

## Pyrolysis of Three Acetates of Methylbicyclo[2.2.1]heptan-2-ols and the Parent Alcohols

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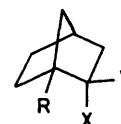
The acetates of *exo*-2-methyl-*endo*-bicyclo[2.2.1]heptan-2-ol, *endo*-2-methyl-*exo*-bicyclo[2.2.1]heptan-2-ol, and 1-methyl-*exo*-bicyclo[2.2.1]heptan-2-ol together the parent alcohols have been pyrolysed at several temperatures and the product distribution determined. The mechanism and direction of elimination in relation to structure are discussed qualitatively. The formation of the principal products is consistent with a concerted elimination involving a six-membered cyclic transition state. Wagner–Meerwein rearrangement occurs as a competing reaction in cases where the formation of a tertiary structure is possible at the expense of a secondary one. In the case studied a two-step reaction is considerably faster than direct pyrolysis of the secondary structure.

Ester pyrolysis has been much studied for decades and there is general agreement about its mechanism.<sup>1–3</sup> The rearrangement products formed in the pyrolysis of bicyclic esters and related compounds cannot however be explained as such by the normal mechanism. According to Emovon,<sup>4</sup> in the pyrolysis of bornyl and isobornyl acetates the rearrangement products, tricyclene and camphene, are formed through a quasi-non-classical ion transition state. Herndon and Manion<sup>5</sup> questioned these results because Emovon had not observed the decomposition of bornylene by a retro-Diels–Alder reaction. They believed that the rearrangement products might be the products of reactions other than the gas-phase unimolecular pyrolysis. According to Sato *et al.*<sup>6</sup> the pyrolysis of the above mentioned acetates may take place through a stepwise reaction. Chuchani *et al.*<sup>7</sup> examined the pyrolysis of isobornyl acetate and found that the rearrangement products resulted from the isomerization of bornylene, the primary product. Holmes *et al.*<sup>8</sup> pyrolysed *exo*-2-norbornyl chloride using compounds labelled with deuterium. A net *trans*-elimination mechanism was unambiguously demonstrated to be the case. They did not notice Wagner–Meerwein rearrangement or any other isomerization of the pyrolysis products, norbornene and nortricyclene, to each other. All the above mentioned studies have been made using a static seasoned reactor except for Sato's group, who used a flow system at reduced pressure. Moreover, Taylor<sup>3</sup> has suggested that the rearrangement products might be formed by a two-step reaction so that Wagner–Meerwein rearrangement takes place before pyrolysis. Wertz and Allinger<sup>9</sup> think that the rearrangement products are explained by ester pyrolysis through surface catalysis.

In connection with our explorative work on the use of some industrially important terpene derivatives pyrolysis of related bicyclic esters and alcohols was studied. Here we report the results of the pyrolysis of the acetates of *exo*-2-methyl-*endo*-bicyclo[2.2.1]heptan-2-ol (1), *endo*-2-methyl-*exo*-bicyclo[2.2.1]heptan-2-ol (2), and 1-methyl-*exo*-bicyclo[2.2.1]heptan-2-ol (3). We believe they give new information about rearrangement reactions in connection with pyrolysis. The reactions of the corresponding alcohols (4)–(6) were examined for comparison. In the acid-catalysed treatment of each of these alcohols an equilibrium mixture is formed in which the 1-methyl derivative (6) is the main product,<sup>10,11</sup> although its formation is very slow.

### Results and Discussion

The studied compounds were pyrolysed, by taking them through a heated quartz tube filled with quartz helices, in the



