Synthesis of Monosubstituted [1.1.1]Propellanes

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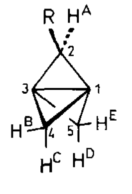
The synthesis (up to the 10-g scale) and purification of alkyl- and methoxyalkyl-substituted [1.1.1]propellanes are described.

[1.1.1]Propellanes undergo ring-opening polymerizations with breaking of the central C–C σ bond[1]. The resulting homopolymers consist of a sequence of bicyclo[1.1.1]pentane repeating units, a structural feature which is associated with an unusual stiffness of the polymer backbone. As a consequence, unsubstituted or insufficiently substituted poly([1.1.1]propellane)s are insoluble and untractable materials[1a,b,d,e]. It has been convincingly shown that the attachment of flexible chains greatly improves the solubility of rigid polymers[2]. In case of the polypropellanes this would require the synthesis of alkyl-chain-substituted [1.1.1]propellanes. Recently, we reported on a convenient route to the pentyl-substituted propellane **1b**[3]. Here, we give a full account on this work which was successfully applied not only to the synthesis of some alkyl-substituted, but also to that of methoxyalkyl-substituted [1.1.1]propellanes. The latter ones are of specific interest in that the methoxyalkyl substituent combines both the positive effect on the solubility and the possibility to introduce various functionalities into the corresponding polymer through displacement reactions of the methoxy function.



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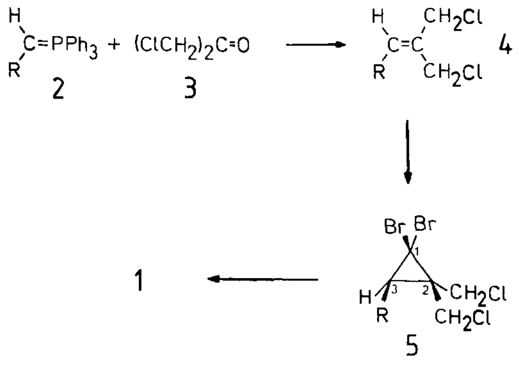
	R
a	H
b	$[CH_2]_4CH_3$
c	$[CH_2]_6CH_3$
d	$[CH_2]_{10}CH_3$
e	$[CH_2]_3OCH_3$
f	$[CH_2]_5OCH_3$

Substituted [1.1.1]propellanes are known[4]. Unfortunately, none of them is an attractive candidate for polymer synthesis. Either the syntheses require far too many steps or the substitution patterns are not useful to tackle the solubility problem. We therefore developed a simple three-step route to monosubstituted propellanes which is a modification of Szeimies' synthesis of the parent [1.1.1]propellane **1a** (Scheme 1)[5]. The substituent R is introduced in the first step using the Wittig reaction of the ylids **2b–f** with 1,3-dichloroacetone (**3**) to give the corresponding olefins **4b–f**. These olefins were then converted into the cyclopropane derivatives **5b–f** by standard carbene chemistry. Except for **4d** and **5d**, which were purified by recrystallization, all compounds were purified by high-vacuum distillation. Upon treatment with methyllithium compounds **5b–f** furnished the propellanes **1b–f** in yields of 40–64% (**1b, c, e, f**) and 21% (**1d**), respectively, and in purities typically better than 90% (by ^1H NMR). Propellanes **1b, c, e** are accessible on the 10-g scale as it was shown for the most important examples **1b, e**. Since the purification of propellane **1d**, carrying a long substituent, requires low-temperature recrystallization the yields are lower, and the amounts of these compounds conveniently prepared are limited to 1–2 g. Table 1 summarizes amounts and yields of the propellanes **1b–f**.

Scheme 1



R: see **1**

Table 1. Amounts [g] of prepared propellanes **1b–f**; yields in parantheses

	b	**c**	**d**	**e**	**f**
1	14.2 (60)	6.8 (54)	1.0 (21)	13.1 (57)	2.0 (40)

The propellanes are accompanied by two kinds of olefinic impurities, those which are present from the very beginning and those which are formed upon standing (under nitrogen) of freshly prepared propellane at room or elevated temperatures. ^1H-NMR-spectroscopical investigations indicate that

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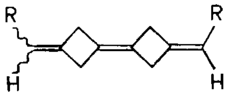
each of the propellanes **1b–f** rearranges to the analogous set of olefins. In case of propellane **1c** one of these latter olefins was characterized as the dimeric compound **6c**[6] presumably formed by an electrophilically catalyzed rearrangement reaction[7].



