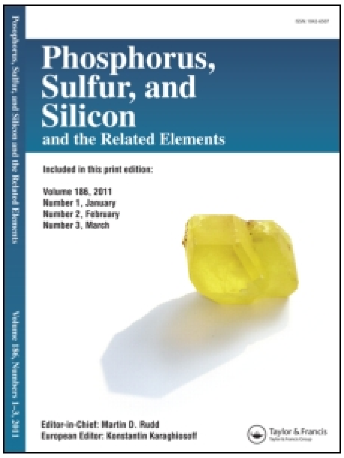


**Phosphorus, Sulfur, and Silicon and the Related Elements**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

# THE EFFECT OF STRUCTURE ON REACTIVITY IN SEMICARBAZONE FORMATION OF SOME SUBSTITUTED 4-THIANONES AND 4-THIANONE-1,1-DIOXIDES

Palaniappan Nanjappan[a]; Kondareddiar Ramalingam[a]; Krishnasamy Ramarajan[b]; K. Darrell Berlin[c]
[a] Department of Chemistry, PSG College of Arts & Sciences, Coimbatore, India [b] Department of Chemistry, CBM College, Coimbatore, India [c] Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma, USA

**To cite this Article** Nanjappan, Palaniappan , Ramalingam, Kondareddiar , Ramarajan, Krishnasamy and Berlin, K. Darrell(1983) 'THE EFFECT OF STRUCTURE ON REACTIVITY IN SEMICARBAZONE FORMATION OF SOME SUBSTITUTED 4-THIANONES AND 4-THIANONE-1,1-DIOXIDES', Phosphorus, Sulfur, and Silicon and the Related Elements, 17: 3, 331 — 341

**To link to this Article: DOI:** 10.1080/03086648308077554

**URL:** http://dx.doi.org/10.1080/03086648308077554

*Phosphorus and Sulfur*, 1983, Vol. 17, pp. 331–341
0308-664X/83/1703-0331/$18.50/0

# THE EFFECT OF STRUCTURE ON REACTIVITY IN SEMICARBAZONE FORMATION OF SOME SUBSTITUTED 4-THIANONES AND 4-THIANONE-1,1-DIOXIDES

PALANIAPPAN NANJAPPAN and KONDAREDDIAR RAMALINGAM*

*Department of Chemistry, PSG College of Arts & Sciences, Coimbatore-641014, India*

KRISHNASAMY RAMARAJAN

*Department of Chemistry, CBM College, Coimbatore-641042, India*

K. DARRELL BERLIN*

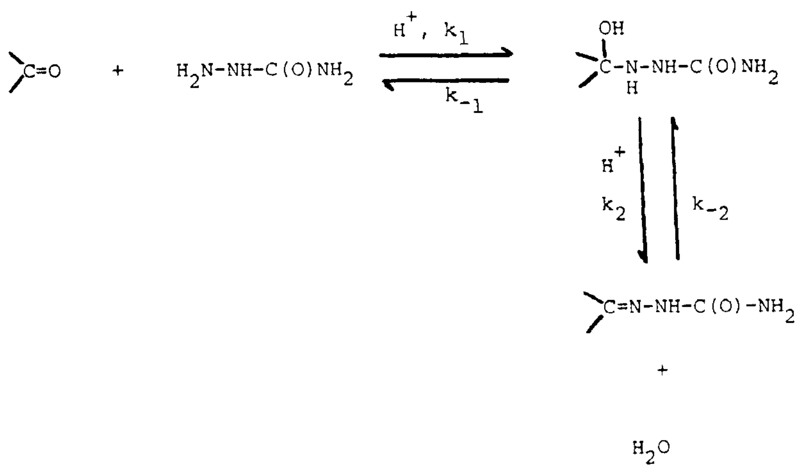
*Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078, USA*

(*Received July 14, 1983*)

The rates of semicarbazone formation of twenty-five heterocyclic ketones (4-thianones and 4-thianone-1,1-dioxides) have been measured at 10°C in 80% ethanol/20% water (v/v) at pH = 6.45 ± 0.05. The data indicate an overall second-order process, first-order each in ketone and semicarbazide. The addition of the semicarbazide is subject to general acid catalysis. In all the cases investigated, the reaction appears to be irreversible under the experimental conditions employed. Increased steric retardation is observed as the steric crowding increases around the carbonyl function, suggesting the rate-determining step is the attack of the semicarbazide on the carbonyl carbon. From the second-order rate constants for the semicarbazone formation from *r*-2,*cis*-6-diphenyl-4-thianone, 2,2-dimethyl-6-phenyl-4-thianone, *r*-2,*cis*-6-di-*p*-chlorophenyl-4-thianone and 2,2-dimethyl-6-*p*-chlorophenyl-4-thianone, the syn-axial interaction energy for $CH_3$—OH has been calculated to be 2.41 kcal $mol^{-1}$.

