

Table 1 The equilibrium constant of the replacement

Ions	Solvent pair	$\epsilon_1$	$K_1$	$-\Delta G$ K cal at 22 C
Co(II)	Water-MeCN	9.04 $\pm$ 0.06	9.05 $\pm$ 0.22	1.29 $\pm$ 0.01
	Water-propanol-1	5.79 $\pm$ 0.0	4.32 $\pm$ 0.22	0.875 $\pm$ 0.03
	Water-propanol-2	5.97 $\pm$ 0.07	5.81 $\pm$ 0.19	1.038 $\pm$ 0.02
	Water-glycol	7.598 $\pm$ 0.19	3.14 $\pm$ 0.1	0.67 $\pm$ 0.02
Ni(II)	Water-MeCN	5.9 $\pm$ 0.13	12.55 $\pm$ 0.05	1.48 $\pm$ 0.003
	Water-propanol-1	5.53 $\pm$ 0.037	6.37 $\pm$ 0.16	1.085 $\pm$ 0.015
	Water-propanol-2	5.43 $\pm$ 0.05	7.59 $\pm$ 0.075	1.196 $\pm$ 0.005
	Water-glycol	6.65 $\pm$ 0.14	4.81 $\pm$ 0.06	0.92 $\pm$ 0.1

> propanol-2 > propanol-1 > glycol. However the donor capacities of water, propanol-1, propanol-2 and glycol are more or less of the same order. This is clear from the fact that the shift of the peak position is very small.

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## DYSENSITIZED PHOTO-OXYGENATION OF SYM-DIPHENYLTHIOUREA

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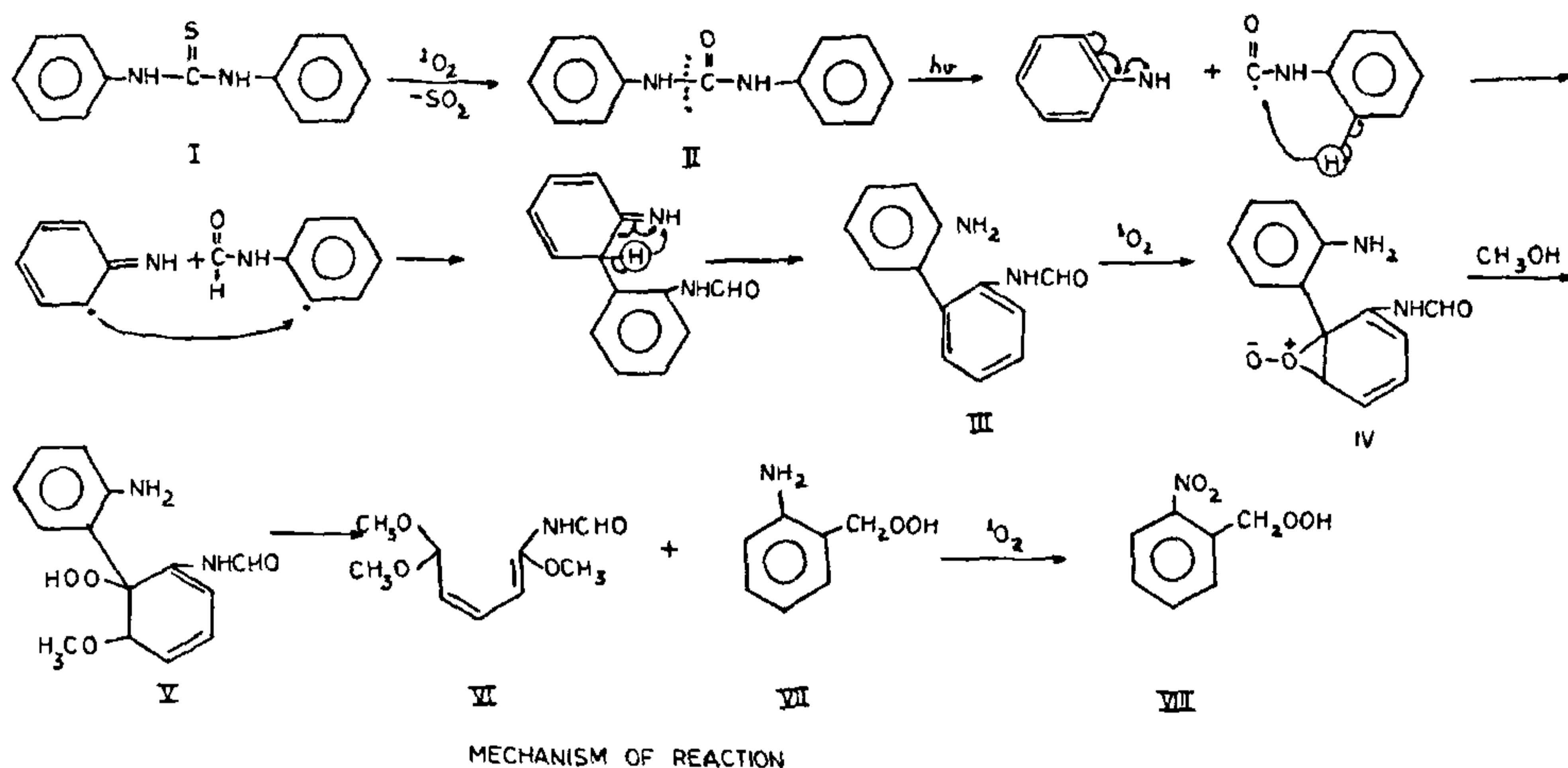
THE photo-oxidation of organic sulphur compounds like sulphides and thioureas has been well investigated<sup>1-3</sup> under different conditions. But no work seems to have been done on the photo-oxidation of sym-oxidation of sym-diphenylthiourea by singlet oxygen. In the present study, dye-sensitized photo-oxygenation of sym-diphenylthiourea has been carried out, and stable peroxide has been isolated.

