The Behaviour of Some Thioxanthene and Thianthrene Derivatives with Hydrazoic Acid

Salvatore Palazzo, Libero Italo Giannola and Sergio Caronna

Applied Pharmaceutical Chemistry Institute, University of Palermo, Palermo, Italy

Received April 1, 1974

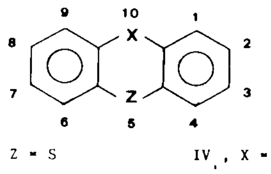
In the Schmidt reaction between carbonyl compounds and hydrazoic acid in the presence of strong protonating agents, it is pertinent that the carbonyl function is attacked by a proton during the first step (1). When this protonation does not occur or is hindered due to the interference of various groups present in the molecule, the Schmidt reaction does not occur at all or occurs only in part. Such is the case, for example, for anthrone, dianthrone, xanthone and thioxanthone which do not react with hydrazoic acid (2).

This behaviour has been attributed to the strong delocalisation of the positive charge from the carbonyl group; inhibition of delocalisation of the positive charge may decrease the stability of the dipolar ion structure and enhance reactivity. Owing to the close analogies between the Schmidt reaction and the Beckmann rearrangement it is plain that the same phenomena may occur either to facilitate or impede both mechanisms.

This is indicated by the behaviour of oximes toward the Beckmann rearrangement (3). Truce and Simms, in fact, observed that electron withdrawing groups caused the Beckmann rearrangement of oximes to proceed much more slowly than in unsubstituted compounds.

Our research was directed toward a comparative study of the reactive behaviour of compounds in the following systems:

SCHEME I



I , X = CO , Z = S
II , X = CO , Z = SO_2
III , X = CO , Z = SO
IV , X = SO , Z = S
V , X = SO , Z = SO
VI , X = SO , Z = SO_2

While compound I did not react at all, compound II underwent a normal Schmidt reaction at the carbonyl group in position 10 and yielded dibenzo[*b,f*][1,4]thiazepin-11(10*H*)one 5,5-dioxide (VIII). Compound III was of interest since it yielded both the corresponding sulfoximine (X) and dibenzo[*b,f*][1,4]thiazepin-11(10*H*)one 5-oxide (IX). Among the compounds of the second series we observed that only compound V reacts to yield the corresponding sulfoximine (XI). In this case, surprisingly, we obtained the same reaction product from either the α or the β isomer (4).

Treatment of sulfoximine X with hydrogen peroxide yielded thioxanthen-10-one 5,5-dioxide (II), convertible to VIII. Compound VIII may also be obtained by oxidation of the normal product IX. Moreover, by reduction with Zn and acetic acid, compound IX yielded compound VII which could not be obtained directly from I.

Oxidation of sulfoximine XI with potassium permanganate yielded the sulfoximine XIII, which could not be obtained directly from thianthrene 5,10,10-trioxide (VI); whereas oxidation with hydrogen peroxide of compound XI yielded thianthrene 5,5,10,10-tetraoxide (XII).

The reaction sequence is shown in the following scheme.

