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-phenyl-sulfonyl- 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)benzonitril-imine, which undergoes 1,3-dipolar cycloaddition in the dipole-LUMO controlled manner.

N-(Phenylsulfonyl)benzohydrazonoyl chloride(1), in contrast to N-phenylbenzo-hydrazonoyl 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 $\underline{1}(1.47g, 5 \text{ mmol})$, 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($\underline{7}$), and N-phenylsulfonyl-N-[N-(phenylsulfonyl) benzohydrazonoyl benzohydrazonoyl chloride(8). 3-Phenyl-1-phenylsulfonyl-3a,7aexo-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-1phenylsulfonyl-pyrazole(4d), the aromatized compound of the corresponding pyrazoline The results are summarized in Table 1. primarily formed. 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,

Table	1.	The	Reac	tion	of	1	in	the
		Pres	sence	of	Zino	3 (Oxid	le

	210001100 01	Dino onico
Olefins	Yields(%) of	<u>4</u> a) Mp(°C)
<u>3</u>	44(<u>4a</u>)	197—199
<u>9</u>	43(<u>4b</u>)	167 — 169
<u>10</u>	4(<u>4c</u>)	198 —199
<u>11</u>	59(<u>4a</u>)	101—102

a) Products <u>4a-d</u> gave reasonable spectral and satisfactory analytical data.

maleate, and benzonitrile.
When silver(I) or copper(I) oxide was used in place of zinc oxide, the formation of 1,3-cycloadduct in a low yield was observed: compounds 6 and 8 were obtained as the major products in these cases. Attempted reactions in the presence of copper(II), aluminium, and magnesium oxide resulted in the recovery of unchanged 1.

Zinc oxide is a typical amphoteric

substance and should be either a Lewis acid or a Lewis base. Based on the fact that Zn(II) ion functions similarly to Ag(I) ion as an effective Lewis acid in S_{N} type reactions, an interaction(denoted with number 12) between 1 and zinc oxide as given below can be postulated in the present reaction. N-(Phenylsulfonyl)benzonitrilimine(13) may be generated from the species, 12, by the concerted or near-concerted elimination of hydrogen chloride. Products 5, 6, 7, and 8 should be

formed by the competitive nucleophilic attack on the imidoyl carbon of 12 by moisture, benzoic acid, 2) 6, and 1 which are contained or generated in the reaction system. Since the Lewis-acid character of silver(I) and copper(I) oxide probably predominates over the Lewis-base character, the nucleophilic reactions, in the presence of these oxides, may precede the nitrilimine-formation process.

N-Phenylbenzonitrilimine derived from 2 acts as both an electron-accepting and -donating 1,3-dipole depending upon the nature of dipolarophiles,³⁾ while the nitrilimine, 13, should function as an electron-accepting one, that is, in the dipole-IUMO controlled manner⁴⁾ because of the strong electron-withdrawing property of phenylsulfonyl group. The reactivity and the regionselectivity observed in the present reaction are in agreement with this theoretical requirement.

References and Notes

- 1) S. Ito, Y. Tanaka, A. Kakehi, and H. Miyazawa, Bull. Chem. Soc. Jpn., <u>50</u>, 2969 (1977).
- 2) Benzoic acid may be generated from 1 and moisture by the action of zinc oxide. The smooth reaction of benzoic acid with 1 giving 6 in an almost quantitative yield was observed when zinc oxide was present. Compound 6 should be the rearrangement product of benzoic hydrazonic anhydride. Cf. R. Huisgen, J. Sauer, and M. Seidel, Chem. Ber., 94, 2503(1961).
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