max} at 546 mμ. This peak showed evidence of an absorbing species at 590–600 mμ. Thus, it seems that the solids from runs 10, 13a and 18 are closely alike but differ from that of run 12. It appears that the tan solid is formed from V at an early stage but is undergoing further reaction corresponding with the slow development of the shoulder at 590 mμ shown in Fig. 2. It is possible that the tan solids represent acceptor molecules in the formation of III, from V, a point which is discussed later. The blue solution obtained by dissolving the tan solid from run 18 in 96% sulfuric acid was found to be paramagnetic. The e.s.r. signal has 5 lines (Fig. 6) but is obviously an unresolved group of more than 5; signs of splitting can be seen in two of the lines. It is to be noted that when this blue solution was mixed with a solution of thianthrene in sulfuric acid the e.s.r. signal obtained (Fig. 6) was similar to that of the thianthrene solution alone and could well be qualitatively mistaken for the thianthrene signal only.

Table I shows that solutions of III in 96% sulfuric acid give about a 35% yield of V. No products other than V and recovered III were found except for the 0.5% of tan solid in run 16. It remains a question whether the V obtained from solutions of III in 96% acid is present in the acid or is formed on pouring the acid onto ice. We have found that when III is dissolving in 96% sulfuric acid no vestige of a maximum at 502 mμ is observed from the time onward of first contact between the acid and III. On the other hand, when III dissolves in 100% sulfuric acid the solutions eventually have the spectral characteristics of V, but if the solutions are concentrated they first show the peak at 546 mμ with a shoulder at 502 mμ. The change corresponding with the shift from 546 to 502 mμ can be seen qualitatively when III dissolves in 100% sulfuric acid; the solution is initially purple and soon becomes amber. It would appear from this that when V is formed from III in 100% acid solution there is an intermediate stage, that responsible for the 546 mμ peak, and that when the V has been formed it can be discerned at first as a shoulder and later as the sole peak. Therefore, we would have thought that if V were present as V to the extent of 35% in solutions of III in 96% acid there would be some sign of its formation in the 502 mμ region.

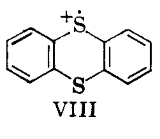
Thianthrene Dioxide (VI).—This oxide in 96% sulfuric acid presents a more complicated case than III and V. We have noted earlier that its extinction coefficient at 502 mμ in 30% fuming sulfuric acid is about four times smaller than those of III and V. Solutions of VI in 96% sulfuric acid are at first pale amber, the same color that V first forms but not at all as intense. This, too, was noted by Fries and Vogt.[14] The solution changes color with time and we have followed the change spectroscopically. It is certainly more complicated than that undergone by V. Initially, the spectrum between 450–1200 mμ is like that of these compounds in 30% fuming sulfuric acid; that is, λ_{max} at 502 mμ and a flat maximum between 725–825 mμ. Quite quickly the 502 mμ peak begins to diminish and the 546 mμ density begins to increase. However, very soon the region near 502 mμ begins to appear again with increasing density and one sees the growth of a doublet at 510 mμ and 546 mμ. The doublet eventually merges to a single, unsymmetrical peak at 546 mμ. While these changes are occurring the flat region of 725–825 mμ gives way first to a group of humps at 825, 920 and 1050 mμ and soon becomes a pronounced flat, but slender, peak between 825 and 920 mμ. These changes are shown in Fig. 7. In Fig. 7 are shown also spectra for solutions of VI that had been standing for 52 days. The eventual formation of twin peaks at 553 and 595 mμ can be seen. These solutions did not obey Beer's law.