	R	X	Y
(1)	H	OAc	Me
(2)	H	Me	OAc
(3)	Me	H	OAc
(4)	H	OH	Me
(5)	H	Me	OH
(6)	Me	H	OH

gas phase at reduced pressure. In these circumstances acetates (1)–(3) gave acetic acid and a mixture of hydrocarbons. These hydrocarbons were in all the cases 1-methyltricyclo[2.2.1.0<sup>2,6</sup>]heptane (7), 2-methylbicyclo[2.2.1]hept-2-ene (8), 2-methylenebicyclo[2.2.1]heptane (9), and a mixture of methylcyclopentadienes. The ethene formed was not analysed. In addition, acetate (3) gave small quantities of 1-methylbicyclo[2.2.1]hept-2-ene (10). No tar-like products were found. The results are presented in Table 1. The results of the pyrolysis of the corresponding alcohols are presented in Table 2. The hydrocarbons formed are the same as with the acetates. In addition to these, (6) gave 1-methylbicyclo[2.2.1]heptan-2-one in small quantities. The amount of the pyrolysis products is given in molal percentages of the total amount of products, while the portion of the retained starting compound is given as a percentage of the original sample. In pyrolysis *exo*-acetate (2) isomerized to some degree to the corresponding *endo*-acetate (1). This did not take place with the other acetates. The analysis of the products was performed with special care. However, the percentage decomposition of the starting materials varied to a degree, but this variation was of no importance as to the product distribution. Nevertheless, it could be clearly seen that *exo*-acetates and alcohols decompose at a lower temperature and to a greater degree than the corresponding *endo*-compounds. The phenomenon has been previously observed in thermal decompositions<sup>4,12–14</sup> and is also typical of the solvolysis reactions of this group of compounds.<sup>15</sup>

To find out the primary pyrolysis products the C<sub>8</sub>H<sub>12</sub> hydrocarbons (7)–(9) were also pyrolysed at 450 °C. In the experimental conditions which were the same as in the pyrolyses of the acetates and alcohols the hydrocarbons

**Table 1.** Results from the pyrolysis of the acetates

	250 °C	300 °C	350 °C	400 °C	450 °C	500 °C
<i>exo</i> -2-Methyl- <i>endo</i> -bicyclo[2.2.1]heptan-2-yl acetate (1)						
Retained acetate <sup>a</sup>	78.3 ± 0.4	59.2 ± 5.0	30.3 ± 1.9	13.2 ± 1.7	3.2 ± 0.3	0.5 ± 0.0
Methylcyclopentadienes			1.1 ± 0.1	11.0 ± 0.5	31.2 ± 0.8	34.7 ± 0.7
(7)	3.1 ± 0.0	2.8 ± 0.1	3.4 ± 0.1	3.8 ± 0.0	3.9 ± 0.1	3.7 ± 0.1
(8)	30.2 ± 0.1	32.6 ± 0.4	31.7 ± 0.2	22.0 ± 0.4	3.0 ± 0.3	
(9)	66.7 ± 0.1	64.5 ± 0.3	63.9 ± 0.1	63.2 ± 0.1	62.0 ± 0.3	61.6 ± 0.6
<i>endo</i> -2-Methyl- <i>exo</i> -bicyclo[2.2.1]heptan-2-yl acetate (2)						
Retained acetate <sup>a</sup>	3.1 ± 0.7	0.6 ± 0.3				
Acetate (1) <sup>a</sup>	2.8 ± 0.1	1.6 ± 0.1	1.5 ± 0.5	0.9 ± 0.1		
Methylcyclopentadienes			1.8 ± 0.4	23.8 ± 1.7	49.6 ± 0.3	57.6 ± 1.8
(7)	0.6 ± 0.0	0.8 ± 0.0	0.9 ± 0.0	0.9 ± 0.0	1.1 ± 0.0	1.1 ± 0.1
(8)	54.3 ± 0.1	50.8 ± 0.3	47.9 ± 0.5	27.6 ± 1.4	3.5 ± 0.7	
(9)	45.1 ± 0.1	48.4 ± 0.3	49.4 ± 0.3	47.6 ± 0.4	45.8 ± 0.8	41.3 ± 1.7
1-Methyl- <i>exo</i> -bicyclo[2.2.1]heptan-2-yl acetate (3)						
Retained acetate <sup>a</sup>		54.0 ± 4.1		17.4 ± 1.3		0.6 ± 0.6
Methylcyclopentadienes				20.1 ± 1.5		59.0 ± 1.6
(10)		0.2 ± 0.0		1.3 ± 0.1		0.1 ± 0.0
(7)		1.2 ± 0.0		1.8 ± 0.0		2.0 ± 0.1
(8)		50.1 ± 0.0		30.5 ± 0.9		0.1 ± 0.0
(9)		48.3 ± 0.0		46.4 ± 0.6		38.9 ± 1.5

<sup>a</sup>% of the original sample, all others % of the total amount of the products.

