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3-BENZYLIDENE-2,4-BIS(TRIMETHYLSILYLOXY)-1,4-PENTADIENE; SYNTHESIS AND ITS DIENE-TRANSMISSIVE DIELS-ALDER REACTION

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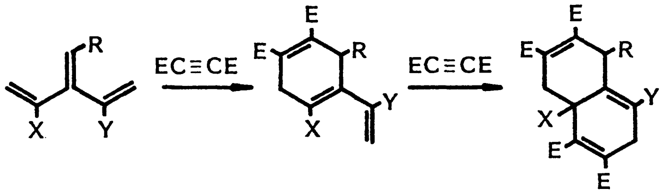
A novel cross-conjugated triene, 3-benzylidene-2,4-bis(trimethylsilyloxy)-1,4-pentadiene, was synthesized and the multiple Diels-Alder cycloaddition reactions to acetylenic dienophiles leading to the dihydronaphthols were demonstrated.

The Diels-Alder reaction is one of the most reliable preparative methods in organic synthesis.$^{1)}$ Recently some examples of the novel conjugated systems which are able to undergo more than two successive Diels-Alder reactions have been developed. These multiple reactions are called Domino,$^{2)}$ Timed,$^{3)}$ and Tandem Diels-Alder reaction$^{4)}$ on the ground of their reaction patterns.

A cross-conjugated triene is one of the systems that function as bis-diene in the multiple Diels-Alder reaction. Conceptually the sequence of multiple Diels-Alder reaction of cross-conjugated triene involves i) the initial cycloaddition reaction across the diene part of the system forming a ring and an endocyclic double bond which shares a newly formed diene structure with the unchanged double bond and ii) the second cycloaddition reaction on the new diene leading to a fused two-ring compound as outlined in Scheme 1. It should be emphasized that the multiple Diels-Alder reaction of cross-conjugated triene exclusively takes place in a regulated order giving no side reaction products whose formation is inevitable in the usual multiple reaction.



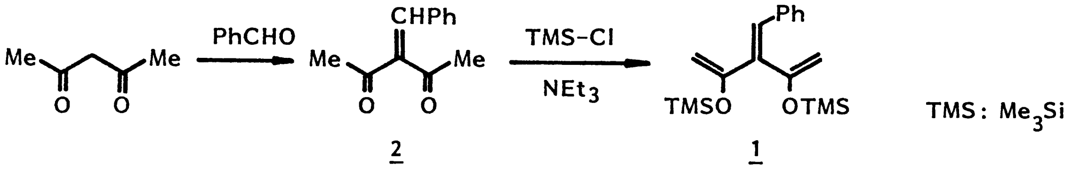
Scheme 1

The only example for the multiple Diels-Alder reaction of cross-conjugated triene was demonstrated by the reactions of 3-methylene-1,4-pentadiene, a parent cross-conjugated triene, with maleic anhydride and several quinones.$^{5)}$ In spite of its elegant ring formation, high instability of the starting triene has discouraged its utilization in organic synthesis. The use of relatively stable and also readily available cross-conjugated triene might widen the generality of the useful multiple Diels-Alder reaction. The appropriately functionalized cross-conjugated triene would facilitate the multiple Diels-Alder reaction leading to the introduction of functionalities (X and Y) onto the bicyclic product (Scheme 1).

In the present communication we wish to describe the convenient synthesis of a cross-conjugated triene, 3-benzylidene-2,4-bis(trimethylsilyloxy)-1,4-pentadiene **1**, and its multiple Diels-Alder reactions to acetylenic dienophiles yielding the 5,8-dihydro-1-naphthols.

Synthesis of A Cross-conjugated Triene 1.

The title compound, 3-benzylidene-2,4-bis(trimethylsilyloxy)-1,4-pentadiene 1, was prepared by the trimethylsilylation of 3-benzylidene-2,4-pentanedione 2 which was easily obtainable from the condensation between benzaldehyde and 2,4-pentanedione in the presence of excess piperidine under reflux in benzene as shown in Scheme 2.



