

## THE SYNTHESSES OF 8-ALKYL DERIVATIVES OF BICYCLO[4,3,0]-3-NONENES

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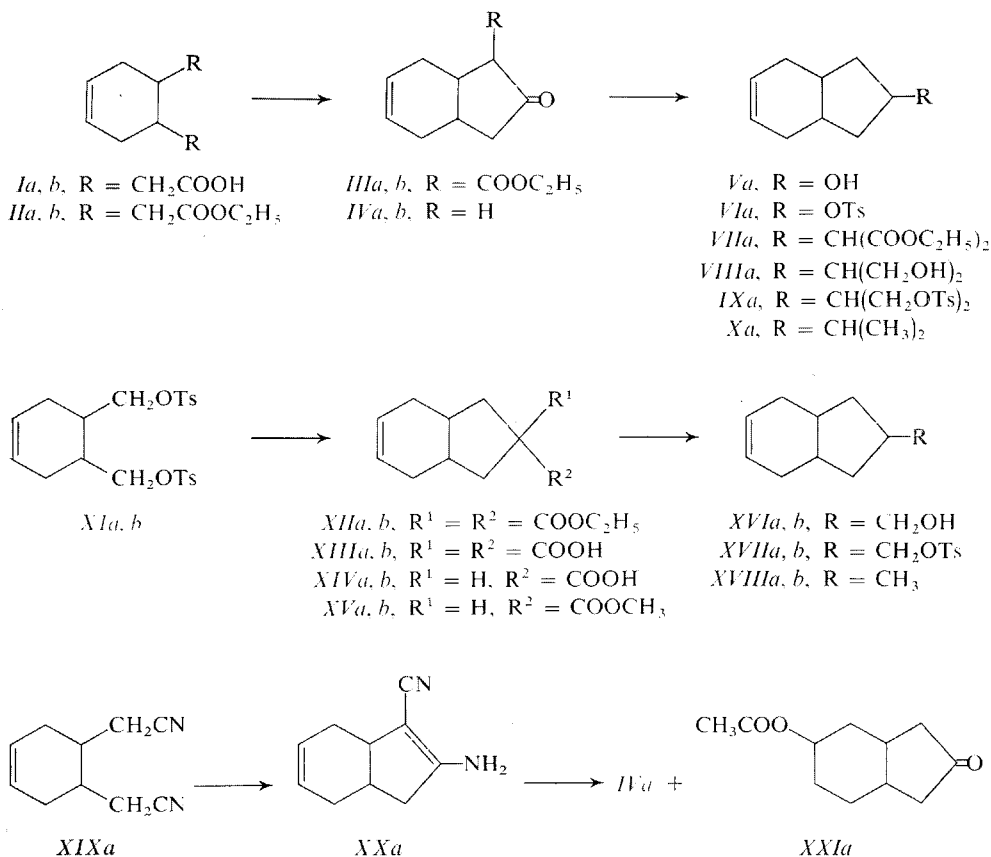
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A series of *cis*- and *trans*-annelated bicyclo[4,3,0]-3-nonenes and bicyclo[4,3,0]-3,7-nonadienes substituted in the position C<sub>(8)</sub> was synthesized.

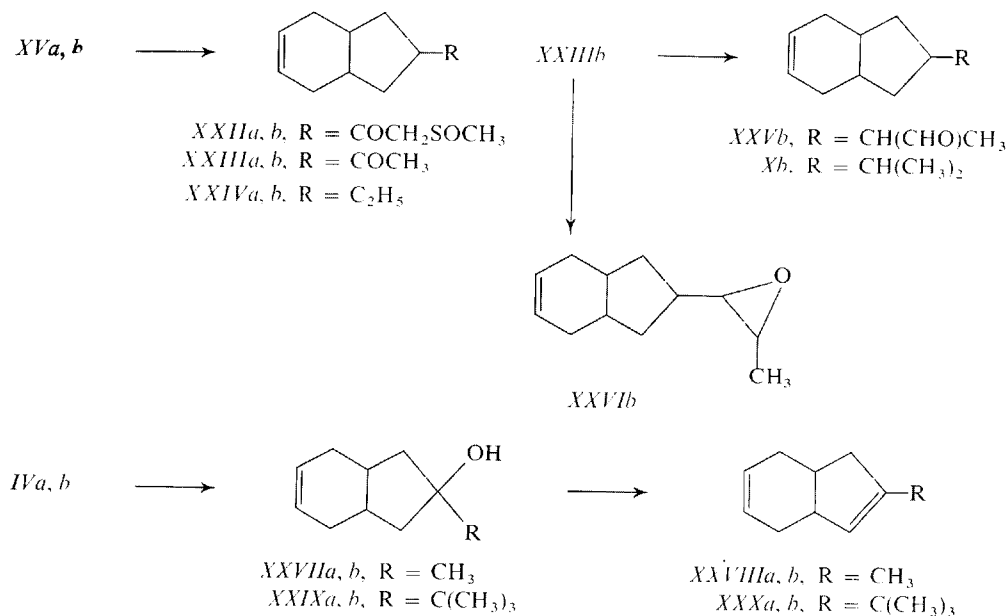
For a study of the retrogression of the Diels–Alder reaction in mass spectrometer we needed a series of substituted bicyclo[4,3,0]-3-nonenes and bicyclo[4,3,0]-3,7-nonadienes with a defined annelation of the rings. In this paper we described the synthesis of derivatives with a substituent in the position C<sub>(8)</sub>.