The E.s.r. Spectra.—The electron spin resonance signal of III in 96% sulfuric acid showed the usual 5-line spectrum. The line width was 0.55 gauss and the splitting was 1.32 gauss. Careful search for other spin signals was in vain. A freshly made solution of V in 96% acid gave the 5-line spectrum with low intensity. The intensity of the signal increased with time. Quantitative measurement of the electron spin resonance intensity as a function of concentration of starting material in old solutions of III, V and VI in 96% sulfuric acid showed clearly that the intensities varied in a linear fashion with the concentration for III and V but did not change linearly for VI. Measurement of spin concentrations in the solutions of III showed a one-to-one correspondence between the concentration of III and the concentration of free radicals. A similar observation was made with the old solutions of V. Solutions of VI did not show this correspondence. An e.s.r. signal from solutions of V and VI in 30% fuming sulfuric acid could not be detected. A very weak signal was detected in a 10^{-3} *M* solution of III in 30% fuming sulfuric acid. This signal was a single broad line of width 2.95 gauss and with an intensity 0.38% of that of 10^{-3} *M* III in 96% sulfuric acid. No signal was detected from a 10^{-5} *M* solution of III in 30% fuming sulfuric acid.

Discussion.—It is now necessary to try to account for these observations. It appears to us that in the sulfuric acid solutions III must be undergoing oxidation. Sulfur dioxide has been noted by all workers when III dissolves in concentrated sulfuric acid. The problem of accounting for a one-electron oxidation (i.e. to give a paramagnetic species) in sulfuric acid solution is not particular to III but applies also to the several cases of polynuclear aromatic hydrocarbons reported by others.[16]

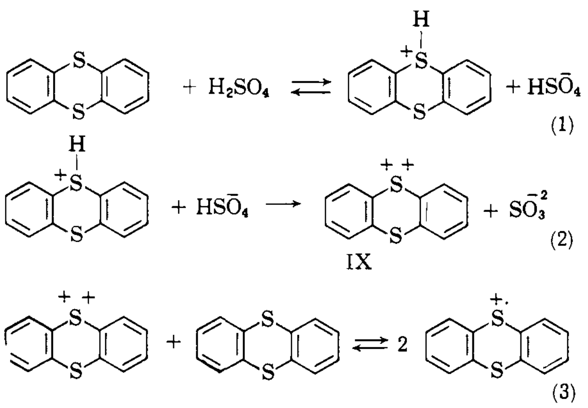
Hoijtink[7] has proposed for some of these hydrocarbons that in sulfuric acid the acceptor may be SO_3, in analogy with results obtained[17] with SO_3 in dimethyl sulfate. However, if this were the case with III one would anticipate that on diluting a solution of III in 96% sulfuric acid with more 96% sulfuric acid some of the radical species would undergo further oxidation and hence Beer's law would not be followed.

In order to account for a one-electron deficient species and a spin signal that would best be attributable to a symmetrical molecule we propose that this species has the structure VIII

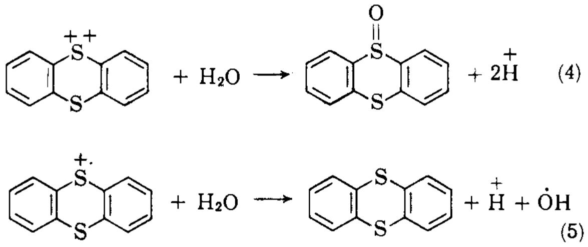


VIII

and that it may be formed by the reactions

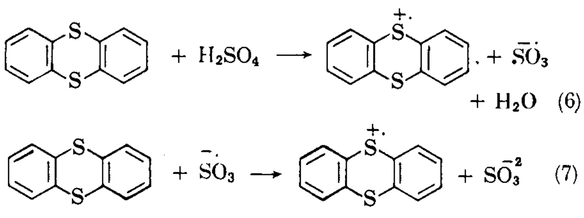


The Beer's law data and the 1:1 correspondence of the radical species with starting concentration of III require that the equilibrium 3 be far to the right. The disturbance of this equilibrium in the direction of IX on pouring a solution of III onto ice would account for the formation of both III and V as products



It should be noted that accounting for the recovery of starting materials from polynuclear hydrocarbon ion-radicals[7] also requires a formulation such as 5. If IX is involved in the formation of VIII from III it is necessary that IX is either rapidly converted to VIII or does not absorb in the region scanned. The reason for this is that the spectrum observable when III is dissolving in 96% sulfuric acid is so uniform as to indicate that only one species is represented.