**Table 2.** Results from the pyrolysis of the alcohols

	300 °C	350 °C	400 °C	450 °C	500 °C
<i>exo</i> -2-Methyl- <i>endo</i> -bicyclo[2.2.1]heptan-2-ol (4)					
Retained alcohol <sup>a</sup>	82.7 ± 2.9	64.1 ± 5.5	56.6 ± 5.4	35.1 ± 4.9	30.7 ± 8.6
Methylcyclopentadienes		0.5 ± 0.1	6.1 ± 0.8	20.6 ± 0.5	22.2 ± 0.66
(7)	6.5 ± 0.1	7.7 ± 0.2	8.8 ± 0.1	9.2 ± 0.2	9.3 ± 0.1
(8)	19.9 ± 0.2	19.3 ± 0.2	14.1 ± 0.4	2.2 ± 0.4	0.6 ± 0.1
(9)	73.6 ± 0.2	72.5 ± 0.3	71.7 ± 0.6	68.0 ± 0.6	68.0 ± 0.7
<i>endo</i> -2-Methyl- <i>exo</i> -bicyclo[2.2.1]heptan-2-ol (5)					
Retained alcohol <sup>a</sup>	51.8 ± 2.8	34.9 ± 4.2	39.9 ± 3.7	33.3 ± 5.5	25.6 ± 3.4
Methylcyclopentadienes		1.3 ± 0.2	15.2 ± 1.3	42.4 ± 0.4	47.7 ± 1.1
(7)	0.6 ± 0.0	0.7 ± 0.0	0.9 ± 0.9	1.0 ± 0.0	1.3 ± 0.0
(8)	48.8 ± 0.1	47.4 ± 0.2	33.8 ± 1.2	6.3 ± 0.7	1.1 ± 0.2
(9)	50.6 ± 0.1	50.5 ± 0.1	50.1 ± 0.2	50.2 ± 0.5	50.0 ± 1.0
1-Methyl- <i>exo</i> -bicyclo[2.2.1]heptan-2-ol (6)					
Retained alcohol <sup>a</sup>	50.9	20.4 ± 1.4	14.3 ± 2.1	7.7 ± 0.3	5.5 ± 0.7
Methylcyclopentadienes		1.5 ± 0.0	15.0 ± 0.1	45.0 ± 1.0	51.8 ± 0.3
(10)	0.4 ± 0.1	0.6 ± 0.0	0.6 ± 0.0	0.1 ± 0.0	0.1 ± 0.0
(7)	1.2 ± 0.1	1.8 ± 0.0	2.1 ± 0.0	2.3 ± 0.0	2.5 ± 0.0
(8)	48.4 ± 0.9	44.9 ± 0.1	32.6 ± 0.2	6.8 ± 0.9	0.8 ± 0.1
(9)	50.0 ± 0.6	51.0 ± 0.1	49.3 ± 0.1	45.0 ± 0.1	43.6 ± 0.2
1-Methylbicyclo[2.2.1]heptan-2-one					
		0.2 ± 0.0	0.5 ± 0.0	0.8 ± 0.0	1.2 ± 0.1

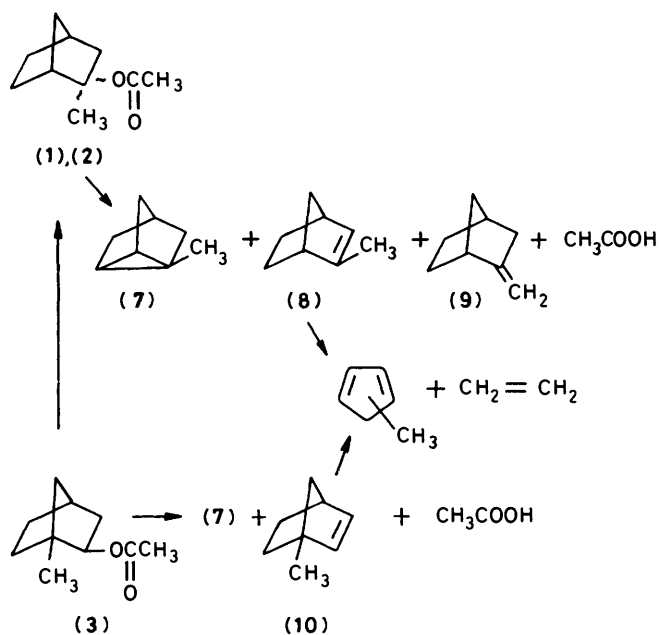
<sup>a</sup>% of the original sample, all others % of the total amount of the products.

