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## 232. The Reaction of Norbornene with Lead Tetraacetate and Thallium Trinitrate

Preliminary Communication

by Jacques Kagan

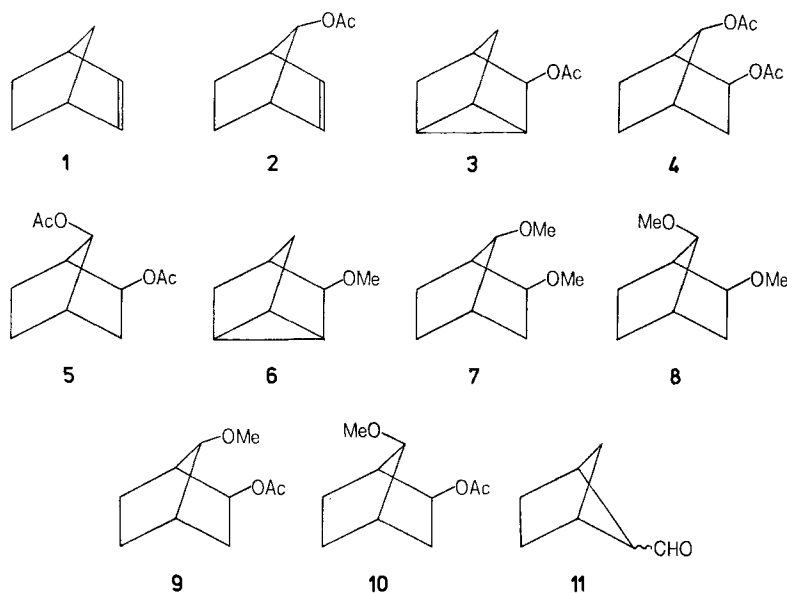
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(24. V. 72)

*Summary.* The reaction of norbornene with lead tetraacetate is found to be much more complex than previously reported. In acetic acid and in benzene, the *syn*-7-norbornenyl, 3-nortricycyl, and *syn* and *anti*-7-acetoxy-*exo*-2-norbornyl acetates were characterized. In methanol, the isolated products represented most of those expected from the competition of methanol and acetate in the neutralization of the intermediate carbocations. The reaction of norbornene with thallium trinitrate in the above solvents yielded very complex mixtures besides the above mentioned products which were formed in about 50% yield.

The reaction of norbornene (**1**) with lead tetraacetate (LTA) was first described by *Alder, Flock & Wirtz* [1]. In acetic acid, they isolated only *exo*-2-*syn*-7-diacetoxynorbornane (**4**) in 85% yield. In benzene, they reported **4** (59%), 3-acetoxy-nortricyclane (**3**, 26%) and one unspecified isomer of 7-acetoxynorbornene (5%). In methanol, finally, they reported *exo*-2-*syn*-7-dimethoxynorbornane (**7**, 43%), 3-methoxynortricyclane (**6**, 4%) and *exo*-2-acetoxy-*syn*-7-methoxynorbornane (**9**, 30%). These results have not been questioned, except in their mechanistic interpretation [2]. The above procedure may even have been utilized for providing an 'authentic' sample of **7** needed in the structure determination of a rearrangement product of 2-chloro-2,3-epoxy-norbornene [**3**]<sup>1</sup>).

<sup>1</sup>) In this work the authors reached stereochemical conclusions by comparing one transformation product with **7**. It is not clear whether they used a sample prepared according to [1], as stated in their text, or according to [4] as indicated in their experimental. Regardless, they found their diacetate **4** to be contaminated by **5** and by another minor product (which we also observed), and it is therefore most likely that their sample of **7** was also contaminated with **8**. This is further suggested by their NMR. spectrum, which resembles that of a mixture of **7** and **8** near 3.5 ppm.



The reaction of **1** with lead tetra acetate at 15° was reinvestigated, and the results are summarized in Table 1.