Alternatively, it may be that VIII is formed directly by reactions such as



but in this case the radical would have to be able to give both III and V when poured onto ice.

The radical VIII has an electron which can appear at every carbon atom of the molecule. Therefore, we might expect either a 9-line e.s.r. signal or a 25-line signal from two sets of four equivalent protons. Since only five lines are observed it appears that there is a strong interaction of the electron with four protons to give the major pattern, and a weaker interaction with the other four

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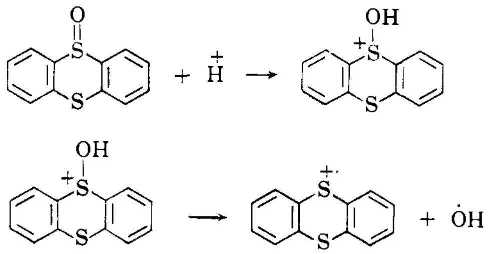
[16] Reference 7 and the references therein.

[17] W. Ij. Aalbersberg, G. T. Hoijtink, E. L. Mackor and W. P. Weijland, *J. Chem. Soc.*, 3055 (1959).

protons which is of a magnitude comparable to the line width and is not resolvable.

In accounting for the formation of VIII from V in 96% sulfuric acid the most straightforward series of reactions, proposed earlier by us,[2a] is



(8)

This sequence of steps was proposed also by Schmidt and co-workers[18a] for the case of diphenyl sulfide[18b] and its monoxide.

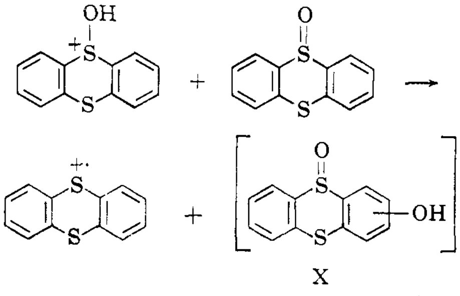
The formation of the hydroxyl radical is not altogether unreasonable. The radical might appear as hydrogen peroxide or as a peroxy-sulfuric acid. It is interesting that Fries and Vogt[14] found that the aqueous solution obtained by pouring a sulfuric acid solution of V into a large volume of water liberated iodine from potassium iodide. These authors felt, however, that the amount of iodine liberated was not as much as expected if hydrogen peroxide had been formed.

The reduction of the sulfoxide that these equations depict is not without precedent. Fries and Vogt[14,19] reported that V dissolves in concentrated hydrochloric acid to give a weakly rose solution, which in time becomes blue and deposits 2-chlorothianthrene. We have observed this ourselves. As soon as the concentrated hydrochloric acid came in contact with the V the solution became pink. The long needles of the V dissolved slowly while the solution slowly became purple. Within about 10 minutes of first contact and long before all of the V had dissolved a fine white solid began to deposit. The deposition of this solid continued while the rest of the V dissolved. By carrying out this reaction in a stoppered cell, and scanning before the solution became too turbid, the visible absorption spectrum was found to have a λ_{max} at 546 mμ. The dioxide VI was found to dissolve very slowly in concentrated hydrochloric acid. The colorless solution turned pink only after standing several days and again the λ_{max} was at 546 mμ. The pink color of the solution increased daily and after 7 days a colorless solid began to deposit and continued to deposit for several days. Fries and Vogt[14,19] have reported 2,7-dichlorothianthrene (*Chemical Abstracts* numbering) as the product of this reaction.

Other examples of the reduction of sulfoxides to sulfides by hydrochloric acid are recorded.[20-22]

However, the simple disproportionation in 8 does not explain why VIII is formed in 96–97% acid but not in 100% acid. This observation and the formation of the tan solids leads to two suggestions for the behavior of V in sulfuric acid.

