

PHOTOCHEMISTRY OF THIOANHYRIDES. PHOTOFRAGMENTATION
 OF CIS-1,2-DIHYDROPHthalic THIOANHYRIDES

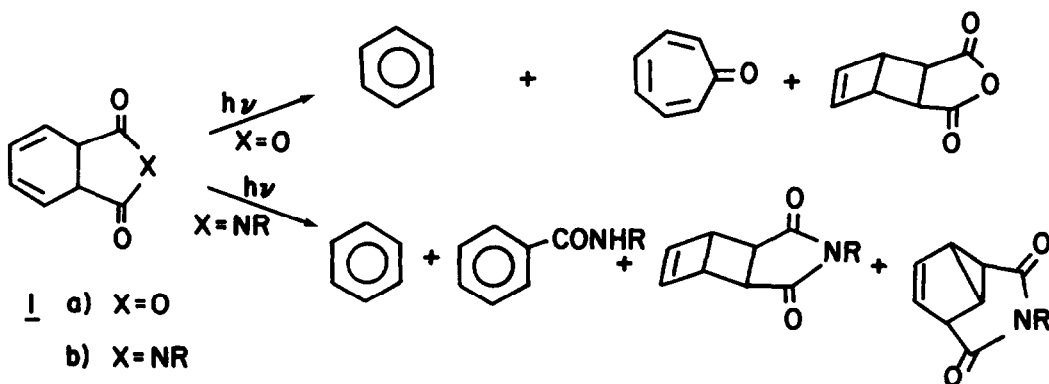
Timor Baasov and Benzion Fuchs*

Department of Chemistry, Tel-Aviv University, Ramat-Aviv, Tel-Aviv, Israel

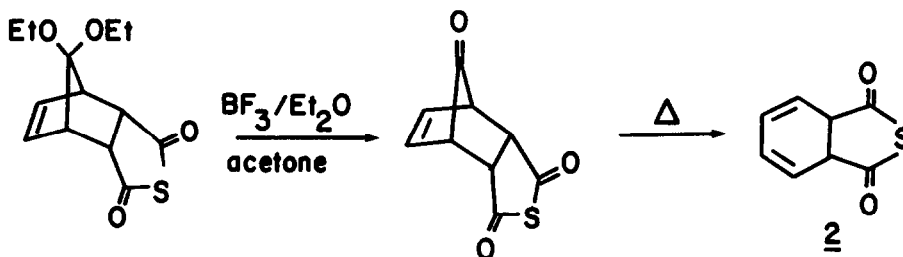
Abstract. CIS-1,2-Dihydrophthalic thioanhydride (2) and some substituted derivatives were prepared and found to undergo irradiation induced, high quantum-yield CO+CO₂ extrusion from a singlet and a (high) triplet excited state.

We have previously reported that irradiation of cis-1,2-dihydrophthalic anhydride (1a)² and imide (1b)³ causes mainly α -cleavage with subsequent fragmentation and rearrangement processes (Scheme 1). Total fragmentation of the anhydride or imide moieties gave benzene whereas partial fragmentation viz. loss of CO₂ or CO led to such products as tropone (from 1a)² or benzamide (from 1b).³ Isomerization processes were also found to occur (Scheme 1)

Scheme 1



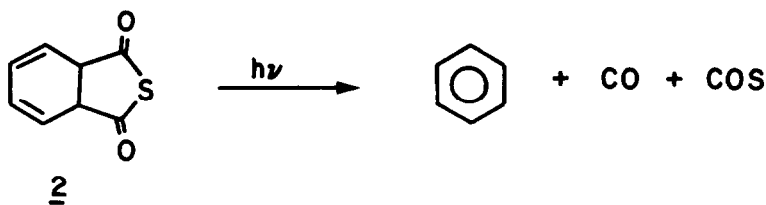
Since the photochemical behavior of thioanhydrides was unknown and we were interested to broaden the scope of the study of dihydrophthalic derivatives, we set out to examine the photochemistry of cis-1,2-dihydrophthalic thioanhydride (2). The latter was prepared (Scheme 2) in a reaction sequence starting with cycloaddition of maleic thioanhydride⁴ with cyclopentadienone-diethylketal⁵ followed by deketalization to norbornen-7-one-1,2-dicarboxylic thioanhydride, this was subjected to thermal decarbonylation to give 1,2-dihydrophthalic thioanhydride (2) in nearly quantitative yield, as a yellow oil, ν_{\max} 1710, 1690 (CO), m/e 166 (M^+ - C₈H₆O₂S), $\delta_{\max}^{\text{MeCN}}$ (ϵ) 255(3,000), 219(8,500), $\delta(\text{CDCl}_3/\text{TMS})$ 5.95(m,4H), 4.05(m,2H).