As starting substances, both in the *cis* and in the *trans* series, bicyclo[4,3,0]-3-nonene-8-ones (*IVa,b*) (ref.<sup>1,2</sup>) and methyl bicyclo[4,3,0]-3-nonene-8-carboxylates (*XVa,b*) were employed. In the subsequent text the substances of the *cis* series are indicated with index *a*, while those of the *trans* series with the index *b*. Ketones *IVa,b* were prepared from acids *Ia,b* (ref.<sup>1,3</sup>) via diethyl esters *IIa,b* which afforded keto esters *IIIa,b* on cyclisation with sodium hydride in tetrahydrofuran<sup>4</sup>. From the keto esters ketones *IVa,b* were obtained on hydrolysis and decarboxylation in moist dimethyl sulfoxide<sup>5</sup>. A shorter procedure, making use of the cyclisation of nitrile *XIXa* to enaminonitrile *XXa* (ref.<sup>6</sup>) and subsequent hydrolysis and decarboxylation in the mixture acetic acid–phosphoric acid–water<sup>7</sup>, afforded a mixture of ketone *IVa* and acetate *XXIa* which was formed under the given conditions by the rather unusual addition of acetic acid to the double bond of the bicyclic skeleton. Esters *XVa,b* were prepared from tosylates *XIa,b* (ref.<sup>3</sup>), which on reaction with the sodium salt of diethyl malonate afforded cyclic esters *XIIa,b*. Their hydrolysis gave acids *XIIIa,b* which were decarboxylated by heating to acids *XIVa,b*. The latter, when esterified with methanol in the presence of *p*-toluenesulfonic acid, gave esters *XVa,b*. Ketone *IVa* was reduced with lithium aluminum hydride in ether to alcohol *Va* which reacted with *p*-toluenesulfonyl chloride in pyridine to tosylate *VIa*. The latter reacted with the sodium salt of diethyl malonate to give ester *VIIa*. Its reduction with lithium aluminum hydride in tetrahydrofuran gave diol *VIIIa* which was tosylated to *IXa* and reduced with lithium aluminum hydride in tetrahydrofuran to *cis*-8-isopropylbicyclo[4,3,0]-3-nonene (*Xa*) as a mixture of two isomers. On reaction with methyl-



magnesium iodide ketones *IVa,b* afforded tertiary alcohols *XXVIIa,b* which were dehydrated with dimethyl sulfoxide<sup>8</sup> to 8-methylbicyclo[4,3,0]-3,7-nonadienes (*XXVIIIa,b*). Reaction of ketones *IVa,b* with tert-butyllithium gave alcohols *XXIXa,b* which were dehydrated with dimethyl sulfoxide to 8-tert-butylbicyclo[4,3,0]-3,7-nonadienes (*XXXa,b*).

Other alkyl derivatives were prepared from esters *XVa,b*. Reduction with lithium aluminum hydride gave alcohols *XVIa,b* which were tosylated to *XVIIa,b* and then converted to 8-methylbicyclo[4,3,0]-3-nonenes (*XVIIIa,b*). On reaction of esters *XVa,b* with the sodium salt of dimethyl sulfoxide<sup>9</sup> strongly enolised ketosulfoxides *XXIIa,b* were obtained which were reduced with aluminum amalgam<sup>9</sup> to ketones *XXIIIa,b*. These were reduced according to Huang–Minlon to 8-ethylbicyclo[4,3,0]-3-nonenes (*XXIVa,b*). Ketone *XXIIIb* was further converted<sup>10</sup> to aldehyde *XXVb* which after reduction according to Huang–Minlon gave *trans*-8-isopropylbicyclo[4,3,0]-3-nonene (*Xb*). In view of the fact that product *Xb* contained about 10%



of compound  $XXIVb$ , an alternative route was tried. Ketone  $XXIIIb$  was reacted with dimethylsulfoxonium methylide<sup>11</sup> to epoxide  $XXVIb$  which was then rearranged under the effect of boron trifluoride etherate<sup>11</sup> to aldehyde  $XXVb$ . This was again reduced according to Huang–Minlon to isopropyl derivative  $Xb$ . As the reaction of ketone  $XXIIIb$  to epoxide  $XXVIb$  did not take place quantitatively, even the isopropyl derivative  $Xb$  prepared in this way contained about 8% of ethyl derivative  $XXIVb$ .

In the case of substances  $Xa$ ,  $XVIIIa$  and  $XXIVa$  the proportion of configurational isomers was analysed by gas chromatography and mass spectrometry. In compounds  $XVIIIa$  and  $XXIVa$  the isomer with a higher retention time distinctly predominates (97%); taking into account its method of preparation we consider that it is probably the more stable isomer. In the case of substance  $Xa$  the isomer with higher retention also prevails, and the determined ratio was 4 : 1. In the trans series only one isomer ( $\pm$ ) can exist, due to reasons of symmetry.