Sym-Diphenylthiourea (I) has been oxidized by singlet oxygen and a stable peroxy compound (VIII) has been isolated. The formation of VIII can be explained as follows (scheme 1).

Sym-Diphenylthiourea (I) reacts with singlet oxygen to give sulphur dioxide and diphenylurea (II) via dioxetane intermediate as proposed by Ishibe *et al*<sup>3</sup>. Sulphur dioxide has been detected by usual dichromate test. In the presence of light II rearranges to III through free radical intermediates. Singlet oxygen, then attacks the intermediate (III) to give peroxide (IV). The formation of peroxide is in agreement with earlier observations<sup>4</sup>. In the presence of methanol and light, IV gives a methanol incorporated compound (V)<sup>5</sup>, which then decomposes to VI and VII. Attempts to isolate VI met with failure. VII is, however, further oxidized to a stable nitroperoxide compound (VIII). The formation of stable peroxide has already been reported in the literature<sup>6</sup>.

The structure of VIII has been confirmed by the elemental analysis, molecular weight determination and spectral data. The electronic absorption spectrum of VIII shows bands at 206 and 274 nm characteristic of nitro group attached to benzene nucleus. The

Scheme 1



infrared spectrum of VIII shows important absorption peaks at  $3020\text{ cm}^{-1}$  (for aromatics),  $1375$  and  $1310\text{ cm}^{-1}$  ( $-\text{NO}_2$  group) and  $910\text{ cm}^{-1}$  (peroxy linkage). The H-NMR of VIII gives complex multiplet in the range of  $2.70$ – $2.90\tau$  for the four aromatic protons. Singlet at  $5.95\tau$  corresponds to two protons of  $-\text{CH}_2$  group. Its low value indicates its attachment to some electronegative group. The low value of  $\tau(1.70)$  for  $-\text{OH}$  group may be attributed to possible hydrogen bonding. The mass spectrum of VIII gives molecular ion peak at  $m/e = 169$  corresponding to the molecular weight of VIII.

The effect of dyes on the yield of the product has been observed keeping the time of irradiation and bubbling constant. The results are given in table 1.

The low yield of the product in the presence of eosin-Y is due to its high  $E_T$  value which generates  $10^1\Sigma_0$  oxygen (number of singlet oxygen molecules in sigma state) for each  $^1\Delta_g$  oxygen (number of singlet oxygen

molecules in delta state). On the other hand methylene blue dye of low triplet energy generates  $^1\Delta_g$  oxygen of longer life time. Rose bengal occupies midposition in triplet energy series. Therefore, it has been concluded that  $^1\Delta_g$  oxygen is the oxidizing agent in the present reaction. This conclusion has been further supported by the fact that the use of singlet oxygen scavengers highly decreases the yield of product.

#### Experimental

Electronic absorption spectrum was recorded on Beckman model 26. Infrared spectrum was scanned on Perkin Elmer Grating 377 infrared spectrophotometer and the spectrum was taken in KBr pallet. H-NMR spectrum was recorded on Perkin Elmer 90 MHz. Mass spectrum was recorded on JEOL JMS DX 300 with JMA 2000 data processing system.

