sealed in a flask and heated at 60 C for 20 hr. The excess ammonia was evaporated off. (iii) The product was then treated with 5 ml of 80 % acetic acid : water for 30 min at room temperature. It was extracted with ether and the aqueous layer was concentrated to get the crude product.

The products were purified by ion-exchange FPLC on Pharmacia Polyanion SI columns and the detailed methods will be reported elsewhere.

The key features of the present method are that (i) a single system of solvents has been used in the assembly procedure, reducing the number of mechanical manipulations, (ii) dichloroacetic acid has been used instead of trifluoro or trichloroacetic acids, as a good compromise between the efficiency of deprotection and minimal depurination, (iii) it avoids the use of troublesome pyridine unlike in most other phosphotriester methods, simultaneously retaining the efficiency of condensation, (iv) it competes effectively with the phosphite method in terms of speed, efficiency and ease, (v) all the protected nucleotides and the functionalised resins were made here at our laboratory using indegenious chemicals and reagents.

The author thanks Mr G V Rajendrakumar and Ms Sivakama Sundari for assistance in performing the experiments.

18 October 1984

1. Gassen, H. G. and Anne Lang (Ed.), *Chemical and enzymatic synthesis of gene fragments*, Verlag Chemie, 1982.
2. Effimov, V. A., Reverdatto, S. V. and Chakhmakhcheva, O. G., *Nucleic Acids Research*, 1982, **10**, 6675.
3. Ti, G. S., Gaffney, B. L. and Jones, R. A., *J. Am. Chem. Soc.*, 1982, **104**, 1316.
4. Gait, M. J., Matthes, H. W. D., Singh, M., Sproat, B. S. and Titmus, R. C., in reference 1, pages 1–42.
5. Owen, G. R., Reese, C. B. and Ransom, C. J., *Synthesis*, 1974, 704.

SENSITISED PHOTOOXYGENATION OF ISORHAMNETIN-4′,5-DIMETHYLETHER

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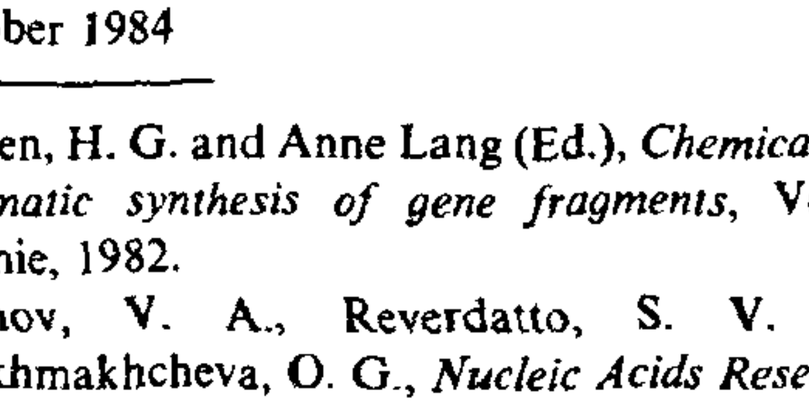
DIOXYGENASE catalysed reactions are similar to sensitised photooxygenation involving singlet oxygen. A variety of reactions have been reported in the literature involving singlet oxygen with heterocyclic compounds[1–4]. The present study reports the reaction of singlet oxygen with isorhamnetin-4′,5-dimethylether.

Isorhamnetin-3,7-diglucoside isolated[5] from the fresh flowers of *Argemona mexicana* Linn. (Papaveraceae) was methylated and hydrolysed. The resulting product, isorhamnetin-4′,5-dimethylether (100 mg) was dissolved in pyridine containing a catalytic amount of the sensitiser (rose bengal, 5 mg). The solution was irradiated with 300 W tungsten lamp and air free from CO_2 was bubbled through it for 14 hr. The solvent was removed under reduced pressure and the residue extracted with ether and ethylacetate. The product was purified and the colourless solid that separated had λ_{max}(MeOH) 233, 264 nm and IR (Nujol mull) peaks at 3550(s), 2990(s), 1700, 1500, 1450(s), 1370, 1320, 1240, 1100 and 990 cm^{-1}.

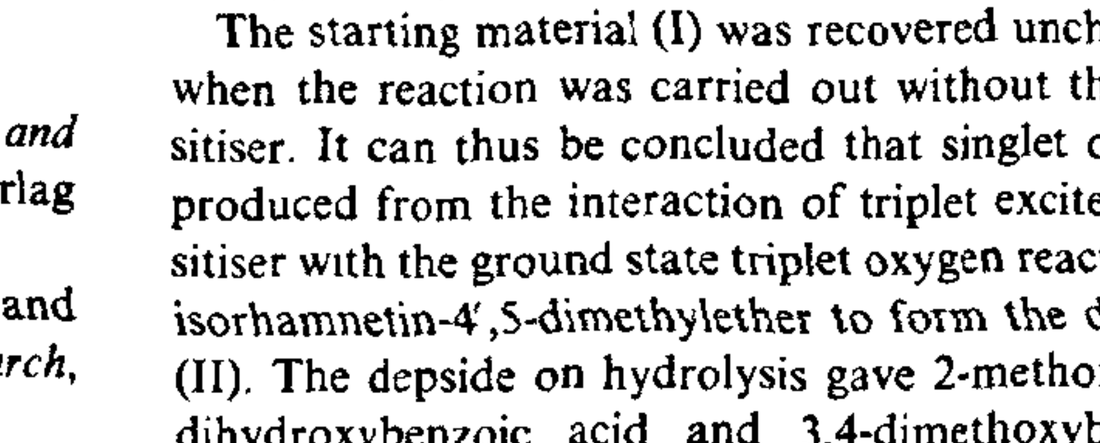
The starting material (I) was recovered unchanged when the reaction was carried out without the sensitiser. It can thus be concluded that singlet oxygen produced from the interaction of triplet excited sensitiser with the ground state triplet oxygen reacts with isorhamnetin-4′,5-dimethylether to form the depsidë (II). The depside on hydrolysis gave 2-methoxy-4,6-dihydroxybenzoic acid and 3,4-dimethoxybenzoic acid both of which were appropriately characterised.

