

Catalyzed Dimerization of 2,5-Dimethyl-2,4-hexadiene. ^1H - and ^{13}C -NMR Studies on *exo*-3-Isopropenyl-*exo*-6-isopropyl-1,*endo*-2,4,4-tetramethylbicyclo[3.1.0]hexane

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2,5-Dimethyl-2,4-hexadiene (**1**) dimerizes under Lewis acid catalysis or in the presence of tris(4-bromophenyl)aminium hexachlorostibate (**4**) mainly to give *exo*-3-isopropenyl-*exo*-6-isopropyl-1,*endo*-2,4,4-tetramethylbicyclo[3.1.0]hexane (**2**). Small amounts of the acyclic dimer 2,5,7,7,10-pentamethyl-2,4,8-undecatriene (**3**) and traces of other unidentified dimeric and trimeric products are formed as well. The latter are the only products in the presence of Brønsted acids, whereas **2** and **3** were not detected under these conditions. The structural assignment of **2** has been carried out by means of 2D-INADEQUATE, -HETCOR, and -COSY spectra.

2,5-Dimethyl-2,4-hexadiene (**1**) has been used as dienophile in radical cation-catalyzed Diels-Alder reactions with 1,3-cyclohexadiene^{1,2}. Although there is no report in the literature on dimerization reactions of **1** itself, we have recently found that **1** dimerizes in the presence of tris(4-bromophenyl)aminium hexachlorostibate (**4**) even in the presence of 1,3-cyclohexadiene^{3,4}. Since this aminium salt is reported to generate cationic reaction pathways as well⁵ we have undertaken a systematic investigation of the acid catalysis in the dimerization of **1**.

Table 1. Dimerization of **1** (1 M) under acidic and radical cation conditions in dichloromethane^{a)}

Entry	Catalyst	Concentration of catalyst [mol %]	Yield [% (%)] ^{b)}		
			2	3	others ^{c)}
1	4	2.5	17 (51)	ca. 1	6 (17)
2 ^{d)}	4 + 5	4 : 5.0 5 : 20	—	—	6 ^{e)}
3 ^{d)}	4 + 5	4 : 50 5 : 55	—	—	2 (3) ^{f)}
4	HSbCl ₅	5.0	12.3 (40)	ca. 1	4 (13)
5	SbCl ₅	2.5	7.4 (44)	ca. 1	3 (17)
6	SbCl ₅	5.0	14.1 (47)	ca. 1	7 (24)
7	TosH	5.0	—	—	3 (35)
8	HCl(gas)	—	—	—	2 ^{g)}

^{a)} Reaction time 30 min at 0°C. — ^{b)} All yields have been determined by GC using camphor or biphenyl as internal standard for the products and toluene for the diene **1**, respectively. (%): Yield with regard to conversion of **1**. — ^{c)} In experiments 1–6 the mixtures of unidentified products show almost the same composition, which, however, differs from those of experiments 7 and 8. In all cases the unidentified products show high molecular weights pointing to, e.g., dimers and trimers of **1**. — ^{d)} Ratio of the components as used in Gassman's experiment⁵. — ^{e)} Conversion of **1**: 4%. — ^{f)} Mainly polymerization of **1**, conversion of **1**: 60%. — ^{g)} In addition to the oligomers (see footnote c) several 1:1 and 2:1 HCl adducts have been detected by GC-MS.

Acid-Catalyzed Dimerization of **1**

The results of the dimerization of **1** to give *exo*-3-isopropenyl-*exo*-6-isopropyl-1,*endo*-2,4,4-tetramethylbicyclo[3.1.0]hexane (**2**) (main product) and 2,5,7,7,10-pentamethyl-2,4,8-undecatriene (**3**) (ca. 10% of **2**) by using either tris(4-bromophenyl)aminium hexachlorostibate (**4**) or antimony pentachloride and other Brønsted acids are summarized in Table 1.