6

R: see **1**

Both kinds of olefins can be removed almost completely by high-vacuum transfer (**1b, c, e, f**) or low-temperature recrystallization (**1d**), respectively. For example, propellane **1e** was obtained in a purity of approx. 97% (by ^1H NMR; Figure 1) in amounts of several grams. Even though purities that high may be considered satisfactory in low-molecular-weight chemistry, higher purities are generally required for polymer synthesis. Unfortunately, up to now there is no procedure known which allows the preparation of absolutely pure [1.1.1]propellanes on the gram or larger scale[9]. We therefore developed a reliable procedure leading to substituted propellanes in large quantities and purities sufficiently high to achieve clean polymerizations. The key step of this procedure (see Experimental) is the photoinitiated polymerization of the respective propellane which is quenched at low conversion. Still unreacted monomer is then recovered from this mixture by vacuum-transfer techniques for its further use. By this means, presumably olefinic impurities susceptible to radicals are removed successfully, a fact which is recognized immediately. Propellanes **1b–f** treated this way, polymerize spontaneously at room temperature[10], whereas they can be stored at this temperature as long as these olefinic inhibitors are present (see below). The nature of the inhibiting impurities was not investigated.

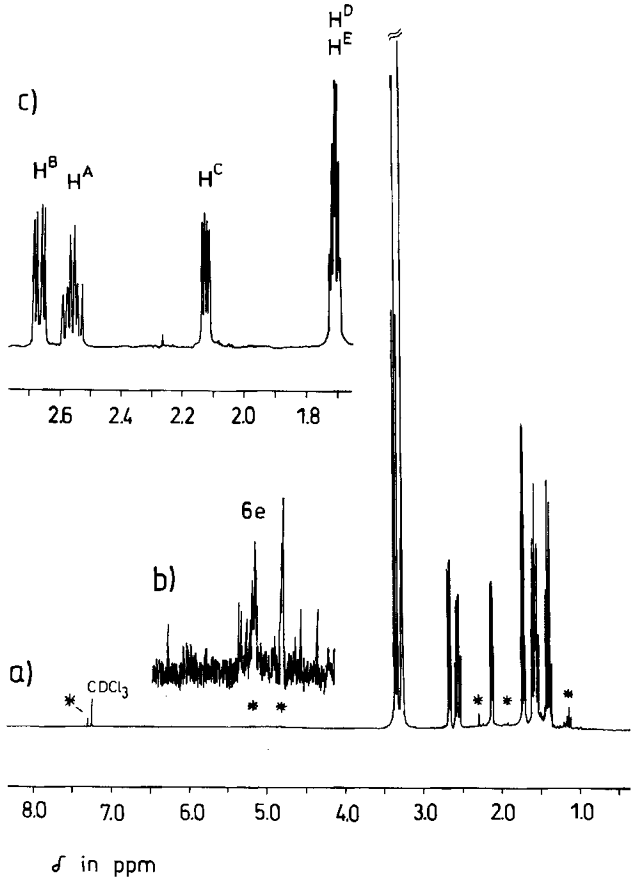


Figure 1. ^1H-NMR spectrum of [1.1.1]propellane **1e** as obtained after purification by high-vacuum transfer (a) with a magnification of the olefinic region (b), and an expansion of the region with the signals of the propellane hydrogen atoms (c); unknown impurities are marked (*)

Propellanes **1b–f** kept under nitrogen can be stored at −40°C. If an inhibitor is present – as is usually the case –, they can even be stored at 5°C as long as traces of electrophiles are suppressed. Best success in this respect was achieved by the additon of about 40% (w/w) triethylamine[11].

For example, propellanes **1c, e** (purity: >95%, inhibiting impurities present) containing this amount of base were kept in ampules sealed with Rotaflo® taps for six weeks at 5°C without any detectable change (^1H NMR).