26 July 1984

1. Sharma, A., Chibber, S. S. and Chawla, H. M., *Indian J. Chem.*, 1980, **B19**, 905 and earlier papers cited therein.



I



II

R_1 = Me, R_2 = H

2. Matsuura, T., Matsushima, H. and Nakashima, R., *Tetrahedron*, 1970, **26,** 435.
3. Hatton, S. and Noguchi, I., *Nature* (*London*), 1959, **184,** 1145.
4. Simpson, F. J., Talbot, G. and Westlake, D. W. S., *Biochem. Biophys. Res. Commun.*, 1960, **2,** 15.
5. Antonyraj, P. and Nagarajan, S., *Proc. Ann. Convention of Chemists*, Madras, December 1981, *Abstr. Org.*, 71.

BIAMPEROMETRIC ESTIMATION OF SOME REDUCTANTS USING CHLORAMINE-T.

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CHLORAMINE T is found to be an excellent oxidant and has been widely employed to estimate more than two hundred compounds. A wide spectrum of techniques like titrimetry using indicators[1,2], potentiometry[3-5], conductometry[6], polarography[7], amperometry[8], spectrophotometry[9] etc have been employed in the determination of various reductants.

The present paper envisages the possibility of employing biamperometric technique to determine reductants like iodide, ferrous, ferrocyanide, ascorbic acid, nitrite, thiocyanate, oxine, thiourea, aminoacids etc by chloramine-T. This technique scores over the other electroanalytical techniques, namely polarography, amperometry and potentiometry by virtue of its simplicity, rapid equilibrium attainment and is temperature independent.

Reagents:

Chloramine-T solution. The solution of Chloramine T (AR) (0.05M) was prepared in double distilled water, stored in amber colored bottles and was standardised by usual methods[10].

In a 100 ml beaker, an aliquot of the reductant was taken and 10–20 ml of 2N HCl or the buffer was added and then suitably diluted with distilled water. In the titration of oxine a pinch of solid KI was added as a catalyst. A suitable voltage (0.6 or 1.00 V) was applied depending on the system employed. The solution was stirred continuously and the initial current was noted.

Chloramine-T is reported to be a powerful oxidising agent in acid medium ($E^\circ = 1.14$ V) than in neutral ($E^\circ = 0.832$) and basic [$E^\circ = 0.499$ V] media[11]. It also gives well-defined reductive wave at a positive potential in an acidic solution[12]. This is found to be due to the reduction of the non-ionised species of N-Chloro-p. toluene sulfonamide and a dichloramine T produced by disproportionation reaction of chloramine T. The possibility of utilising this behaviour of chloramine-T at platinum electrode is exploited in this investigation. A potential of 0.6 V is applied as the polarising potential. In certain instances a voltage of 1.0 volt has to be applied, because of low initial current in the system.

When the polarising potential is 0.6 V, the current either remains constant or slightly decreases after the end point. This is probably due to the following reaction.

CAT in acidic medium gives

$$RNCl^- + H^+ \rightarrow RNHCl \ (R = CH_3C_6H_4SO_2)$$

$$2RNHCl \rightarrow RNCl_2 + RNH_2$$

The free acid dichloramine-T predominate in strongly acidic medium. After the end point the two species RNHCl and $RNCl^-$ can form a redox couple as,

$$RNHCl + H^+ + 2\,e \rightarrow RNH_2 + Cl^-$$

$$RNCl^- + Cl^- \rightarrow RNCl_2 + 2e$$

Hence even though chloramine T is irreversible the redox couple formed by the two species of chloramine T accounts for the increase in current. A polarising potential of 0.6 V is not sufficient to oxidise the above mentioned species. Hence in that case the current remains constant due to the irreversible nature of chloramine T.

The stoichiometry of the reductants with respect to the oxidant was reported by the earlier workers in

Table 1 *Estimation of inorganic compounds*

Reductant	Applied Voltage (V)	Taken (mg)	Found (mg)	% Error
Fe^{2+}	0.6	7.65	7.60	−0.7
		21.30	21.38	+0.4
		39.21	39.10	−0.3
$[Fe(CN)_6]^{4-}$	0.6	8.92	8.88	−0.5
		26.20	26.28	+0.3
		42.00	41.90	−0.2
KI	0.6	6.52	6.55	+0.5
		16.60	16.56	−0.2
		36.21	36.10	−0.3
NO_2^-	1.0	13.81	13.90	+0.7
		30.24	30.09	−0.5
CNS^-	1.0	9.72	9.80	+0.8
		29.56	29.41	−0.5