## EXPERIMENTAL

The melting points were determined on a Kofler block. The infrared spectra were measured on a UR-10, Zeiss, Jena, spectrophotometer, in tetrachloromethane, unless stated otherwise. The  $^1H$ -NMR spectra were measured on a JEOL JNM-PS-100 instrument in tetrachloromethane, using hexamethyldisiloxan as internal standard. The mass spectra were measured on the spectrometers MCH-1303, 100 eV, using the method of direct introduction of the sample into the source (spectra marked M), and JEOL D-100, 75 eV, either in connection with a gas chromatograph

or using the above direct inlet technique (spectra marked J). Gas chromatographic analyses were carried out on CHROM 31 chromatograph, Laboratorní přístroje, Prague, with flame ionization detection, on the following columns: (A) GE-SE-30 2.40 m/6 mm, 6% on Chromaton NAW-DMCS; (B) GE-SE-52, 2.40 m/6 mm, 7% on porovina; (C) GE-XE-60, 2.40 m/6 mm, 11% on Chromaton NAW-DMCS; (D) poly(ethylene glycol adipate) 1.20 m/6 mm, 4% on porovina, (E) dinonyl phthalate, 1.20 m/6 mm, 5% on Chromaton NAW-DMCS; (F) Apiezon K, 2.40 m/6 mm, 10% on Chromaton NAW-DMCS. The observation of the reaction courses by thin layer chromatography was carried out on Silufol plates from Kavalier, Votice. The expression "worked up" means that the extract was dried over magnesium sulfate and that the solvent was evaporated *in vacuo*.

#### Diethyl (4-Cyclohexene-1,2-diacetate) (IIa,b)

*Ester IIa*: Acid *Ia* was esterified by the procedure described in ref.<sup>12</sup>, giving 79% yield. The product had b.p. 109–111°C/0.5 Torr; IR: 1740, 1725, 1645, 1190  $\text{cm}^{-1}$ . For  $\text{C}_{14}\text{H}_{22}\text{O}_4$  (254.3) calculated: 66.12% C, 8.72% H; found: 66.33% C, 8.65% H.

*Ester IIb* was prepared analogously from acid *Ib* in a 74% yield, b.p. 105–107°C/0.5 Torr; IR: 1735, 1640, 1185  $\text{cm}^{-1}$ ; for  $\text{C}_{14}\text{H}_{22}\text{O}_4$  (254.3) calculated: 66.12% C, 8.72% H; found: 66.40% C, 8.75% H.

#### Ethyl 8-Oxobicyclo[4,3,0]-3-nonene-7-carboxylate (IIIa,b)

*Ketoester IIIa*: A suspension of sodium hydride in mineral oil (2.65 g of a 60% suspension, 66 mmol of hydride) was washed with three 10 ml portions of pentane, 40 ml of tetrahydrofuran were added, the mixture was heated and 15 g (59 mmol) of ester *IIa* in 30 ml of tetrahydrofuran were added to the mixture under argon, while refluxing. After the lively reaction had subsided the mixture was further refluxed for 4 hours, then cooled, added with 10 ml of acetic acid and the solvent was distilled off in a vacuum. The residue was mixed with 100 ml of water and the mixture extracted with five 20 ml portions of ether and then worked up. After distillation 10.5 g (89%) of an oil were obtained, b.p. 95–97°C/0.6 Torr, which crystallized on standing, m.p. 36–38°C. For  $\text{C}_{12}\text{H}_{16}\text{O}_3$  (208.3) calculated: 69.21% C, 7.74% H; found: 69.65% C, 7.82% H; IR: 1753, 1722, 1655, 1440, 1410, 1370, 1160  $\text{cm}^{-1}$ ; MS (J): 208 (5.0), 207 (3.7), 190 (5.0), 175 (7.1), 163 (20.9), 154 (23.7), 135 (16.6), 130 (100), 115 (17.9), 108 (43.7), 102 (26.7), 91 (34.1), 84 (62.0), 79 (50.9), 77 (29.1), 57 (25.4), 55 (27.0), 53 (25.4), 43 (27.0), 41 (42.6), 39 (30.0).

*Ketoester IIIb* was prepared in an analogous manner from ester *IIb* in a 92% yield. B.p. 110°C/0.6 Torr, m.p. 42–45°C; for  $\text{C}_{12}\text{H}_{16}\text{O}_3$  (208.3) calculated: 69.21% C, 7.74% H; found: 69.50% C, 7.70% H; IR: 1740, 1719, 1640, 1435, 1370, 1130  $\text{cm}^{-1}$ ; MS(J): 208 (15.6), 163 (19.7), 162 (28.0), 130 (11.2), 108 (15.1), 105 (10.0), 93 (11.5), 92 (16.0), 91 (29.4), 84 (100), 79 (25.1), 77 (18.0), 67 (9.5), 65 (9.4), 53 (14.8), 41 (20.4), 39 (22.1).