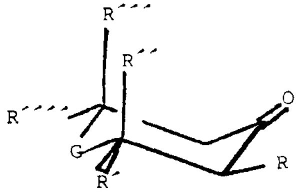
## INTRODUCTION

Addition of semicarbazide to aromatic aldehydes has been the subject of extensive study in simple systems, notably by Jencks and co-workers.[1–4] Several investigators have established that the rate-determining attack of weakly basic semicarbazide with aldehydes and ketones is usually subject to general acid catalysis.[1,4–8] Semicarbazone formation takes place in two steps, i.e. according to Eq. (1) the first step is rate-determining at acidic pH and the dehydration step is rate-determining at neutral and alkaline pH values.[1,2] The studies on para-substituted acetophenones[9] and benzaldehydes[10] (at pH = 6.40) have shown that the rate-controlling step is



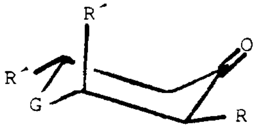
(1)

simply the rate of addition of semicarbazide to the carbonyl group. Although a large amount of work has been done on the reaction of semicarbazide with aliphatic and aromatic ketones, work on the six-membered heterocyclic ketones is rare. The purpose of this investigation was to measure the rates of semicarbazone formation of various substituted-4-thianones and 4-thianone-1,1-dioxides and to study the effect of substituents on the reactivity of the carbonyl group. In view of the known ring flattening of thianones,[11] some anomalies might be anticipated with large substituents adjacent to the C=O group. In the present work, the rates of formation of semicarbazone with 4-thianones (**1–4**, **6–10**, **15–18**, **22**, **23**) and the corresponding 1,1-dioxides (**5**, **11–14**, **19–21**, **24**, **25**) have been measured at 10°C in 80% ethanol/20% water (v/v) buffered at pH = 6.45 ± 0.05. The reaction was followed by iodine titration of the unreacted semicarbazide,[5] and the kinetic results have been summarized in Tables I–V. In all cases examined, no measurable hydrolysis of the semicarbazone could be found and care was taken to maintain the constancy of the pH during the progress of the reaction.

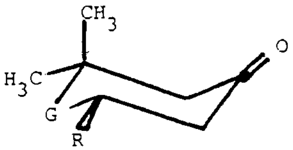


| | G | R | R′ | R″ | R‴ | R⁗ |
|---|---|---|---|---|---|---|
| **1** | S | H | H | H | H | H |
| **2** | S | $i$-$C_3H_7$ | H | H | H | H |
| **3** | S | H | H | H | $CH_3$ | $CH_3$ |
| **4** | S | H | $CH_3$ | $CH_3$ | $CH_3$ | $CH_3$ |
| **5** | $SO_2$ | $i$-$C_3H_7$ | H | H | H | H |

| | G | R | R′ |
|---|---|---|---|
| **6** | S | H | $C_6H_5$ |
| **7** | S | H | $p$-Cl-$C_6H_4$ |
| **8** | S | H | $p$-$CH_3O$-$C_6H_4$ |
| **9** | S | $CH_3$ | $C_6H_5$ |
| **10** | S | $C_2H_5$ | $C_6H_5$ |
| **11** | $SO_2$ | H | $C_6H_5$ |
| **12** | $SO_2$ | H | $p$-Cl-$C_6H_4$ |
| **13** | $SO_2$ | $CH_3$ | $C_6H_5$ |
| **14** | $SO_2$ | $C_2H_5$ | $C_6H_5$ |



| | G | R | R′ |
|---|---|---|---|
| **15** | S | H | $C_6H_5$ |
| **16** | S | H | $p$-$CH_3O$-$C_6H_4$ |
| **17** | S | $CH_3$ | $C_6H_5$ |
| **18** | S | $C_2H_5$ | $C_6H_5$ |
| **19** | $SO_2$ | H | $C_6H_5$ |
| **20** | $SO_2$ | $CH_3$ | $C_6H_5$ |
| **21** | $SO_2$ | $C_6H_5$ | $C_6H_5$ |



| | G | R |
|---|---|---|
| **22** | S | $C_6H_5$ |
| **23** | S | $p$-Cl-$C_6H_4$ |
| **24** | $SO_2$ | $C_6H_5$ |
| **25** | $SO_2$ | $p$-Cl-$C_6H_4$ |

TABLE I

Second-order rate constants of semicarbazone formation of some substituted 4-thianones and 4-thianone-1,1-dioxides

| Compd. (4-thianone) | $k_2/10^{-2}\,\mathrm{l\,mol^{-1}\,s^{-1}}$ | Compd. (4-thianone-1,1-dioxide) | $k_2/10^{-2}\,\mathrm{l\,mol^{-1}\,s^{-1}}$ |
|---|---|---|---|
| **1** | 18.35 ± 0.06 | **5** | 0.37 ± 0.01 |
| **2** | 0.24 ± 0.01 | **11** | 16.65 ± 0.03 |
| **3** | 0.37 ± 0.01 | **12** | 17.21 ± 0.03 |
| **4** | 0.051 ± 0.01 | **13** | 2.19 ± 0.02 |
| **6** | 11.51 ± 0.03 | **14** | 0.91 ± 0.03 |
| **7** | 11.25 ± 0.09 | **19** | 3.51 ± 0.02 |
| **8** | 10.88 ± 0.08 | **20** | 0.18 ± 0.01 |
| **9** | 1.77 ± 0.02 | **21** | 0.14 ± 0.01 |
| **10** | 0.63 ± 0.01 | **24** | 0.52 ± 0.01 |
| **15** | 2.48 ± 0.02 | **25** | 0.54 ± 0.01 |
| **16** | 2.20 ± 0.04 | | |
| **17** | 0.12 ± 0.01 | | |
| **18** | 0.096 ± 0.01 | | |
| **22** | 0.36 ± 0.01 | | |
| **23** | 0.34 ± 0.01 | | |

Solvent = 80% ethanol/20% water (v/v), pH = 6.45 ± 0.05, $I$ = 0.075 M, Temp. = 10°C.

