large chain lengths, first order in H_2O_2. Table 1 and Fig. 4 demonstrate that these are experimentally realized. The apparent first-order rate constant includes a square-root dependence on dose rate which is again in agreement with the experimental results. Assuming a value of $2k_{14} = 2.4 \times 10^9$ (12) for the bimolecular termination reaction, a rate constant for the chain propagating reaction may be estimated as $k_{13} = (4.0 \pm 0.4) \times 10^4\ M^{-1}\ s^{-1}$. This is somewhat less than the rate constant found by Seddon and Allen (4) for the propagating reaction in the ethanol/H_2O_2 chain reaction. It may be noted that the rate constant for reduction of ferricyanide by $\dot{C}H_2OH$ is slightly less than that for reduction by $CH_3\dot{C}HOH$ (8).

The small yield of ethylene glycol found (G(glycol) ~ 0.5) represents approximately 20% of the termination reaction. In the photolysis of methanol–water solutions (13), the major product of radical combination was said to be ethylene glycol.

At high concentrations of either alcohol the yield of the chain reaction is decreased. This phenomenon has previously been reported for the photo-induced reaction in mixed water–alcohol systems (5) and in the radiation-induced oxidation of 2-propanol (1). In the latter case the decreased yield was attributed to a decrease in the rate of reaction [7], as a result of the decreasing dielectric constant of the medium at alcohol concentrations sufficiently high to make reaction [7] rather than reaction [8] the rate-determining propagation step.

Summary

The principal numerical results are summarized in Table 2. We have demonstrated that the two-radical model for the chain oxidation of alcohols by H_2O_2, as developed for 2-propanol, is applicable also to ethanol but that a one-radical model accounts satisfactorily for the features of the oxidation of methanol.

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Structure of a product obtained on treatment of 1-thioacetoacetanilide with sulfuryl chloride

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Received April 3, 1970

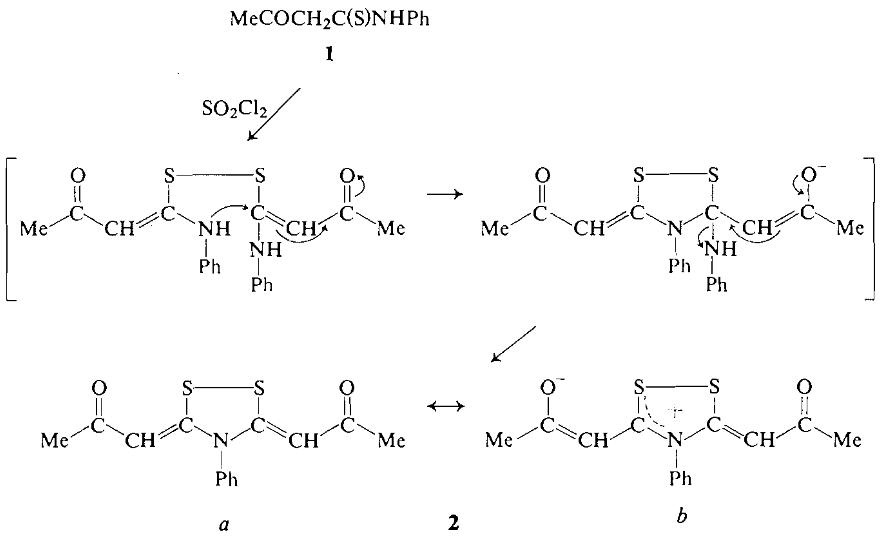
Treatment of 1-thioacetoacetanilide with sulfuryl chloride or thionyl chloride produced a crystalline compound identified as 3,5-diacetonylidene-4-phenyl-1,2,4-dithiazolidine. The absence of carbonyl absorption in the infrared spectrum of the compound indicated that it should be represented by a resonance structure (**2**) involving non-carbonyl components.

Canadian Journal of Chemistry, **48**, 2632 (1970)

In connection with our synthetic work on pesticides, the preparation of 2-chloro-1-thioacetoacetanilide was required. Accordingly 1-thioacetoacetanilide (**1**) was treated at room temperature with an equimolar quantity of sulfuryl chloride. Reaction occurred readily; but instead of the desired product, a chlorine-free crystalline compound (m.p. 195–195.5°) was obtained.