Table 1. *The reaction of norbornene with LTA*

(The yields are obtained from the GLC. measurements and are based on reacted **1**)

Solvent	Products (% yield)
Acetic acid	<b>2</b> (1), <b>3</b> (11), <b>4</b> (59), <b>5</b> (27)
Benzene	<b>2</b> (8), <b>3</b> (21), <b>4</b> (55), <b>5</b> (6)
Methanol	<b>4</b> (tr), <b>5</b> (tr), <b>6</b> (2), <b>7</b> (31), <b>8</b> (21), <b>9</b> (46), <b>10</b> (tr)

*Alder, Flock & Wirtz* separated their reaction products by distillation, but the isomers **2** and **3**, **4** and **5**, **7** and **8** and **9** and **10** could not be separated by this method. However, these products were easily detected and separated by GLC. using polar stationary phases such as XE-60 or OF-1. The structural assignments (Table 2) are based on the NMR. spectra of the pure products, isolated by preparative GLC. The spectrum of **2** was available for comparison [5], and the assignments for the three *syn-anti* pairs were based on the deshielding of the C(7) proton by the oxygenated *exo*-2-substituent in the *anti* with respect to the *syn* isomer. Compound **10** was not actually isolated, but its presence was inferred from a small GLC. peak, barely resolved from that of **9**, and by the NMR. of this product which showed a minor impurity with a C(7) proton as a broad singlet at 3.65 ppm, 0.15 ppm downfield from that of **9**, as expected from the *syn*-7-proton of **10**.

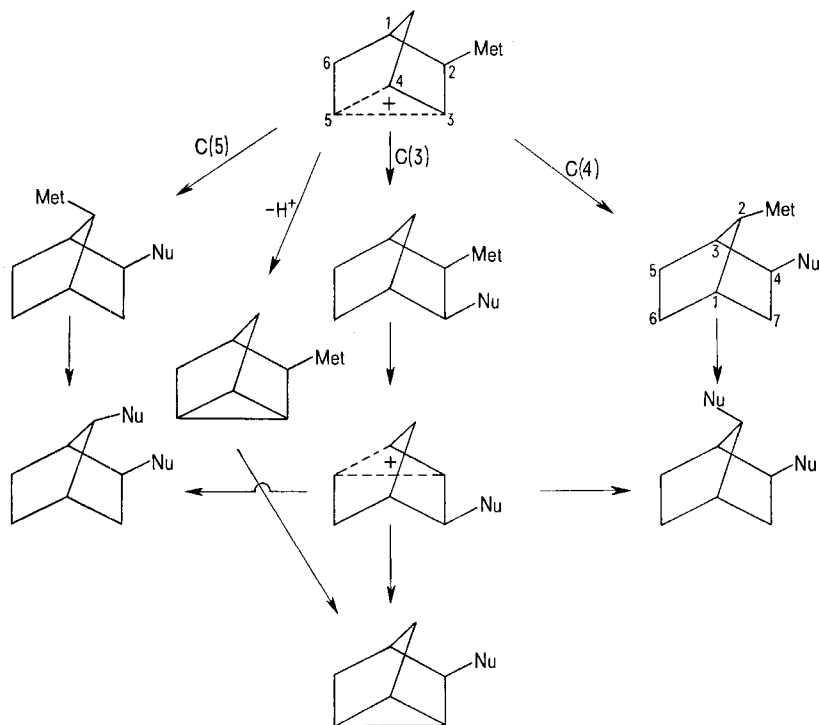
The product distribution in methanol indicated that the solvent (the better nucleophile) had competed with the acetate ion. The formation of **2** and **3**, as well as that of the 7-acetoxy and 7-methoxy-2-norbornenes was therefore expected. But if formed

at all, these were present in very small amounts, and a more refined GLC. analysis is needed in order to clarify this point.