#### Bicyclo[4,3,0]-3-nonen-8-one (IVa,b)

*Ketone IVa*: *Ketoester IIIa* (10.4 g, 50 mmol) was heated at 155°C for 4 hours with 2 ml of water in 45 ml of dimethyl sulfoxide, under argon. After cooling the mixture was poured into 150 ml of water, extracted four times with 25 ml of light petroleum and then worked up. After distillation 6.2 g (95%) of product were obtained, b.p. 50–53°C/0.3 Torr (literature<sup>2</sup> gives 100°C/10 Torr), which was pure according to chromatography on columns A, C and D. IR: 1745, 1655, 1445, 1410  $\text{cm}^{-1}$ ; MS(J): 136 (59.8), 108 (38.4), 94 (30.8), 93 (38.1), 91 (22.3), 82 (28.0), 79 (100), 77 (30.8), 67 (31.4), 58 (33.0), 54 (84.0), 41 (31.4), 39 (38.4).

*Ketone IVb* was prepared in analogous manner in a 96% yield, m.p. 63–65°C (ref.<sup>1</sup> gives 66–67°C). IR: 1740, 1645, 1450, 1415  $\text{cm}^{-1}$ ; MS (J): 136 (73.8), 108 (35.4), 94 (32.4), 93 (41.3) 92 (37.8), 91 (30.1), 82 (34.5), 79 (100), 67 (32.5), 54 (34.5), 41 (30.1), 39 (46.0).

*cis*-Bicyclo[4,3,0]-3-nonen-8-ol (*Va*)

*Ketone IVa* (700 mg) was reduced with 100 mg of lithium aluminum hydride in 15 ml of ether. The excess of hydride was hydrolysed with sodium sulfate solution and the mixture was worked up. The product (667 mg, 95%) was chromatographically inseparable on column C and D. For  $\text{C}_9\text{H}_{14}\text{O}$  (138.2) calculated: 78.21% C, 10.21% H; found: 78.73% C, 10.44% H; IR: 3620, 3380, 1656, 1440, 1100, 1065, 1050, 1040, 1025  $\text{cm}^{-1}$ ; MS (M): 138 (3.1), 120 (56.0), 110 (6.0), 105 (13.3), 95 (10.0), 94 (10.0), 93 (10.0), 92 (42.7), 91 (44.0), 79 (100), 78 (28.0), 77 (17.3), 67 (12.7), 66 (12.7).

*cis*-Bicyclo[4,3,0]-3-nonen-8-yl *p*-Toluenesulfonate (*VIa*)

Alcohol *Va* (650 mg) and *p*-toluenesulfonyl chloride (1.05 g) in pyridine (5 ml) were allowed to stand at 0°C for 96 hours and the reaction course was observed by thin layer chromatography on Silufol, with chloroform as solvent. Icy water (100 ml) was then added to the reaction mixture and the separated oil extracted three times with 20 ml of chloroform. The extract was washed with 20 ml of 1M-HCl, 20 ml of 5% sodium hydrogen carbonate and water and further worked up. The oily product (1.25 g, 91%) was used for further reaction without purification.

Diethyl *cis*-Bicyclo[4,3,0]-3-nonen-8-yl Malonate (*VIIa*)

A suspension of sodium hydride in mineral oil (330 mg of suspension, 8.2 mmol of hydride) was washed three times with 10 ml of pentane and 1.3 g (8.2 mmol) of diethylmalonate in 15 ml of dioxan were added to it under argon. After homogenization (5 minutes) 1.24 g (4.3 mmol) of tosylate *VIa* in 10 ml of dioxan were added and the mixture refluxed for 12 hours. The separated sodium *p*-toluenesulfonate was filtered off, the filtrate was additioned with 0.5 ml water and 30 ml of ether, and the mixture was worked up as usual. The crude product was distilled at 140°C/0.4 Torr (bath temperature) and 1.20 g (90%) of ester *VIIa* were obtained. For  $\text{C}_{16}\text{H}_{24}\text{O}_4$  (280.4) calculated: 68.55% C, 8.63% H; found: 69.06% C, 8.74% H; IR: 1739, 1656, 1468, 1448, 1415, 1392, 1370  $\text{cm}^{-1}$ .

2-(*cis*-Bicyclo[4,3,0]-3-nonen-8-yl)-1,3-propanediol (*VIIIa*)

Ester *VIIa* (1.180 g) was reduced with 300 mg of lithium aluminum hydride in 20 ml of tetrahydrofuran for three hours under reflux. A solution of sodium sulfate was added to the solution and the mixture worked up. Yield 700 mg (85%) of product m.p. 47–55°C. For  $\text{C}_{12}\text{H}_{20}\text{O}_2$  (196.3) calculated: 73.43% C, 10.27% H; found: 73.61% C, 10.27% H; IR (chloroform) 3625, 3400, 1656, 1438, 1048, 1028  $\text{cm}^{-1}$ .