## RESULTS AND DISCUSSION

### *Effect of Varying Ionic Strength*

The effect of ionic strength on the reaction rate was determined by performing the kinetic runs in the presence of various concentrations of potassium chloride. The results in Table II indicate that the reaction rate is independent of ionic strength, and this can be interpreted only as showing the rate-controlling step does not likely occur between ions, but may involve reaction between uncharged molecules or between an ion and an uncharged molecule.

TABLE II

Effect of varying ionic strength on the reaction rate

| $[\mathrm{ketone}]/10^{-4}\,\mathrm{mol\,l^{-1}}$ | $I/\mathrm{mol\,l^{-1}}$ | $k_2/10^{-2}\,\mathrm{l\,mol^{-1}\,s^{-1}}$ |
|---|---|---|
| | *r*-2,*cis*-6-Diphenyl-4-thianone (**6**) | |
| 33.48 | 0.065 | 11.51 ± 0.03 |
| 33.48 | 0.081 | 11.44 ± 0.02 |
| 33.42 | 0.093 | 11.69 ± 0.02 |
| 33.46 | 0.12 | 11.31 ± 0.01 |
| | *r*-2,*cis*-6-Diphenyl-*trans*-3-methyl-4-thianone (**9**) | |
| 32.74 | 0.065 | 1.77 ± 0.02 |
| 32.76 | 0.081 | 1.74 ± 0.02 |
| 32.74 | 0.093 | 1.76 ± 0.02 |
| 32.70 | 0.12 | 1.74 ± 0.02 |

Solvent = 80% ethanol/20% water (v/v), [semicarbazide] = 78.04 × $10^{-4}$ M, pH = 6.45 ± 0.05, Temp. = 10°C.

TABLE III

Dependence of rate on ketone concentration

| [semicarbazide]/$10^{-4}$ mol $l^{-1}$ | [ketone]/$10^{-4}$ mol $l^{-1}$ | $k_1/10^{-4}$ $s^{-1}$ | $k_2/10^{-2}$ l $mol^{-1}$ $s^{-1}$ |
|---|---|---|---|
| | *r*-2,*cis*-6-Diphenyl-4-thianone (**6**) | | |
| 17.92 | 384.10 | 43.85 | 11.42 |
| 17.92 | 241.40 | 27.81 | 11.52 |
| 17.92 | 182.70 | 20.78 | 11.37 |
| 17.92 | 121.40 | 14.21 | 11.71 |
| | *r*-2,*cis*-6-Diphenyl-*trans*-3-methyl-4-thianone (**9**) | | |
| 18.28 | 498.40 | 8.77 | 1.76 |
| 18.28 | 338.10 | 6.05 | 1.79 |
| 18.28 | 220.70 | 3.80 | 1.72 |
| 18.28 | 127.10 | 2.17 | 1.71 |

Solvent = 80% ethanol/20% water (v/v), pH = 6.45 ± 0.05, $I = 0.075$ M, Temp. = 10°C.

### *Dependence of Rate on 4-Thianone Concentration*

In Table III are recorded values of $k_1$ (pseudo-first-order rate constants) for various runs with large excess of initial concentrations of 4-thianones **6** and **9** at constant pH (6.45 ± 0.05). The increase in ketone concentration under pseudo-first-order conditions increases the rate of semicarbazone formation. The values of $k_1$, the pseudo first-order rate constants, when divided by ketone concentration, gave the second-order rate constants $k_2$ which were found to be constant. This infers that the reaction rate is proportional to the first power of the ketone concentration.

### *Effect of Varying Semicarbazide Concentration*

The rate constants $k_1$ measured on solutions with different semicarbazide concentrations, but at constant ketone concentration and at constant pH (6.45 ± 0.05), revealed the first-order dependence with respect to semicarbazide. In Table IV are shown values of pseudo-first-order rate constants ($k_1$) for *r*-2,*cis*-6-diphenyl-*trans*-3-ethyl-4-thianone (**10**) for runs with four different initial concentrations of semicarbazide.

Thus, the kinetic data indicate that the semicarbazone formation is a second-order reaction, first-order with respect to the semicarbazide and first-order with respect to the 4-thianone.

