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A NOVEL REACTION OF CHLORANIL WITH 1,4-DISUBSTITUTED PIPERAZINEDIONES

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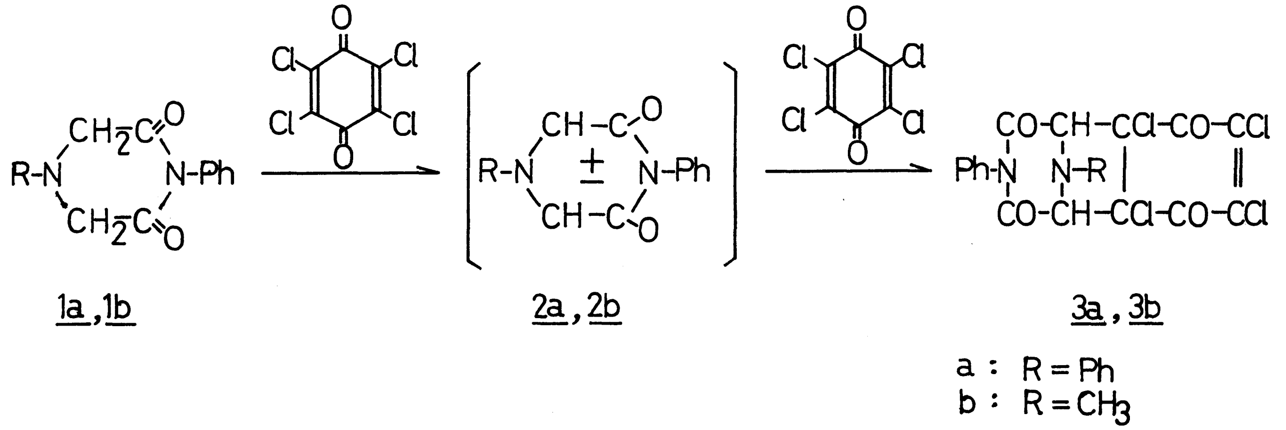
Reaction of 1,4-diphenyl-2,6-piperazinedione with chloranil in benzene at refluxing temperature afforded an adduct, 2,4,5,7-tetrachloro-10,12-diphenyl-3,6,9,11-tetraoxo-10,12-diaza-tricyclo-$[6.3.1.0^{2,7}]$-4-dodecene, which was formed through dehydrogenation followed by 1,3-dipolar cycloaddition of chloranil to the intermediate mesoionic species. 4-Methyl-1-phenyl-2,6-piperazinedione reacted with chloranil to give a similar adduct.

Honzl, Šorm and Hanuš[1)] reported that mesoionic 1,4-disubstituted-2,6-piperazinediones having phenylthio groups at the 3 and 5 positions were obtained by heating 1,4-disubstituted-2,6-piperazinediones with arylsulfonyl chloride in pyridine. In this reaction, dehydrogenation and substitution occurred concurrently at positions 3 and 5, but the reaction mechanism was not elucidated. Huisgen and Mäder[2)] reported that the irradiation of 1-arylaziridine-2,3-dicarboxylic N-methylimide in the presence of a 1,3-dipolarophile yielded a cycloadduct via the intermediacy of mesoionic 2,6-piperazinedione or its azomethine ylide species.

These results prompted us to investigate the behavior of 2,6-piperazinediones towards various dehydrogenating reagents and, when chloranil was used as a dehydrogenating reagent, we have found a novel reaction where dehydrogenation of 2,6-piperazinediones followed by 1,3-dipolar cycloaddition of chloranil to the intermediate mesoionic species took place. Although the utility of chloranil as dehydrogenating reagent is well known and its potency as a dienophile in Diels-Alder reaction is already reported, reaction of chloranil as both dehydrogenating reagent and 1,3-dipolarophile has not yet been reported.



The reaction of 1,4-diphenyl-2,6-piperazinedione (1a) with chloranil in benzene at refluxing temperature for 24 hr gave an adduct (3a) in 59% yield, pale yellow needles, mp 218-220°C (chloroform-petroleum ether). When recrystallized from benzene, the adduct formed an addition compound with benzene (a half molecule of benzene for 1 molecule of 3a), which was removed by heating in vacuo at 170°C for 10 hr. Anal. Found: C, 51.85; H, 2.35; N, 5.60%. Calcd for $C_{22}H_{12}O_4N_2Cl_4$: C, 51.78; H, 2.38; N, 5.49%. IR(KBr): 1752, 1720, 1705, 1600, 1569, 1498 cm^{-1}. NMR(τ): 2.50-3.40(10H, m, aromatic H), 4.20(2H, s, methine H). Mass: m/e 508(M^+). These data are consistent with the structure of 2,4,5,7-tetrachloro-10,12-diphenyl-3,6,9,11-tetraoxo-10,12-diaza-tricyclo[$6.3.1.0^{2,7}$]-4-dodecene (3a) with an unknown stereochemistry. The present reaction is presumed to occur via intermediacy of mesoionic or azomethine ylide species (2a), which was trapped by chloranil.

Similar reaction of chloranil with 4-methyl-1-phenyl-2,6-piperazinedione (1b) gave an adduct (3b) in 31% yield, colorless plates, mp 200-202°C(dec.)(benzene). Anal. Found: C, 45.71; H, 2.25; N, 6.13%. Calcd for $C_{17}H_{10}O_4N_2Cl_4$: C, 45.47; H, 2.25; N, 6.25%. IR(KBr): 1750, 1718, 1690, 1565 cm^{-1}. NMR(τ): 2.45-2.95(5H, m, aromatic H), 5.13(2H, s, methine H), 7.25(3H, s, methyl H). Mass: m/e 446(M^+).

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