

CROSS TYPE OF DIENE-TRANSMISSIVE DIELS-ALDER REACTION

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The first example of cross type of diene-transmissive Diels-Alder reaction is presented by the reactions of an activated cross-conjugated triene, 3-(methoxymethylene)-2,4-bis(trimethylsilyloxy)-1,4-pentadiene, with cyclic olefins as the first dienophiles and then with acetylenes as the second.

The previous communication has shown that an activated cross-conjugated triene, 3-(methoxymethylene)-2,4-bis(trimethylsilyloxy)-1,4-pentadiene 1, reacts with such cyclic olefins as maleimides and maleic anhydride leading to the selective formation of mono- and bis-cycloadducts depending upon the amounts of dienophiles used.¹⁾ This result indicates that two different dienophiles may be orderly incorporated in the bis-cycloadduct of 1 if these olefins are employed as the first dienophile.

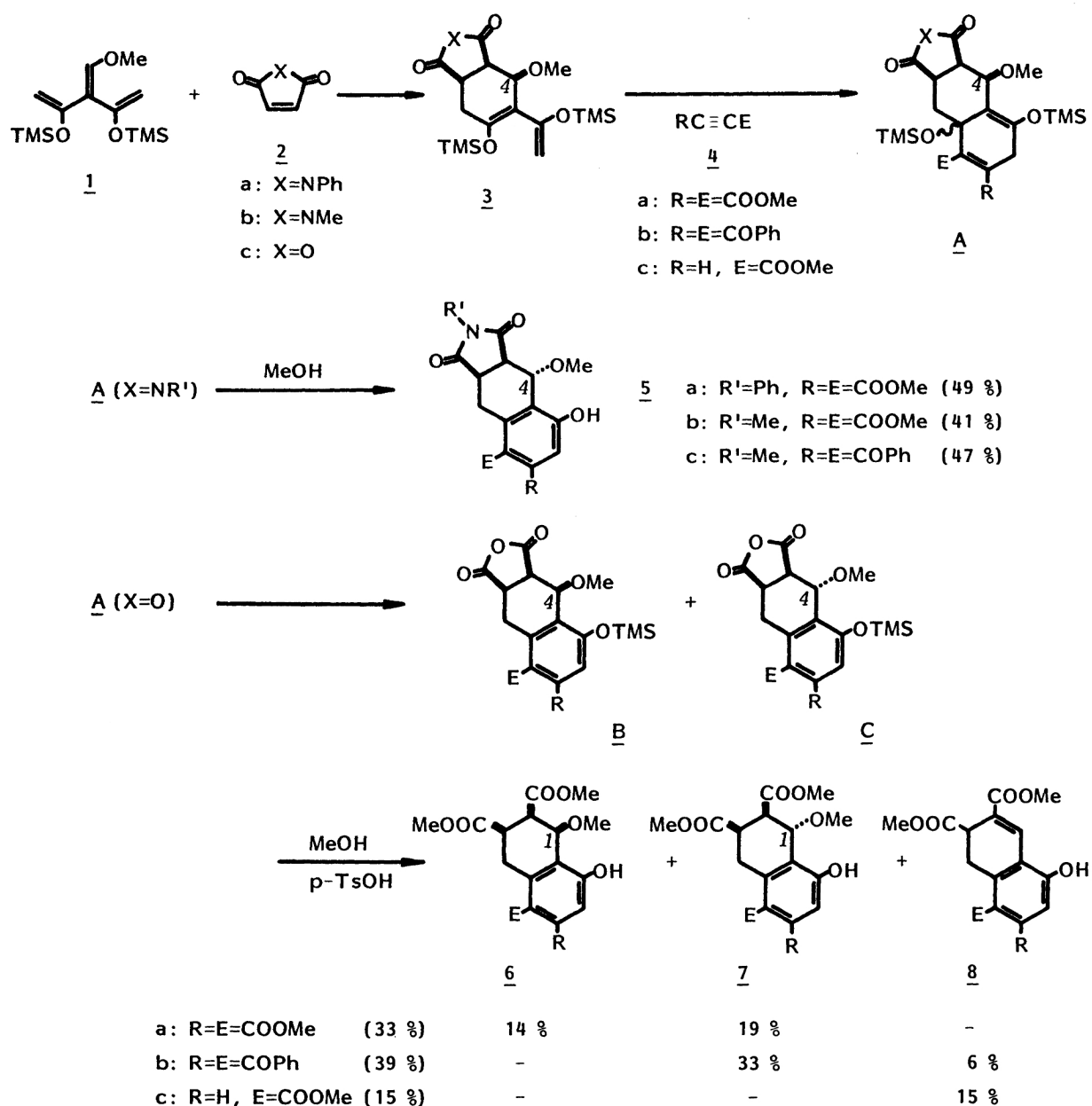
The present communication presents the first example of cross type of diene-transmissive Diels-Alder reaction in which cyclic olefinic and acetylenic dienophiles are used as the first and second dienophiles, respectively.²⁾

