# PHOTOCHEMICAL REACTION OF 2,5-DIPHENYL-1,3,4-OXADIAZOLE

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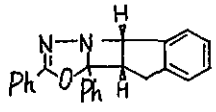
The photochemical reactions of 2,5-diphenyl-1,3,4-oxadiazole (1) with indene, benz[b]thiophene, indazole and its methyl derivatives are reported. Irradiation of 1 with indene in benzene solution gave the diazetidine derivative 5 whose structure corresponded to that of the compound derived from an 1:2 adduct of 1 and indene with the elimination of oxgen atom, while in the presence of iodine (20 mole % to 1) the cis-1:1 cycloadduct 6 was only formed. In ethylether solution, however, the oxadiazepine derivative 7 was obtained in addition to 5. On heating in refluxing xylene 7 was easily isomerized into 3-benzoylindene=benzoylhydrazone (9), and treatment of 7 with water in $CCl_4$ afforded 1-benzoyl-2-hydroxyindane=benzoylhydrazone (10). 7 reacted with aryl isocyanate to give an 1:1 adduct 13, which was hydrolyzed with NaOH aqueous solution to afford the urethane derivative 14.

Although the photochemical reaction of 1 with thiophene did not take place without iodine, irradiation of 1 with benz[b]thiophene in benzene solution without iodine gave a trans-1:1 cycloadduct 15, which on treatment with NaOH aqueous solution was isomerized into 3-benzoylbenz[b]thiophene=benzoylhydrazone (16). Reduction of 15 with $NaBH_4$ afforded a dihydro compound 17 with ring opening of the azetidine moiety of 15. The photochemical reaction of 1 with benz[b]thiophene in ethylether solution gave the 1,5-adduct 19, which was easily converted into 16 on heating or treatment with an alkaline solution. However, 19 which had the oxadiazepine structure like 7, did not react with aryl isocyanate.

Finally, the photochemical reaction of 1 with indazoles has been investigated. Contrary to expectation, 1 did not react with the pyrazole rings, but 1 attacked on the benzene rings in indazoles. On irradiation in ethylether, indazole and 3-methylindazole afforded the corresponding 7-benzoylindazole=benzoylhydrazones (27a, 27d). Under similar conditions, however, 4-methyl- and 7-methylindazole gave 6-benzoyl-4-methylindazole= (27b) and 5-benzoyl-7-methylindazole=benzoylhydrazone (27c) respectively. The reaction pathway is also discussed.



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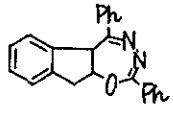

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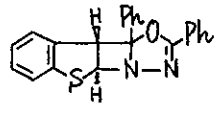

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