*cis*-8-Isopropylbicyclo[4,3,0]-3-nonene (*Xa*)

Diol *VIIIa* (660 mg, 3.36 mmol) was tosylated with 1.52 g (8 mmol) of *p*-toluenesulfonyl chloride in 7 ml of pyridine by the procedure given for compound *VIa*. Oily *IXa* was obtained (1.120 g; 66%) which was reduced without further purification with 150 mg of lithium aluminum hydride in 10 ml of tetrahydrofuran. After 15 hours refluxing 20 ml of ether were added and the mixture

worked up as in the case of compound *Va*. The crude product was distilled at 140°C/10 Torr (bath temperature) to yield 190 mg (57%) of *Xa* in the form of a mixture of 20% of the isomer with lower retention and 80% of the isomer with higher retention (column C, 104°C). For C<sub>12</sub>H<sub>20</sub> (164.3) calculated: 87.73 C, 12.27% H; found: 87.09% C, 12.11% H; IR: 1662, 1475, 1455, 1440, 1388, 1370, 670 cm<sup>-1</sup>; MS (M): 164 (8.8), 149 (4.1), 135 (0.8), 122 (13.4), 121 (100), 120 (7.0), 109 (4.4), 107 (4.7), 93 (16.7), 91 (9.6), 81 (10.4), 79 (27.4), 77 (9.6), 67 (18.9).

#### Diethyl *cis*-Bicyclo[4,3,0]-3-nonene-8,8-dicarboxylate (*XIIa*)

Ester *XIIa* was prepared analogously as *trans*-isomer *XIIb* (ref.<sup>3</sup>) in 53% yield, b.p. 110°C/0.4 Torr. For C<sub>15</sub>H<sub>22</sub>O<sub>4</sub> (266.3) calculated: 67.65% C, 8.32% H; found: 67.78% C, 8.40% H. Acid *XIIIA* (m.p. 183–185°C) and *XIVa* (oil) were prepared analogously as in the *trans* series<sup>3</sup> in a 90% or 93% yield, respectively. For C<sub>10</sub>H<sub>14</sub>O<sub>2</sub> (*XIVa*) (166.2) calculated: 72.26% C, 8.49% H; found: 72.88% C, 8.60% H; IR (*XIVa*): 3500, 3100, 1704, 1652, 1460, 1432, 1235 cm<sup>-1</sup>.

#### Methyl Bicyclo[4,3,0]-3-nonene-8-carboxylate (*XVa,b*)

*Ester XVa*: Acid *XIVa* (2.6 g), 50 ml of methanol and 0.5 g of *p*-toluenesulfonic acid were refluxed for 6 hours, methanol was distilled off under reduced pressure, and the residue was diluted with 30 ml of 5% sodium hydrogen carbonate. The mixture was extracted with two 15 ml portions of chloroform, the extract was dried over calcium chloride and the chloroform was evaporated under reduced pressure and the residue distilled *in vacuo*. Yield 2.49 g (89%) of product, b.p. 74°C/0.6 Torr. For C<sub>11</sub>H<sub>16</sub>O<sub>2</sub> (180.2) calculated: 73.30% C, 8.95% H; found: 73.97% C, 9.11% H; IR: 1718, 1652, 1450, 1435, 1360, 1220, 1200, 1175 cm<sup>-1</sup>; MS (M): 180 (37.5), 165 (1.5), 149 (26.4), 148 (75.0), 130 (5.4), 121 (68.1), 120 (100), 111 (5.7), 107 (5.8), 106 (6.0), 105 (12.1), 94 (58.3) 93 (27.8), 92 (40.2), 91 (40.2), 79 (82.0), 77 (25.0), 67 (36.1), 66 (19.4), 55 (16.7).

*Ester XVb* was prepared in an analogous manner in 92% yield, b.p. 59°C/0.3 Torr. For C<sub>11</sub>.H<sub>16</sub>O<sub>2</sub> (180.2) calculated: 73.30% C, 8.95% H; found: 73.52% C, 9.02% H; IR: 1730, 1640, 1450, 1440, 1360, 1200, 1175 cm<sup>-1</sup>. MS (M): 180 (48.4), 165 (2.4), 149 (23.4), 148 (34.4), 121 (78.1), 120 (100), 107 (9.1), 106 (9.7), 105 (11.6), 94 (75.0), 93 (27.5), 92 (27.2), 91 (35.9), 87 (72.5), 79 (84.4), 67 (21.9), 59 (10.6), 55 (20.6).

#### (Bicyclo[4,3,0]-3-nonen-8-yl)methanol (*XVIa,b*)

Esters *XVa,b* were reduced with lithium aluminum hydride in ether to corresponding alcohols *XVIa,b* in a 90% yield. *XVIa*: For C<sub>10</sub>H<sub>16</sub>O (152.2) calculated: 78.90% C, 10.59% H; found: 79.33% C, 10.72% H; IR: 3630, 3380, 1656, 1450, 1435, 1055, 1035, 1025 cm<sup>-1</sup>; MS (M): 152 (20.4), 134 (51.0), 121 (73.4), 119 (44.9), 106 (25.6), 105 (19.4), 93 (49.0), 92 (67.4), 91 (63.3), 80 (44.9), 79 (100), 78 (20.4), 77 (30.6), 67 (30.6), 55 (14.3). *XVIb*: For C<sub>10</sub>H<sub>16</sub>O (152.2) calculated: 78.90% C, 10.59% H; found: 79.10% C, 10.63% H; IR: 3625, 3340, 1642, 1455, 1440, 1385, 1050 cm<sup>-1</sup>; MS (M): 152 (22.3), 134 (79.2), 121 (65.0), 119 (63.6), 106 (37.7), 105 (28.6), 94 (23.4), 93 (89.6), 92 (100), 91 (94.7), 80 (32.5), 79 (100), 77 (45.4), 67 (31.2) 55 (16.9).