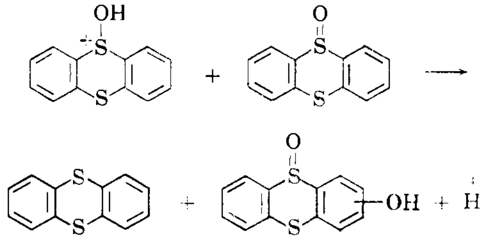
The first is that in less than 100% sulfuric acid V is not fully protonated so that unprotonated V may act as an acceptor from protonated V leading to hydroxylated radicals, X, which would then



X

correspond with the tan products obtained by pouring onto ice.

The second is that V may act as an acceptor of the HO+ ion from protonated V



In this case the III so formed would undergo subsequent oxidation to VIII. Also the hydroxythianthrene monoxide would eventually form the hydroxy radical-ion corresponding with VIII. If this sequence is correct and III is formed as a precursor to VIII it is also possible that some hydroxylation of III by HO^+ transfer from protonated V will occur.

The lack of symmetry and the evidence of line splitting in the e.s.r. spectrum of a sulfuric acid solution of the tan solid from run 18 (Fig. 6) is in accord with proposing a substituted thianthrene structure for the tan solid. Furthermore, work now in progress in our laboratory (Lubbock) has shown that while 1-substituents in thianthrene do not markedly affect the character of the e.s.r. spectrum in sulfuric acid solution, some 2-substituents cause a considerable alteration in the symmetry and hyperfine structure. Hence, the indications are that the tan solid probably carries a 2- (or 2,7-) substituent(s), and that the four protons in VIII with the major interaction constant are those at positions 2, 3, 7 and 8. This division of the eight protons is similar to that for the anthracene semiquinone negative ion-radical[23,24] and of the anthracene[25] and 9,10-dimethylanthracene[26] positive ion-

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(18) (a) U. Schmidt, K. Kabitze and K. Markau, *Angew. Chem.*, **72**, 708 (1960); (b) in our laboratory we have found that the red color of solutions of diphenyl sulfide in sulfuric acid [H. H. Szmant and G. A. Brost, *J. Am. Chem. Soc.*, **73**, 4175 (1951)] is due to the presence of diphenyl disulfide and thianthrene. Carefully purified diphenyl sulfide does not form colored solutions in 96% sulfuric acid. Therefore, interpretations of the chemistry of this sulfide in sulfuric acid based on the red color of the solutions are in error. A later paper will deal in detail with this sulfide and its oxides.

(19) K. Fries and W. Vogt, *Ber.*, **44**, 756 (1911).

(20) Th. Zincke and P. Jorg, *ibid.*, **42**, 3365 (1909).

(21) E. de Barry Barnett and S. Smiles, *J. Chem. Soc.*, **97**, 186 (1909).

(22) H. Gilman and J. Eisch, *J. Am. Chem. Soc.*, **77**, 3862 (1955).

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(25) A. Carrington, F. Dravnieks and M. C. R. Symons, *ibid.*, 947 (1959).

radicals; in the positive ion-radicals, however, the larger splitting constant is assigned to the alpha protons rather than the beta.

Experimental

Materials.—Thianthrene (K and K Laboratories, Long Island, N. Y.) was recrystallized from acetone after boiling the solution with activated charcoal; m.p. 155–157°. Thianthrene monoxide was prepared by the method of Fries and Vogt.[14] The crude product (94.5% yld.), had m.p. 141–142°. After several crystallizations from 95% ethanol the product with m.p. 143–143.5° was used for subsequent work.

Thianthrene dioxide (*cis*) was prepared by the method of Fries and Vogt.[19] The crude product had m.p. 274–276°. Recrystallization from benzene failed to raise the melting point. Recrystallization from acetic acid gave a product in which acetic acid was retained very tenaciously. The final product, after two crystallizations from benzene and three from acetic acid, was heated for 2 days with refluxing toluene in a drying pistol containing solid sodium hydroxide. The odor of acetic acid was no longer detected. The product had m.p. 281.5–282° (lit. 284°), corrected against 284.8° for recrystallized anthraquinone.[27]

Diphenyl disulfide was prepared by oxidation of thiophenol with iodine in sodium hydroxide solution. Recrystallization from 95% ethanol gave m.p. 59–60°.