Scheme 2

The reaction of 2 (16.9 g, 0.09 mol) with trimethylsilyl chloride (24.5 g, 0.22 mol) in the presence of triethylamine (63 ml) in dry N,N-dimethylformamide (100 ml), at 90-95 °C under a nitrogen atmosphere for 48 h, gave 1 in 55 % yield after the crude product obtained was quickly chromatographed over silica gel using benzene-hexane (1 : 9) as an eluent. The cross-conjugated triene 1 is stable enough to be purified without any serious decomposition by bulb-to-bulb distillation (bp 115 °C/0.8 torr (bath)) and enough to be stored at least two weeks in a freezer.6) The structure of 1 is confirmed on the basis of the spectral data as well as the micro analysis:7)

1: IR (neat) 1625, 1595 (C=C), 1245, and 830 cm^{-1}; ^{1}H-NMR (CCl$_4$) δ 0.17, 0.27 (each 9H, s, Me$_3$-Si), 4.17, 4.38 (each 1H, d, J$_{gem}$= 1.0 Hz, 1- and/or 5-CH$_2$), 4.35, 4.69 (each 1H, dd, J= 1.0 and 0.6 Hz, 1- and/or 5-CH$_2$), 6.72 (1H, t, J= 0.6 Hz, PhCH=), and 7.00-7.46 ppm (5H, m, Ph); ^{13}C-NMR (CCl$_4$) δ 0.00, 0.10 (each q, Me$_3$Si), 94.83, 95.95 (each t, 1- and 5-C), 153.06, and 155.30 ppm (each s, 2- and 4-C); MS m/e 332 (M$^+$, base peak).

The Multiple Diels-Alder Reactions of 1 with Acetylenic Dienophiles.

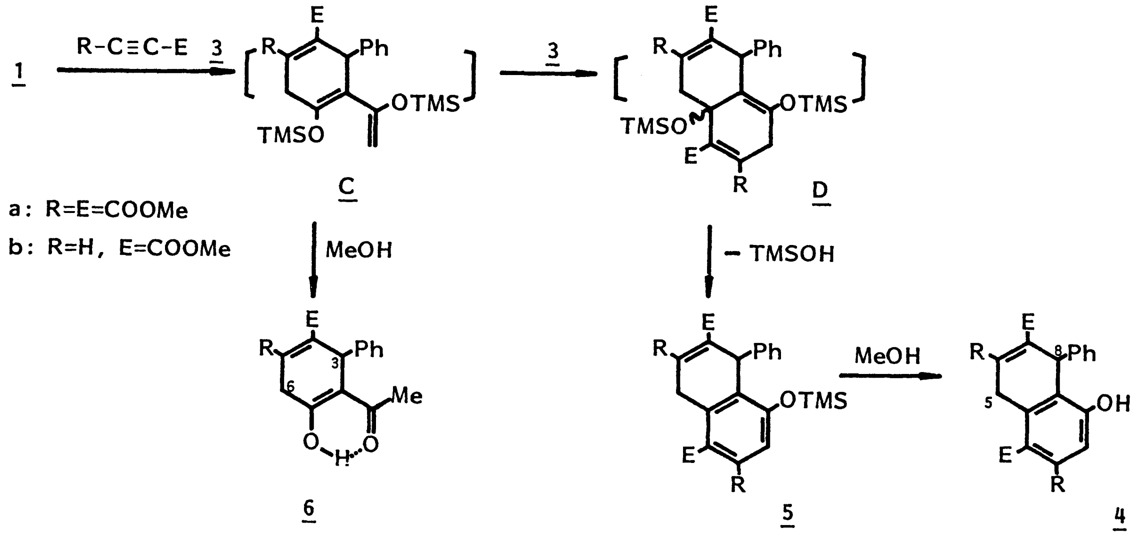
The multiple Diels-Alder reactions of the cross-conjugated triene 1 with dimethyl acetylenedicarboxylate 3a and methyl propiolate 3b gave 5,8-dihydro-1-naphthol derivatives 4a and 4b, respectively, as the major products in fair yields as shown in Scheme 3.