TABLE IV

Dependence of rate on semicarbazide concentration *r*-2,*cis*-6-diphenyl-*trans*-3-ethyl-4-thianone (**10**)

| [semicarbazide]/$10^{-4}$ mol $l^{-1}$ | $k_1/10^{-5}$ $s^{-1}$ |
|---|---|
| 8.64 | 4.97 ± 0.02 |
| 12.06 | 4.91 ± 0.01 |
| 17.46 | 5.02 ± 0.01 |
| 23.61 | 4.94 ± 0.01 |

Solvent = 80% ethanol/20% water (v/v), pH = 6.45 ± 0.05, $I = 0.075$ M, Temp. = 10°C, [ketone] = 286.4 × $10^{-4}$ M.

TABLE V

Dependence of rate on acidity at constant pH
*r*-2,*cis*-6-diphenyl-*trans*-3-methyl-4-thianone (9)

| [acetic acid]/mol $l^{-1}$ | [acetate]/mol $l^{-1}$ | $k_2/10^{-2}$ l $mol^{-1}$ $s^{-1}$ |
|---|---|---|
| 0.025 | 0.025 | 1.77 ± 0.02 |
| 0.050 | 0.050 | 2.94 ± 0.01 |
| 0.060 | 0.060 | 3.45 ± 0.01 |
| 0.075 | 0.075 | 4.15 ± 0.02 |

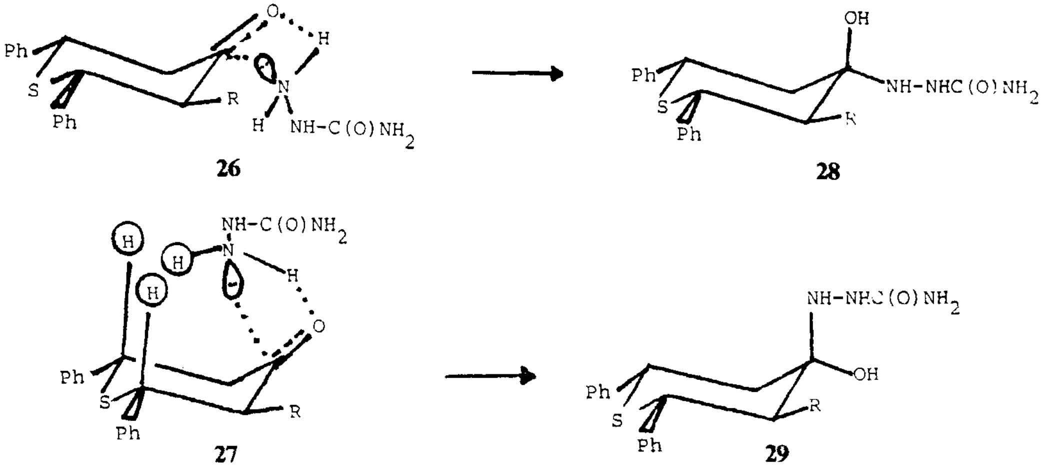
Solvent = 80% ethanol/20% water (v/v), pH = 6.45 ± 0.05, $I$ = 0.18 M, Temp. = 10°C, [ketone] = $33.48 \times 10^{-4}$ M, [semicarbazide] = $84.65 \times 10^{-4}$ M.

## *Demonstration of General Acid Catalysis*

The kinetic runs show that the reaction of the 4-thianone with semicarbazide is subject to general acid catalysis. The method used was related to that of Bronsted and Guggenheim[12] in which the same pH was maintained constant but the concentrations of acetic acid and acetate ion were varied. This was accomplished by adding to each solution sufficient acetate anion to make the ratio of the concentration of acetate to that of acetic acid the same in all solutions. It is evident from Table V and Figure 1 (a graph of $k_2$ versus [acetic acid]) that the second-order rate constants for semicarbazone formation increase with increasing acetic acid concentration although the pH remains constant (6.45 ± 0.05). The catalyst may therefore be presumed to increase the positive charge on the carbonyl carbon, facilitating the attack of semicarbazide on the carbonyl carbon.

## *Evaluation of Data*

Two transition states **26** and **27** are possible for the addition of semicarbazide to the 4-thianone which is anchored in a single chair conformation. In **26**, the semicarbazide may approach the 4-thianone from the equatorial side and in **27** the approach may be from the axial side. Transition state **26** should afford a carbinolamine **28** with an axial hydroxyl group while **27** would give a carbinolamine **29** with an equatorial hydroxyl group.