#### (Bicyclo[4,3,0]-3-nonen-8-yl)methyl *p*-Toluenesulfonate (*XVIIa,b*)

Alcohols *XVIa,b* were tosylated with *p*-toluenesulfonyl chloride in pyridine at 0°C for 72 hours and isolated using the procedure given for substance *Via*. The products (*XVIIa* liquid, *XVIIb*, m.p. 75–76°C) were used for further reaction without purification. IR (*XVIIa*): 1656, 1602, 1500, 1465, 1440, 1375, 1190, 1175 cm<sup>-1</sup>; IR (*XVIIb*): 1646, 1604, 1500, 1470, 1455, 1374, 1191, 1180 cm<sup>-1</sup>.

*cis*-8-Methylbicyclo[4,3,0]-3-nonene (*XVIIIa*)

Tosylate *XVIIa* (1.4 g) was reduced with 200 mg of lithium aluminum hydride in 30 ml of tetrahydrofuran under refluxing for 72 hours. After isolation by the procedure described for substance *Va* 472 mg (71%) of product were obtained, b.p. 59°C/12 Torr, which was a mixture of 3% of the isomer with the lower retention time and 97% of the isomer with the higher retention time (column C, 88°C). For C<sub>10</sub>H<sub>16</sub> (136.2) calculated: 88.16% C, 11.84% H; found: 87.49% C, 11.52% H; IR: 1656, 1467, 1452, 1437, 1377, 671, 641 cm<sup>-1</sup>; MS (M): 136 (55.3), 121 (100), 108 (14.3), 107 (25.0), 95 (41.1), 94 (75.7), 93 (46.4), 81 (52.1), 80 (27.5), 79 (60.7), 67 (62.6).

*trans* Isomer *XVIIIb* was prepared in an analogous manner in a 60% yield, b.p. 49°C/10 Torr. The product was chromatographically pure (columns A, B, C, F, 88°C). For C<sub>10</sub>H<sub>16</sub> (136.2) calculated: 88.16% C, 11.84% H; found: 87.80% C, 11.70% H; IR: 1644, 1460, 1435, 1374, 663 cm<sup>-1</sup>; MS (M): 136 (64.3), 121 (100), 107 (29.2), 95 (66.5), 94 (79.4), 93 (49.4), 81 (30.1), 80 (30.1), 79 (66.5), 77 (20.4), 67 (39.7).

Bicyclo[4,3,0]-3-nonene-8-carbonylmethylsulfinylmethane (*XXIIa,b*)

*Keto sulfoxide* *XXIIa*: Ester *XVa* (500 mg, 2.78 mmol) in 5 ml of tetrahydrofuran was added under stirring at 0°C and under argon to 8 mmol of sodium salt of dimethyl sulfoxide<sup>9</sup> in 8 ml of dimethyl sulfoxide. The mixture was stirred at 0°C for 30 minutes, and at 25°C for another two hours. 1M-HCl (100 ml) was then added and the mixture extracted six times with 15 ml portions of chloroform. After the usual work-up the greater part of the dimethyl sulfoxide taken along with the residue was eliminated by distillation at 50°C/0.3 Torr and the semi-crystalline product was used for further processing without purification. IR (chloroform): 3680, 3400 (enol), 1710, 1658, 1458, 1442, 1410, 1055 cm<sup>-1</sup>.

*Keto sulfoxide* *XXIIb* was prepared in an analogous manner. IR: 3680, 3420 (enol), 1715, 1682, 1442, 1055 cm<sup>-1</sup>.

8-Acetylbicyclo[4,3,0]-3-nonene (*XXIIIa,b*)

*Ketone* *XXIIIa*: Crude keto sulfoxide *XXIIa* was reduced with 2 g of aluminum amalgam<sup>9</sup> in 15 ml of 90% aqueous tetrahydrofuran. After 2 hours' refluxing (the conversion was followed by thin layer chromatography on Silufol in chloroform) 20 ml of ether were added, the remains of amalgam were filtered off, washed with ether, and the filtrate was worked up. The crude product was distilled at 90°C/0.4 Torr (bath temperature) yielding 400 mg (89% when referred to ester *XVa*) of compound *XXIIIa*. For C<sub>11</sub>H<sub>16</sub>O (164.2) calculated: 80.44% C, 9.82% H; found: 80.91% C, 9.90% H; IR: 1718, 1664, 1455, 1438, 1362 cm<sup>-1</sup>; MS (J): 164 (18.8), 149 (10.2), 146 (34.4), 131 (21.3), 121 (26.1), 117 (16.2), 106 (38.2), 94 (60.6), 91 (38.2), 79 (71.7), 77 (27.1), 71 (62.1), 67 (47.8), 43 (100), 41 (36.7), 39 (34.4).

