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**PHOTO-SENSITIZED OXIDATION OF
6, 7, 8, 9, 10, 10-HEXACHLORO-1, 5, 5a, 6, 9, 9a-
HEXAHYDRO-6, 9-METHANO-2, 4, 3-
BENZODIOXATHIEPIN-3-OXIDE
(ENDOSULFAN) BY SINGLET OXYGEN**

V. K. VAIDYA*, R. L. PITLIYA, H. S. SHARMA
and SURESH C. AMETA†

*Department of Chemistry, M. L. V. Govt. College (PG),
Bhilwara 311 001, India*

*†Department of Chemistry, College of Science, Sukhadia
University, Udaipur 313 001, India*

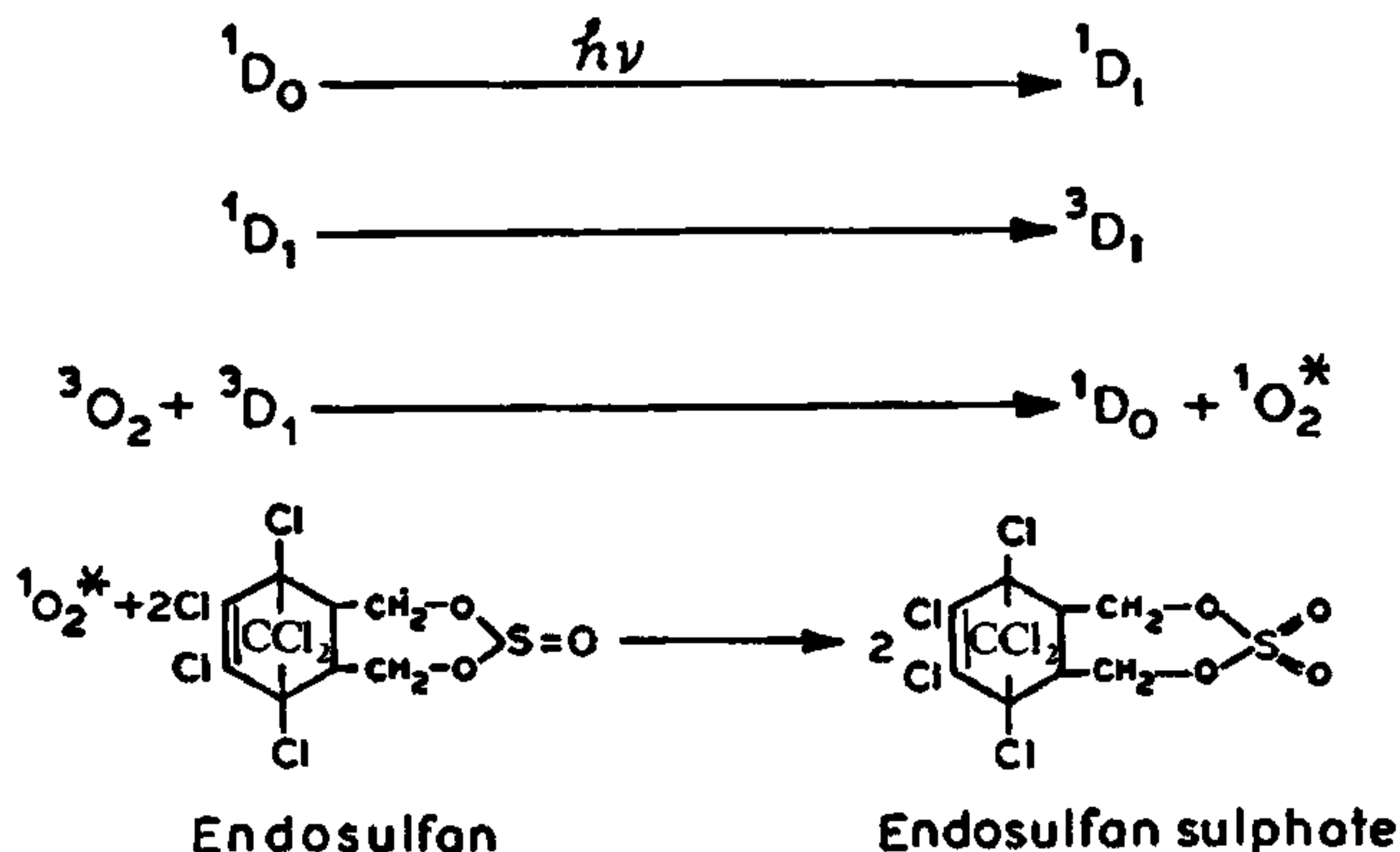
GUNTHER¹ observed that DDT lost its toxic effects quickly when sprayed in the field during summer.

*For correspondence

It was further studied by various workers²⁻⁵. Photodecomposition of aldrin and dieldrin was reported by Henderson and Crosby⁶, whereas Benson *et al.*⁷ characterized the photoproducts of chlordane. Photodecomposition of the chlorinated hydrocarbon endosulfan was observed by Archer *et al.*^{8,9}, while Dureja and Mukerjee¹⁰ did not observe any photosensitization product.