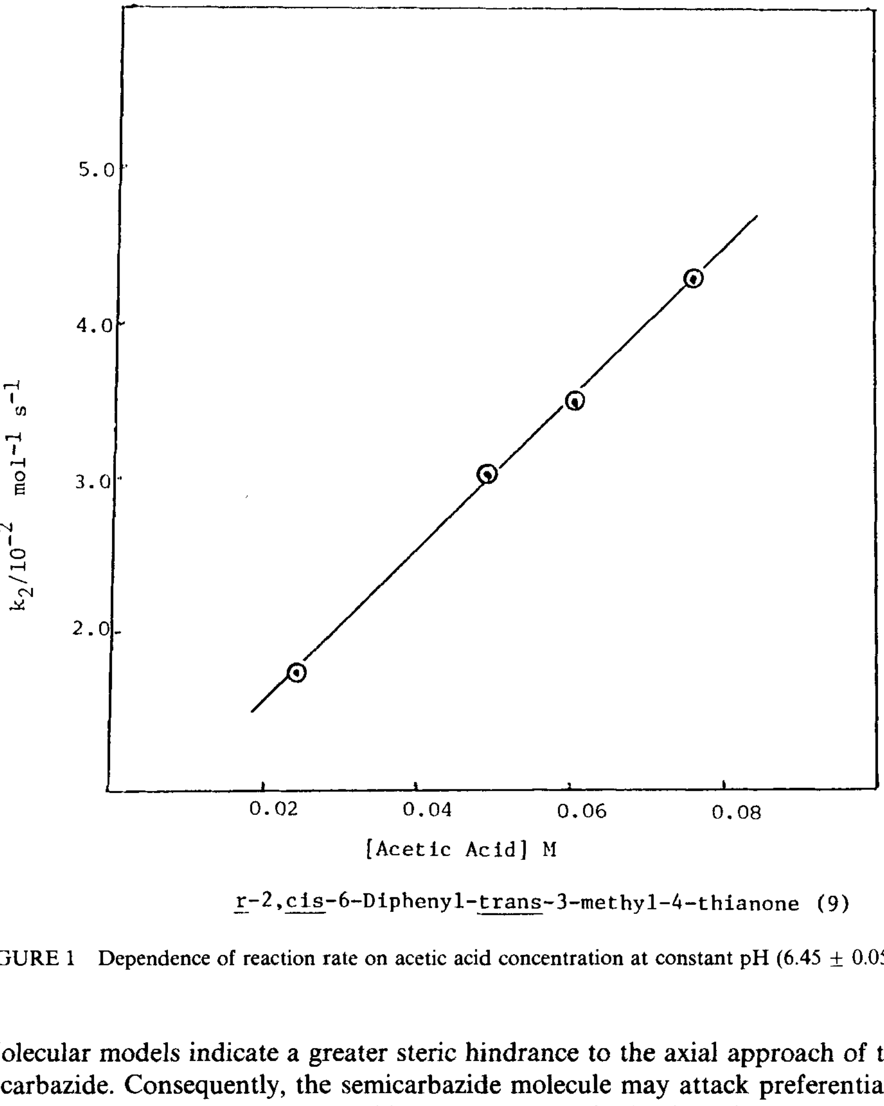


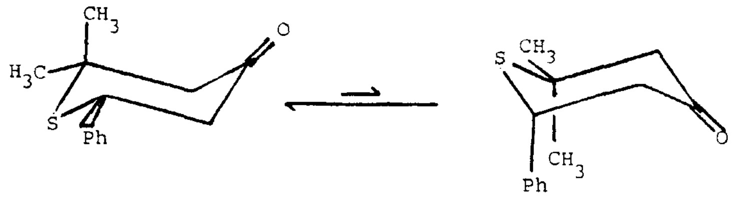
FIGURE 1 Dependence of reaction rate on acetic acid concentration at constant pH (6.45 ± 0.05).

Molecular models indicate a greater steric hindrance to the axial approach of the semicarbazide. Consequently, the semicarbazide molecule may attack preferentially from the equatorial side of the 4-thianone. The carbinolamines **28** and **29** will develop non-bonded interactions between the two newly formed groups (—OH and —$NHNHCONH_2$) and 2,6-hydrogens (axial) and also with adjacent hydrogens. Such steric interactions should retard the addition step but accelerate the second step.

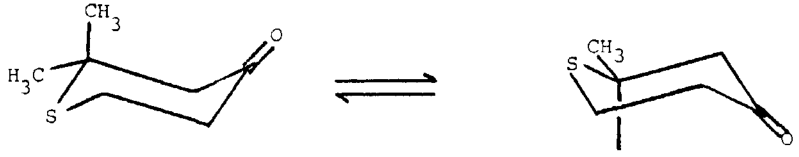
The rate constants for the formation of semicarbazones with **6**, **7** and **8** do not differ significantly. The near equal rate constants suggest that the substituent on the phenyl group does not influence the rate of semicarbazone formation appreciably. The rate constants for *r*-2,*cis*-6-diphenyl-4-thianone (**6**) and *r*-2,*cis*-6-diphenyl-*trans*-3-methyl-4-thianone (**9**) do indicate the influence of a steric factor on the rate of semicarbazone formation. Thus, the introduction of a methyl group at the 3-position (alpha to the carbonyl) lowers the rate by about 8.4 times. The introduction of an ethyl group alpha to the carbonyl (ketone **10**) lowers the rate even to a much smaller value. The rate constants decrease in the order H > Me > Et. The large steric effect seems to suggest that the addition of semicarbazide is rate-limiting. If dehydration of the carbinolamine is rate-determining, a steric acceleration should have been witnessed. The chromic acid oxidation of secondary alcohols[13,14] and the dissociation constants of cyanohydrins of ketones[15,17] belong to this second category. The steric retardation in semicarbazone formation is even more striking than the steric acceleration previously found in the cyanohydrin formation.[17]

The second-order rate constants for formation of semicarbazones from 4-thianones **15–18** are significantly smaller than those of their corresponding *cis*-epimers (wherein the two phenyl groups are *cis*-oriented). The smaller rate constants for semicarbazone formation with compounds **15–18**, when compared with those for semicarbazone formation with compounds **6–10**, surely arise because of the increased unfavorable steric crowding due to the bulky *axial* phenyl group. Similarly, the lower second-order rate constants for semicarbazone formation with **3**, **22** and **23**, when compared to that of 4-thianone **6**, may be attributed to the increased $CH_3$—OH 1,3-interaction in the carbinolamine developed.

