158. Synthesis and Photochemistry of 2,2-Dimethyl-3(2*H*)-thiophenone, a Ketonic Tautomer of 3-Hydroxythiophene

Preliminary Communication

by **Elke Anklam, Ramin Ghaffari-Tabrizi, Hermann Hombrecher, Sabine Lau** and **Paul Margaretha***

Institut für Organische Chemie, Universität, D-2000 Hamburg 13

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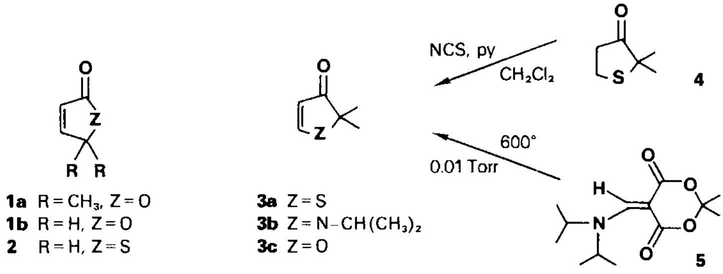
Summary

On irradiation (λ = 366 nm), the 4-thia-2-cyclopentenone **3a** behaves in complete analogy to the oxa-enone **3c** undergoing regio- and stereospecific cyclodimerization, regiospecific cycloaddition with 2-methylpropene and cycloaddition with 2,3-dimethyl-2-butene to afford cyclobutane derivatives. In contrast, the 4-aza-2-cyclopentenone **3b** does not undergo the above-mentioned reactions but only slow photodecomposition.

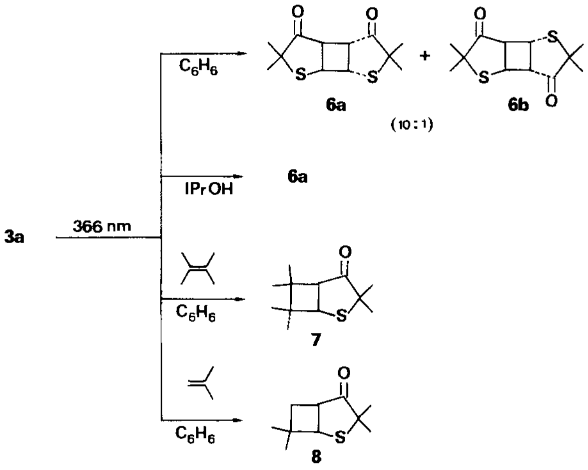
We have recently shown that the ketonic tautomers of 2-hydroxythiophene and 2-hydroxyfuran exhibit a dissimilar photochemical behaviour. While the 5(2*H*)-furanones **1** undergo ordinary bimolecular enone reactions, *e.g.* [2+2]-cycloadditions with olefins or photoreduction in easily oxidizable solvents [1], the unsaturated thiolactone **2** is photosolvolized in alcohols affording 4-mercaptocrotonates, which themselves undergo further light-induced reactions [2]. We have now synthesized the ketonic tautomers of 3-hydroxythiophene and 3-hydroxypyrrole, **3a** and **3b**, respectively, to compare their photochemical behaviour to that of the well-investigated [3] [4] 2,2-dimethyl-3(2*H*)-furanone (**3c**) (*Scheme 1*).

Thia-enone **3a** was obtained by dehydrogenation of 2,2-dimethylthiolan-3-one (**4**); in this reaction *N*-chlorosuccinimide [5] proved to be a much more efficient reagent

Scheme 1



Scheme 2



than 2,3-dichloro-5,6-dicyanoquinone. Aza-enone **3b** was obtained by pyrolysis [6] of the diisopropylaminomethylene analogue **5** of *Meldrum*'s acid.

