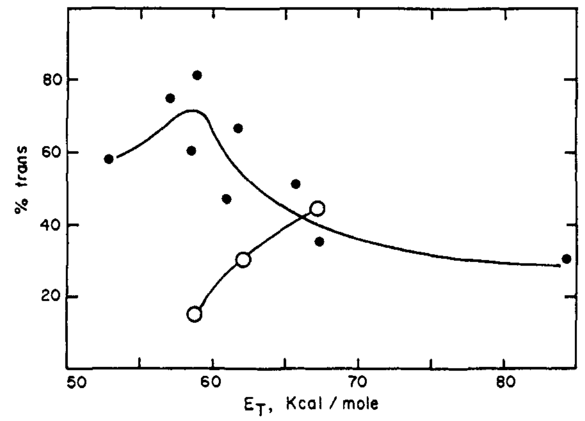

Figure 1. Photostationary states of 2-benzal-5-methylcyclopentanone (1) as a function of sensitizer triplet energy: ●, unselective sensitizers; ○, selective sensitizers.

predicts the selectivities of sensitizers with $E_T > 59$ kcal/mol but fails to predict that all lower energy sensitizers are unselective.[4] This result is predictable if there is an isomer of 1 having a ~59-kcal/mol T_2 state with π,π^* character. Lower energy potentially selective sensitizers would then have insufficient energy to populate the T_2 state, and exothermic energy transfer would ensue causing population of the T_1-n,π^* hydrogen abstraction intermediate. The observed occurrence of isomerization even with the lower energy sensitizers could be due to competing nonvertical energy transfer to give a distorted $^3(\pi,\pi^*)$ state or to isomerization of the T_1 ^{3}(n,π^*) state.

The changes in the photostationary ratios on reducing the triplet energies of the sensitizers also suggest a T_2-π,π^* state of **1**. The *decrease* in the trans–cis ratio with lower energy *selective* sensitizers suggests that the cis-π,π^* triplet is more energetic than the trans-π,π^* triplet and therefore is populated less efficiently on lowering the sensitizer energies. The *increase* in the trans–cis ratio with lower energy *unselective* sensitizers implies that, conversely, with these sensitizers the efficiency of excitation to the trans-π,π^* triplet falls off faster than to the cis-π,π^* triplet. Analogy with sensitization of oxygen to its $^1\Sigma_g{}^+$ state suggests that excitation to T_2 states may fall off rapidly with sensitizers having energies up to 10 kcal/mol above the T_2 energy.[5] Thus if the π,π^* triplet of *trans*-**1** is a T_2 state, excitation to this state with unselective sensitizers could become inefficient earlier than excitation of *cis*-**1** to its higher energy T_1 π,π^* state.

(4) This is strictly true only if the nearly identical triplet energies given for the two phenylnaphthalene sensitizers are reversed.

(5) D. R. Kearns, R. A. Hollins, A. V. Khan, R. W. Chambers, and P. Radlick, *J. Amer. Chem. Soc.*, **89**, 5455 (1967).

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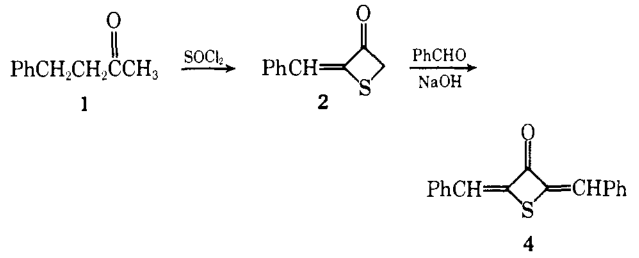
Oxidations by Thionyl Chloride. II. 3-Thietanones from Ketones

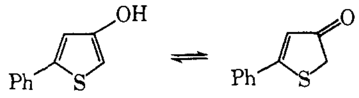
Sir:

Thionyl chloride, in the presence of catalytic amounts of pyridine, reacts abnormally with aliphatic carboxylic acids to afford α-chloro-α-chlorosulfenyl acid chlorides[1] and—with 3-arylpropanoic acids—benzo[*b*]thiophenes.[1a] Formation of the former can be rationalized mechanistically in terms of a Hell–Volhard–Zelinsky (HVZ) type addition of thionyl chloride to the enol of the carboxylic acid chloride to afford an α-sulfinyl chloride which may be converted to the sulfenyl chloride by a sequence of steps finding close analogy in the Pummerer rearrangement.[1a] The operation of this mechanism in the case of ketones might be surprising, since not only does that group appear to be inert to the action of thionyl chloride,[2] but also, if reaction did occur, a *gem*-dichloride might be expected instead.[3] During attempts to detect the operation of the HVZ- and Pummerer-type mechanisms with ketones, an unexpected cyclization occurred which led to a new one-step synthesis of a relatively unfamiliar class of compounds, the 3-thietanones.[4]