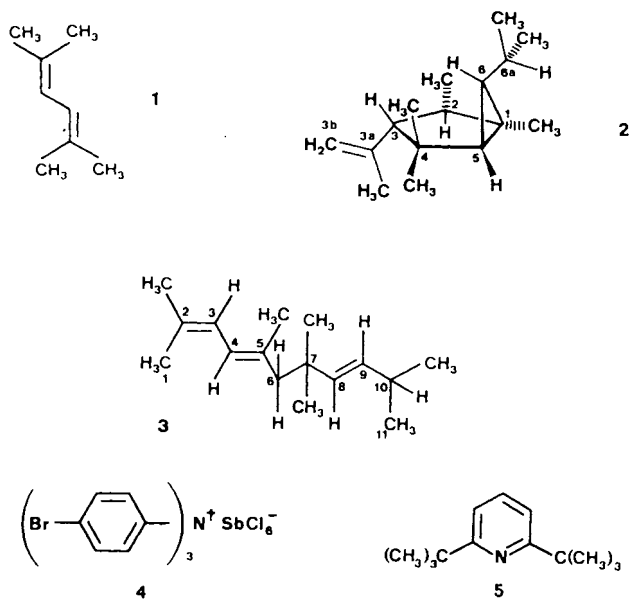
The following aspects are noteworthy:

(1) The bicyclic dimerization product **2** is only formed in the presence of **4**, SbCl₅, or HSbCl₆.

(2) The radical cation catalyst **4** has no effect in the presence of 2,6-di-*tert*-butylpyridine (**5**)⁵. However, under Gassman's conditions (entry 3) small amounts of unidentified dimeric and trimeric products are formed.

(3) Brønsted acids such as *p*-toluenesulfonic acid (entry 7) and gaseous HCl (entry 8) do not work.

These results clearly show that both **2** and **3** are formed in the presence of the Lewis acid SbCl₅. Proton acids only lead to the formation of di- and trimeric products of **1**, which have not been

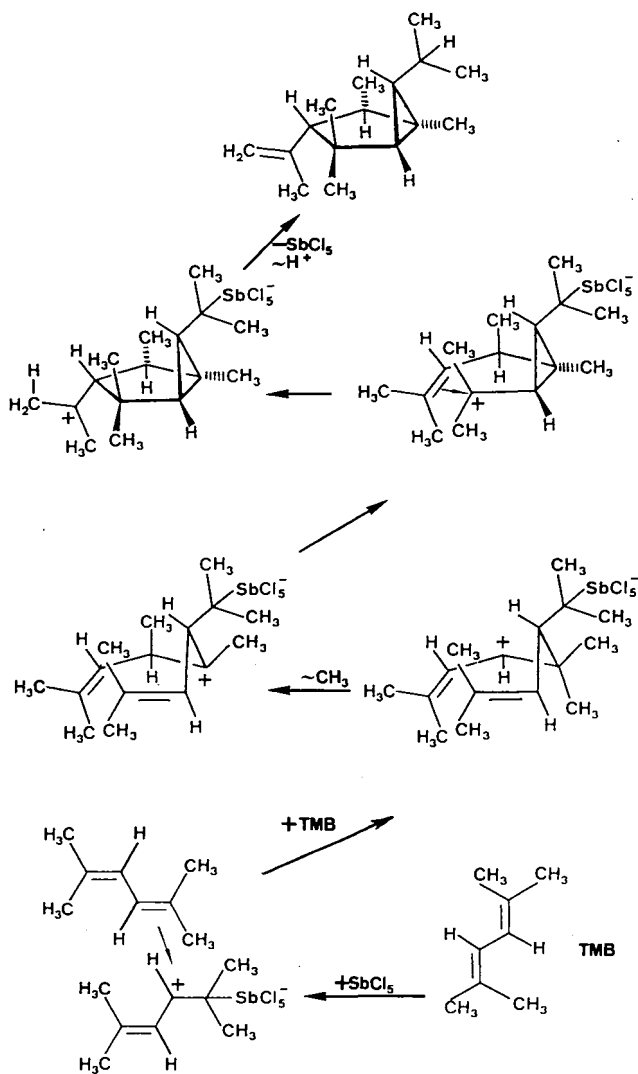


identified yet due to their small yields. At first sight a radical cation route to **2** or **3** may be excluded since the aminium salt **4** does not show any effect in the presence of the pyridine base **5**⁵. However, the following observation should be noted: **4** decomposes very fast in the presence of **5**, which can be followed by the disappearance of the blue color of **4** after addition of **5**. Therefore, the failure of **4** in experiments 2 and 3 might be due to the fact that **4** decomposes before it can generate radical cations from **1**. We, therefore, do not completely exclude a radical cation route to **2** under these conditions, although other electron acceptors such as pyrylium salts, chloranil, and 1,4-dicyanonaphthalene, which work photochemically, do not show any effect^{3,4}. In addition, by comparison of experiment 1 with the experiments 4–5 a higher efficiency of **4** has to be noted.