Irradiation (λ = 366 nm) of **3a** in benzene affords a 10:1 mixture of dimers **6a** and **6b**, while in i-PrOH **6a** is formed exclusively. The head-to-head structure and assignment of the *anti*-configuration for dimer **6a** results from the ^{1}H-NMR data and from an enantioselective GC analysis [7]. Irradiation of **3a** in the presence of 2,3-dimethyl-2-butene or 2-methylpropene affords the thiabicyclo[3.2.0]heptanones **7** and **8**, respectively, this latter product again being formed regiospecifically (for spectroscopic and analytical data *cf.* the *Table*). The photochemical behaviour of **3a** thus fully matches that of the oxa-enone **3c** [4] *(Scheme 2)*.

Aza-enone **3b** exhibits a totally different behaviour. On irradiation (λ = 366 nm) in a variety of solvents (CH_2Cl_2, CH_3CN, i-PrOH) either in the presence or absence of the above-mentioned olefins, **3b** only undergoes slow photodecomposition to unidentified material. Such a sluggishness in photochemical reactivity has already been observed for other pyrrolinones [8]. A plausible explanation for this observation can be given by the following reaction sequence, wherein self-quenching occurs *via* electron transfer from a ground- to an excited-state molecule followed by electron back-transfer between the two ion radicals *(Scheme 3)*.

Although we have not measured the oxidation potentials for compounds **3**, it can be assumed that their ease of oxidation will parallel the series *N,N*-dimethylaniline, thioanisole and anisole ($E_{\frac{1}{2}}$ *vs.* SCE: 0.71, 1.56 and 1.76 V, resp. [9]). It thus becomes obvious that aza-enones have a much higher probability to undergo the deactivation reaction described above than the corresponding sulfur or oxygen heterocycles.

Scheme 3

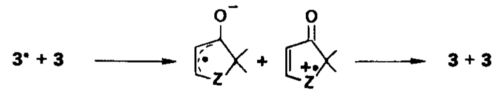


Table. *Spectroscopic and Analytical Data of Enones* **3a** *and* **3b**, *and of Photoproducts* **6**, **7**, *and* **8**

Compound	UV	^{1}H-NMR ($CDCl_3$)	MS	E_{p_c} a)
3a	310 (3.75)b) 352 (sh, 2.34) 366 (sh, 1.90)	8.27 and 6.12 (*AB*, $J = 6.0$) 1.52 (*s*, 6H)	128 (M^+) *59*	– 2.42 V
3b	322 (3.97)c)	7.92 and 5.10 (*AB*, $J = 3.4$); 3.63 (*m*, 1H); 1.30 (*d*, 6H); 1.23 (*s*, 6H)	153 (M^+) *110*	> – 2.85 V
6ad)		3.71 and 3.57 (*AA'BB'*, $J_{AB} = 7.4$, $J_{AB'} = -1.4$, $J_{AA'} = 4.4$, $J_{BB'} = 2.4$); 1.47 (*s*, 6H); 1.40 (*s*, 6H)	256 (M^+) *128*	
6be)		3.95 and 3.44 (*AA'BB'*, $J_{AB} = 7.5$, $J_{AB'} = 3.3$, $J_{AA'} = 3.1$, $J_{BB'} = 1.3$); 1.50 (*s*, 6H); 1.42 (*s*, 6H)	256 (M^+) *128*	
7		3.45 and 3.05 (*AB*, $J = 7.5$); 1.35 (*s*, 6H); 1.20 (*s*, 6H); 1.15 (*s*, 3H); 1.00 (*s*, 3H)	212 (M^+) *84*	
8		3.50 (*ddd*, $J = 7.2, 2.2, 0.6$, H_1)f)); 3.30 (*ddd*, $J = 10.0, 7.2, 6.7$, H_2); 2.18 (*ddd*, $J = 11.8, 10.0, 2.2$, H_3); 2.00 (*ddd*, $J = 11.8, 6.7, 0.6$, H_4); 1.42 (*s*, 3H); 1.38 (*s*, 3H); 1.26 (*s*, 3H); 1.05 (*s*, 3H)	184 (M^+) *128*	

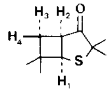
a) Measured *vs.* Ag/Ag^+ (10^{-1} M in CH_3CN), sweep rate = 100 mV/s. The value for **3c** is –2.75 V.

b) In cyclohexane.

