

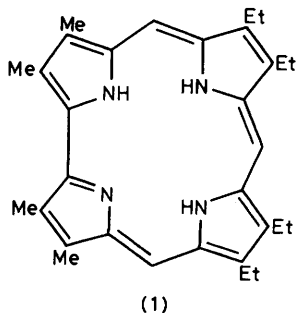
## Hydrogen Transfer Photo-catalysed by Corrole in Visible Light: Reduction of Benzaldehyde with Benzenethiol

By YUKITO MURAKAMI,\* YASUHIRO AOYAMA, and KOJI TOKUNAGA

(Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Fukuoka 812, Japan)

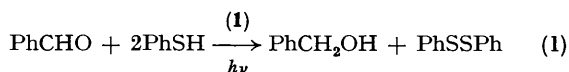
**Summary** Corrole effectively catalysed the photo-reduction of benzaldehyde to benzyl alcohol with benzenethiol in visible light; in a separate experiment without benzaldehyde, photo-bleaching of corrole took place with benzenethiol, while under appropriate conditions, photo-induced redox re-cycling of the catalyst was observed.

CHLOROPHYLLS and porphyrins are known to catalyse certain photochemical redox reactions for which the sensitizers mediate electron (hydrogen) transfer from an appropriate electron (hydrogen) donor to an acceptor *via* a redox process of the excited sensitizers. The reducible substrates so far investigated include dyes,<sup>1</sup> quinones,<sup>2</sup> riboflavin,<sup>3</sup> NAD,<sup>4</sup> azobenzene,<sup>1</sup> and nitrobenzene.<sup>5</sup> In general, the photo-catalysed reduction of a less readily reducible substrate (having more negative redox potential) is an important process for successful conversion of solar energy into chemical energy. We report here the first example, to the best of our knowledge, of the photo-reduction of a simple carbonyl substrate in visible light which is sensitized by metal-free corrole. Corrole is a unique cyclic tetrapyrrole which is characterized by direct linkage between the A and D rings.



A solution of benzaldehyde (0.28 mol l<sup>-1</sup>), benzenethiol (0.045 mol l<sup>-1</sup>), and a catalytic amount of 2,3,17,18-tetramethyl-7,8,12,13-tetraethylcorrole (**1**) (0.001 mol l<sup>-1</sup>) in methanol (10 ml) containing acetic acid (0.08 mol l<sup>-1</sup>) was

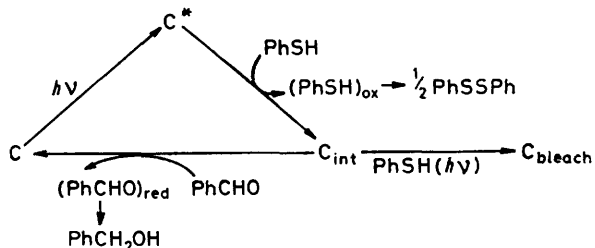
degassed by freeze-pump-thaw cycles. Irradiation of this solution for 8 h at 0–5 °C was carried out with filtered light for a 250-W tungsten lamp; water with a path length of *ca.* 1 cm was used as a heat filter, and naphthalene in iso-octane (0.1 mol l<sup>-1</sup>) with a path length of 1 cm as a u.v. filter. The photo-reaction resulted in the reduction of benzaldehyde to benzyl alcohol along with the concomitant oxidation of benzenethiol to diphenyl disulphide. The amount of diphenyl disulphide thus produced was nearly equivalent to that of benzyl alcohol, consistent with the redox stoichiometry in equation (1). Benzyl alcohol



(*ca.* 50% yield based on the limiting substrate, benzenethiol) was isolated and identified by means of high performance liquid chromatography, t.l.c., and i.r. spectroscopy. Hydrobenzoin, another possible reduction product from benzaldehyde, was not detected by t.l.c. analysis. The redox reaction did not occur either in the dark or in the absence of (**1**), indicating that hydrogen transfer from the thiol to the aldehyde was mediated by redox recycling of (**1**).