In order to check the possibility of a dimerization under high pressure conditions we have heated **1** to 150°C at 14 kbar⁶. However, no dimeric products have been detected, and **1** could be recovered up to 90%.

Whereas the dimerization of **1** to **3** does not require any skeletal rearrangement (a deconjugation of **1** leading to 2,5-dimethyl-1,4-hexadiene as an intermediate may simply explain its formation), one methyl group has to be rearranged during the formation of **2**. A possible mechanism is shown in the scheme. A radical cation route should also involve similarly structured intermediates.

Scheme



NMR Analysis of **2**

The ^{13}C - and ^1H -NMR spectroscopic data are presented in Table 2. A thorough use of the 2D-NMR methods was made because of the complex nature of spectra. The CC and CH connectivity schemes and the assignments presented result from the analysis of the 2D-INADEQUATE, -HETCOR, and -COSY spectra.

Table 2. ^{13}C - and ^1H -NMR spectroscopic data of **2** in C_6D_6

Atom	$\delta^{13}\text{C}$	$^1J_{\text{CH}}$	$\delta^1\text{H}^{\text{a)}$	^1H -mult./J
1	30.87	-	-	
2	42.82	125	1.98	dq $J_{23} \cdot 11.0$, $J_{2-\text{CH}_3} \cdot 6.4$ Hz
3	59.69	125	1.33	br. d $J_{23} \cdot 11.0$ Hz
4	41.36	-	-	
5	42.70	156	0.37	d $J_{56} \cdot 3.4$ Hz
6	29.80	154	0.26	dd $J_{56} \cdot 3.4$, $J_{66a} \cdot 9.0$ Hz
1- CH_3	15.86	125	1.15	s
2- CH_3	14.10	124	0.84	d $J_{2-\text{CH}_3} \cdot 6.4$ Hz
3a	143.41	-	-	
3b	113.05	155	4.65	ddq $^2J_{3b} \cdot 2.3$, $J_{33b} \cdot 1.0$, $J \cdot 0.8$ Hz
			4.91	dq $^2J_{3b} \cdot 2.3$, $J_{33b} \cdot 1.4$ Hz
3a- CH_3	23.77	126	1.65	ddd $J \cdot 1.4$, 0.8, 0.4 Hz
4- CH_3	25.22	125	0.83	s
4- CH_3	26.19	125	1.00	s
6a	28.80	128	1.00	m
6a- CH_3	22.82	126	0.94	br. d $J_{6a,6a-\text{CH}_3} \cdot 5.4$ Hz
6a- CH_3	23.05	125	1.00	m

^{a)} The chemical shift differences in CS_2 as solvent are within 0.1 ppm.

Typical features in the ^1H -NMR spectra are:

- Two cyclopropane protons at $\delta = 0.26$ and 0.37 revealing a typical small *trans* coupling of 3.4 Hz⁷,
- an allylic proton at only $\delta = 1.33$, whereas a "normal" cyclopentane proton is observed at $\delta = 1.98$,
- an at first sight "hidden" isopropyl group because the isopropyl proton at $\delta = 1.00$ is chemically almost equivalent to the isopropyl methyl groups,
- two cyclopentane protons exhibiting a large vicinal coupling constant of $J_{23} = 11.0$ Hz.

The ^1H -chemical shifts of 2-, 3-, and 6a-H are clearly influenced by the diamagnetic anisotropic effect of the cyclopropane ring⁷. Thus, 2-H and 6a-H are in the shielding zone of the cyclopropane ring. These features, combined with the basic CC and CH connectivity scheme and with the *trans* relation of 5- and 6-H (point i), resulted in the depicted structure. The configuration at C-2, however, is not certain. Here it is assumed that the large coupling for J_{23} (point iv) results from the sterical more stable *trans* 2-H–3-H configuration and a conformation where the H–C²–C³–H dihedral angle is near 180° . However, the alternative *cis* configuration where the dihedral angle is near zero can not be excluded.