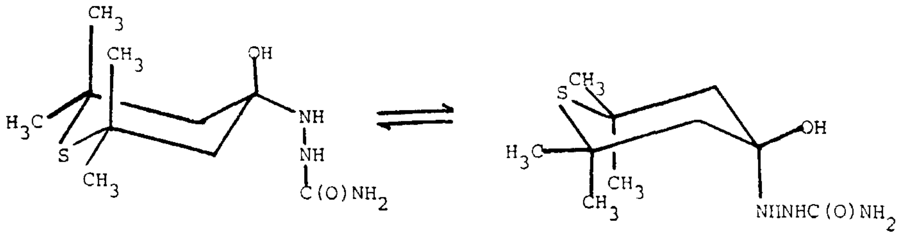
2,2-Dimethyl-6-phenyl-4-thianone (**22**) may be considered as a biased system whereas 2,2-dimethyl-4-thianone (**3**) is a mobile system. Nevertheless, both have identical rate constants for semicarbazone formation. The almost identical rate constants for semicarbazone formation with **3**, **22** and **23** suggest that the phenyl group at the 2-position has little effect. However, 2,2,6,6,-tetramethyl-4-thianone (**4**) reacts very slowly with semicarbazide, i.e. 36 times slower than the unsubstituted 4-thianone (**1**). The principle factor contributing to this smaller value is probably the non-bonded steric interaction between the axial methyl groups and the hydroxyl group during formation of the product **30**.



**22** **22′**



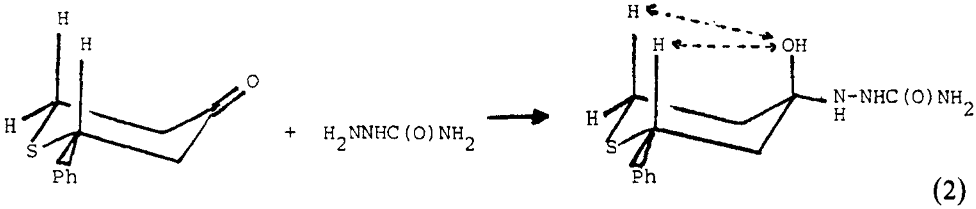
**3** **3′**



**30** **30′**

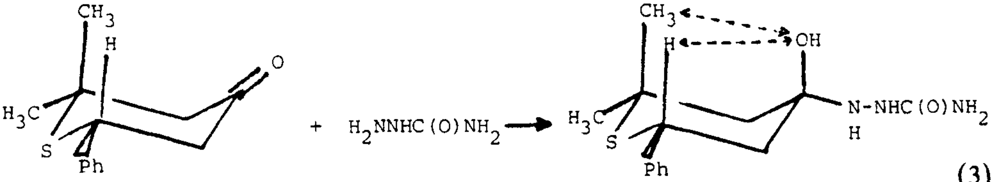
In general, 4-thianone-1,1-dioxides **5**, **11–14**, **19–21**, **24** and **25** react somewhat at a higher rate with semicarbazide when compared with their corresponding 4-thianones. The rate increase is explicable on the basis of the enhanced electron-withdrawing effect of the sulfonyl (—$SO_2$—) group which influences the rate-limiting attack of the semicarbazide on the ketonic group. It also appears that the conversion of sulfide to sulfone flattens the thianone ring system[11,18] and this flattening of the ring presumably reduces the 1,3-interactions in the carbinolamine developed and increases the rate of the reaction.

The second-order rate coefficients for semicarbazone formation from *r*-2,*cis*-6-diphenyl-4-thianone (**6**) and 2,2-dimethyl-6-phenyl-4-thianone (**22**) may be utilized



**6**

(2)



**22**

(3)

to compute $CH_3$—OH syn-axial, non-bonded interaction energy. The rate-limiting step involved may be represented as follows. If $\Delta G^{\ddagger}_{H}$ and $\Delta G^{\ddagger}_{CH_3}$ are the free energies of activation for reactions Eq. (2) and Eq. (3), respectively, then the difference between these free energies of activation is related to the corresponding second-order rate coefficients $k_H$ and $k_{CH_3}$ by the Eyring equation, i.e. Eq. (4) is pertinent.

$$\Delta G^{\ddagger}_{CH_3} - \Delta G^{\ddagger}_{H} = RT \ln \frac{k_H}{k_{CH_3}} \qquad (4)$$

