TETRACYCLO[5.1.0.0^{1,6}.0^{2,7}]OCTANE: SOME UNEXPECTED ADDITION REACTIONS AND A NEW SYNTHESIS[†] Johannes Belzner and Günter Szeimies^{*} Institut für Organische Chemie der Universität München Karlstrasse 23, D-8000 München 2, Germany

<u>Summary</u>: Besides carbon tetrachloride and tri-n-butyltin hydride, alkyl halides and even diethyl ether could be added to the central carbon-carbon bond of the title compound $\frac{2}{2}$ via radical chain processes. Allylic carbone cyclization of $\frac{14}{2}$ leading to $\frac{2}{2}$ has been established as a new route to the [1.1.1]propellane framework.

Recently Wiberg has communicated the results of radical chain addition reactions to [1.1.1]propellane $\underline{1}$, 1,2 including carbon tetrachloride, chloroform, acetaldehyde, cyanogen bromide, diphenyl disulfide, iodine, and *tert*-butyl hypochlorite, which all proceeded by cleavage of the central bond of $\underline{1}$. 3,4 We wish to report on some addition reactions to the [1.1.1]rivative $\underline{2}$, 2 which seem to take place in the same fashion.



Whereas solutions of $\underline{2}$ in ether remained unchanged in the absence of oxygen over periods of several days, $\underline{2}$ was consumed within 47 h upon irradiation with a mercury high pressure lamp in a quartz vessel, and the ether adduct $\underline{3}\underline{a}$ was formed in 13% yield, accompanied by a 12% yield of $\underline{4}\underline{a}$, by a 5% yield of $\underline{5}\underline{a}$ and by polymeric material. It should be noted that the intended synthesis of

the [2.1.1]propellane $\underline{\delta}$ in ether at room temperature led to the corresponding ether adduct of $\underline{\delta}$ as the main product, even when daylight was excluded.⁵

As expected, a solution of $\underline{2}$ in carbon tetrachloride was quickly converted into $\underline{3}\underline{b}$ in 54% yield, along with a 4% yield of $\underline{4}\underline{b}$. When $\underline{2}$ was dissolved in bromochloromethane, a slow reaction took place affording a 31% yield of $\underline{3}\underline{c}$.

To our surprise, $\underline{2}$ also reacted with monohalides: after 12 h at 40°C, $\underline{2}$ and iodomethane gave rise to a 25% yield of $\underline{3}\underline{d}$. Probably caused by traces of unknown electrophiles, $\underline{3}\underline{d}$ showed a pronounced tendency to rearrange in a poorly controlled reaction to an isomer, the structure of which could be $\underline{7}\underline{a}$ or \underline{b} .⁶ A sole product ($\underline{7}\underline{c}$ or \underline{d}) was isolated in 35% yield from the reaction of ethyl iodide and $\underline{2}$ after 17 h at 50°C and distillative workup. When a solution of $\underline{2}$ in *tert*-butyl bromide, sealed in an NMR tube, was kept at 20°C for 72 h, no decrease in the concentration of $\underline{2}$ was observed. However, when this experiment was repeated at 80°C with a trace of dibenzoyl peroxide, $\underline{3}\underline{e}$ was formed in 36% yield. This bromide could be distilled without rearranging to the isomer of type $\underline{7}$. Dibenzoyl peroxide was also added as a radical chain initiator for the reaction of $\underline{2}$ with benzyl bromide at 80°C, which afforded a 50% yield of $\underline{3}\underline{f}$. $\underline{3}\underline{f}$ showed a slight propensity towards isomerization to $\underline{7}$.

Tri-*n*-butyltin hydride was added to the central bond of $\underline{2}$ in ether at room temperature without initiation, giving rise to a 72% yield of $\underline{3\underline{g}}$.⁷ The conversion of the propellane $\underline{2}$ into the tricyclic hydrocarbon $\underline{3\underline{h}}$ was achieved in 63% yield by refluxing a solution of $\underline{2}$ in ethylamine in the presence of dissolved lithium for 14 h, followed by aqueous workup.



When dichlorocarbene was generated from chloroform and potassium *text*-butoxide in pentane in the presence of $\underline{2}$, a 1.0:1.1 mixture of $\underline{8a}$ and $\underline{2a}$ was isolated in a total yield of 34%, along with an 11% yield of the 2:1 adduct $\underline{10a}$. Similar results were obtained, when bromoform was used instead of chloroform ($\underline{8b}$: $\underline{2b}$: $\underline{10b}$ = 1.0:1.4:0.3).