EXPERIMENTAL

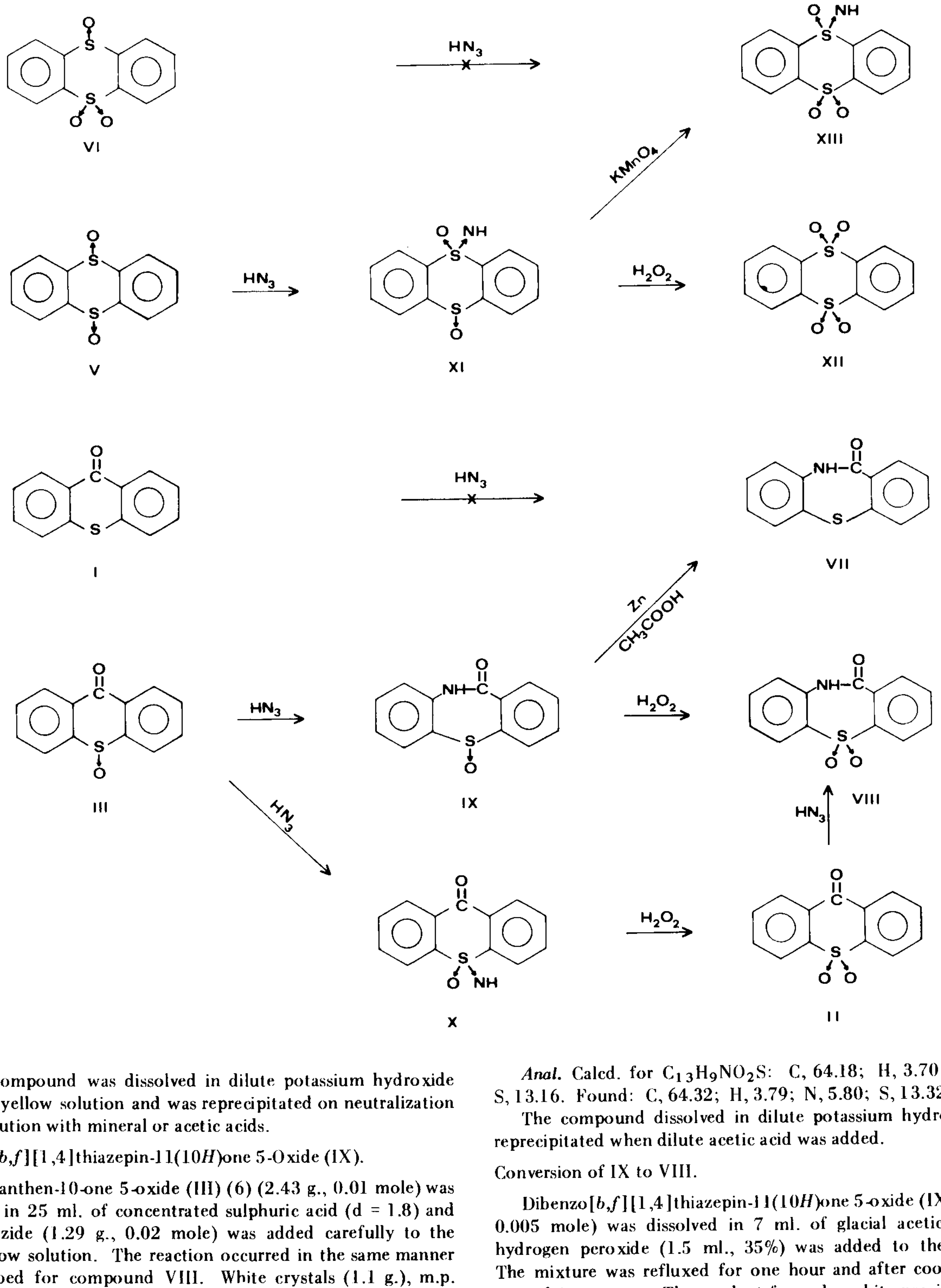
Melting points were determined on a Büchi-Tottoli capillary apparatus and are uncorrected. Ir spectra were recorded on a Perkin-Elmer model 157 infrared spectrometer as nujol mulls. The purity of the compounds was confirmed by tlc on silica-gel Merck platten 0.25 mm. using the solvent system benzene:ethyl acetate = 3:7.

Dibenzo[*b,f*][1,4]thiazepin-11(10*H*)one 5,5-Dioxide (VIII).

To a solution of thioxanthen-10-one 5,5-dioxide (II) (5) (2.59 g., 0.02 mole) in 13 ml. of concentrated sulphuric acid (d = 1.8) was added sodium azide (1.29 g., 0.02 mole) in small portions. A slow reaction occurred and gas was evolved. After standing overnight, the reaction mixture was poured onto crushed ice and the product was collected, washed, dried and crystallized from ethanol. Pale yellow crystals (2.1 g.) which melted at 296-298° were obtained; ir: 3100 (NH), 1640 (C=O), 1160 and 1310 cm^{-1} (SO_2).

Anal. Calcd. for $C_{13}H_9NO_3S$: C, 60.23; H, 3.50; N, 5.40; S, 12.35. Found: C, 60.42; H, 3.65; N, 5.65; S, 12.65.

SCHEME II



The compound was dissolved in dilute potassium hydroxide to give a yellow solution and was reprecipitated on neutralization of the solution with mineral or acetic acids.

Dibenzo[*b*,*f*][1,4]thiazepin-11(10*H*)one 5-Oxide (IX).

Thioxanthen-10-one 5-oxide (III) (6) (2.43 g., 0.01 mole) was dissolved in 25 ml. of concentrated sulphuric acid (d = 1.8) and sodium azide (1.29 g., 0.02 mole) was added carefully to the deep yellow solution. The reaction occurred in the same manner as described for compound VIII. White crystals (1.1 g.), m.p. 314-316°, were obtained; ir: 3120 (NH), 1665 (C=O) and 1025 cm^{-1} (SO).

Anal. Calcd. for $C_{13}H_9NO_2S$: C, 64.18; H, 3.70; N, 5.76; S, 13.16. Found: C, 64.32; H, 3.79; N, 5.80; S, 13.32.

The compound dissolved in dilute potassium hydroxide, and reprecipitated when dilute acetic acid was added.

Conversion of IX to VIII.

Dibenzo[*b*,*f*][1,4]thiazepin-11(10*H*)one 5-oxide (IX) (1.22 g., 0.005 mole) was dissolved in 7 ml. of glacial acetic acid and hydrogen peroxide (1.5 ml., 35%) was added to the solution. The mixture was refluxed for one hour and after cooling it was poured into water. The product formed a white precipitate (1.1 g.) which was collected, washed, dried and crystallized from ethanol. White crystals, m.p. 296-298°, were obtained.

