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SYNTHESIS OF 1-ALKYNYLBICYCLO[1.1.1]PENTANES

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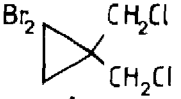
Summary: Radical chain addition of 1,1,1-trichloroethane and, respectively, 1,1-dichloroethane to [1.1.1]-propellane led to bicyclo[1.1.1]pentane derivatives **5** and **6** which could be converted by sodium amide into the acetylenes **9** and **10**. Glaser type coupling afforded the diacetylenes **12** and **13**.

Since [1.1.1]propellane **1**[1] has become an easily accessible compound,[2] its chemistry has been investigated intensively.[3] Radical chain addition reactions to **1** and its derivatives lead to bridgehead substituted bicyclo[1.1.1]pentanes of type **2**. In some cases, formation of telomers of type **3** has also been observed as a major reaction path, and polymerization of **1** has been achieved, too.[3g,4] Kaszynski and Michl proposed the name "[*n*]staffanes" for **3** and they have pointed out the importance of **1** as a building block for the "construction of molecular-size mechanical structures".[3g]


1

2

3



4

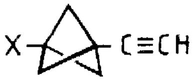
5

6

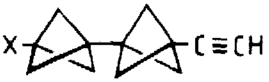
7

5,6,7	R	X
a	CCl_2Me	Cl
b	CCl_2Me	H

8

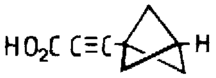


9

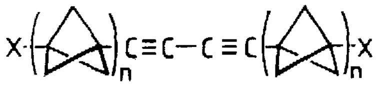


10

9,10	X
a	Cl
b	H



11



12: n = 1, X = Cl
13: n = 2, X = H

For the synthesis of rigid molecular systems, the combination of bicyclo[1.1.1]pentane and acetylene subunits could lead to interesting molecules. We report here on the synthesis of alkynyl-substituted bicyclo[1.1.1]pentanes starting from **1**. The procedure is based on the observation that a bridged derivative of **1** reacted with some selected alkyl halides under radical chain initiation affording 1-halo-3-alkyl-bicyclo[1.1.1]pentanes.[3e] When **1**, generated from the tetrahalide **4** with lithium according to ref. [2b], was irradiated with a 150-W high-pressure mercury lamp in a solution of 1,1,1-trichloroethane at -30°C for 24 h, the bicyclo[1.1.1]pentanes **5a** and **6a** were isolated in yields given in Table 1. Not unexpectedly, **1** and 1,1-dichloroethane under the same reaction conditions led to the formation of **5b**, **6b** and even a small portion of **7b**. In this case, the type **8** radical abstracts a hydrogen from 1,1-dichloroethane rather than a chlorine atom. It should be noted that the yields of Table 1 are based on the tetrahalide **4**. According to our previous results, the yields of **1** when generated from **4** were between 25% and 38%.[2b] As the sum of the yields of **5a** and **6a** and, respectively, **5b**, **6b** and **7b** is within that same range (see Table 1), we conclude that practically all of the propellane **1** is converted into product. This is further verified by the photoaddition of methyl iodide to **1**, which gave rise to a 42% yield of **5c**.

Table 1. Yields of the Bicyclo[1.1.1]pentanes **5**, **6** and **7**$^{a)}$ and Alkynes **9** and **10**

	X	R	**5**	**6**	**7**	Σ **5**, **6**, **7**	**9**	**10**
a	Cl	CCl_2CH_3	18	18	-	36	71	58
b	H	CCl_2CH_3	21	14	2	37	32$^{b)}$	85

a) Yields based on **4**. Ratio of **1** to halides at the beginning of irradiation approximately 1:100.

b) Isolated yield; the yield of **9b** as determined by ^{1}H NMR spectroscopy was 80%.

The structures of **5**, **6** and **7** are in accordance with analytical and spectrosopic data, a selection of which is given in Table 2.