in question did not isomerize to each other. 1-Methyltricyclo[2.2.1.0<sup>2,6</sup>]heptane (7) and 2-methylenebicyclo[2.2.1]heptane (9) did not give any decomposition products. Instead, 2-methylbicyclo[2.2.1]hept-2-ene (8) was partly decomposed by retro-Diels-Alder reaction into a mixture of methylcyclopentadienes. These results agree with the previous results from the pyrolyses of related bicyclo[2.2.1]hept-2-enes.<sup>5,8,16</sup> Only the Chuchani group<sup>7</sup> has found isomerization products in the pyrolysis of 1,7,7-trimethylbicyclo[2.2.1]hept-2-ene.

A change in temperature had no noteworthy effect on the primary product distribution in the pyrolyses of the acetates. Still, in all cases the total amount of bicyclic *endo*-alkene and methylcyclopentadienes grew a little at the expense of bicyclic *exo*-alkene when the temperature got higher. The decomposition

of 2-methylbicyclo[2.2.1]hept-2-ene started at about 350 °C and was nearly complete at 500 °C.

According to the general view ester pyrolysis takes place by *cis*-1,2-elimination through a six-membered cyclic transition state in a semiconcerted process.<sup>3</sup> According to Taylor<sup>3</sup> the reaction is, in addition, non-sensitive to surface effects. This mechanism explains many of the results obtained in this study as such. The main products in the pyrolyses of acetates (1) and (2) are normal elimination products no Wagner-Meerwein rearrangement products were found. Instead, in both cases, a small quantity of tricyclic product was formed. The main products of acetate (3) are both rearranged compounds. This is possible according to the above mentioned mechanism, if the reaction takes place mostly in two stages so that first there

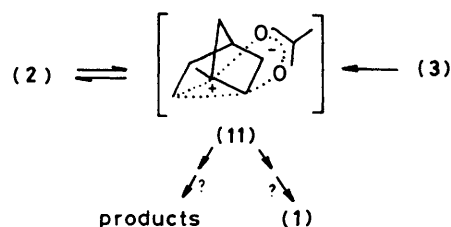


Scheme. Product formation from acetates (1)–(3)

occurs the rearrangement of (3) to (2) and then the pyrolysis of (2) (Scheme). The product distribution from (2) and (3) is the same within experimental error (Table 1). Direct pyrolysis of ester (3) may also take place as a competing reaction, but this is notably slower. It is difficult to estimate the degree of the reaction, because its primary product, 1-methylbicyclo[2.2.1]hept-2-ene (10), probably continues to decompose. The quantity of (10) is however small even at lower temperatures and thus the reaction in question is probably a minor pathway. The rearrangement is comprehensible if the reaction takes place as does ester pyrolysis under kinetic control,<sup>17</sup> because then tertiary structures prevail. According to Haseltine,<sup>18</sup> in the bicyclo[2.2.1]heptane system the tertiary cation is *ca.* 23 kJ mol<sup>-1</sup> more stable than the secondary.

Of the effects influencing the direction of elimination both *endo*- and *exo*-acetate (1) and (2) have the same statistical and electronic effects. The formed pyrolysis products are also the same. However, (1) and (2) have different product distributions, which differ unmistakably from the composition of the thermodynamic equilibrium mixture of these compounds,<sup>19</sup> which is (9) 60%, (8) 21%, (7) 14%, and (10) 5%. Neither (1) nor (2) have a statistical product distribution, which would mean a ratio of 1:3 in the case of *cis* elimination. However, the deviation is greater for (2) than for (1). Since the energy difference between the *exo*- and *endo*-forms in bicyclo[2.2.1]heptane derivatives is not in general very great<sup>15</sup> and the interactions in the ground state, when examined with the help of models, are approximately the same, the difference in the product distribution is likely to be due to steric interactions in the transition state. As for (2), with the formation of a bicyclic *exo*-alkene the coplanar transition state causes a hydrogen atom of the methyl group to come very close to *endo*-H(6). There is no corresponding interaction in the transition state with the formation of a bicyclic *endo*-alkene. With (1) the interactions in the transition state are very alike in the case of both bicyclic *exo*- and *endo*-alkenes.