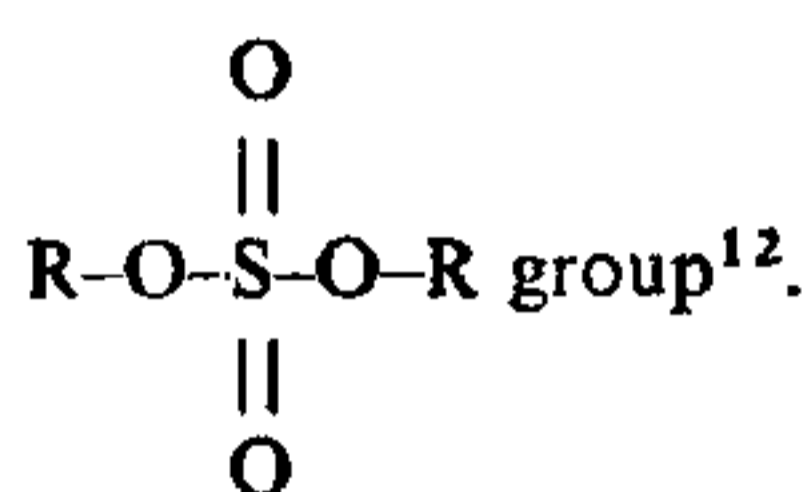
Endosulfan (technical grade) (6, 7, 8, 9, 10, 10-hexachloro-1, 5, 5a, 6, 9, 9a-hexahydro-6, 9-methano-2, 4, 3-benzodioxathiepin-3-oxide), 1, 4-diazobicyclo-(2, 2, 2)-octane (DABCO), methylene blue (CI-52015) and methanol (BDH) were used. All other chemicals used were of SM grade. Endosulfan was used after recrystallization (m.p. 95°C). A 200 W tungsten lamp was used for irradiating the reaction mixture; IR radiations were cut off using a water filter. The reaction mixture was prepared by adding four drops of methylene blue (2×10^{-6} M) in methanolic solution of endosulfan (8% v/v) and was aerated for 5 h in the presence of light. The progress of the reaction was followed by TLC. Some suspension was observed in the reaction mixture after 3 h.

A white substance that settled in the reaction mixture after 5 h was separated by decantation. The methylene blue was removed by the addition of activated charcoal. Dureja and Mukerjee¹⁰ did not observe any photoproduct in methanolic solution with methylene blue in the presence of light from a tungsten lamp while we have obtained a photoproduct, which has been characterized as the sulphate derivative (recrystallized, m.p. 178°C). The following were the results of elemental analysis: found



Scheme 1

C=25.53%, H=1.50%, Cl=50.15%; and calculated for $C_9H_6Cl_6O_4S$, C=25.53%, H=1.41%, Cl=50.35%. Further, the endosulfan and the photoproduct were hydrolysed with alkali and the hydrolysed solutions gave positive test for sulphite and sulphate ions respectively¹¹. The bromo derivatives of endosulfan and its photoproduct were prepared; the m.p.'s were 85 and 55°C, respectively. New bands were seen in the IR spectra of the photoproduct at 1445, 1230 and 645 cm^{-1} , which are characteristic of



However, the NMR spectra of endosulfan and its photoproduct are almost identical. The product of photo-sensitized oxidation of endosulfan was the same as that of oxidation carried out in the dark using $H_2O_2 + NaOCl$ mixture as the oxidant.

It was confirmed that the C=C bond remained unattacked during oxidation¹³ and therefore the site of attack in endosulfan is the sulphur atom. The participation of singlet oxygen as the active oxidizing species in the photo-oxidation was confirmed by using singlet oxygen scavengers, where the yield was considerably reduced¹⁴.

The experimental data suggest the mechanism shown in scheme 1. The primary process of the photo-chemical reaction involves the absorption of radiation while the secondary reactions lead to the transformation of the various electronically excited states to give chemical products.

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SYNTHESIS OF SOME 2-AMINO-3-CYANO-4,6-DISUBSTITUTED PYRIDINE DERIVATIVES AND THEIR ANTIBACTERIAL ACTIVITY

L. PRAKASH, SHAIHLA, SEEMA MALIK and R. L. MITAL

Department of Chemistry, University of Rajasthan, Jaipur 302 004, India

CYCLIZATION of chalcones with dicyanomethane in 1:1 molar ratio in the presence of ammonium acetate, gives 2-amino-3-cyano-4,6-disubstituted pyridines through Michael reaction.

Cyanopyridines with different alkyl and aryl groups have been found to have antimicrobial^{1,2}, fungicidal³⁻⁵, antihypertensive⁶⁻⁸, cardiovascular⁹, and other activities. Only a few cyanopyridines have been synthesized by Michael reaction¹⁰, and by other methods¹¹⁻¹⁵, during the past few years. Keeping in view the biological activity of the cyanopyridine derivatives, we have synthesized some new cyanopyridine derivatives.

The condensation of acetophenone (1 mol) with benzaldehyde (1 mol) in the presence of sodium hydroxide and ethanol resulted in the formation of