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[2 + 2] CYCLODIMERIZATION OF N-VINYLCARBAZOLE IN ACETONE UNDER THE CONDITION OF SINGLET OXYGEN REACTION

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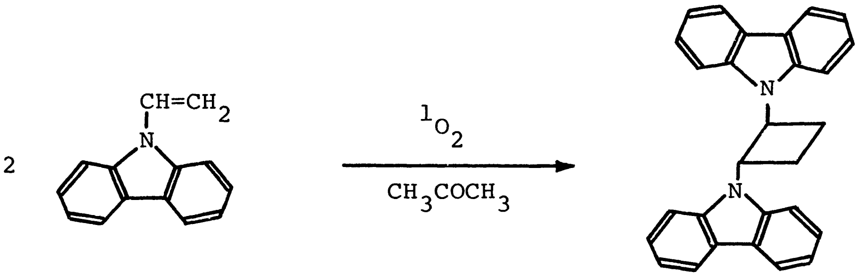
In the presence of singlet molecular oxygen generated by means of the microwave discharge or the decomposition of triphenyl phosphite ozonide, N-vinylcarbazole was converted to trans-1,2-dicarbazylcyclobutane in good yields in acetone solution.

Photosensitized [2 + 2] cyclodimerization of N-vinylcarbazole (NVC) to give trans-1,2-dicarbazylcyclobutane (DCB) in the presence of catalytic amounts of molecular oxygen was first reported by Ledwith et al..1) A few works have subsequently been accomplished on the catalytic feature of molecular oxygen in the photochemical cyclodimerization of NVC in various solvents.2,3) In this work, the reaction of NVC in the presence of singlet molecular oxygen was carried out in order to elucidate whether molecular oxygen participates in the cyclodimerization in its electronically ground or excited state.



NVC DCB

Two methods were employed for the generation of singlet oxygen: (a) the microwave discharge in gaseous oxygen (physical method)4) and (b) the decomposition of triphenyl phosphite ozonide (chemical method).5) In method (a), gaseous oxygen was passed over mercury warmed at 35° and fed into the discharge cavity through a quartz tube at ca. 10 Torr. The microwave discharge was operated at 70 W and 2450 MHz. The emerging singlet oxygen stream was bubbled for 5 hr into a solution of NVC (4.19 mmol) in 18 ml acetone at -70°. In method (b), triphenyl phosphite (TPP) was ozonized in 100 ml acetone at -78° to prepare TPP ozonide. After removal of the excess ozone with nitrogen stream, a cold solution of NVC (4.96 mmol) in 50 ml acetone was added. The reaction mixture was stirred with nitrogen stream for ca. 4 hr until it was warmed up to room temperature.

The reactions of NVC in the presence of singlet oxygen were carried out in the dark. The resulting reaction mixtures were concentrated to ca. 10 ml on a rotary evaporator and poured into 150 ml methanol. DCB precipitated gradually as white

Table. Reactions of N-Vinylcarbazole in the Presence of Singlet Oxygen in Acetone

Source of $^1O_2$	Run	Initial concn. x10^2 M			Product	Yield %[a)]
		NVC	TPP	DABCO		
a. Microwave discharge	1	23	0	0	DCB	50
	2	23	0	5.3	No reaction	
b. $(PhO)_3P-O_3$ decompn.	3	3.3	2.2	0	DCB	31
	4	3.3	4.5	0	DCB	60
	5	3.3	11	0	DCB	84
	6	3.3	4.4	3.3	No reaction	

a) Determined by gravimetry.

needles and was isolated by filtration. The structure of DCB[6)] was confirmed by the following data: mp 191-192° ; IR(KBr) 1230, 1210 cm^{-1}; NMR($CDCl_3$) δ 2.3-3.3 (broad, 4H), 5.9-6.3 (broad, 2H), 6.9-8.0 (m, 16H); Mass m/e 386 (M^+). Found: C, 87.20; H, 5.80; N, 7.14%. Calcd for $C_{28}H_{22}N_2$: C, 87.00; H, 5.75; N, 7.25%.

Table shows some representative results. Oxygen-containing products could not be detected in the present systems. The yield of DCB increased with the initial concentration of TPP ozonide (Runs 3-5). The reaction was entirely inhibited by the addition of 1,4-diazabicyclo[2.2.2]octane (DABCO) which is a well-known quencher of singlet oxygen to the reaction system (Runs 2 and 6). Since no reaction occurred without the microwave discharge in method (a), molecular oxygen in the ground state is not responsible for the formation of DCB. Furthermore, DCB was not yielded in the experiment with the use of TPP ozonide solution after warmed up to room temperature. This suggests that NVC may undergo the cyclodimerization in the presence of singlet oxygen.

It is also possible that the species such as ozone, atomic oxygen, or TPP ozonide[7)] participate in the formation of DCB. Nevertheless, the results obtained in this work lead to a suggestion that singlet molecular oxygen potentially plays an important catalytic role in the [2 + 2] cyclodimerization of NVC in acetone. Further detailed studies on the reaction of NVC in the presence of singlet oxygen will be reported in a subsequent paper.

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