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Experimental

2,5-Dimethyl-2,4-hexadiene (**1**) has been purchased from Janssen and was further purified by distillation under argon. No isomers of **1** have been detected by GC-MS analysis. The aminium salt **4** has been synthesized according to a procedure from the literature^{8,9}, HSbCl_6 was simply formed from SbCl_5 and gaseous HCl at -30°C in 1,1,2-trichloro-1,2,2-trifluoroethane as described by Gassman et al.⁹. SbCl_5 and **5** were used as commercially available (from Janssen). Dichloromethane was purified by distillation and by filtration over basic alumina, which had been activated by annealing at 0.01 Torr. All procedures for purification and syntheses were carried out under argon.

^1H and ^{13}C NMR: Varian EM 390 (90 MHz) and Varian CFT 20 (20 MHz), Bruker WM 400 (400 MHz). — IR: Perkin-Elmer 377. — GC-MS: Varian MAT 212. — Analytic GC: Carlo Erba Fractovap 2101 with Apiezon L. — Prep. GC: Hupe Busch and F + M 720 with OV 101.

Preparation of 2 and 3: 5.1 g (25 mmol) of the aminium salt **4** was added to a solution of 27.6 g (250 mmol) of 2,5-dimethyl-2,4-hexadiene (**1**) in 250 ml of dichloromethane at 0°C under argon. After 50 min the solvent was distilled off at room temperature, and the products were extracted with hexane. The hexane solution was filtered over activated basic alumina, and the product mixture was isolated by distillation: b. p. $45-50^\circ\text{C}/0.25$ Torr, yield 2.7 g (20%); colorless oil. The dimers **2** and **3** were separated by semipreparative GC.

exo-3-Isopropenyl-exo-6-isopropyl-1,endo-2,4,4-tetramethylbicyclo[3.1.0]hexane (2): For NMR data see Table 2. — IR (cap.): 3070 cm^{-1} ($=\text{CH}$); 2950, 2920, 2860 (CH); 1640, 1630 ($\text{C}=\text{C}$). — MS: m/z (%) = 222 (0.7, $\text{M}^+ + 2$), 221 (7.5, $\text{M}^+ + 1$), 220 (40.0, M^+), 205 (2.6), 138 (26.5), 123 (30.4), 121 (35.7), 111 (100, $1^+ + 1$), 110 (19.0, 1^+), 109 (34.0), 69 (71.3).

$\text{C}_{16}\text{H}_{28}$ (220.5) Calcd. C 87.16 H 12.84
Found C 87.38 H 12.95

2,5,7,7,10-Pentamethyl-2,4,8-undecatriene (3): ^1H NMR (90 MHz, C_6D_6): δ = 0.98 (d, 6H, J = 6.8 Hz, $2 \times 10\text{-CH}_3$); 1.03 (s, 6H, 7- CH_3); 1.7 (br. s, 9H, $2 \times 2\text{-CH}_3$, 5- CH_3); 2.08 (br. s, 2H, 6-H); 2.2 (m, 1H, 10-H); 5.27 (dd, 1H, J = 15.5, 5.5 Hz, 9-H); 5.44 (d, 1H, J = 15.5 Hz, 8-H); 6.07 (br. s, 2H, 3,4-H). — ^{13}C NMR (20 MHz, C_6D_6): δ = 18.14, 19.37 (2- CH_3 , 5- CH_3); 22.90 ($2 \times 10\text{-CH}_3$); 26.34 (2- CH_3); 28.02 ($2 \times 7\text{-CH}_3$); 31.55 (C-10); 36.75 (C-7); 54.37 (C-6); 122.39, 125.38 (C-3,4); 132.79 (C-9); 138.06 (C-8); 131.93, 133.21 (C-2,5). — MS: m/z (%) = 222 (0.2, $\text{M}^+ + 2$), 221 (2.3, $\text{M}^+ + 1$), 220 (13.2, M^+), 111 (100, $1^+ + 1$), 110 (26.8, 1^+), 109 (55.4), 69 (88.9).

Dimerization of 1 Under Acid Catalysis: The acid catalyst was added to **1** (1.1 g, 10 mmol) in dichloromethane (for further experimental conditions see Table 1). The reaction was controlled by GC analysis. After the reaction mixture had been stirred at 0°C for 30 min, triethylamine (3 ml) was added for quenching the acid. The solvent was removed by distillation, and the products were extracted with diethyl ether (10 ml), tetrahydrofuran (3 ml), and triethylamine (2 ml). The products were isolated by semipreparative GC.

CAS Registry Numbers

1: 764-13-6 / **2:** 114564-55-5 / **3:** 114564-56-6 / **4:** 24964-91-8 / **5:** 585-48-8

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