The structures of the new propellanes were proven by ^1H- and ^{13}C-NMR spectra as well as by the fact that they can be polymerized with formation of the corresponding homopolymers[10]. Particularly informative are the chemical shifts of the carbon atoms of the strained unit which are characteristic for [1.1.1]propellanes[12]. The signals of comparable carbon atoms of the propellanes **1b–f** appear within ±0.5 ppm at the same shift (Table 2) and were assigned according to the literature[4]. The proton signals of comparable hydrogen atoms also absorb at very similar shifts (±0.1 ppm) and show identical coupling patterns (Table 3). The signals were assigned (Figure 1) on the basis of both a COSY experiment using propellane **1c** as a representative example and data from literature[4,13]. The signal of H^D appears as a doublet centered in the middle of the signal of H^E which appears as a doublet of doublets. The coupling constants [Hz] are very similar for all propellanes: $J_{A,C}$ = 4.5, $J_{A,\text{alkyl CH}_2}$ = 7.3, $J_{B,C}$ = 2.3, $J_{B,E}$ = 7.6, $J_{D,E}$ = 1.7.

Table 2. Selected ^{13}C-NMR shifts of the propellanes **1b–f** in $CDCl_3$

	C-1	C-2	C-3	C-4	C-5
1b–f	5.3	91.0	5.3	69.2	71.9

Table 3. Selected ^1H-NMR shifts of the propellanes **1b–f** in $CDCl_3$

	H^A	H^B	H^C	H^D	H^E
1b–f	2.60	2.69	2.16	1.74	1.74

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Experimental

Apparatuses used were as described[14]. 4-Bromobutyl methyl ether and 6-bromohexyl methyl ether were prepared according to literature procedures[15]. All other chemicals were purchased from Fluka or Aldrich Chemical Co.

1. *Synthesis of the Olefins* **4**. – *General Procedure:* A 4-l three-necked flask equipped with mechanical stirrer, dropping funnel and reflux condenser is charged with a mixture of the respective alkyl bromide or methoxyalkyl bromide (0.5 mol), triphenylphosphine [131 g (0.5 mol)], and toluene (100 ml) and heated to reflux. After 3 d, the obtained viscous material is disperged in diethyl ether (1.5 l), and a 1.6 N solution of butyllithium in hexane [315 ml (0.5 mol)] is added slowly. The obtained red mixture is then stirred for 2 h before it is cooled to –70°C and a solution of **3** [63 g (0.5 mol)] in diethyl ether (500 ml) is added such that the temperature does not exceed –55°C. After the addition, the mixture is allowed to warm to room temp. and is then stirred for 1 h. The precipitate formed is recovered by filtration and washed with diethyl ether whereupon the solvent is removed in vacuo.

a) *1-Chloro-2-(chloromethyl)-2-decene* (**4c**): The viscous residue is destilled in high vacuum (0.002 mbar) to yield a colorless oil: 54 g (48%); bp 76°C. Except for the alkyl signals the NMR data are almost identical with those reported for **4b**[3].

$C_{11}H_{20}Cl_2$ (223.2) Calcd. C 59.20 H 9.03 Cl 31.77
Found C 59.06 H 9.12 Cl 31.59

b) *1-Chloro-2-(chloromethyl)-2-tetradecene* (**4d**): The viscous residue is purified by recrystallization from ethanol (400 ml) at –35°C to yield a colorless oil: 54 g (39%). Except for the alkyl signals the NMR data are very similar to those reported for **4b**[3].

$C_{15}H_{28}Cl_2$ (279.3) Calcd. C 64.51 H 10.11 Cl 25.39
Found C 64.35 H 10.12 Cl 24.91

c) *1-Chloro-2-(chlormethyl)-6-methoxy-2-hexene* (**4e**): It is recommended that the phosphonium salt is prepared as described, however, at an internal temperature not exceeding 70°C. The viscous residue is distilled in high vacuum (0.002 mbar) to yield a colorless oil: 38–42 g (38–42%); bp 74°C. – ^{1}H NMR (CDCl$_3$): δ = 1.64 (tt, 2H, 5-H), 2.19 (dt, 2H, 4-H), 3.27 (s, 3H, OCH$_3$), 3.31 (t, 2H, 6-H), 4.15 (s, 2H, CH$_2$Cl), 4.21 (s, 2H, CH$_2$Cl), 5.72 (t, 1H, 3-H). – ^{13}C NMR (CDCl$_3$): δ = 24.4, 28.6 (2 t, C-4, -5), 38.8 (CH$_2$Cl), 47.3 (CH$_2$Cl), 58.4 (OCH$_3$), 71.3 (t, C-6), 133.0 (s, C-2), 135.5 (d, C-3).