The di- and trihalides **5** and **6** were suitable precursors for the formation of the corresponding alkynes **9** and **10**, which were obtained from the halides by treatment with sodium amide in liquid ammonia,[5] followed by addition of ammonium chloride and evaporation of ammonia. In one dehydrohalogenation experiment of **5b**, carbon dioxide was bubbled through the reaction mixture prior to the addition of ammonium chloride, which led to the formation of acetylenic acid **11** in 16% yield. The yields of the alkynes **9** and **10** are given in Table 1. **9b** is a highly volatile liquid, and although its yield as determined by ^{1}H NMR spectroscopy was 80%, the greater part of the material was lost in the workup process.

Alkynes **9a** and **10b** were oxidized in yields of 69% and 50% to the diacetylenes **12** and **13** by following a modification of the Glaser coupling reaction, using stochiometric amounts of CuCl and N,N'-tetramethylethylenediamine.[6] Again, the structures of the alkynes **9** - **13** are based on analytical and spectral data, some of which are collected in Table 2.

Table 2. NMR Data (in $CDCl_3$) of **5a**, **b**, **6a**, **b**, **9a**, **b**, **10a**, **b**, **12**, and **13**

5a:	m.p. 54-57°C; ^{1}H NMR: δ 2.09 (s, 3 H), 2.25 (s, 6 H); ^{13}C NMR: δ 34.53 (q), 47.55 (s), 48.31 (s), 55.31 (m), 85.99 (s).
5b:	m.p. 30°C; ^{1}H NMR: δ 1.90 (s, 6 H), 2.05 (s, 3 H), 2.55 (s, 1 H); ^{13}C NMR: 24.55 (d), 33.81 (q), 48.14 (m, CH_2) 53.16 (m, CH), 87.97 (s).
6a:	m.p. 125-128°C; ^{1}H NMR: δ 1.75 (s, 6 H), 2.03 (s, 6 H), 2.05 (s, 3 H); ^{13}C NMR δ 33.86 (q), 35.20 (s), 36.89 (s), 47.95 (m, CH_2), 48.31 (s), 48.37 (s), 56.28 (m, CH_2), 87.96 (s).
6b:	m.p. 64.5°C; ^{1}H NMR: δ 1.66 (s, 6 H), 1.69 (s, 6 H), 2.04 (s, 3 H), 2.41 (s, 1 H); ^{13}C NMR: δ 26.72 (d), 33.92 (q), 36.53 (s), 44.31 (s), 47.37 (m, CH_2), 47.98 (s), 49.22 (m, CH_2), 88.66 (s).
9a:	m.p. 34-35°C; ^{1}H NMR: δ 2.13 (s, 1 H), 2.38 (s, 6 H); ^{13}C NMR: δ 26.35 (s), 48.37 (s), 60.73 (m, CH_2), 69.63 (d), 79.45 (s).
9b:	^{1}H NMR: δ 2.01 (s, 1 H), 2.08 (s, 6 H), 2.24 (s, 1 H); ^{13}C NMR: δ 29.78 (d), 32.37 (s), 54.21 (t), 66.39 (d), 83.14 (s).
10a:	m.p. 162°C; ^{1}H NMR: δ 1.91 (s, 6 H), 1.98 (s, 6 H), 2.06 (s, 1 H); ^{13}C NMR: δ 27.29 (s), 36.98 (s), 40.16 (s), 48.25 (s), 54.01 (m, CH_2), 56.28 (m, CH_2), 67.97 (d), 88.84 (s).
10b:	m.p.63-64°C; ^{1}H NMR: δ 1.63 (s, 6 H), 1.90 (s, 6 H), 2.08 (s, 1 H), 2.38 (s, 1 H); ^{13} C NMR: δ 26.53 (d), 42.07 (s), 44.48 (s), 47.35 (s), 49.25 (m, CH_2), 53.54 (m, CH_2), 67.41 (d), 83.72 (s).
12:	dec. 221°C; ^{1}H NMR: δ 2.38 (s); ^{13}C NMR: δ 26.87 (s), 48.26 (s), 61.06 (m, CH_2), 65.82 (s), 74.06 (s).
13:	dec. 230°C; 1.63 (s, 12 H), 1.89 (s, 12 H), 2.38 (s, 2 H).

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