Conversion of IX to VII.

Dibenzo[*b,f*][1,4]thiazepin-11(10*H*)one 5-oxide (IX) (2.43 g., 0.01 mole) was dissolved in 5 ml. of glacial acetic acid and zinc dust (0.1 g.) was added to the solution. The mixture was heated under reflux for 3 hours and then poured into water. The white product precipitated (2.2 g.) and was collected, washed, dried and crystallized from ethanol. White crystals, m.p. 263-265°, were obtained; ir: 3090 (NH), 1638 (C=O), and 1575 cm^{-1} (NH).

Anal. Calcd. for $C_{13}H_9NOS$: C, 68.72; H, 3.99; N, 6.17; S, 14.09. Found: C, 68.85; H, 3.90; N, 5.98; S, 14.41.

Thioxanthen-10-one Sulfoximine (X).

Addition of sodium carbonate to alkalinity to the acidic mother liquor from which dibenzo[*b,f*][1,4]thiazepin-11(10*H*)one 5-oxide (IX) separated caused a pale red product to precipitate (1.2 g.). The product was collected, washed and crystallized from water using charcoal. Yellow crystals, m.p. 164-165°, were obtained; ir: 3050 (NH), 1655 (C=O), 1570 (NH) and 1015 cm^{-1} (SO).

Anal. Calcd. for $C_{13}H_9NO_2S$: C, 64.20; H, 3.70; N, 5.76; S, 13.16. Found: C, 64.35; H, 3.81; N, 5.79; S, 13.48.

The compound dissolved in dilute cold sodium hydroxide solution, and was reprecipitated by neutralizing with dilute acetic acid. It was soluble in an excess of acid.

Conversion of X to II.

Compound X (0.24 g., 0.001 mole) was dissolved in 5 ml. of glacial acetic acid and hydrogen peroxide (2 ml., 35%) was added to the solution which was heated under reflux for 30 minutes. Cooling caused fine needles to crystallize. The reaction mixture was poured into water and the yellow product (0.2 g.) which separated was collected, washed, dried and crystallized from ethanol. Pale yellow needles, m.p. 184-187°, were obtained and the compound was identified as thioxanthen-10-one 5,5-dioxide. The compound afforded a picrate which melted at 233-235°.

Thianthrene 5-Oxide Sulfoximine (XI).

Thianthrene 5,10-dioxide (2 g., 0.008 mole) (either the α (*anti-cis*) m.p. 298° or the β (*trans*) m.p. 249° (7) isomer) was dissolved in 10 ml. of concentrated sulphuric acid (d = 1.8) and to the solution was carefully added 1.5 g. (0.023 mole) of sodium azide in small portions. The dark red solution of the α isomer became violet and finally blue. The violet solution of the β isomer became dark violet. A slow reaction occurred and gas was evolved. After standing overnight the reaction mixture was poured onto ice and the product was collected, washed, dried and crystallized from ethanol. White crystals (1.1 g.), m.p. 240-242° were obtained; ir: 3110 (NH), 1562 (NH) and 1025 cm^{-1} (SO).

Anal. Calcd. for $C_{12}H_9NO_2S_2$: C, 54.75; H, 3.42; N, 5.32; S, 24.33. Found: C, 54.78; H, 3.48; N, 5.37; S, 24.67.

Additional product (0.8 g.) was obtained from the mother liquor by adding sodium carbonate, total yield 98%.

Oxidation of XI.

1) With Hydrogen Peroxide (35%).

Compound XI (1 g., 0.004 mole) was suspended in acetic acid (10 ml.) to which hydrogen peroxide (2 ml.) was added. This suspension was heated and the product dissolved. In a few minutes a white product separated and the mixture was refluxed for two hours. The white precipitate (0.7 g.) was collected, washed and crystallized from acetic acid and it melted at 325-327°. It was identified as thianthrene 5,5,10,10-tetraoxide (XII).

2) With Potassium Permanganate (5%).

Compound XI (1 g., 0.004 mole) was dissolved in acetic acid (15 ml.) and to the solution 15 ml. of potassium permanganate was added. The mixture was heated for 10 minutes, filtered and poured into 150 ml. of water. A white product separated (0.8 g.). Crystallization from ethanol afforded a product which melted at 288-292°; ir: 3100 (NH), 1560 (NH), 1160 and 1320 (SO_2) and 1040 cm^{-1} (SO).

Anal. Calcd. for $C_{12}H_9NO_3S_2$: C, 51.61; H, 3.22; N, 5.01; S, 22.93. Found: C, 51.83; H, 3.32; N, 5.02; S, 23.12.

The product was identified as thianthrene 5,5-dioxide sulfoximine (XIII).

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