$C_8H_{14}Cl_2O$ (197.1) Calcd. C 48.75 H 7.17 Cl 35.97
Found C 48.69 H 7.17 Cl 35.08

d) *1-Chloro-2-(chloromethyl)-6-methoxy-2-octene* (**4f**): The viscous residue is distilled under high vacuum (0.002 mbar) to yield a colorless oil: 38 g (32%); bp 88°C. Except for some of the alkyl signals the NMR spectra are very similar to those of **4e**.

$C_{10}H_{18}Cl_2O$ (225.2) Calcd. C 53.34 H 8.06
Found C 53.22 H 8.16

2. *Synthesis fo the Dibromocarbene Adducts* **5**. – *General Procedure:* To a mixture of the respective olefin **4** (0.25 mol), bromoform (0.50 mol), dichloromethane (70 ml), trimethyl(phenyl)ammonium chloride (1.1 g), and ethanol (1.1 ml) is added under vigorous stirring a 50% (w/w) aqueous solution of NaOH (100 ml). This mixture is stirred for 4 d at room temperature followed by aqueous workup. The organic layer is separated, dried with MgSO$_4$, concentrated in vacuo, and distilled in high vacuum (0.002 mbar) to yield a pale yellow, viscous liquid in yields ranging between 20 and 50%. Unreacted starting material is recovered as the first fraction after removal of the excess bromoform with losses of the order of 10% and can be reused. After three such cycles conversions of up to 80% can be achieved without intermediate workup. Despite various attempts, it was not possible to obtain satisfactory data from elemental analyses for compounds **5e, f**. The C values are too low by about 1.3%.

a) *1,1-Dibromo-2,2-bis(chloromethyl)-3-heptylcyclopropane* (**5c**): Yield: 20–47 g (20–48%); bp 105–108°C (0.002 mbar). Except for the alkyl signals the NMR spectra are very similar to those reported for **5b**[3].

$C_{12}H_{20}Br_2Cl_2$ (395.9) Calcd. C 36.49 H 5.10 Br 40.46 Cl 17.59
Found C 36.66 H 5.11 Br 40.63 Cl 18.03

b) *1,1-Dibromo-2,2-bis(chloromethyl)-3-undecylcyclopropane* (**5d**): The purification by high-vacuum distillation leads to losses of material due to the required high temperatures. It is therefore recommended to purify compound **5c** by crystallization from low-boiling petroleum ether (200ml) at –40°C. Yield: 65 g (57%, after 4 cycles). Except for the alkyl signals the NMR spectra are very similar to those reported for **5b**[3].

$C_{16}H_{28}Br_2Cl_2$ (451.1) Calcd. C 42.60 H 6.26 Br 35.43 Cl 15.72
Found C 42.38 H 6.34 Br 35.35 Cl 15.68

c) *1,1-Dibromo-2,2-bis(chloromethyl)-3-(3'-methoxypropyl)cyclopropane* (**5e**): Yield: 25–35 g (27–38%); bp 104°C (0.002 mbar). – ^{1}H NMR (CDCl$_3$): δ = 1.57–1.75 (m, 5H, 1'-, 2'-, 3-H), 3.29 (s, 3H, OCH$_3$), 3.40 (t, 2H, 3'-H), 3.76–4.00 (m, 4H, CH$_2$Cl). – ^{13}C-NMR (CDCl$_3$): δ = 24.3, 28.0 (2 t, C-1', -2'), 36.7, 39.9 (2 s, C-1, -2), 41.0 (d, C-3), 43.9 (CH$_2$Cl), 49.5 (CH$_2$Cl), 58.5 (OCH$_3$), 71.6 (t, C-3').

d) *1,1-Dibromo-2,2-bis(chloromethyl)-3-methoxypentylcyclopropane* (**5f**): Yield: 27 g (27%); bp 114°C (0.002 mbar). Except for some of the alkyl signals the NMR spectra are very similar to with those of **5e**.

