

ZINC OXIDE-INDUCED DEHYDROCHLORO-CYCLOADDITION
OF N-(PHENYLSULFONYL)BENZOHYDRAZONOYL CHLORIDE

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N-(Phenylsulfonyl)benzohydrazonoyl chloride reacts with electron-rich olefins such as bicyclo[2.2.1]hept-2-ene to give 1-phenylsulfonyl- Δ^2 -pyrazoline derivatives in the presence of zinc oxide. Zinc oxide may cause the dehydrochlorination of the hydrazonoyl chloride to lead to the formation of N-(phenylsulfonyl)benzotrilimine, which undergoes 1,3-dipolar cycloaddition in the dipole-LUMO controlled manner.

N-(Phenylsulfonyl)benzohydrazonoyl chloride(1), in contrast to N-phenylbenzohydrazonoyl chloride(2), does not afford nitrilimine on treatment with triethylamine and the exclusive formation of dihydrotetrazine via the nucleophilic attack of hydrazonoyl chloride N-anion on 1 was observed in the presence of dipolarophiles.¹⁾

During the course of the investigation concerning reactions of hydrazonoyl halides, we have found that zinc oxide causes the 1,3-cycloadduct formation in the reaction of 1 with electron-rich olefins. No other studies using zinc oxide as a dehydrohalogenating agent for the generation of 1,3-dipoles have been reported.

A mixture of 1(1.47g, 5 mmol), bicyclo[2.2.1]hept-2-ene(3, 0.47g, 5 mmol), and dioxane(30 ml) was stirred with an excess amount of finely ground zinc oxide(0.82g, 10 mmol) for 2 days at room temperature. After removal of inorganic substances by filtration, the dioxane solution was concentrated and chromatographed(silica gel, benzene-ether-ethanol), giving 3-phenyl-1-phenylsulfonyl-3a,7a-exo-4,7-methano-3a,4,5,6,7,7a-hexahydro-indazole(4a) along with N'-phenylsulfonyl-benzohydrazide(5), N'-benzoyl-N'-phenylsulfonyl-benzohydrazide(6), N'-phenylsulfonyl-N'-[N-(phenylsulfonyl)benzohydrazonoyl]-benzohydrazide(7), and N-phenylsulfonyl-N-[N-(phenylsulfonyl)benzohydrazonoyl]benzohydrazonoyl chloride(8). 3-Phenyl-1-phenylsulfonyl-3a,7a-exo-4,7-methano-3a,4,7,7a-tetrahydro-indazole(4b) and 3,5-diphenyl-1-phenylsulfonyl- Δ^2 -pyrazoline(4c) were obtained from bicyclo[2.2.1]hepta-2,5-diene(9) and styrene(10), respectively, in the same manner. Ethyl vinyl ether(11) gave 3-phenyl-1-phenylsulfonyl-pyrazole(4d), the aromatized compound of the corresponding pyrazoline primarily formed. The results are summarized in Table 1. The use of acetone, benzene, THF, or chloroform in lieu of dioxane led to a decrease in yields of 4a-d.

No 1,3-cycloadducts were obtained from ordinary cycloalkenes, and from electron-deficient dipolarophiles such as dimethyl acetylenedicarboxylate, fumarate,

