The Diels—Alder reaction between substituted 6,6-dimethyl-2-vinylnorpinenes and maleic anhydride

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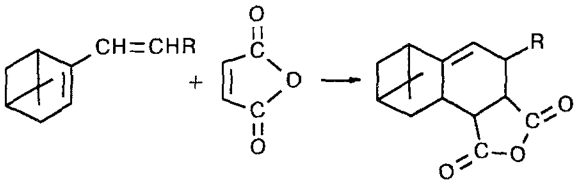
Cycloaddition of substituted 6,6-dimethyl-2-vinylnorpinenes with maleic anhydride occurs *via* the attack of a dienophile on diene from the less hindered side of the bicyclic fragment. IR, UV, CD, and ^{1}H NMR spectra of adducts have been studied.

Key words: substituted 6,6-dimethyl-2-vinylnorpinenes, maleic anhydride, Diels—Alder reaction, IR, UV, CD, and NMR spectra.

Diene synthesis involving bicyclic terpene dienes is of interest for preparing various polycyclic fragments. For example, tricyclic hydrocarbons were synthesized by cycloaddition reactions of the simplest dienes based on α-pinene and 3-carene.[1—5]

We studied the reaction of diene synthesis of substituted vinylnorpinenes containing a functional group at the terminal carbon atom of the *exo*-double bond. Initial dienes (**1a—d**) were synthesized from myrtenal and corresponding phosphonates in the presence of NaH in THF according to Horner—Emmons reactions.[6] Maleic anhydride (**2**) was used as a dienophile. Crystalline adducts **3** were obtained on heating reagents **1** and **2** (Scheme 1).

Scheme 1



1a—d **2** **3a—d**

R = CN (**a**), COOMe (**b**), COOEt (**c**), CONEt$_2$ (**d**)

The bands at ~1840 to 1780 cm^{-1} corresponding to C=O groups in saturated dicarboxylic anhydrides[7] are observed in IR spectra of adducts **3**. The band of the nitrile group is observed at 2260 cm^{-1} in the IR spectrum of **3a**; the bands of the ester group are observed at 1730 cm^{-1} in the spectra of **3b,c**; and the band of the amide group at 1636 cm^{-1} is observed in the spectrum of **3d**.

Strong absorption in the UV region, which is characteristic of conjugated systems (~278 nm), is observed for initial dienes **1a—d**, while adducts **3a—d** are characterized by low-intensity bands at 218 and 222 nm, which are typical of the double bond of the pinene fragment.

It is known that stereochemistry of cycloaddition depends on electronic, orbital, and steric effects of reagents.[8—10] In the majority of cases, cycloaddition occurs with the predominant formation of *endo*-adducts.[9]

The spatial structures of adducts **3a—d** are studied by the ^{1}H NMR method. The ^{1}H NMR spectrum of compound **3a** is presented in Fig. 1, *a*. The signals were assigned by the subsequent selective decoupling of the spin-spin interaction of protons (Table 1).

It is seen from Table 1 that the values of $^3J_{\text{H-1,H-2}}$ and $^3J_{\text{H-2,H-3}}$ are similar (8.42 and 9.37 Hz, respectively) and correspond to the *cis*-orientation of H-1, H-2, and H-2, H-3. Thus, the principle of *cis*-addition is fulfilled.[11]

Starting from the Karplus dependence,[12,13] we have calculated dihedral angles of some vicinal-bonded protons according to the known procedure[14] (Table 2). These data suggest the nearly coplanar arrangement of H-2 and H-3 and *cis—gauche*-orientation of bonds with H-3 and H-4 protons.

Thus, the analysis of the ^{1}H NMR spectra of compound **3a** allows us to draw a conclusion that dienophile **2** attacks diene **1a** from the side, which is less sterically hindered relative to the bicyclic fragment (*anti-endo*).

Experimental

^{1}H NMR spectra were recorded on Bruker MSL-400 (**3a,b**) and Varian T-60 (**3c,d**) instruments. Selective homonuclear double resonance was used to assign signals in the ^{1}H NMR spectra of **3a,b**. IR spectra were recorded on an UR-20