A solution of 1 and excess of 3a in dry benzene was refluxed for 72 h under nitrogen and then the reaction mixture was treated with methanol. The chromatographic separation of the crude product afforded the colorless di-adduct 4a, mp 171-173 °C, in 51 % yield. Although the formation of the mono-adduct 6a was observed by the ^{1}H-NMR analysis of the crude reaction mixture, its isolation by column chromatography failed because of the too poor yield.8)

The structure of 4a is identified as 5,8-dihydro-3,4,6,7-tetrakis(methoxycarbonyl)-8-phenyl-1-naphthol on the basis of the spectral data.9) The ^{13}C-NMR spectrum shows a methylene and a methine carbon at 29.12 and 42.08 ppm, respectively, and a singlet signal characteristic of the C-1 carbon of phenol at 153.99 ppm. The considerably large long-range couplings observed between the 5-methylene and 8-methine hydrogens (J= 4.0 and 2.8 Hz) and the large geminal coupling (21.8 Hz) are consistent with the values reported for 1,4-dihydronaphthalene-1-carboxylic acid.10)

A similar reaction of 1 with excess of 3b in benzene under reflux gave the trimethylsilylated di-adduct 5b, mp 143-145 °C, in 37 % yield, after evaporation of all the voratile materials in vacuo and crystallization of the residue. On the other hand, the detrimethylsilylated di-adduct 4b, mp 179-181

°C, was isolated in 47 % yield together with a trace (2 % yield) of mono-adduct 6b, bp 120 °C/1.5 torr (by bulb-to-bulb distillation), when the crude product was treated with methanol. It is clear that the product 4b has been formed through the intermediary trimethylsilylated compound 5b, since 5b was quantatively convertible into 4b on the treatment with methanol.



Scheme 3

The structures of 4b, 5b, and 6b are again confirmed on the basis of the spectral data.[11] The orientation of 4b, as well as that of 5b, is easily determined by the fact that an olefinic and an aromatic hydrogens from the dienophile 3b couple with the methylene hydrogens at the 5-position (J_{5-6}= 5.2 and 3.2 Hz) and the aromatic one at the 2-position (J_{2-3}= 8.5 Hz), respectively. The ^{1}H-NMR spectrum indicates that 6b is almost completely enolized in a chloroform solution (a broad singlet at 15.96 ppm), and that the regiochemistry of 6b is the same to that of the initially formed ring of the di-adduct 4b (J_{5-6}= 4.8 and 3.2 Hz for 6b). These structural assignment shows that every step in the multiple Diels-Alder reaction of 1 with the unsymmetrically substituted dienophile 3b has taken place in a highly regioselective manner.

As mentioned above, the cross-conjugated triene has undergone the multiple Diels-Alder reactions with acetylenic dienophiles giving fair yields of the di-adducts. These reactions probably proceed through the steps shown in Scheme 3, which involve the initial cycloaddition reaction forming an intermediate C that carries a diene moiety activated by the two trimethylsilyloxy substituents, the second cycloaddition reaction leading to another intermediate D, a 1,4-elimination of trimethylsilanol into 5, and hydrolysis into the final products 4. The high regioselectivity for both the initial and the second Diels-Alder reactions can be explained in terms of ortho- and para-orientation rule which usual single-step Diels-Alder reactions obey.

We would like to designate the multiple Diels-Alder reaction of cross-conjugated triene as "Transmissive Diels-Alder reaction", this reaction being able to transmit a diene functionality in order during the reaction.

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5) A. T. Blomquist and J. A. Verdol, ibid., 77, 81 (1955); W. J. Bailey and J. Economy, ibid., 77, 1133 (1955); W. J. Bailey, C. H. Cunov, and L. Nicholas, ibid., 77, 2787 (1955).

6) The compound 1 may be stored in a freezer under nitrogen in the presence of hydroquinone. No detectable decomposition was observed by NMR analysis after two weeks under the above conditions.

7) All the compounds reported in the present communication gives the satisfactory analytical results.

8) The ^{1}H-NMR spectrum of the crude product reveals an enolic hydrogen as a broad singlet at 15.9 ppm.