In the present publication we provide evidence establishing the structure of this compound.

The molecular formula $C_{14}H_{13}NO_2S_2$, estab-



SCHEME 1

lished by elemental analysis and high-resolution mass spectrometry, indicated that the product was formed from two reactant molecules with loss of two hydrogen atoms and the elements of aniline.

The nuclear magnetic resonance (n.m.r.) spectrum shows aromatic absorption centered at 2.5 τ and singlets at 4.59 and 7.94 τ. The intensities of the peaks are in the ratios 5:2:6, respectively.

Consideration of the foregoing data indicated structure **2***a* (3,5-diacetonylidene-4-phenyl-1,2,4-dithiazolidine) for the compound under study.

The mechanism postulated for the conversion of 1-thioacetoacetanilide (**1**) to **2***a* is indicated in Scheme 1. The initial oxidative step, involving a thiol form of **1**, is consistent with early work on the action of sulfuryl chloride on mercaptans (1, 2). The latter were found convertible to the corresponding disulfides according to eq. [1].

$$[1]\quad 2RSH + SO_2Cl_2 \rightarrow RSSR + 2HCl + SO_2$$

Interestingly, when 1-thioacetoacetanilide and sulfuryl chloride were used in the proportions indicated by this equation, the yield of product was increased from 60 to 96%.

The conversion of mercaptans to disulfides and analogous oxidations of thioureas to 1,1′-dithiodiformamidine derivatives on treatment with thionyl chloride have also been reported (2, 3). Oxidation of 1-thioacetoacetanilide (**1**) by this method led to an almost quantitative yield of the same dithiazolidine derivative.

Although the data presented above appear entirely consistent with structure **2***a*, the infrared (i.r.) spectrum of the product indicated a modification of this structure to be necessary. The i.r. spectrum shows no absorption attributable to a normal conjugated carbonyl group; within the 1700–1600 cm^{-1} range there is only one broad peak at 1610 cm^{-1}.

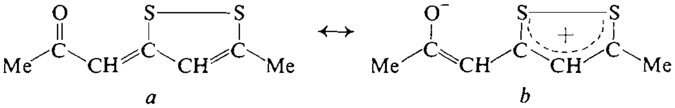
The necessary modification was suggested by earlier work on the structure of the related (5-methyl-1,2-dithiol-3-ylidene)-2-propanone (**3**) (4). The i.r. spectrum of this compound also lacks bands in the carbonyl region and thus indicated that formula **3***a* is an inadequate representation of the molecule. X-ray crystallographic studies (5, 6) supported this conclusion and appear consistent with a resonance hybrid **3** including non-carbonyl components **3***b* (7).

Similarly it can be concluded that structure **2***a* should be replaced by a resonance hybrid involving, besides **2***a*, ionic structures such as **2***b*.

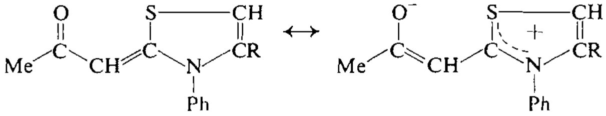
Confirmatory evidence was obtained from a study of (3,4-diphenyl-4-thiazolin-2-ylidene)-2-propanone (8) and (4-methyl-3-phenyl-4-thiazolin-2-ylidene)-2-propanone, prepared by reaction of 1-thioacetoacetanilide (**1**) with 2-bromoacetophenone and chloroacetone, respectively. As expected of structures **4***a* and *b* the i.r. spectra of these compounds showed no absorption in the usual conjugated carbonyl region.

Experimental

The i.r. spectra were recorded on a Perkin–Elmer 521 i.r. spectrophotometer. Accurate mass measurement of



3



4

a R = Ph
b R = Me

the molecular ion was carried out on a CEC 110B double-focusing mass spectrometer by reference to appropriate peaks in the spectrum of perfluorokerosene, through the courtesy of Professor D. B. MacLean of McMaster University, Hamilton, Ontario.