The first reaction of 1 with an equivalent of N-phenylmaleimide 2a in benzene at room temperature for 24 h followed by the second reaction with an equivalent of dimethyl acetylenedicarboxylate 4a under reflux for 20 h afforded, after the work up with methanol, the cross bis-adduct 5a (mp 230 °C). The structure of 5a was confirmed on the basis of the spectral data as well as the elemental analysis.³⁾ This reaction involves the selective formation of mono-cycloadduct 3 (X=NPh),⁴⁾ the second cycloaddition reaction of 3 to 4a leading to the cross bis-cycloadduct A (X=NPh), and the hydrolytic desilylation during which the configuration at the 4-position was inverted.⁵⁾

The similar reactions of 1 with N-methylmaleimide 2b and then 4a or with 2b and then dibenzoylacetylene 4b gave the cross bis-adducts 5b (mp 248 °C) or 5c (mp 160-162 °C), respectively.

When maleic anhydride 2c was used as the first dienophile, the cycloaddition reaction was completed in 2 h at room temperature. The second reactions with acetylenes 4 were followed under reflux in benzene for 24 h (for 4a and 4b) or 48 h (for methyl propiolate 4c) to give three kinds of bis-adducts 6, 7, and 8 after the esterification of the reaction mixture. Their ratios are not so important because 6 gradually changes into 7 when heated or treated with methanol in the presence of p-toluenesulfonic acid and because 8 is closely related to the other two products. The structures of 6 and 7 were confirmed mainly on the basis of the coupling constant between the 1-H and 2-H (6.0 Hz for 6a and 3.0 Hz for 7a).

The ¹H-NMR analysis of the reaction of the isolated mono-cycloadduct 3 (X=O) with 4a showed the formation of the desilylated bis-cycloadducts B and C (R=E=COOMe) whose isolation failed. Their ratio was found to change depending upon the reaction temperature and time: Only B (after 24 h at room temperature), a mixture of B and C (4 : 3, after 24 h under reflux in benzene), and only C (after a week at room temperature or after 3 days under reflux in benzene) were formed, indicating that the cis B and trans isomer C are kinetically and thermodynamically controlled products, respectively.



Thus the cross type of diene-transmissive Diels-Alder reaction of 1 takes place through an endo approach of the first cycloaddition reaction between 1 and cyclic olefins 2.

References

- 1) O. Tsuge, S. Kanemasa, H. Sakoh, and E. Wada, Chem. Lett., 1984, the preceding paper.
- 2) Active acetylenes have been employed as the second dienophiles since the bis-adducts obtained in the reactions of 1 with cyclic olefins are rather unstable (Ref. 1).
- 3) 5a: IR (KBr) 3400 (OH), 1775, 1720, 1685 cm^{-1} (C=O); $^1\text{H-NMR}$ (CDCl_3) δ 2.70-3.90 (4H, m, CH_2 , 3a-H, 9a-H), 3.11 (3H, s, OMe), 3.81, 3.82 (each 3H, s, COOMe), 5.40 (1H, d, $J=3.0$ Hz, 4-H), 7.10-7.56 ppm (7H, m, ArH, =CH, OH); Mass m/e 439 (M^+). All the new compounds reported herein gave satisfactory elemental analyses.
- 4) The mono-adduct was actually isolated in 73% yield (Ref. 1).
- 5) The configuration at the 4-positions of mono- 3 (X=NPh) and bis-cycloadduct A (X=NPh) was tentatively assigned as shown in the above scheme because the endo mono-cycloadduct 3 (X=O) does not isomerize into the exo isomer when refluxed in benzene for a long time. Such high endo selectivity has been reported (O. Tsuge, E. Wada, and S. Kanemasa, Chem. Lett., 1983, 1525).

(Received November 4, 1983)