9) 4a: IR (KBr) 3360 (OH), 1725, 1715, and 1665 cm^{-1} (CO); ^{1}H-NMR (CDCl$_3$) δ 3.64 (1H, dd, J_{5-8}= 2.8, J_{gem}= 21.8 Hz, one of 5-CH$_2$), 3.64, 3.74, 3.76, 3.89 (each 3H, s, COOMe), 3.95 (1H, dd, $J_{5-8'}$= 4.0, J_{gem}= 21.8 Hz, the other of 5-CH$_2$), 5.30 (1H, dd, 8-H), and 7.04-7.16 ppm (6H, m, Ph and 2-H); ^{13}C-NMR (CDCl$_3$) δ 29.12 (t, 5-C), 42.08 (d, 8-C), 52.55, 52.80 (each q, COOMe), 114.78 (d, 2-C), 153.99 (s, 1-C), 166.27, 167.74, 168.15, and 169.43 ppm (each s, COOMe), MS m/e 454 (M$^+$, 10 %).

10) J. L. Marshall and T. K. Folson, J. Org. Chem., 36, 2011 (1971).

11) 4b: IR (KBr) 3230 (OH) and 1720-1660 cm^{-1} (CO); ^{1}H-NMR (CDCl$_3$) δ 3.67, 3.84 (each 3H, s, COOMe), 4.08 (1H, dt, J_{5-6}= J_{5-8}= 3.2, J_{gem}= 23.0 Hz, one of 5-CH$_2$), 4.15 (1H, ddd, $J_{5'-6}$= 5.2, $J_{5'-8}$= 2.6, J_{gem}= 23.0 Hz, the other of 5-CH$_2$), 5.41 (1H, dd, 8-H), 6.60 (1H, d, J_{2-3}= 8.5 Hz, 2-H), 7.00-7.34 (6H, m, Ph and 6-H), and 7.76 ppm (1H, d, 3-H); ^{13}C-NMR (CDCl$_3$) δ 30.65 (t, 5-C), 39.39 (d, 8-C), 51.78 (q, COOMe), 113.31 (d, 2-C), 120.30 (s, 4-C), 136.85 (d, 6-C), 157.04 (s, 1-C), 166.85, and 167.73 ppm (each s, COOMe); MS m/e 338 (M$^+$, 83 %).

5b: IR (KBr) 1720, 1700 (CO), 1250, 875, and 840 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ 0.13 (9H, s, Me$_3$-Si), 3.67, 3.83 (each 3H, s, COOMe), 4.09 (1H, dt, J_{5-6}= J_{5-8}= 3.3, J_{gem}= 22.5 Hz, one of 5-CH$_2$), 4.15 (1H, ddd, $J_{5'-6}$= 5.2, $J_{5'-8}$= 2.6, J_{gem}= 22.5 Hz, the other of 5-CH$_2$), 5.30 (1H, dd, 8-H), 6.62 (1H, d, J_{2-3}= 8.5 Hz, 2-H), 7.00-7.30 (6H, m, Ph and 6-H), and 7.76 ppm (1H, d, 3-H); ^{13}C-NMR (CDCl$_3$) δ 0.00 (q, Me$_3$Si), 30.41 (t, 5-C), 39.69 (d, 8-C), 51.25 (q, COOMe), 115.43 (d, 2-C), 120.77 (s, 4-C), 135.80 (d, 6-C), 156.34 (s, 1-C), 166.03, and 167.14 ppm (each s, COOMe); MS m/e 410 (M$^+$, base peak).

6b: IR (neat) 3400 (OH), 1720, 1660, 1600 (CO), and 1245 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ 2.05 (3H, s, COOMe), 3.27 (1H, ddd, J_{6-3}= 3.0, J_{6-5}= 4.8, J_{gem}= 22.0 Hz, one of 6-CH$_2$), 3.37 (1H, ddd, $J_{6'-5}$= 3.2, $J_{6'-3}$= 3.7, J_{gem}= 22.0 Hz, the other of 6-CH$_2$), 3.68 (3H, s, COOMe), 4.83 (1H, dd, 3-H), 6.83 (1H, dd, 5-H), 7.10-7.24 (5H, br. s, Ph), and 15.96 ppm (1H, br. s, OH); ^{13}C-NMR δ 25.60 (t, 6-C), 32.58 (q, COMe), 41.80 (d, 3-C), 51.72 (q, COOMe), 109.56 (s, 2-C), 165.68 (s, COOMe), 177.89 (s, COMe), and 199.20 ppm (s, 1-C); MS m/e 272 (M$^+$, base peak).

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