Sulfuric acid was either Baker analyzed 96.8% (J. T. Baker Co.) or C.P. reagent 96.6% (General Chemical Division, Allied Chemical and Dye Corp.). To this was added the appropriate amount of fuming sulfuric acid (Baker analyzed, 30–33%). Acid concentrations were determined in each case on three samples weighed in glass stoppered weighing bottles. Small chips of ice were added to the weighed acid and the bottles were re-stoppered. The acid was titrated with base after washing from the weighing bottle. Where, in the thianthrene work, we refer to 96% the concentration actually determined was 96.17%; 97% was actually 96.93%; and 100% was titrated as 100.15%.

Ice used in product recovery was made from distilled water and was used mostly as uncrushed cubes. If the ice was crushed a plastic bag was used so as to avoid lint or rust contamination.

Diphenyl Disulfide (I) in Sulfuric Acid.—Two experiments were performed in each of which 2 g. of I was stirred by magnet with 20 ml. of 99.95% sulfuric acid in an ice-bath. In one experiment stirring was continued for 30 min.; in the other, for 60 min. The I was added to partly solidified acid at 0°. In each case a pale green color developed and changed to purple within 30 sec. Pouring the slush onto ice gave clear, colorless solutions from which there deposited 0.018 g. (0.9 weight %) and 0.0185 g. (1.06 weight %) of solid.

In a third experiment 1 g. of finely ground diphenyl disulfide was placed in a coarse grade 15-ml. sintered glass funnel. The funnel was fitted to a 1-l. filtering flask filled with crushed ice. To the sintered funnel was fitted a dropping funnel protected by a drying tube, and in this funnel was placed 100 ml. of cold 99.95% sulfuric acid. The acid was drawn by suction in about 5-ml. increments through the disulfide, a procedure which took about 5 min. The acid coming through the sinter was pale-green in color. As soon as it contacted the ice the color was dispelled and a curdy, white precipitate formed. The solid filtered from the aqueous acid weighed 0.731 g. (91% of the dissolved disulfide) and had m.p. 57–60°.

Thianthrene and Its Oxides. Preparation of Solutions.—Thianthrene dissolves only slowly in sulfuric acid of strength 96–97%. On the other hand, the monoxide and *cis*-dioxide dissolve very rapidly. Therefore, in preparing the initial 10^{-2} *M* thianthrene solutions that were mostly used in this work the thianthrene was weighed accurately on a slip of aluminum foil and transferred to a long-necked 250-ml. volumetric flask *via* a long-stemmed funnel. Through this funnel was poured quickly 100 ml. of the appropriate acid, washing in any solid adhering to the funnel. The funnel was removed carefully and the flask stopper, greased with Heavy Celvacene (Distillation Products Industries), was wired on. The flask was placed on a "hand-action" shaker (Palo Laboratory Supplies, Inc., New York) and swirled until the solid was completely dissolved; no contact with the greased stopper occurred. This took about 5 days and, therefore, 5 days were used as a standard preparatory time in most cases for not only solutions of thianthrene but also of the oxides. After the appropriate time for dissolution the solution was used for the spectroscopic work and/or for product analysis.

Spectroscopic Work (Sulfuric Acid).—A Beckman model DK-2 recording spectrophotometer was used. The cells were ground-glass stoppered silica (Pyrocell Manufacturing Co., New York). All spectra were traced in absorption but optical densities were calculated after switching the instrument to transmission and measuring the % transmission. For observing III dissolve in 96% and 100% sulfuric acid the III was added to the acid in the cell and scanning was carried out with intermittent shaking of the cell.