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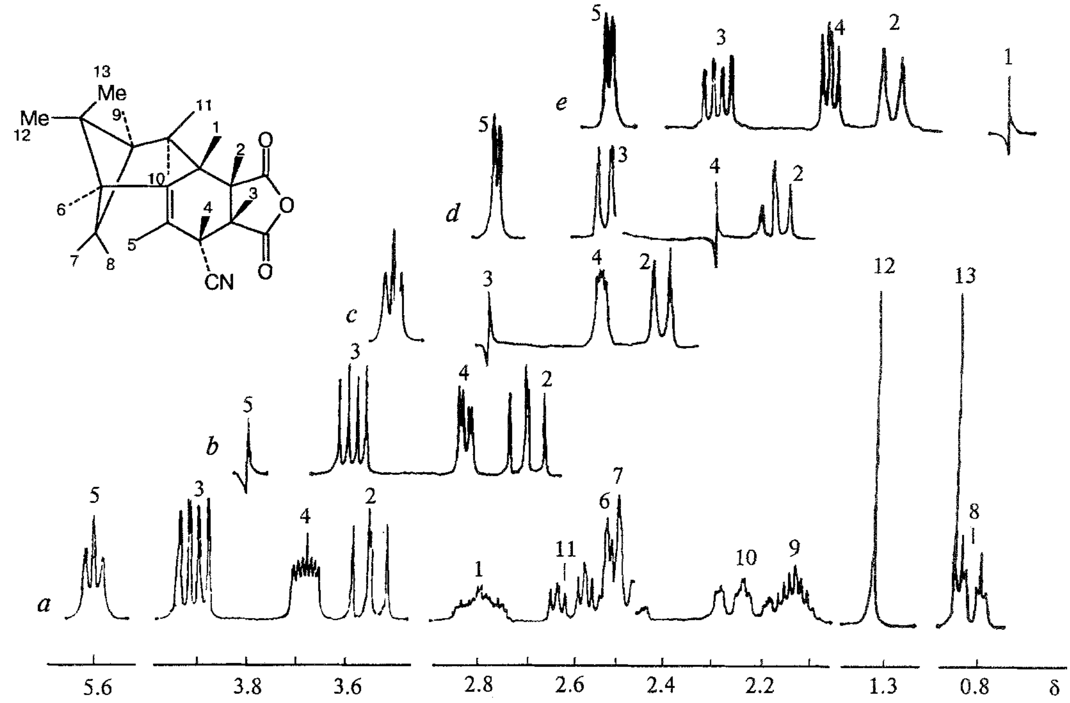

Fig. 1. ^1H NMR of compound **3a**: the total spectrum (*a*); the spectra of the homonuclear H{H} decoupling (*b*—*e*) of protons H-5 (*b*); H-3 (*c*); H-4 (*d*), and H-1 (*e*).

Table 1. ^1H NMR spectrum of compound **3a**

Proton	δ	*J*/Hz	$\{H_n\}H_k$*
H-1	2.77	$J_{H-1,H-2}$ = 8.42, $J_{H-1,H-5}$ = 2.95,** $J_{H-1,H-4}$ = 1.69, $J_{H-1,H-11}$ = 5.60, $J_{H-1,H-10}$ = 13.22	1→5, 11, 4, 10, 2
H-2	3.50	$J_{H-2,H-3}$ = 9.37, $J_{H-1,H-2}$ = 8.42	2→3, 1
H-3	3.90	$J_{H-3,H-2}$ = 9.37, $J_{H-3,H-4}$ = 4.70, $J_{H-3,H-5}$ = 0.70	3→2, 4, 5
H-4	3.67	$J_{H-4,H-3}$ = 4.70, $J_{H-4,H-5}$ = 3.32, $J_{H-1,H-4}$ = 1.69	4→3, 5, 1
H-5	5.60	$J_{H-5,H-3}$ = 0.70, $J_{H-5,H-4}$ = 3.32, $J_{H-5,H-1}$ = 2.95	5→3, 4, 1
H-6	2.57		
H-7	2.51		
H-8	0.80		
H-9	2.13	$J_{H-9,H-10}$ = 2.10, $J_{H-9,H-6}$ = 5.05, $J_{H-9,H-11}$ = 5.05	9→10, 6, 11, 7
H-10	2.23	$J_{H-10,H-1}$ = 13.22, $J_{H-10,H-9}$ = 2.10, $J_{H-10,H-11}$ = 14.41	10→1, 9, 11, 7
H-11	2.60	$J_{H-11,H-10}$ = 14.41, $J_{H-11,H-1}$ = 5.63, $J_{H-11,H-9}$ = 5.05	11→10, 1, 9
anti-Me	1.31		
syn-Me	0.84		

* H_n is the "selectively" irradiated proton; H_k are the protons bound to H_n by spin-spin interaction. ** Long-range spin-spin coupling constant characteristic of cyclic allyl systems.[12]

spectrophotometer; UV spectra were recorded on a Specord M-40 spectrophotometer in MeCN; and CD spectra were recorded on a Jasco 500A spectropolarimeter (Japan) in MeCN. Values of specific rotation were determined on a Polamat A polarimeter. Melting points were measured on a Boetius block.