*Ketone* *XXIIIb* was prepared in an analogous manner in a total yield of 91%. The product was distilled at 85°C/0.35 Torr (bath temperature) and it was chromatographically pure on column C and E (136°C). For C<sub>11</sub>H<sub>16</sub>O (164.2) calculated: 80.44% C, 9.82% H; found: 81.05% C, 9.84% H; IR: 1718, 1648, 1451, 1442, 1362 cm<sup>-1</sup>.

*cis*-8-Ethylbicyclo[4,3,0]-3-nonene (*XXIVa*)

Ketone *XXIIIa* (200 mg) was heated with 200 mg of hydrazine hydrate (100%) in 5 ml of diethylene glycol at 135°C for 2 hours. Potassium hydroxide (250 mg) was added and the mixture heated under argon at 220°C for 5 hours. After cooling 20 ml of water were added, the mixture

was extracted with three 5 ml portions of pentane and worked up. The product was distilled at 90°C/10 Torr (bath temperature) and 124 mg (76%) of product *XXIVa* were obtained in the form of a mixture of 3% of the isomer with lower retention time and 97% of the isomer with higher retention. For  $C_{11}H_{18}$  (150·3) calculated: 87·93% C, 12·07% H; found: 87·41% C, 11·88% H; IR: 1658, 1463, 1438, 1377, 672, 658  $cm^{-1}$ ; MS (M): 150 (15·0), 135 (1·8), 121 (100), 109 (7·1), 108 (7·1), 107 (6·2), 95 (8·7), 94 (10·4), 93 (13·4), 81 (11·8), 80 (7·7), 79 (26·2), 67 (32·8),

*trans*-Isomer *XXIVb* was prepared analogously in 77% yield. The product was distilled at 75°C/11 Torr, and on columns A, B, C, E and F (88°C) it was chromatographically pure. For  $C_{11}H_{18}$  (150·3) calculated: 87·93% C, 12·07% H; found: 87·46% C, 11·97% H; IR: 1644, 1473, 1454, 1440, 1382, 663  $cm^{-1}$ ; MS (M) 150 (30·0), 135 (3·4), 121 (100), 109 (16·5), 108 (5·8), 107 (5·8), 95 (8·7), 94 (19·4), 93 (20·6), 81 (13·5), 80 (11·6), 79 (37·6), 67 (31·2).

#### 2-(*trans*-Bicyclo[4,3,0]-3-nonen-8-yl)propanal (*XXVb*)

a) *From ketone XXIIIb*: 2·2 ml of 0·9M *n*-butyllithium in benzene were added to a solution of 442 mg (2 mmol) of diethyl(*N*-pyrrolidylmethylphosphonate)<sup>10</sup> in 5 ml of tetrahydrofuran under argon at -78°C. After one hour's stirring 180 mg (1·15 mmol) of ketone *XXIIIb* in 5 ml of tetrahydrofuran were added dropwise and the mixture was stirred at -78°C for 4 hours and at 25°C for 20 hours. Three ml of 1M-HCl were added and the mixture refluxed for 4 hours. After cooling 10 ml of water were added and the mixture extracted four times with 10 ml of ether and worked up. The crude product was distilled at 110°C/0·4 Torr. Yield 115 mg (59%) of a mixture of 10% of ketone *XXIIIb*, 80% of aldehyde *XXVb* and 10% of two further, unidentified compounds (column C, 136°C). For  $C_{12}H_{18}O$  (178·3) calculated: 80·85% C, 10·18% H; found: 81·62% C, 10·44% H.

b) *From epoxide XXVIb*: Boron trifluoride etherate<sup>11</sup> (400 mg) was added under argon at 0°C and under stirring to a solution of 285 mg of epoxide *XXVIb* in 10 ml of ether and the mixture was stirred at 0°C for 20 minutes and at 25°C for another 20 minutes. Sodium hydrogen carbonate (5%; 20 ml) was then added and the aqueous phase extracted with three 10 ml portions of ether. After working up and distillation 270 mg (95%) of a mixture of 8% of ketone *XXIIIb*, 77% of aldehyde *XXVb*, and 15% of another two unidentified substances with a higher retention were obtained.

#### 2-(*trans*-Bicyclo[4,3,0]-3-nonen-8-yl)-2-methyloxiran (*XXVIIb*)

Dimethyl sulfoxide (5 ml) was added under argon and stirring to a mixture of 650 mg of trimethylsulfoxonium iodide<sup>11</sup> and 70 mg of sodium hydride and when the evolution of hydrogen ceased 380 mg of ketone *XXIIIb* in 5 ml of dimethyl sulfoxide were added dropwise. The mixture was stirred at 25°C for 15 minutes and at 60°C for 2 hours, then cooled and poured into 50 ml of water and the product was extracted four times with 10 ml of pentane. After working up and distillation at 100°C/0·4 Torr (bath temperature) 300 mg (73%) of a mixture of 8% of ketone *XXIIIb* and 92% of epoxide *XXVIIb* (column C, 140°C) was obtained. For  $C_{12}H_{18}O$  (178·3) calculated: 80·85% C, 10·18% H; found: 81·33% C, 10·21% H.