Substitution of values for $k_H$ and $k_{CH_3}$ in Eq. (4) leads to 1.95 kcal $mol^{-1}$ as this difference. If one also assumes that the free-energy difference between the transition states of these two reactions is equivalent (or nearly equivalent) to that difference between the carbinolamines, it is possible to relate the above difference in the free-energies of activation to the difference in the syn-axial non-bonded interactions as follows:

$$\begin{aligned}\Delta G^{\ddagger}_{CH_3} - \Delta G^{\ddagger}_{H} &= 1.95 \text{ kcal mol}^{-1} \\ &= (CH_3\text{—OH interaction})\text{–}(H\text{—OH interaction}) \qquad (5)\end{aligned}$$

This also assumes that there is no change in the $CH_3$—OH syn-axial interaction between the reactant and the transition state of ketone **22**. Adding to the above difference the H—OH interaction energy (0.45 kcal $mol^{-1}$),[19] a value at 2.40 kcal $mol^{-1}$ is obtained as the $CH_3$—OH interaction energy. A similar calculation utilizing rate coefficients for compounds **7** and **23** gave 2.42 kcal $mol^{-1}$ as the $CH_3$—OH interaction energy. The mean value 2.41 kcal $mol^{-1}$ is in good accord with the best value (2.4 kcal $mol^{-1}$) available in the literature for other six-membered rings. Consequently, it does not appear that ring flattening in these thianones exerts a significance difference on the 1,3-interaction of axial $CH_3$—OH groups.

## EXPERIMENTAL

Compounds 1,[22] 2,[17] 3,[23] 4,[24] 5,[17] 6,[25] 7,[26] 8,[27] 9,[11] 10,[11] 12,[26] 13,[11] 14,[11] 15,[25] 16,[28] 17,[11] 18,[11] 19,[26] 20–22,[11] 23,[29] 24,[11] and 25[30] were prepared according to published procedures.

*Reagents.* Ethanol used for the kinetic study was purified by the literature method.[31] The reaction medium [ethanol : $H_2O$; 80% v/v] was prepared by diluting a mixture of 100 mL of 0.25 M acetic acid and 100 mL of 0.25 M sodium acetate to one liter with ethanol in a volumetric flash (Solution A). Its pH was found to be 6.45 ± 0.05 (measured with a Elico pH meter, model LI-10).

Semicarbazide hydrochloride was purified by dissolving a sample in a minimum amount of water (10 g in 20 mL of water) and saturating with hydrogen chloride. Three such crystallizations yielded a product which was dried *in vacuo* over calcium chloride and sodium hydroxide. The semicarbazide solution was prepared by dissolving a weighed quantity ($\cong$ 0.04 moles) of semicarbazide hydrochloride into ethanol in a standard flask. The free hydrogen chloride in the semicarbazide solution was neutralized by adding a calculated amount of standard sodium hydroxide. Then acetic acid-acetate buffer was added until the final solution was 80% (v/v) with a pH of 6.45 ± 0.05; this was similar to the reaction medium of ethanol and was labeled (Solution B).

*Kinetic measurements.* The titrimetric method reported by Conant and Bartlett[5] and refined by Price and Hammett[7] was followed to estimate the semicarbazide concentration for all the kinetic runs. In general, the molar concentration of semicarbazide was twice that of the 4-thianone. The alcohol and semicarbazide [Solutions (A) and (B)] were equilibrated at 10.00°C in a MLW Ultracryostat, Type MK 70, with an accuracy of ±0.02°C. A weighed quantity of the ketone (0.002–0.003 moles) was dissolved in 20 mL of the cold alcohol Solutions (A) and kept at 10.00°C. The ionic strength of the solution was maintained constant by the addition of potassium chloride. At the time of mixing, 5 mL of the semicarbazide Solution (B) was added to the ketone solution. A stop-watch was started immediately and 2 mL of the reaction mixture was pipetted out into a stoppered flask containing an excess of standard iodine (5 mL, $\simeq$ 0.03 N) in a phosphate buffer (5 mL, pH 7). Then 5 mL of standard sodium thiosulfate solution ($\simeq$ 0.03 N) was added to the same flask. The unreacted thiosulfate was titrated [after diluting the contents of the flask to about 50 mL with ice-cold water] against standard iodine solution ($\simeq$ 0.006 N) using 1% starch as indicator. This method gave the initial concentration of the semicarbazide in the reaction mixture. Similarly, 2 mL aliquots were withdrawn at suitable time intervals and titrated. The data obtained were substituted into the second-order rate equation for unequal concentrations of the reactants. In studies concerning the dependence of rate upon the concentrations of ketone and carbonyl reagents, the rate constants $k_1$ were calculated from the first-order rate equation.

In the semicarbazone formation of any carbonyl compound, the possibility exists for hydrolysis of the semicarbazone (reverse reaction). Such hydrolysis, if it occurs, would complicate the mathematical treatment of the experimental data. To determine whether the reverse reaction was operative, a known weight of pure semicarbazone of a selected 4-thianone was dissolved in a known amount of buffer solution (Solution A) at 10°C. Immediately after complete solution, an aliquot was removed and subjected to analysis as described above. At subsequent times, aliquots were removed and analyzed. The titer value in all cases remained constant and no semicarbazide resulted via hydrolysis.

