

DIOXOPYRROLINE, AN AMBIDENT DIENOPHILE IN DIELS-ALDER REACTION

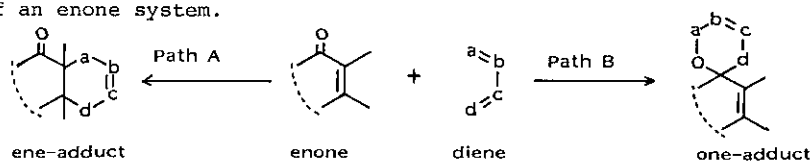
Yoshisuke Tsuda and Takeshi Oshima

Faculty of Pharmaceutical Sciences, Kanazawa University, Takara-machi,
Kanazawa-920, Japan.

Takehiro Sano and Jun Toda

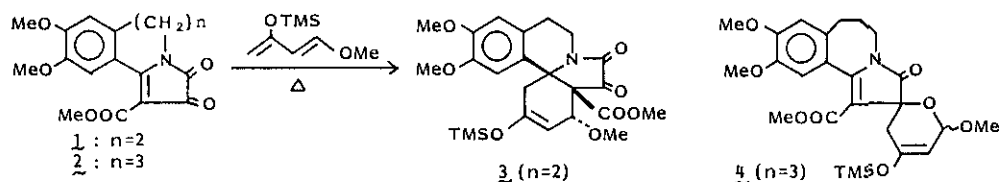
Showa College of Pharmaceutical Sciences, Setagaya, Tokyo-154, Japan.

Enones as a dienophile in Diels-Alder reaction must be inherently ambident (path A and B). We now present examples, which we believe the first, of path B reaction of an enone system.



The Diels-Alder reaction of dioxopyrroline **1** with 1-methoxy-3-trimethylsilyloxy butadiene produced the normal 1,4-adduct **3** (path A). On the other hand, dioxopyrroline **2** on similar Diels-Alder reaction predominantly afforded the path B adduct **4** which was characterized as the corresponding desilylated compounds.

This unusual Diels-Alder reaction is attributable to the steric hindrance originated from the non-planarity of the aromatic ring with dioxopyrroline ring in the dienophile **3**.



That the steric hindrance is a factor which influences the pathway of Diels-Alder reaction was also shown by the following examples. On the similar Diels-Alder reaction, the dioxopyrrolines **5** predominantly produced the path A adduct, when R=H or CH₃, while **5** having more bulky N-substituents such as C₂H₅, i-Pr produced only the path B adduct. Rotational inhibition of phenyl group produced the steric hindrance which prohibits path A approach of the diene to the dienophile.