Product Analyses.—A solution from which the products were to be isolated and identified was poured in a fine stream from its flask into a 1-l. beaker full of ice cubes. The ice was kept moving as a mass while the acid was poured onto it. The flask was rinsed in ice water. The acidic solution was allowed to stand overnight and the solid product was filtered off through Whatman No. 50 paper in a tared Hirsch funnel. The product and funnel were washed well with water; unless this was done the solid on the sides of the funnel became blue when drying in the vacuum desiccator; the blue color disappeared on removal from the desiccator. The aqueous solution and washings were extracted with three or four portions of cyclohexane (either Phillips or Distillation Products). The cyclohexane extract was dried over magnesium sulfate, made up to volume after suction filtration and analyzed spectrophotometrically for thianthrene and thianthrene monoxide.

The aqueous solutions obtained from pouring the acids onto ice were colorless when thianthrene had been the solute. The solid obtained from these solutions was always flocculent and white. With the exception of the 1-min. experiment (run 9) the aqueous solutions obtained from thianthrene monoxide in 96% acid were amber or reddish-brown and the solids were fine, powdery and light tan. The aqueous solutions obtained from thianthrene dioxide in 96% acid were wine-colored while the solid was dark tan. The color of the colored aqueous solutions faded overnight in all cases.

A portion of the solid product was placed under cyclohexane and shaken mechanically. The products from the thianthrene oxides contained an insoluble tan component and this always separated as a very fine powder. In these cases, therefore, gentle shaking was continued for several hr. until the insoluble matter was completely dispersed and uniform. Where the tan component was absent or in very small amount, as in the thianthrene experiments, the solids dissolved quite readily during about 30 min. The cyclohexane solution was filtered through a tared funnel and analyzed

TABLE II

PRODUCT BALANCE IN ANALYSES OF SOLIDS[a]

Run	Original solute	Wt. of portion, g.	V, g.	III, g.	Tan solid, g.	Total found	Error, %
1	III	0.1033	0.0505	0.0573	....	0.1078	4.3
2	III	.0736	.0294	.0427	....	.0721	2.0
4	III	.1252	.0617	.0669	....	.1286	2.7
5	III	.1534	.1481	.0120	....	.1601	2.6
7	III	.1400	.1300	.0075	....	.1375	1.8
11	III	.1255	.0589	.0694	....	.1283	1.2
16	III	.1454	.0685	.0768	0.0008	.1461	0.5
6	V	.1610	.1472	.0062	....	.1534	4.7
9	V	.1582	.1478	.0049	....	.1527	3.5
10	V	.1136	.0171	.0591	.0353	.1115	1.8
12	V	.1755	.0603	.0530	.0546	.1679	4.3
13a	V	.1774	.0234	.1010	.0490	.1734	2.2
18	V	.1344	.0188	.0742	.0402	.1332	0.9
17	VI	.0862	.0035	.0059	.0684	.0778	9.7

[a] In these spectrophotometric analyses the extinction coefficients used were: III, 3.98 × 10^4 (258.7 mμ) and 1.80 × 10^4 (247.7 mμ); V, 0.95 × 10^4 (258.7 mμ) and 1.94 × 10^4 (247.7 mμ).

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[26] J. A. Brivati, R. Hulme and M. C. R. Symons, *Proc. Chem. Soc.*, 384 (1961).

[27] S. Bunce, *Anal. Chem.*, **25**, 825 (1953).

spectrophotometrically. In no case was a spectrum obtained that appeared to contain anything but thianthrene and monoxide. Computation on this basis always agreed well with the weight of the portion analyzed. A summary of product balance for solid analyses is given in Table II. A summary of the total products is given in Table I.

The Tan Solids.—Part of each of the solids from runs 10, 12, 13a, 17 and 18 was placed under 95% ethanol and warmed at 50° for several hours. The solids, except that from run 12, did not dissolve completely. The ultraviolet spectra of the ethanol solutions differed from that of VI. Solutions of the solids from runs 10, 12, 13a and 18 had broad shoulders at 312 and 250 mμ and a broad maximum at 239 mμ. The solution of the solid from run 17 had a broad shoulder at 312 mμ, a sharp shoulder at 276.5 mμ, humps at 250 and 239 mμ, and increasing absorption at lower wave lengths. The dioxide VI has sharp shoulders at 269.5 and 276.5 mμ with increasing absorption at lower wave lengths.