Treatment at room temperature of 4-phenyl-2-butanone, **1**, with an excess of thionyl chloride in the presence of catalytic amounts of pyridine gave rise to a vigorous, exothermic reaction which afforded 2-benzylidene-3-thietanone, **2**, 37.5%, mp 113.1–113.9°; the remaining material was intractable. The structure was established through analysis of the infrared (λ_{max}^{KBr} 5.75 μm), nmr (CCl_4, three singlets at τ 2.66, 2.78, and 5.75 in the ratio 5:1:2), and ultraviolet (λ_{max}^{EtOH} 361.5 (log ϵ 4.20), 292 (infl., 3.41), 265 (infl., 3.80), 242 (4.20), and 235 (infl., 4.17) nm) spectra which clearly differentiated **2** from an alternative product, 5-phenylthiophen-3-ol[10] (**3**). Base-catalyzed condensation of **2** with benzaldehyde yielded bisbenzylidene-3-thietanone, **4**, mp 168–169°. The structure of the latter was



1 **2** **4**



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(1) (a) A. J. Krubsack and T. Higa, *Tetrahedron Lett.*, 5149 (1968); (b) M. S. Simon, J. B. Rogers, W. Saenger, and J. Z. Gougoutas, *J. Amer. Chem. Soc.*, **89**, 5838 (1967).

(2) G. Büchi and G. Lukas, *ibid.*, **86**, 5654 (1964); V. J. Dalvi and G. V. Jadhav, *J. Indian Chem. Soc.*, **34**, 324 (1957).

(3) A. Schönberg and R. von Ardenne, *Chem. Ber.*, **101**, 346 (1968); A. Schönberg and A. F. A. Ismail, *J. Chem. Soc.*, 200 (1945).

(4) Five 3-thietanones have been reported: 3-thietanone,[5] 2,2,4,4-tetramethyl-3-thietanone,[6] 3-thietanone-2-acetic acid,[7] 2-(2-propenyl)-3-thietanone,[8] and 2,2,4,4-tetraphenyl-3-thietanone.[9]

(5) R. Mayer and K. F. Funk, *Angew. Chem.*, **73**, 578 (1961); H. Prinzbach and G. v. Veh, *Z. Naturforsch., B*, **16**, 763 (1961); K. K. Maheshwari and G. A. Berchtold, *Chem. Commun.*, 13 (1969).

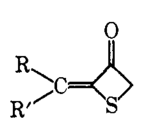
(6) G. Claeson and A. Thalen, *Acta Chem. Scand.*, **17**, 1172 (1963); G. Claeson, A. Thalen, and L. Schotte, *Ark. Kemi*, **21**, 295 (1963).

(7) G. Claeson and A. Thalen, *Acta Chem. Scand.*, **17**, 2763 (1963).

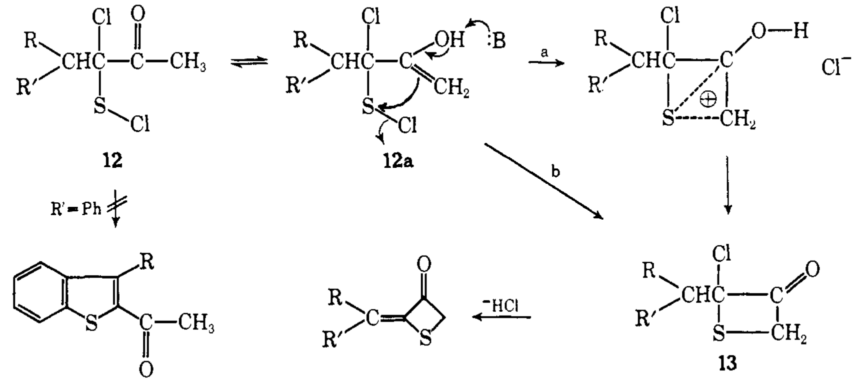
(8) W. C. Lumma, Jr., and G. A. Berchtold, *J. Org. Chem.*, **34**, 1566 (1969).

(9) R. Rioult and J. Vialle, *Bull. Soc. Chim. Fr.*, 2883 (1967).

(10) A. J. Kosak, R. J. F. Palchak, W. A. Steele, and C. M. Selwitz, *J. Amer. Chem. Soc.*, **76**, 4450 (1954). The reported melting point of **3**, 78°, is much lower than that of **2**. Furthermore, **3** is reported to be oxidized readily by atmospheric oxygen; **2** is stable under these conditions.