Scheme 2

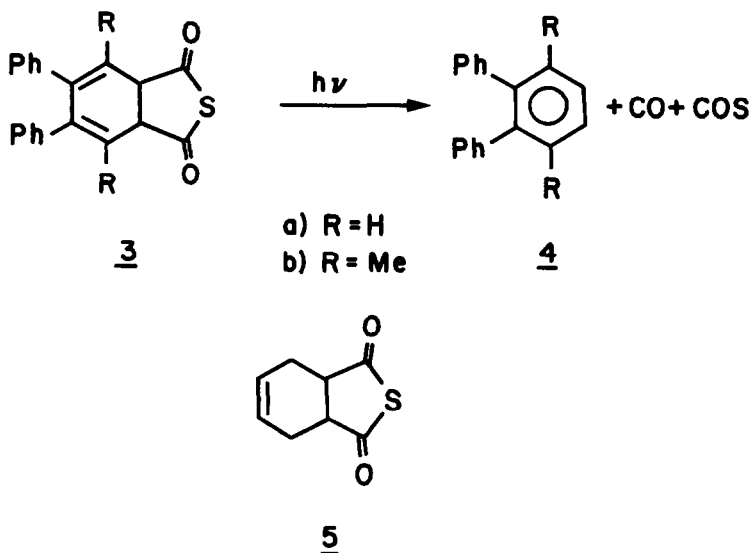
Direct irradiation of 2 at all absorbing wavelengths (230-350 nm) provided, surprisingly, only one product benzene (Scheme 3). Quantum yields of benzene formation were measured at several wavelengths and found to be constant in the range 230-285 nm, namely $\phi = 0.3$ with 60% chemical yield at 280 nm.

Sensitization with xanthen-9-one or acetophenone ($E_T = 74$ kcal/mol) failed to cause any fragmentation but yielded only photo-dimers of (2). Quenching attempts, however, using cis-piperylene ($E_T = 58$ kcal/mol) at 300 nm actually succeeded and a non-linear Stern-Volmer plot could be obtained. We tried therefore acetone as sensitizer ($E_T = 78$ kcal/mol) and could indeed observe definite, albeit inefficient photosensitized benzene formation.

All this leads us to the conclusion that photofragmentation is the only unimolecular process of 2 occurring via both a singlet and (a higher) triplet excited state, its fast rate making the fragmentation highly competitive to the point of exclusivity. The lowest triplet, on the other hand, leads to dimerization. This awaits confirmation from photophysical measurements now in course.

Scheme 3

In continuation of the mechanistic study, we looked carefully for other products or intermediates (like tropone², etc.) and none could be found. This striking exclusiveness and efficiency of benzene formation by irradiation induced CO + COS fragmentation (as shown by mass-spectrometric analysis of the gaseous photoproducts), appears to indicate a concerted extrusion process. A possible rationale could be found in the rather close heats of formation⁸ of CO(-26.4 kcal/mol) and COS(-33.8 kcal/mol) as compared to CO₂(-94.1 kcal/mol), this could explain the concerted fragmentation in 2 in contrast to the stepwise CO₂ and CO expulsion from 1a, via an incipient biradical.²



To be able to generalize, we prepared the substituted 1,2-dihydrophthalic thioanhydrides (3a & b), in analogy with the corresponding anhydrides.^{6,7} Direct irradiation (254 nm) of 3a and 3b provided the *o*-terphenyls 4a and 4b in 50% and 70% yield, respectively, and no other product was isolated (besides photopolymeric material).

Finally, since this is to our knowledge the first photochemical study of thioanhydrides, a control experiment was carried out, in that 1,2,3,6-tetrahydrophthalic thioanhydride (5)⁹ was subjected to direct irradiation in solution and found to be completely inert. Hence we can conclude by firmly asserting that the efficient photofragmentation is due to: 1) kinetic preference of α -cleavage because of the rigid five-membered thioanhydride ring which prevents electrocyclic opening¹⁰, 2) thermodynamic favoring of concerted CO + COS elimination and 3) triggering by the excitation of the homo-conjugated thio-carbonyl chromophore

References and Notes

1. Photochemical Studies Part 22. Part 21. B Fuchs and M. Pasternak, Tetrahedron, 1981, 37, 2501
2. B Fuchs and G. Scharf, Isr J. Chem., 1977, 16, 335.
3. B. Fuchs and G. Scharf, J Org. Chem., 1979, 44, 604.
4. Y. Tamura, K. Imanishi, Y. Miki and M. Ikeda, Synthesis, 1977, 559
5. P.E. Eaton and R.H. Hudson, J Am. Chem. Soc., 1965, 87, 4629.
6. C.F H Allen, and J.A Van Allan, J. Am Chem. Soc , 1942, 64, 1261.
7. B. Fuchs, J. Chem Soc. (C), 1968, 68.
8. R.H Perry, and C.H. Chilton, "Chemical Engineer's Handbook", 5th Ed., p. 3-139, McGraw-Hill, New York, 1973.
9. M. Verbeek, H.D. Scharf, and F Korte, Chem. Ber., 1969, 102, 2471.
- 10 See following communication.

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