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PHOTOLYSIS OF 3,3,6,6-TETRAMETHYL-1-THIACYCLOHEPTANE-4,5-DIONE - A PRODUCT STUDY

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Reports on the photolyses of non-enolizable cyclic α-diones[1,2] and on the effects of amines and sulfides on the mechanisms of the photolyses of α-diones[3,4] and ketones[5,6] leads us to report our preliminary results on the photolysis of 3,3,6,6-tetramethyl-1-thiacycloheptane-4,5-dione(I) in t-butyl alcohol and Freon 113. Products are given in Fig. 1 and yields and other data in Table 1.

Fig. 1

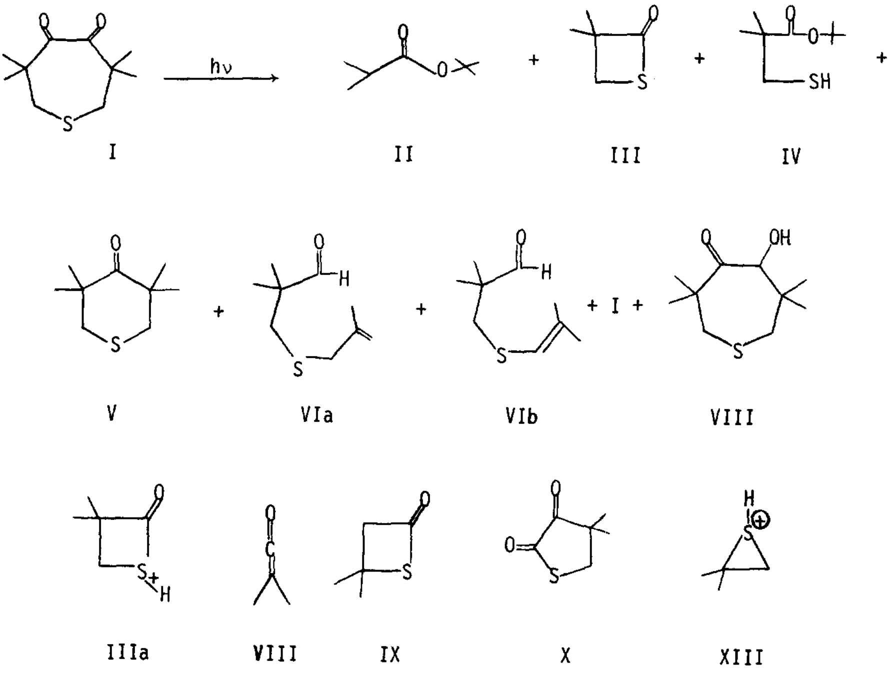


Table 1

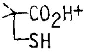
Run	Apparatus	Solvent	Time	Yield of Products[a] (average of several runs)
A	450 watt Hanovia Pyrex Filter	*t*-BuOH (2%I)	10 hr[b]	II (5-10%, variable), III (47%), IV (trace), V (2.5%), VIa (2.0), VIb (2.5), I (15%)
B	450 watt Hanovia Pyrex Filter	Freon 113 (2%I)	3 hr[c]	polymer, III (35%), V (3.5%), VIa (3.0%), VIb (3.8%), I (38%)
C	Rayonet 3500 A° source	*t*-BuOH (2%I)	6.5 hr[d]	II (5-10%, variable), III (52%), IV (1%), V (14%), VIa (5.5%), VIb (6.5%), I (5%), VII (trace)
D	Rayonet 3500 A° source	Freon 113 (2%I)	3.5 hr[c]	polymer, III (49%), V (19%), VIa (8%), VIb (9%), I (2%), VII (trace)

a, Yields are based on internal standard and analyses were performed on 6 ft. 10% carbowax and 8 ft. 10% Se30 GLC columns.

b, When Runs *A* and *B* were pushed till the yield of I neared zero, there was an overall decrease in all products, especially V and VI.

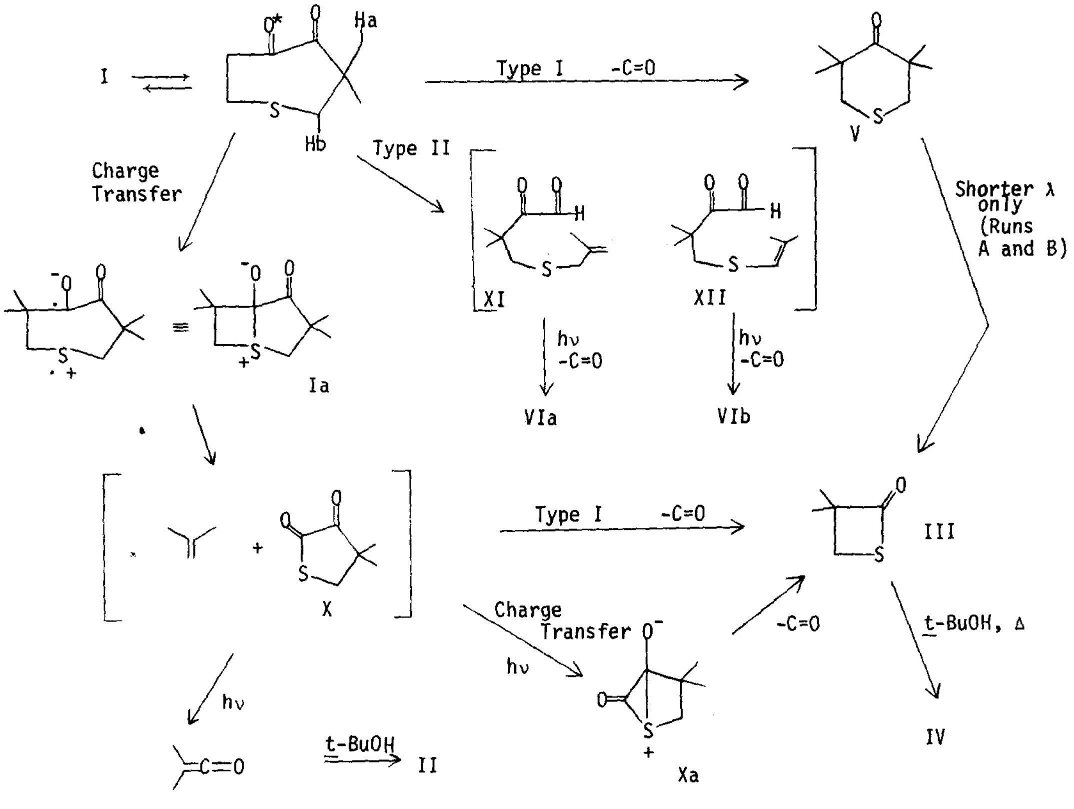
c, The photolyses in Freon 113 (1,1,2-trichlorotrifluoroethane) slowed as time progressed due to a polymer coating on the sides of the photolysis vessel. The reaction would stop in about 3 hr. In runs *D* the sides of the photolysis vessel were wiped as needed in order to get more complete reaction.