Compared with ester pyrolysis alcohol pyrolysis has been less studied.<sup>1,2</sup> The pyrolysis of alcohols is above all complicated by the absence of a uniform decomposition path, because both water and hydrogen can be eliminated. In addition, the reaction has been explained to take place by a radical chain mechanism,



except for tertiary alcohols.<sup>20</sup> The pyrolysis temperatures needed are also in general higher than with the corresponding esters.

The decomposition of the alcohols studied here [(4)–(6)] occurred to a somewhat smaller degree than that of the corresponding esters, even though there were no great differences. The product distributions of the pyrolyses did not differ very much from those of the acetates either. With *endo*-alcohol (4) the portion of bicyclic *endo*-alkene is, however, smaller than with the corresponding acetate. The portion of tricyclic product is somewhat larger. As with acetates (1) and (2), Wagner–Meerwein rearrangement was not observed with alcohols (4) and (5). Instead, with alcohol (6) this rearrangement took place either before elimination or during it. There was also some direct pyrolysis of a secondary alcohol, as seen in the formation of 1-methylbicyclo[2.2.1]hept-2-ene (10) and 1-methylbicyclo[2.2.1]heptan-2-one.

As stated above, a pure concerted pyrolysis mechanism explains the ratio of (8) and (9). Other observations like (2) being pyrolysed more easily than (1) as well as the acetates at lower temperatures than the corresponding alcohols require modified procedures. Semi-ionic species [like (11)] may account for the various reactions including isomerization. The elimination step is tentatively concluded to be kinetically controlled while the initial step is thermodynamically controlled, no matter whether the actual reactive form is regarded as classical or non-classical in nature.<sup>21</sup>

## Experimental

M.p.s were determined with a Büchi 510 m.p. apparatus equipped with calibrated thermometers. Densities were measured with 0.5 cm<sup>3</sup> Ostwald pycnometer. I.r. spectra were recorded with a Perkin-Elmer 297 spectrophotometer. <sup>1</sup>H N.m.r. spectra were taken on a JEOL JNM-PMX60 spectrometer using 1% tetramethylsilane as an internal standard. In some cases the structures were further checked with a Bruker AM 250–Aspect 3000 n.m.r. system. Low-resolution electron-impact mass spectra were recorded with a JEOL JMS-D300/JMA-3500 double-focusing mass spectrometer. The preparative g.l.c. work was carried out with a Carlo Erba Fractovap 2450 gas chromatograph using a 4 m × 10 mm i.d. stainless steel column filled with 10% Carbowax on Chromosorb G/AW 60–80 mesh or a 2 m × 10 mm i.d. column filled with 7% FFAP on Chromosorb G/AW 60–80 mesh.

**Starting Materials.**—*exo*-2-Methyl-*endo*-bicyclo[2.2.1]heptan-2-ol (4) was prepared by the Grignard reaction from norbornan-2-one,<sup>13</sup> which was prepared from norborn-2-ene.<sup>22</sup> Compound (4) had m.p. 31.3–32.3 °C, b.p. 68–69 °C at 11 Torr (lit.,<sup>23</sup> m.p. 31.4–32.6 °C, b.p. 55–56 °C at 7 Torr; <sup>1</sup>H n.m.r. spectrum;<sup>24</sup> e.i.-m.s.<sup>25</sup>).

The acetate (1) was prepared by acetylation of the corresponding alcohol.<sup>26</sup> The b.p. of the crude product was 73–74 °C at 11 Torr. The product was purified with preparative g.l.c., *n*<sub>D</sub><sup>20</sup> 1.4543, *d*<sub>4</sub><sup>20</sup> 1.0111 g cm<sup>-3</sup> (lit.,<sup>23</sup> b.p. 79–80 °C at 11 Torr, *n*<sub>D</sub><sup>20</sup> 1.4584, *d*<sub>4</sub><sup>20</sup> 1.0089 g cm<sup>-3</sup>; i.r. spectrum<sup>27</sup>).

*endo*-2-Methyl-*exo*-bicyclo[2.2.1]heptan-2-ol (5) was pre-

pared by the method of Toivonen *et al.*<sup>13</sup> Purification was carried out by crystallization from ligroin–benzene (1:1), m.p. 84.5–84.8 °C (lit.,<sup>23</sup> m.p. 84–85 °C; <sup>1</sup>H n.m.r. spectrum;<sup>24</sup> e.i.-m.s.<sup>25</sup>).