Whereas $\underline{1}$ and iodine afforded $\underline{11}$,^{3,8} which did not show any tendency to isomerize to $\underline{12}$, the reaction of $\underline{2}$ with one equiv. of iodine in $C_6 D_6$ led to $\underline{7e}$ as the sole product in 77% yield. Monitoring this reaction by ¹H NMR spectroscopy did not provide any evidence for the intermediacy of $\underline{3i}$. At present it is not clear, if $\underline{7e}$ is the result of a fast ionic rearrangement of $\underline{3i}$, which could have been formed by a radical chain process, or if $\underline{7e}$ is the outcome of an ionic reaction of iodine with $\underline{2}$.

The dijodide $\underline{\underline{7}e}$ opened a new synthesis of the [1.1.1]propellane framework. When treated with methyllithium in ether at -30°C, $\underline{\underline{7}e}$ was converted into $\underline{\underline{2}}$ in 43% yield. In addition, an 18% yield



of $\underline{3}\underline{d}$, the reaction product of methyl iodide with $\underline{2}$, was also isolated. Reaction intermediates on the route from $\underline{7}\underline{e}$ to $\underline{2}$ could be the carbenoid $\underline{1}\underline{3}$ and the carbene $\underline{1}\underline{4}$, the intramolecular cycloaddition of which would account for the formation of $\underline{2}$.⁹ Related cyclization reactions of allylcarbene derivatives have previously proved to be successful in the synthesis of [3.1.1]- and [4.1.1]propellanes.^{10,11,12}

The structures of the new compounds mentioned in this article are based mainly on the NMR spectra, a selection of which is given in Table I.

<u>Acknowledgement</u>: This work was supported by the <u>Deutsche Forschungsgemeinschaft</u> and by the <u>Fonds</u> der Chemischen Industrie.

References and Notes:

- † Dedicated to Professor Kenneth B. Wiberg on the occasion of his 60th birthday.
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- 7. The three-bond coupling constant of 3g between ¹³C of position 7 and ¹¹⁹Sn showed a remarkably high value of 129 Hz.
- 8. We have repeated the reaction of $\underline{1}$ with iodine and fully confirm the results of ref. 3.
- 9. As <u>7e</u> was obtained from <u>2</u> by reaction with iodine, the regeneration of <u>2</u> from <u>7e</u> might seem to be of limited value as a new route to the [1.1.1]propellane framework. However, the use-fulness of the carbene path to [1.1.1]propellanes was demonstrated by the synthesis of <u>2</u> and, respectively, <u>i</u> from <u>ii</u> on reaction with lithium diisopropylamide, and, respectively, from <u>iii</u> on reaction with butyllithium: W. Schmid, B. Gareiß and G. Szeimies, unpublished.



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Table I. NMR Data of $\underline{3a}$, $\underline{3e}$, $\underline{3g}$, $\underline{3h}$, $\underline{7a}$ or \underline{b} , $\underline{7e}$, $\underline{8a}$, and $\underline{9a}$