The following observations are relevant to the elucidation of the mechanism. (i) A solution of (**1**) and the aldehyde exhibited no spectral change upon irradiation, whereas a solution of (**1**) and the thiol (0.27 mol l<sup>-1</sup>) was readily photo-bleached in 40 min at 0–5 °C. This suggests that successive hydrogenation of the macrocycle takes place.<sup>6</sup> Exposure of this solution to the air resulted in colour changes (sequentially colourless, green, blue, and finally purple) and regeneration of (**1**) (*ca.* 50% yield by spectroscopic analysis) at the end. (ii) A solution of (**1**) and the thiol (0.27 mol l<sup>-1</sup>) was irradiated as above. After photo-bleaching was completed, benzaldehyde (0.27 mol l<sup>-1</sup>) was added anaerobically. The resulting solution showed no tendency to regenerate (**1**) in the dark or upon irradiation for 8 h. Chromatographic analysis of the irradiated solution indicated that benzyl alcohol, if any, was present only in a trace amount. (iii) The recovery of (**1**) after irradiation of the system containing (**1**), benzaldehyde, and

benzenethiol for 8 h was dependent on the relative amounts of both reactants. Thus, for a solution rich in the thiol (benzenethiol,  $0.27 \text{ mol l}^{-1}$ ; benzaldehyde,  $0.046 \text{ mol l}^{-1}$ ) the recovery of (1) was  $< 10\%$ , whereas for solutions rich in the aldehyde (benzenethiol,  $0.056 \text{ mol l}^{-1}$ ; benzaldehyde,  $0.32, 0.46,$  and  $0.93 \text{ mol l}^{-1}$ ) the recovery yields were much improved (30, 70, and  $80\%$ , respectively).



From the above observations the mechanism in the Scheme can be deduced. The electron (hydrogen) transfer from the thiol to the excited (1) ( $C^*$ ) is the primary photo-reaction. The resulting reduced intermediate of (1) ( $C_{int}$ ) may either reduce the aldehyde with concomitant regeneration of (1) or undergo further reduction with benzenethiol giving rise to the bleached product of (1) ( $C_{bleach}$ ).<sup>6</sup> The relative importance of these two processes is dependent on the relative amounts of benzaldehyde and benzenethiol. It must be noted here that the bleached reduction product of (1) cannot reduce the aldehyde. A critical evaluation of the mechanism and the general application of (1) as a photocatalyst in visible light to other redox reactions are in progress. It would be of particular interest to discover a possible correlation between the strain energy in (1) and its photo-activity.

(Received, 9th July 1979; Com. 735.)

<sup>1</sup> G. R. Seely, *J. Phys. Chem.*, 1965, **69**, 2779.

<sup>2</sup> F. M. Huennekens and M. Calvin, *J. Amer. Chem. Soc.*, 1949, **71**, 4031; K. Kano, K. Takuma, T. Ikeda, D. Nakajima, and T. Matsuo, *Photochem. and Photobiol.*, 1978, **27**, 695.

<sup>3</sup> A. A. Krasnovskii, *Doklady Akad. Nauk S.S.S.R.*, 1948, **61**, 91.

<sup>4</sup> A. A. Krasnovskii, G. P. Grin, and N. N. Drozdova, *Doklady Akad. Nauk S.S.S.R.*, 1963, **150**, 1157.

<sup>5</sup> Y. Harel and J. Manassen, *J. Amer. Chem. Soc.*, 1977, **99**, 5817.

<sup>6</sup> For photo-reduction of chlorophyll: see A. A. Krasnovskii and G. P. Grin, *Doklady Akad. Nauk S.S.S.R.*, 1949, **67**, 325; for photo-reduction of porphyrins: see D. Mauzerall, *J. Amer. Chem. Soc.*, 1962, **84**, 2437; also ref. 5 and references cited therein; for the chemical hydrogenation of corrole: see A. W. Johnson and I. T. Kay, *J. Chem. Soc.*, 1965, 1620.