The observation that the reaction of **1** with LTA led predominantly to a mixture of *exo*-2-*syn*-7 and *exo*-2-*anti*-7 disubstituted norbornanes has an analogy in the reaction of **1** with peroxy acids, which also was proved to give the corresponding isomeric glycols [3] [6].

The oxythallation reaction of substituted norbornenes is of current interest [7] and **1** itself has been treated with thallium triacetate by *Pande & Winstein* in 1964, yielding **3**, **4** and **5** in unspecified yields [8]. Thallium trinitrate is now much preferred for oxythallation reactions, since it reacts considerably faster with double bonds [9].

When **1** was treated with thallium trinitrate<sup>2)</sup> either in acetic acid or in methanol, the products described above for the reaction of **1** with these solvents were observed in similar ratios. The combined yield of these products in each case was about 50%, the other half of the reaction mixture consisting of a dozen components. Unlike the quantitative conversion of cyclohexene into cyclopentanecarbaldehyde reported with this reagent [9], there was no sign of ring contraction to a bicyclo [2.1.1] hexane-carbaldehyde (**11**) having taken place, since no carbonyl absorption could be detected by infrared analysis of the crude reaction mixture in aqueous or anhydrous methanol, even after treatment with aqueous acid in order to hydrolyse the eventual acetal of **11**.



The oxythallation-demetallation reactions of **1**

Met:  $\text{Pb}(\text{OAc})_3$  or  $\text{Tl}(\text{NO}_3)_3$ ; Nu: the nucleophile, OAc or  $\text{OCH}_3$

<sup>2)</sup> This experiment was suggested by Prof. C. W. Jefford.

Table 2. NMR. spectra in  $CCl_4$  of the reaction products from **1**  
br: broad, m: multiplet

Compound	H—C(2)	H—C(7)	OCH <sub>3</sub>	OCOCH <sub>3</sub>	H—C(1)	H—C(4)	Others
<b>2</b>	5.98 (H <sub>2</sub> +H <sub>3</sub> )	4.42		1.92	~2.93br		0.9–2.2
<b>3</b>	4.67			1.98			1.1–2.0
<b>4</b>	4.70 <sup>m</sup>	4.60		1.98	2.3br	2.5br	1.0–2.2
<b>5</b>	4.60 <sup>m</sup>	4.90		2.0	~2.3br		1.0–2.2
<b>6</b>	3.40		3.26				1.0–2.0
<b>7</b>	~3.15	3.45	3.15		2.15br	2.32br	0.9–2.0
<b>8</b>	~3.15	3.67	3.17			2.0–2.4	0.9–2.0
			3.12				
<b>9</b>	4.60 <sup>m</sup>	3.50	3.24	1.94	2.17br	2.33br	0.9–2.0

A mechanism accounting for the observed products in the reaction of **1** with lead tetra acetate and thallium trinitrate is presented in Scheme. It assumes non-classical norbornyl carbonium ions intermediates [10].

The identification of all the products formed in the reactions of **1** with lead tetra acetate and thallium trinitrate will be completed and the results incorporated in the full account of this work.

The hospitality of the Department of Organic Chemistry, University of Geneva, the generosity of Prof. C. W. Jefford, who spared valuable laboratory space and supplies, and the discussions with Dr. M. H. Laffer are gratefully acknowledged.

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### 233. $\sigma$ , $\pi$ -Isomerisierungen von Monohetero- $\sigma$ -bishomobenzol-Derivaten

Vorläufige Mitteilung<sup>1)</sup>

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(23. VI. 72)

*Summary.* The *cis*-oxa- (**13a–d**) and -aza- $\sigma$ -bishomobenzene (**13e**) derivatives have been synthesized; they are sufficiently stable to be isolated in pure form. On heating, **13a–e** are easily isomerized into the  $\pi$ -bishomobenzene analogues **14a–e**, the processes **13a**  $\rightleftharpoons$  **14a**, **13b**  $\rightleftharpoons$  **14b**

<sup>1)</sup> Eine ausführliche Mitteilung soll in Helv. erscheinen.