Solutions of the solids in 96.9% sulfuric acid were made by weighing 3 mg. of each and dissolving in 25 ml. of acid. Assuming the molecular weight to be 232 (V) these solutions were approx. 5×10^{-4} *M*. Absorption spectra were run on solutions diluted to 10^{-4} *M*. Each solution had a broad maximum near 900 and 1000 mμ. Each of the solutions for runs 10, 13a, 17 and 18 had a peak in the range 594–598 mμ and a shoulder at 560 mμ. On the other hand, the solution for run 12 had its maximum at 546 mμ showing signs of absorption on one side of the peak near 590 mμ. The optical densities at the large peaks of the 10, 12, 13a and 18 solutions were about the same and double that of the 17 solution.

E.s.r. Spectra.—A Varian Associates spectrometer was used with 100 Kc. field modulation. Varian Associates aqueous-type cells were used. The spectra were calibrated with a solution of potassium nitrosodisulfonate (K and K Laboratories) in saturated sodium carbonate solution. It is interesting to note that the shape and line width of a freshly made solution of III in sulfuric acid did not differ from a solution that was 17 months old.

Acknowledgments.—This work was generously supported by the Robert A. Welch Foundation, Houston, Texas, and the United States Air Force (AFOSR Grant AF-AFOSR-61-48). Helpful discussions with Dr. Fausto Ramirez are acknowledged with pleasure.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILL.]

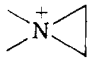
Small Charged Rings. II. The Synthesis of Aziridinium Salts[1-3]

BY NELSON J. LEONARD AND KLAUS JANN

RECEIVED JULY 19, 1962

In a reaction patterned after the nucleophilic attack of diazomethane on the ketone carbonyl, we have found that a similar attack on a ternary iminium perchlorate (I) or fluoborate can give the corresponding aziridinium salt II in high yield. The prototype for the general method of synthesis of aziridinium salts was the conversion of N-cyclohexylidenepyrrolidinium perchlorate (IV) to 2,2-pentamethylene-1,1-tetramethyleneaziridinium perchlorate (V). Characterization of the three-membered ring was achieved by chemical means, including thiosulfate titration, hydrolysis, alcoholysis and hydrogenolysis, all suggesting new synthetic utility, and by physical methods, including molecular weight determination and infrared and n.m.r. spectroscopy. Other diazoalkanes and ternary iminium salts react in the same manner to give variously substituted aziridinium salts.

The first postulate of the existence of an ethylenimonium or aziridinium compound was that of

( X$^-$)

Marckwald and Frobenius[4] for the product of treatment of 1-β-chloroethylpiperidine hydrochloride with limited base. The conditions of the reaction and of product purification were such as to suggest a bis-piperizinium salt structure as more reasonable.[5] Evidence has been provided for the aziridinium cation as an intermediate in the hydrolysis of certain α-bromo-β-3°-aminoketones,[6-8] and it has been recognized as the key intermediate in chemical reactions of the nitrogen mustards, β-haloethyl-*tert.*-amines.[9-18] Moreover, aziridinium cation intermediates (EI-ions) may serve as pharmacologically active species[9,19-23] in alkylating functional groups of compounds of biological importance, in adrenergic blocking and in antiadrenaline and antihistamine activity.

Thus far, aziridinium intermediates have been trapped only in the form of unwieldy salts.[10,20,22,24,25]

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[1] For the first article in the series, see N. J. Leonard and K. Jann, *J. Am. Chem. Soc.*, **82**, 6418 (1960).

[2] This investigation was supported by a research grant (USPHS-RG5829) from the National Institutes of Health, U. S. Public Health Service.

[3] Presented at the Seventeenth National Organic Chemistry Symposium of the American Chemical Society, June, 1961, Bloomington, Ind.; see Abstracts, pp. 1-10.

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