The acetate (2) was prepared as mentioned before. Its b.p. was 77 °C at 11 Torr. The product was purified with preparative g.l.c.,  $n_D^{20}$  1.4618,  $d_4^{20}$  1.0142 g cm<sup>3</sup> (lit.,<sup>23</sup> b.p. 76–78 °C at 8 Torr,  $n_D^{20}$  1.4669,  $d_4^{20}$  1.0135; i.r. spectrum<sup>27</sup>).

1-Methyl-*exo*-bicyclo[2.2.1]heptan-2-ol (6) was prepared by hydrolysis of the corresponding acetate (3) and purified by sublimation, m.p. 75.8–77 °C (lit.,<sup>27</sup> m.p. 76 °C, <sup>1</sup>H n.m.r. spectrum).

The acetate (3) was prepared by the Bertram–Walbaum method.<sup>28</sup> Purification was carried out by preparative g.l.c. — purity was >97%, with alcohols (4)–(6) present = *ca.* 2% and acetates (1)–(2) in *ca.* 1%,  $n_D^{20}$  1.4567,  $d_4^{20}$  0.9938 g cm<sup>-3</sup> (lit.,<sup>23</sup>  $n_D^{20}$  1.4564,  $d_4^{20}$  1.0031 g cm<sup>-3</sup>; i.r. spectrum<sup>27</sup>).

All the substances were racemic mixtures.

**Pyrolysis System.**—The pyrolysis apparatus was modified from the apparatus of Seybold<sup>29</sup> and Brown.<sup>30</sup> A 30 cm × 2 cm (i.d.) quartz tube filled with quartz helices was heated with Nichrome resistance wire. The temperature was measured with chromel–alumel thermocouples situated in a ‘pocket’ middle of the tube. The samples (50–100 mg) were sublimed or vaporized in a stream of dry nitrogen (10 cm<sup>3</sup> min<sup>-1</sup>) and carried into the pyrolysis tube, the temperature of which was kept constant to ±2 °C during the pyrolysis experiments. Pressure was 10–20 Torr throughout the line. The products were condensed in a series of traps placed between the quartz tube and a vacuum pump. The traps were cooled with liquid nitrogen. After pyrolysis, the traps were washed with *n*-pentane or diethyl ether. The pyrolysis experiments were performed at least five times at each temperature and the results averaged.

**Analysis of Pyrolysis Products.**—For the identification of pyrolysis products authentic hydrocarbons (7)–(9) were prepared. Dehydration<sup>31,32</sup> of alcohol (4) with KHSO<sub>4</sub> gave 1-methyltricyclo[2.2.1.0<sup>2,6</sup>]heptane (7) 13%, 2-methylbicyclo[2.2.1]hept-2-ene (8) 17%, and 2-methylenebicyclo[2.2.1]heptane (9) 69%. These compounds were separated and purified with preparative g.l.c. using the FFAP column. They were identified by their retention times, <sup>1</sup>H n.m.r., and mass spectra. A mixture of methylcyclopentadienes was prepared from methylcyclopentadiene dimer and further purified by g.l.c. The sample used was at least a mixture of two isomers, as was the one formed in the pyrolysis reaction. The pyrolysis products were identified by comparing their retention times with those of the model compounds. The results were verified by simultaneous injection into the g.l.c. apparatus of a mixture of the pyrolysis product mixture and the sample of the model compound in question. The pyrolysis products were also individually confirmed by mass spectrometric analysis. The composition of the sample did not change even after a long time.

The quantitative analyses of the pyrolysis product mixtures were performed on a Carlo Erba Fractovap 4160 gas chromatograph equipped with an on-column injection system using 25 m glass capillary column OV-17 and/or on a Carlo Erba Fractovap 2450 gas chromatograph with a 2 m × 2 mm i.d. glass column filled with 4% FFAP on Chromosorb G/AW 60—

80 mesh. The analyses were determined by comparison of peak areas with the standard solution of the model compounds *cis*- or *trans*-decalin as internal standard, using a Hewlett–Packard 3390 A integrator. The analyses were performed at least thrice and the results averaged.

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