- $\underline{\underline{3}}_{a} = {}^{1}\text{H NMR (CDCL}_{3}): \delta 1.02 (d, J = 6 \text{ Hz}, 3 \text{ H}), 1.17 (t, J = 6 \text{ Hz}, 3 \text{ H}), 1.30 1.75 (m, 7 \text{ H}), 1.45 (broad s, 2 \text{ H}), 2.23 2.50 (m, 1 \text{ H}), 2.30 (s, 1 \text{ H}), 3.43 (q, J = 6 \text{ Hz}, 1 \text{ H}), 3.45 (q, J = 6 \text{ Hz}, 2 \text{ H}).$ ${}^{13}\text{c NMR (CDCL}_{3}): \delta 15.75 (q), 16.78 (q), 18.60 (t), 21.57 (t, 2 \text{ C}), 30.53 (d), 42.89 (t), 49.80 (s), 54.94 (d), 55.91 (d), 64.61 (t), 71.45 (d).$
- $\underline{\underline{3}}_{\underline{6}} = {}^{1}\text{H NMR} (CDCL_{3}): \delta 0.95 (s, 9 \text{ H}), 1.53 1.83 (m, 6 \text{ H}), 1.82 (s, 2 \text{ H}), 2.53 (m, 2 \text{ H}).$ ${}^{13}\text{c NMR} (CDCL_{3}): \delta 14.42 (t), 19.78 (t, 2 \text{ C}), 28.08 (q), 32.56 (s), 44.59 (s), 50.28 (s),$ 53.19 (t), 61.58 (d, 2 C).
- $\underline{\underline{3}}_{g} \qquad {}^{1}\text{H NMR (CDCL}_{3}): \quad \delta \ 0.68 \ \ 1.94 \ (m, \ 33 \ \text{H}), \ 1.60 \ (s, \ 2 \ \text{H}), \ 2.52 \ (mc, \ 2 \ \text{H}), \ 2.69 \ (s, \ 1 \ \text{H}). \\ \\ \underline{1^{3}\text{C NMR (CDCL}_{3}): \quad \delta \ 9.09 \ (t, \ {}^{1}\text{J}[^{119}\text{Sn}^{13}\text{C}] = \ 313 \ \text{Hz}, \ 3 \ \text{C}), \ 13.78 \ (q, \ 3 \ \text{C}), \ 19.26 \ (t), \ 24.47 \\ \\ (t, \ 2 \ \text{C}), \ 27.65 \ (t, \ 3 \ \text{C}), \ 29.56 \ (t, \ 3 \ \text{C}), \ 40.19 \ (d, \ {}^{3}\text{J}[^{119}\text{Sn}^{13}\text{C}] = \ 129 \ \text{Hz}), \ 41.50 \ (s, \ {}^{1}\text{J}[^{119}\text{Sn}^{13}\text{C}] = \ 281 \ \text{Hz}), \ 48.98 \ (t), \ 62.27 \ (d, \ 2 \ \text{C}). \\ \end{array}$
- $\underline{\underline{3h}} \qquad {}^{1}\text{H NMR (CDCL}_{3}): \quad \delta \ 1.44 \ \ 1.81 \ (\text{m, 6 H}), \ 1.49 \ (\text{s, 2 H}), \ 2.29 \ (\text{s, 2 H}), \ 2.43 \ (\text{mc, 2 H}). \\ \\ \underline{\underline{3h}} \qquad {}^{13}\text{C NMR (CDCL}_{3}): \quad \delta \ 19.32 \ (\text{t}), \ 21.67 \ (\text{t, 2 C}), \ 36.62 \ (\text{d, }^{1}\text{J}[{}^{13}\text{C}^{1}\text{H}] \ = \ 161 \ \text{Hz}, \ 2 \ \text{C}), \ 44.19 \\ \\ (\text{t, }^{1}\text{J}[{}^{13}\text{C}^{1}\text{H}] \ = \ 143 \ \text{Hz}), \ 47.25 \ (\text{d, }^{1}\text{J}[{}^{13}\text{C}^{1}\text{H}] \ = \ 147 \ \text{Hz}, \ 2 \ \text{C}). \end{cases}$
- $\underline{\underline{Za}} \underline{\underline{D}} = {}^{1}\text{H} \text{ NMR} (C_{6}D_{6}); \qquad \delta \text{ 0.63 } -2.03 \text{ (m, 6 H), 1.74 (s, 3 H), 2.60 (d, J = 14 Hz, 1 H), 3.49 (m, 1 H), 3.58 (d, J = 14 Hz, 1 H), 5.11 (m, 1 H).$ $<math>{}^{13}\text{C} \text{ NMR} (C_{6}D_{6}); \qquad \delta \text{ 20.38 (t), 21.63 (t), 25.05 (t), 29.29 (q), 33.47 (s), 54.64 (t), 60.15 (d), 116.70 (d), 137.30 (s). }$
- $\underline{\underline{7}}_{\underline{P}} = {}^{1}\text{H NMR (CCL}_{4}): \quad \delta \ 0.97 \ \ 2.21 \ (\text{m, 6 H}), \ 3.13 \ \ 3.50 \ (\text{m, 1 H}), \ 3.73 \ (\text{d, J} = 15 \ \text{Hz}, 1 \ \text{H}), \\ 4.45 \ (\text{d, J} = 15 \ \text{Hz}, 1 \ \text{H}), \ 5.50 \ (\text{m, 1 H}). \\ {}^{13}\text{C NMR (CDCL}_{3}): \ \delta \ -3.82 \ (\text{s}), \ 19.20 \ (\text{t}), \ 24.69 \ (\text{t}), \ 30.83 \ (\text{t}), \ 63.64 \ (\text{t}), \ 66.06 \ (\text{d}), \\ 118.76 \ (\text{d}), \ 134.39 \ (\text{s}). \end{cases}$
- <u>Sea</u> ¹H NMR (CDCL₃): δ 1.45 2.32 (m, 6 H), 3.40 (mc, 2 H), 4.76 (s, 2 H). ¹³C NMR (CDCL₃): δ 17.45 (t), 34.29 (t, 2 C), 52.37 (d, 2 C), 99.95 (t), 105.81 (s), 141.93 (s), 147.87 (s).
- $\underline{\underline{22}} = {}^{1}\text{H NMR (CDCL}_{3}): \delta 1.45 2.30 (m, 6 H), 3.28 (m, 3 H), 5.40 (m, 1 H). \\ {}^{13}\text{C NMR (CDCL}_{3}): \delta 20.81 (t), 25.05 (t), 25.20 (t), 40.53 (t), 49.34 (d), 111.15 (s), \\ 116.82 (d), 132.97 (s), 139.36 (s).$

(Received in Germany 25 March 1987)

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