4-Cyanotricyclo[7.1.1.0^{2,7}]undec-2-en-5,6-dicarboxylic anhydride (3a). A mixture of 6.5 g (24 mmol) of 6,6-dimethyl-2-cyanovinylnorpinene and 2.4 g (24 mmol) of maleic anhydride was heated for 3 h at 120 °C. After cooling ether was added, and crystals that precipitated were separated and recrystallized from MeOH. Yield 25.6 %; m.p. 194.5—196 °C; $[\alpha]_D^{20}$ −6.1 (*c* 8.4, MeCN). Found (%): C, 70.90; H, 6.45; N, 5.33. $C_6H_{17}NO_3$. Calculated (%): C, 70.85; H, 6.30; N, 5.16. IR, ν/cm^{-1}: 2260 (C≡N); 1850, 1780 (C(O)—O—C(O)); 1658 (C=C); 1465 (≡C—H); 1380 (Me—C—Me). UV (MeCN), λ_{max}/nm: 217.5 (logε 3.72); 222.4 (logε 3.65). CD, λ_{max}/nm: 222.4 (Δε −1). The ^1H NMR data are presented in Table 1.

4-Carbomethoxytricyclo[7.1.1.0^{2,7}]undec-2-en-5,6-dicarboxylic anhydride (3b) was prepared from diene **1b** similarly to

Table 2. Dihedral angles θ and values of spin-spin coupling constants of some protons in compound **3a**

Protons	*J*/Hz	θ^*_{calc}/deg
H-1, H-2	8.42	23.1
H-2, H-3	9.37	14.2
H-3, H-4	4.70	50.1
H-1, H-11	5.63	41.6
H-1, H-10	13.22	114.7

* Dihedral angles calculated by the known[14] equation

$$^3J_{H,H'} = \begin{cases} 10\cos^2\theta, & 0 \le \theta \le 90° \\ 16\cos^2\theta, & 90° \le \theta \le 180° \end{cases}.$$

compound **3a**. Yield 26 %; m.p. 210.5—212 °C; $[\alpha]_D^{20}$ −3.5 (*c* 4.8, MeCN). Found (%): C, 66.95; H, 6.44. $C_{17}H_{20}O_5$. Calculated (%): C, 67.10; H, 6.58. IR, ν/cm^{-1}: 1730 (C=O); 1655 (C=C). ^{1}H NMR (CD_3CN, δ): 0.79 (d, 1 H); 0.85 (s, 3 H, *syn*-Me); 1.26 (s, 3 H, *anti*-Me); 2.11 (m, 1 H); 2.49 (m, 1 H); 2.52 (m, 1 H); 2.60 (m, 1 H); 2.83 (m, 1 H); 3.37 (m, 1 H); 3.59 (q, 1 H); 3.82 (s, 3 H, MeO); 4.08 (q, 1 H); 5.96 (t, 1 H).

4-Carbethoxytricyclo[7.1.1.0^{2,7}]undec-2-en-5,6-dicarboxylic anhydride (3c) was prepared from diene **1c** similarly to compound **3a**. Yield 25 %; m.p. 172.5—174 °C; $[\alpha]_D^{20}$ −5.85 (*c* 7.96, MeCN). Found (%): C, 67.70; H, 6.78. $C_{18}H_{22}O_5$. Calculated (%): C, 67.92; H, 6.92. IR, ν/cm^{-1}: 1843, 1776 s (CO—O—CO); 1736 (CO—OR). UV, λ_{max}/nm: 217.2 (logε 4.05); 222 (logε 3.97). CD, λ_{max}/nm: 215 (Δε +2); 223 (Δε −5); 284 (Δε −3.3). ^{1}H NMR ($CDCl_3$, δ): 0.78 (s, 3 H, *syn*-Me); 0.87 (m, 1 H); 1.23 (s, 3 H, *anti*-Me); 1.32 (t, 3 H, Me); 2.00—4.10 (m, 9 H); 4.27 (q, 2 H); 5.93 (t, 1 H).

4-Diethylcarbamidotricyclo[7.1.1.0^{2,7}]undec-2-en-5,6-dicarboxylic anhydride (3d) was prepared from diene **1d** similarly to compound **3a**. Yield 30.0 %; m.p. 198.5—200 °C; $[\alpha]_D^{20}$ −3.6 (*c* 1.9, acetone). Found (%): C, 69.22; H, 7.71; N, 4.00; $C_{20}H_{27}NO_4$. Calculated (%): C, 69.56; H, 7.82; N, 4.05. IR, ν/cm^{-1}: 1858 (C=O); 1775 (C=O); 1636 (C=O). UV, λ_{max}/nm: 217.8 (logε 4.19); 222.4 (logε 4.11). CD, λ_{max}/nm: 216 (Δε +1.8); 226 (Δε −4.3); 286 (Δε +2.8). ^{1}H NMR ($(CD_3)_2CO$, δ): 0.83 (s, 3 H, *syn*-Me); 0.89 (m, 1 H); 1.13 (m, 6 H, 2 Me); 1.27 (s, 3 H, *anti*-Me); 2.00—4.20 (m, 13 H); 5.03 (m, 1 H).

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