1-Thioacetoacetanilide (1)

This compound was prepared by the method of Worrall (9): reaction of phenylisothiocyanate with the sodio derivative of acetylacetone and deacetylation of the 2-acetyl-1-thioacetoacetanilide produced with alkali. The sodio derivative of acetylacetone was conveniently prepared by use of sodium hydride in place of the sodium employed in the original method.

3,5-Diacetonylidene-4-phenyl-1,2,4-dithiazolidine (2)

(*1*) To a stirred solution of 1-thioacetoacetanilide (19.3 g, 0.10 mole) in benzene (150 ml) was added dropwise sulfuryl chloride (6.8 g, 0.05 mole) over 0.5 h. The reaction mixture was stirred for a further 3 h and then cooled. The precipitate was collected, washed with cold benzene, and then treated with boiling benzene. The insoluble material (aniline hydrochloride) was removed by filtration. Crystallization from the concentrated filtrate afforded material melting at 185–187°. Recrystallization from benzene gave crystals (14 g, 96%) of m.p. 190–191°. Two more recrystallizations from acetonitrile gave an analytical sample, m.p. 195–195.5°. The i.r.: ν_{max} (KBr and $CHCl_3$) 1610 (broad), no other absorption in the 1700–1600 cm^{-1} region; n.m.r.: 2.5 (5H, multiplet), 4.59 (2H, singlet), 7.94 τ (6H, singlet).

Anal. Calcd. for $C_{14}H_{13}NO_2S_2$ (291.0388): C, 57.73; H, 4.50; N, 4.82; S, 21.97. Found (mass spectroscopy 291.0395): C, 57.65; H, 4.29; N, 4.87; S, 21.81.

When equimolar quantities of the two reagents were used, the product was obtained in 60% yield.

(*2*) To a stirred solution of 1-thioacetoacetanilide (9.6 g) in benzene (100 ml) was added dropwise thionyl chloride (3.0 g) over 15 min. The temperature of the reaction mixture during the addition and for a further hour was kept at 10–15°. Then it was allowed to rise to 25° within 20 min. The crystalline product was collected and washed with cool benzene. Then it was treated with boiling benzene and the insoluble material removed by filtration. Crystallization from the concentrated filtrate afforded material (7.2 g, 99%) of m.p. 194–195°. The identity of this product with that obtained by the sulfuryl chloride method was established by comparison of i.r. spectra and determination of the m.p. of a mixture of the two specimens.

(3,4-Diphenyl-4-thiazolin-2-ylidene)-2-propanone (4a)

This compound was prepared by the reaction of 1-thioacetoacetanilide and 2-bromoacetophenone, according to the procedure of Borisevich *et al.* (8). The i.r.: ν_{max} ($CHCl_3$) 1595 and 1585, no absorption in the 1700–1600 cm^{-1} region; n.m.r.: 2.8 (10H, multiplet), 3.61 (1H, singlet), 4.47 (1H, singlet), 7.99 τ (3H, singlet).

(4-Methyl-3-phenyl-4-thiazolin-2-ylidene)-2-propanone (4b)

1-Thioacetoacetanilide (3.1 g) and chloroacetone (2.1 g) were dissolved in ethanol (30 ml); the resulting solution was heated under reflux for 3 h and then left to stand at room temperature for 42 h. The hydrochloride obtained after removal of the ethanol was recrystallized from acetonitrile to give material (1.3 g) of m.p. 250–255° decomposition. From the mother liquors an additional amount (0.3 g) of product was crystallized.

The hydrochloride was chromatographed on neutral alumina with ethanol as eluent. The free base was thus obtained (1.1 g, 37%), m.p. 155–157°. Two recrystallizations from ethanol–water yielded an analytical sample of m.p. 157–158.5°. The i.r.: ν_{max} ($CHCl_3$) 1592 and 1577, no absorption in the 1700–1600 cm^{-1} region; n.m.r.: 2.6 (5H, multiplet), 3.88 (1H, singlet), 4.73 (1H, singlet), 8.01 (3H, singlet), 8.10 τ (3H, singlet).

Anal. Calcd. for $C_{13}H_{13}NOS$: C, 67.52; H, 5.67; N, 6.06. Found: C, 67.46; H, 5.70; N, 5.81.

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