8, R = R′ = CH_3
9, R = H; R′ = $(CH_3)_2CH$
10, R = R′ = C_2H_5
11, R = R′ = Ph



established by unambiguous synthesis. Acid-catalyzed condensation of ethylene glycol with 1,3-dibromo-2-propanone, obtained by Jones oxidation of 1,3-dibromo-2-propanol, afforded 1,3-dibromo-2,2-ethylenedioxypropane, **5**. Treatment of **5** with anhydrous sodium sulfide in hot ethylene glycol furnished 3,3-ethylenedioxythietane, **6**, which in turn was hydrolyzed to the known[5] 3-thietanone, **7**. Base-catalyzed condensation of **7** with benzaldehyde yielded the bis adduct, **4**, shown by mixture melting point and by comparison of the ir and nmr spectra to be identical with the bis adduct obtained from **2**.

Both **2** and **4** appear to be single isomers, as judged by sharp melting points and by the nmr spectra, which consist of sharp singlets in the case of **2** and one sharp singlet at τ 2.62 in the case of **4**. A shoulder on the upfield side of the aromatic proton peak of **4** in the 100-MHz spectrum explained the apparent disappearance of the vinyl protons.

Other 3-thietanones have also been synthesized in one step from readily available ketones by the above procedure. 4-Methyl-2-pentanone afforded thietanone **8**, λ_{max}^{neat} 5.75 μm, τ (CCl_4) 5.98 (s, 2 H), 7.86 (s, 3 H), and 8.27 (s, 3 H), in 25% yield, as an oil which polymerized readily at room temperature. 5-Methyl-2-hexanone furnished thietanone **9**, λ_{max}^{neat} 5.68 μm, τ (CCl_4) 3.66 (d, 1 H), 5.80 (s, 2 H), 7.68 (m, 1 H), and 8.87 (d, 6 H) in 16% yield. 4-Ethyl-2-hexanone gave thietanone **10**, λ_{max}^{neat} 5.74 μm, τ (CCl_4) 5.96 (s, 2 H), 7.40 (q, 2 H), 7.93 (q, 2 H), 8.90 (t, 3 H), and 8.94 (t, 3 H) in 12% yield. And 4,4-diphenyl-2-butanone furnished thietanone **11**, mp 130–131°, λ_{max}^{KBr} 5.75 μm, τ ($CDCl_3$) 2.62 and 2.64 (two overlapping singlets, 10 H) and 5.82 (s, 2 H), in 17.1% yield. Both **9** and **10** are relatively stable oils. The stereochemistry of **9** is assigned as indicated on the basis of the diamagnetic anisotropy effect of the carbonyl group and the chemical shifts of the corresponding aliphatic groups in **8** and **10**.

On the assumption that sulfenyl chloride **12** is formed by an HVZ- and Pummerer-type of sequence, capture of its enol, **12a**, by either (a) addition of the sulfenyl chloride group to the carbon–carbon double bond or (b) nucleophilic attack of the terminal methylene carbon atom upon sulfur, displacing chloride ion, would give rise to thietanone **13**. Elimination of hydrogen chloride from **13** would yield the unsaturated 3-thietanones. The role which pyridine plays in the sequence may be to assist in the enolization process or in the elimination of hydrogen chloride from **12a**, for example. Qualitative studies have thus far indicated merely that its presence enhances the rate of reaction.

The observation of 3-thietanones from reactions of thionyl chloride with 4-phenyl-2-butanones is in marked contrast to the formation of benzo[*b*]thiophene derivatives from hydrocinnamic and cinnamic acids.[1a] Apparently the propensity for presumed intermediate sulfenyl chloride **12** to enolize and form a four-membered ring by intramolecular addition to the enolic carbon–carbon double bond is much greater than that for formation of a five-membered ring by intramolecular addition to the aromatic ring.

We are pursuing experiments aimed at further defining the mechanistic and stereochemical consequences of these reactions.

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Calorimetric Study of the Solvation of a Stable Free Radical

Sir:

Recent studies of solvent effects on rate constants for radical termination and chain transfer have suggested that certain free radicals, particularly small relatively unstable ones, may be especially well solvated in aromatic media.[1] We have measured[2] the partial molal heats of solution at substantially infinite dilution of the stable free radical di-*tert*-butyl nitroxide (**1**) and its nonradical

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(1) S. A. Weiner and G. S. Hammond, *J. Amer. Chem. Soc.*, **91**, 986 (1969); R. D. Burkhart, *ibid.*, **90**, 273 (1968); *J. Phys. Chem.*, **73**, 2703 (1969).

(2) The calorimeter used is a modification of the design of E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. M. Duggleby, *J. Amer. Chem. Soc.*, **87**, 1541 (1965). Values plotted are averages of three to five heats determined by successive injections of solute. Final solute concentrations were in the range 4–8 × 10^{-3} *M*. No regular trends suggestive of solute–solute interaction were noted with successive solute additions. Maximum standard deviations in measured heats for the radical were 20 cal/mol. Those for the hydroxylamine are shown in Figure 1.