Because of the known significant effect of pH on the rate of this type of reaction, care was taken to establish the constancy of the pH during the course of the kinetic experiments. Samples of the reaction mixture were withdrawn at appropriate time intervals and the pH was measured. In all the cases, the adequacy of the buffer system was confirmed, establishing the invariance of the environment with regard to pH during the progress of the reaction.

## ACKNOWLEDGMENTS

We thank Professor D. K. P. Varadarajan, Principal, PSG College of Arts and Science, Coimbatore and Mr. G. Varadaraj, Managing Trustee, PSG Institutions, Coimbatore for interest and financial support. We also thank the University Grants Commission, New Delhi, for the award of a research grant to P. N. and the College of Arts and Sciences at OSU for financial support to K.D.B.

## REFERENCES

1. W. P. Jencks, *J. Am. Chem. Soc.*, **81**, 475 (1959).
2. B. M. Anderson and W. P. Jencks, *J. Am. Chem. Soc.*, **82**, 1773 (1960).
3. R. Wolfenden and W. P. Jencks, *J. Am. Chem. Soc.*, **83**, 2763 (1961).
4. E. H. Cordes and W. P. Jencks, *J. Am. Chem. Soc.*, **84**, 4319 (1962).
5. J. B. Conant and P. D. Bartlett, *J. Am. Chem. Soc.*, **54**, 2881 (1932).
6. F. H. Westheimer, *J. Am. Chem. Soc.*, **56**, 1962 (1934).
7. F. P. Price, Jr. and L. P. Hammett, *J. Am. Chem. Soc.*, **63**, 2387 (1941).
8. G. H. Stempel, Jr. and G. S. Schaffel, *J. Am. Chem. Soc.*, **66**, 1158 (1944).
9. R. P. Cross and P. Fugassi, *J. Am. Chem. Soc.*, **71**, 223 (1949).
10. D. S. Noyce, A. T. Bottini and S. G. Smith, *J. Org. Chem.*, **23**, 752 (1958).
11. K. Ramalingam, K. D. Berlin, E. A. Loghry, D. Van der Helm and N. Satyamurthy, *J. Org. Chem.*, **44**, 477 (1979). In view of the known "flattening" in thianone ring systems, greater eclipsing of $R(3_e)$ with the C=O group would expectedly retard semicarbazone formation as $R''''$ increases in size.
12. J. N. Bronsted and E. A. Guggenheim, *J. Am. Chem. Soc.*, **49**, 2554 (1927).
13. J. A. Richer, L. A. Pilato and E. L. Eliel, *Chem. Ind. (London)*, 2007 (1961).
14. E. L. Eliel, S. H. Schroeter, T. J. Brett, F. J. Biros and J. C. Richer, *J. Am. Chem. Soc.*, **88**, 3327 (1966).
15. O. H. Wheeler and J. Z. Zabicky, *Can. J. Chem.*, **36**, 656 (1958).
16. O. H. Wheeler and E. Granell, *J. Org. Chem.*, **29**, 718 (1964).
17. P. Nanjappan, N. Satyamurthy and K. Ramalingan, *J. Chem. Soc. Perkin II.*, 714 (1980).
18. N. Satyamurthy, R. Sivakumar, K. Ramalingam, K. D. Berlin, R. A. Loghry and D. van der Helm, *J. Org. Chem.*, **45**, 349 (1980).
19. E. L. Eliel, N. L. Allinger, S. J. Angyal and G. A. Morrison, "Conformational Analysis," Interscience Publishers, New York (1965), p. 52.
20. E. L. Eliel and H. Haubenstock, *J. Org. Chem.*, **26**, 3504 (1961).
21. S. J. Angyal, V. A. Pickles and R. Ahluwahlia, *Carbohydrate Research*, **1**, 365 (1966).
22. C. Barkenbus, V. C. Midkiff and R. M. Newman, *J. Org. Chem.*, **16**, 232 (1951).
23. P. Y. Johnson and C. A. Berchtold, *J. Org. Chem.*, **35**, 584 (1970).
24. R. F. Naylor, *J. Chem. Soc.*, 2749 (1949).
25. K. Ramalingam, K. D. Berlin, N. Satyamurthy and R. Sivakumar, *J. Org. Chem.*, **44**, 471 (1979).
26. V. Baliah and T. Chellathurai, *Indian J. Chem.*, **9**, 424 (1971).
27. I. El-Sayed, El-Kholy and F. K. Rafla, *Tetrahedron Lett.*, 1437 (1965).
28. V. Baliah and N. Bhavani, *Indian J. Chem.*, **16B**, 776 (1978).
29. P. K. Subramanian, K. Ramalingam, N. Satyamurthy and K. D. Berlin, *J. Org. Chem.*, **46**, 4376 (1981).
30. P. Nanjappan, Ph.D. Thesis, University of Madras, India (1981).
31. A. Weissberger and E. S. Proskauer, Eds., "Technique of Organic Chemistry, Organic Solvents, Physical Properties and Methods of Purification, Vol. III," Interscience Publisher, Inc., New York (1955), p. 337.