d, Continued photolysis in runs *C* and *D* showed no loss of products V or VI as was noted in runs *A* and *B* (see note b).

The products were identified by their spectral properties and/or synthesis. Dione I was synthesized according to published procedures in high yield[7]: UV λ max (ETOH) 219 nm (ε 720), 300 nm (ε 53), 335 nm (ε 45); mass spect (70 eV, rel intensity) m/e 200 (12, m^+), 172 (10, V), 144 (4), 117 (20, IIIa), 88 (10), 56 (100). *t*-Butylester II was synthesized from isobutyric acid and isobutylene in 80% yield: ir (CCl_4) 1738 cm^{-1}; mass spect (70 eV, rel intensity) m/e 144 (4, m^+), 129 (11), 88 (9), 70 (38, VIII), 57 (100). β-Thiolactone III was characterized by complete spectral data and by comparison to data of its isomer IX[5]: ir (CCl_4) 2955 (m), 2915(w), 2855 (w), 1769 (s), 1465 (w), 1446 (w), 1380 (w), 1370 (w), 975 (m), 912 (m) cm^{-1}; nmr $\left(^{\text{TMS}}_{\text{CCl}_4}\right)$ δ 1.34 (S, 6), 2.73 (S, 2); mass spect (70 eV, rel intensity) m/e 116 (5, m^+), 73 (9), 70 (13, VII, absent in IX), 56 (100). Mercapto-*t*-butylester IV was identified by its mass spect only: (70 eV, rel intensity) m/e 190 (1, m^+), 134 (24, ), 117 (17, IIIa), 89 (25, XIII), 57 (100). Keto-sulfide V was synthesized according to published procedures from dione I[8]: ir (CCl_4) 1695 cm^{-1}; mass spect (70 eV, rel intensity) m/e 172 (28, m^+), 144 (8, -c=o), 129 (3), 117 (22, IIIa), 89 (5), 88 (14), 56 (100). Products VI (a and b) have been shown to be unsaturated aldehydes [ir (CCl_4) 2860, 2798, 2700, 1730, 1675, (VIa 3), 1600 (VIb) cm^{-1}] with molecular weight 172. The m+2 peak in the mass spect indicates one sulfur in the molecules. The fragmentation pattern of the mass spectrums and meta-stable peak analysis are in line with structures VI (a and b).

While work on the mechanism of this novel photochemical reaction is still in progress, several conclusions can be drawn. The build up of ketone V and its lack of photochemical reaction at longer wavelengths (runs C and D) indicate that V is probably not the main precursor of III in the photolysis of I at either wavelength employed. Inspection of products indicates several reaction pathways may be operating including type I and II processes as well as charge-transfer processes as visualized in Fig. 2.

Fig. 2



α-Diones X, XI and XII would be expected to further photolyze at any of the wavelengths employed in this study. We are currently attempting to prove that X photolyses to III under our reaction conditions. Charge-transfer mechanisms have been postulated for both 7-membered (Ia)[5] and 5-membered

(Xa) rings.[9,10] Turro[4] has stated that the singlet and triplet states of α-diones (biacetyl) can best be described as being derived from n, π* states on monoketones. He has also shown that the triplet state of α-diones can be quenched by amines and proposes a charge-transfer mechanism similar to that proposed by other workers for the quenching of monoketones in the presence of amines[11,12] and sulfides[5,6]. *The n-π* absorbtion of α-diketones is strongly dependent upon the dihedral angle* between the α-dicarbonyls. The long-wavelength n-π* transition occurs at 420-450 nm for either cisoid or transoid coplanar α-dicarbonyl systems and is shifted to much higher energies (λ max < 400 nm) when the dihedral angle deviates significantly from 0° or 180°[13]. Comparison of the UV spectrum of I[14] with carbocyclic analogs shows the dihedral angle between the α-dicarbonyls to be about 90° for I, thus the interaction between the two carbonyls should be minimal for α-dione I. In view of the above discussion we feel I can be viewed as a keto-sulfide and its photolysis described in terms of monoketones as in Fig. 2.

The photolyses of the N and O substituted analogs of I and X are currently under study and will be reported later.

Acknowledgments

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