#### (1) Methylene blue sensitized photo-oxygenation of sym diphenylthiourea

Sym-Diphenylthiourea (2 g) was dissolved in pure methanol (100 ml). To this, dilute methanolic solution of methylene blue (2 ml,  $1.0 \times 10^{-4}\text{ M}$ ) was added. The reaction mixture was irradiated with tungsten light (500 W) with continuous bubbling of oxygen through the solution. A distance of 30 cm was maintained between the reaction flask and tungsten lamp. After about 12 hr the reaction mixture gave a new spot on

Table 1. Effect of dyes on the yield of product in photo-oxygenation of sym-diphenylthiourea

Dyes used	$E_T(\text{Kcal/mole})^{7,8}$	Approximate percent yield of the product
Methylene blue	34	25%
Rose bengal	39.5–42.2	23%
Eosin-Y	43.2–46.0	20%



TLC plate in addition to the spot of original substrate. The solvent from the reaction mixture was then evaporated to dryness. The dry mass was again dissolved in a small quantity of benzene to remove the dye. The benzene was then evaporated and the white solid mass was subjected to column chromatography to separate the product in first fraction by using benzene as eluent. The ratio of silicagel compound was 20:1 (w/w). The yield of the product after 12, 24, 36 and 48 hours was about 10, 18, 25 and 30% respectively (m.p. 84°C). Calculated C, 49.7; H, 4.1 and N, 8.2 for  $C_7H_7NO_4$  found C, 49.4; H, 4.3 and N, 8.0%.

(II) *Rose bengal sensitized photo-oxygenation of sym-diphenylthiourea*

Under exactly identical conditions as in experiment (i), solution of rose bengal sensitizer (2 ml,  $1 \times 10^{-4}$  M) was added in place of methylene blue. The same product was formed as shown by TLC. The yield was determined after 36 hr (about 23%).

(III) *Eosin-Y sensitized photo-oxygenation sym-diphenylthiourea*

Under similar experimental conditions as in experiments (i) and (ii), the oxidation of diphenylthiourea was carried out using solution of eosin-Y (2 ml,  $1 \times 10^{-4}$  M) instead of methylene blue or rose bengal. The same product was formed as shown by TLC. Yield was 20% after 36 hr.

Photo-oxygenation was also carried out in the presence of nickel chloride and cobalt chloride as singlet oxygen scavengers. The yield of the product was considerably decreased.

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**SUCCESSFUL COLONIZATION OF *LACCOTREPHESS GRISEUS* (HEMIPTERA: NEPIDAE)**

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INFORMATION available on aquatic hemipterans are related to their biology, feeding habits and predatory behaviour<sup>1-5</sup>. Most of the nepids are continuous breeders with marked seasonal fluctuations. Thorough scanning of the literature revealed a paucity of information on the colonization of these animals. *Laccotrephes griseus* (Hemiptera: Nepidae) is a predaceous aquatic bug commonly called as nepa or water scorpion. It inhabits the littoral zones of ponds and temporary water system. Attempt was made to colonize the nepa in the laboratory for the following reasons:

- (i) it is a potential feeder on mosquito larvae<sup>6</sup>
- (ii) larval and adult stages of nepa co-exist with the mosquito larvae and hence it can be used as a tool for biological control
- (iii) all the stages of this insect are easily adapted to varying conditions of laboratory rearing and
- (iv) this bug reproduces throughout the year.

To get uniform and continuous production of the predaceous bug, attempt has been made to identify a set of standardized conditions for colonizing *L. griseus* in the laboratory. Final instar nymphs of *L. griseus* were collected from the ponds and maintained in the laboratory in a plastic aquarium. They were fed *ad libitum* with larvae of the mosquito *Culex quinquefasciatus*. Freshly emerged adult bugs were identified and sexed. 10 pairs (1♂ : 1♀) were introduced into an aquarium floored with fine sand and elevated sand margins (figure 1). Pebbles, the macrophyte *Chara fragilis* were also provided in the aquarium. Individuals were fed daily with *C. quinquefasciatus* larvae. Mating and reproductive behaviour of *L. griseus* were observed continuously. No detectable courtship behaviour was observed. Mating occurred after 15 days of adult emergence; though copulation was completed within a short period, (about 3-5 minutes), the pairs remained together even 2 days after