3. *Synthesis and Purification of the [1.1.1]Propellanes* **1c–f**. – *Typical Procedure:* To a solution of **5c** [30 g (76 mmol)] in diethyl ether (100 ml) at –40°C is added of a 1.6 N solution of methyllithium [100 ml (160 mmol)] whereupon the mixture is warmed to room temperature and stirred for 90 min. Then degassed water (100 ml) is added slowly, the resultant layers are separated, and the organic phase is dried with MgSO$_4$. MgSO$_4$ is removed with a Schlenk frit. Most of the diethyl ether is removed in vacuo (12 mbar) at –20°C, remaining traces (^{1}H NMR) are removed in high vacuum (0.002 mbar) at –30°C. Propellane **1c** is then vacuum-transferred at a temperature not exceeding 35°C [30°C (**1e**); 50°C (**1f**)] into a cooled ampule or a flask with a Rotaflo® tap (–78°C) onto triethyl amine [ca. 1 ml (10% w/w)]. Yield (without NEt$_3$): 6.8 g (54%). The purity of this material is typically between 90 and 96% (^{1}H NMR). – It is recommended to purify propellane **1d** not by the described vacuum-transfer technique since the required temperatures favor rearrangement reactions, but rather by low-temperature recrystallization (–40°C) from low-boiling petroleum ether under nitrogen. Typical yields of the propellanes **1c–f** as well as the NMR-spectroscopical data are given in Tables 1–3.

Typical Procedure for Further Purification of [1.1.1]Propellanes: Propellane **1e** [2.5 g (purity 90–96%)], triethylamine (250 mg) and benzophenone (2 mol-%) are placed in a quartz tube. This mixture is irradiated at 10°C with a high-pressure Hg lamp (100 W; light with λ < 290 nm was filtered out) until a conversion of about 10–15% is reached (ca. 90 min). The remaining propellane together with the triethylamine is transferred in high vacuum (0.002 mbar) into an ampule or a flask for its further use. Propellanes treated this way cannot be stored at room temperature and have to be used immediately. Otherwise they start polymerizing even without addition of an initiator[10].

CAS Registry Numbers

1b: 119298-85-0 / **1c**: 131042-19-8 / **1d**: 131042-20-1 / **1e**: 131042-21-2 / **1f**: 131042-22-3 / **3**: 534-07-6 / **4b**: 119326-88-4 / **4c**: 131042-12-1 / **4d**: 131042-13-2 / **4e**: 131042-14-3 / **4f**: 131042-15-4 / **5b**: 119326-89-5 / **5c**: 131042-16-5 / **5d**: 131042-17-6 / **5e**: 131065-60-6 / **5f**: 131042-18-7 / $Br(CH_2)_7CH_3$: 111-83-1 / $Br(CH_2)_{11}CH_3$: 143-15-7 / $Br(CH_2)_4OCH_3$: 4457-67-4 / $Br(CH_2)_6OCH_3$: 50592-87-5

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[6] **6c**: ^{1}H NMR ($CDCl_3$): $\delta = 0.87$ (t, 6H, CH_3), 1.10–1.50 (m, 20H, alkyl H), 1.89 (m, 4H, Ch_2), 3.14 (br. s, 8H, CH_2), 5.23 (t, 2H, CH). – ^{13}C NMR ($CDCl_3$): $\delta = 14.07-31.90$ (alkyl C), 36.12, 37.64 (2 t, CH_2), 122.14 (d, CH), 125.17, 133.71 (2 s). – Both NMR spectra show one set of lines each, even though it is reasonable to assume that two isomers are formed (*cisoid* or *transoid* arrangement of the alkyl chains). We assume that besides compounds of type **6** dimers are also formed which carry the alkyl chains at the four-membered ring(s). – MS (70 eV): m/z (%) = 328 (18) [M^+].

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