c) In benzene.

d) Separation factor = 1.029 on a 15-m fused silica capillary coated with *XE-60-L*-valine-(*S*)-α-phenylethylamide.

e) Not isolated, data from product mixture **6a**/**6b** (irradiation in cyclohexane).

f) 

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Experimental Part

General. Absorptions in the UV spectra are given in nm (logε). Chemical shifts in the 400-MHz ^{1}H-NMR spectra are given in ppm relative to TMS (= 0 ppm) as internal standard. The mass spectra were measured at 70 eV. Cathodic peak potentials were measured with a Pt-electrode using TBAP (10^{-1}M) as electrolyte.

Starting Materials. 2,2-Dimethylthiolan-3-one (**4**) was synthesized according to the procedure in [10]. 2,3-Dimethyl-2-butene and 2-methylpropene were purchased from *Fluka AG*. All solvents used for photolyses were of spectral grade.

*2,2-Dimethyl-3(2*H*)-thiophenone* (**3a**). To an ice-cooled, well stirred solution of 2.6 g ($2 \cdot 10^{-2}$ mol) **4** and 1.6 g ($2 \cdot 10^{-2}$ mol) pyridine in 50 ml CH_2Cl_2, 2.7 g ($2 \cdot 10^{-2}$ mol) of NCS [5] was added within 10 min. Stirring was continued for 5 h at r.t. CH_2Cl_2 was removed under vacuum and replaced with 50 ml of Et_2O. The precipitate was removed by filtration and washed with 10 ml Et_2O. The combined ethereal extract was dried ($MgSO_4$) and distilled to afford 1.0 g (38%) **3a**, b.p. 78–80°/12 mm.

*(5-(*N,N*-Diisopropylaminomethylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione* (**5**). Following the procedure of *Bihlmayer et al.* [11], the reaction of *Meldrum*'s acid, ethyl orthoformate and $(i\text{-}Pr)_2NH$ afforded **5** in 78% yield, m.p. 118° (from cyclohexane), ^{1}H-NMR ($CDCl_3$): 8.21 (*s*, 1H); 4.87 (*m*, 1H); 3.81 (*m*, 1H); 1.68 (*s*, 6H); 1.35 (*d*, 6H); 1.28 (*d*, 6H).

N-*Isopropyl-5,5-dimethyl-2-pyrrolin-4-one* (**3b**). Following the procedure of *McNab* [6], flash vacuum pyrolysis of **5** gave **3b** in 67% yield, m.p. 57° (from cyclohexane).

Photolyses. Irradiations were performed with a 400-W medium-pressure Hg-lamp using a liquid filter solution (7 g $Pb(NO_3)_2$ + 750 g NaBr/l H_2O) with a cut-off at $\lambda > 340$ nm. The concentration of **3a** or **3b** in all experiments was $2 \cdot 10^{-1}$M.

cis-transoid-cis-*4,4,9,9-Tetramethyl-3,10-dithiatricyclo[5.3.0.0^{2,6}]decan-5,8-dione* (**6a**). A degassed solution of 26 mg **3a** in 1 ml i-PrOH was irradiated for 14 h. The white crystalline precipitate was filtered, dried and recrystallized from pentane/Et_2O. The yield of **6a** (m.p. 175–177°) is 90%.

3,3,6,6,7,7-Hexamethyl-2-thiabicyclo[3.2.0]heptan-4-one (**7**). A degassed solution of 26 mg **3a** and 300 mg 2,3-dimethyl-2-butene in 1 ml benzene was irradiated for 14 h. After evaporation of the solvent the residue was purified by bulb-to-bulb distillation (120°/0.1 Torr) to afford 38 mg (90%) **7**.

3,3,7,7-Tetramethyl-2-thiabicyclo[3.2.0]heptan-4-one (**8**). A solution of 26 mg **3a** in 1 ml of benzene was saturated with 2-methylpropene and irradiated for 14 h. Workup as described above and bulb-to-bulb distillation (100°/0.1 Torr) afforded 32 mg (88%) **8**.

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