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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.

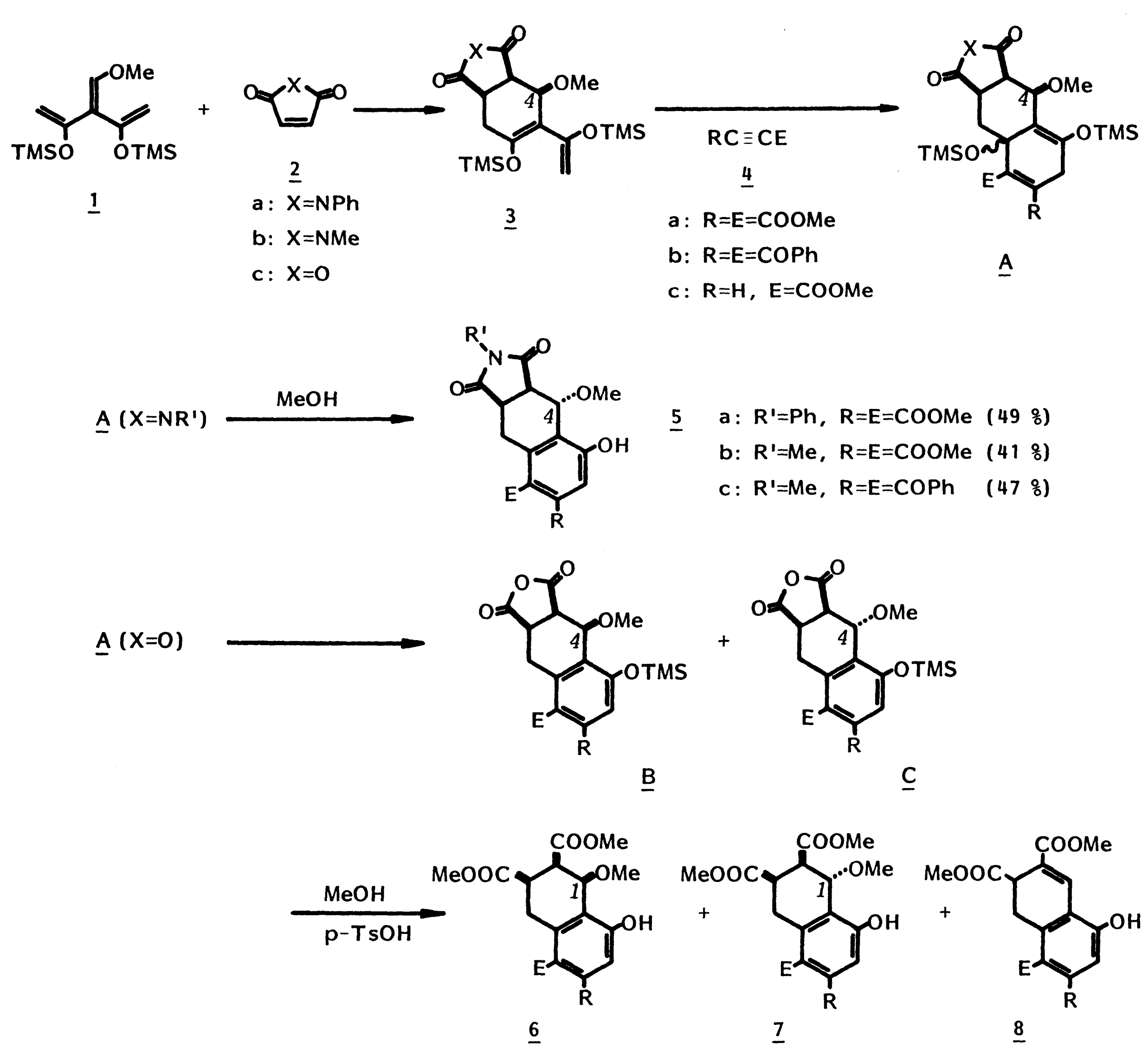
The present communication presents the first example of cross type of diene-transmissive Diels-Alder reaction in which cyclic olefinic and acetylenic dienophiles are used as the first and second dienophiles, respectively.2)

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 benbenzene 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 ^{1}H-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.



2 a: X=NPh
b: X=NMe
c: X=O

4 a: R=E=COOMe
b: R=E=COPh
c: R=H, E=COOMe

5 a: R'=Ph, R=E=COOMe (49 %)
b: R'=Me, R=E=COOMe (41 %)
c: R'=Me, R=E=COPh (47 %)

		6	7	8
a: R=E=COOMe	(33 %)	14 %	19 %	-
b: R=E=COPh	(39 %)	-	33 %	6 %
c: R=H, E=COOMe	(15 %)	-	-	15 %

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}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).

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