#### *trans*-8-Isopropylbicyclo[4,3,0]-3-nonene (*Xb*)

Aldehyde *XXVb* was reduced by the procedure mentioned for compound *XXIVa*, giving a 41% yield. The crude product was distilled at 90°C/11 Torr. The distillate consisted of 8–10% of compound *XXIVb* and 90–92% of compound *Xb* (column C, 104°C). The infrared spectra of the products prepared from aldehyde obtained as under a) and b) were identical. For  $C_{12}H_{20}$  (164·3)



calculated: 87.73% C, 12.27% H; found 88.12% C, 12.49% H; IR: 1642, 1472, 1451, 1441, 1387, 1371, 662  $\text{cm}^{-1}$ ; MS (M): 164 (28.2), 135 (1.2), 121 (100), 109 (2.4), 108 (4.7), 107 (3.6), 95 (10.4), 94 (13.8), 93 (22.4), 81 (21.2), 80 (9.4), 79 (34.5), 67 (22.9).

#### 8-Methylbicyclo[4,3,0]-3-nonen-8-ol (XXVIIa,b)

*Alcohol XXVIIa*: Ketone *IVa* (300 mg, 2.2 mmol) in 10 ml of ether was added under stirring to a solution of 5 mmol of methylmagnesium iodide in 10 ml of ether and the mixture was refluxed for 30 minutes. After cooling at 0°C 10 ml of water and 10 ml of ether were added to the mixture and the ethereal phase was dried over sodium sulfate, filtered and the solvent evaporated under reduced pressure. Yield, 306 mg (91%) of product containing traces of ketone *IVa* only and which was used for further work without additional purification. IR: 3610, 3400, 1654, 1470, 1452, 1375, 1118, 1102  $\text{cm}^{-1}$ .

*Alcohol XXVIIb* was prepared analogously in 93% yield. IR: 3610, 3370, 1647, 1462, 1380, 1115  $\text{cm}^{-1}$ .

#### cis-8-Methylbicyclo[4,3,0]-3,7-nonadiene (XXVIIIa)

*Alcohol XXVIIa* (290 mg) was heated with 8 ml of dimethyl sulfoxide under argon at 170°C for 6 hours. After cooling 80 ml of water were added and the mixture extracted with three 15 ml portions of pentane, and worked up. The crude product was distilled at 70°C/11 Torr (bath temperature) to give 120 mg of compound *XXVIIIa* which was chromatographically pure (columns A, C, 88°C). For  $\text{C}_{10}\text{H}_{14}$  (134.2) calculated: 89.49% C, 10.51% H; found: 89.15% C, 10.33% H; IR: 1665, 1646, 1448, 1383, 677, 662  $\text{cm}^{-1}$ ; MS (M): 134 (21.7), 119 (12.3), 117 (2.8), 115 (2.5), 93 (4.4), 92 (4.4), 91 (9.6), 80 (100), 79 (28.0), 78 (7.9), 77 (8.9), 65 (3.8), 39 (9.4).

*trans-Isomer XXVIIIb* was prepared analogously in a 44% yield. The product was distilled at 60°C/11 Torr (bath temperature) and it was chromatographically pure (columns A, C, 88°C). For  $\text{C}_{10}\text{H}_{14}$  (134.2) calculated: 89.49% C, 10.51% H; found: 88.90% C, 10.19% H; IR: 1642, 1450, 1358, 663  $\text{cm}^{-1}$ ; MS (M): 134 (21.7), 119 (12.3), 117 (2.6), 115 (2.5), 106 (3.5), 105 (4.1), 93 (5.6), 92 (9.4), 91 (17.3), 80 (100), 79 (13.6), 77 (6.5), 41 (3.9), 39 (4.2).

#### 8-Tert-butylbicyclo[4,3,0]-3-nonen-8-ol (XXIXa,b)

*Alcohol XXIXa*: Ketone *IVa* (280 mg, 2.06 mmol) in 5 ml of ether was added under argon to a solution of 5 mmol of tert-butyllithium in a mixture of 10 ml of benzene and 5 ml of ether. The addition was carried out under cooling at -10°C and stirring, which was continued for another hour at 0°C, then for 4 hours at 25°C, and finally at boiling temperature for 2 hours. After cooling 20 ml of 0.1M-HCl were added and the organic phase was washed with 10 ml of 5% sodium hydrogen carbonate, then dried over sodium sulfate, and finally evaporated *in vacuo*. The crude product contained about 30% of the starting ketone *IVa* (estimated from the IR spectrum). The mixture was reduced with sodium borohydride in methanol and alcohol *Va* was separated by column chromatography on silica gel (chloroform) to yield 255 mg (60%) of the product, *XXIXa*. For  $\text{C}_{13}\text{H}_{22}\text{O}$  (194.3) calculated: 80.35% C, 11.41% H; found: 80.59% C, 11.48% H; IR: 3610, 3450, 1655, 1480, 1445, 1390, 1372  $\text{cm}^{-1}$ . *Alcohol XXIXb* was prepared analogously in a 45% yield. For  $\text{C}_{13}\text{H}_{22}\text{O}$  (194.3) calculated: 80.35% C, 11.41% H; found: 80.74% C, 11.55% H; IR: 3615, 3450, 1645, 1481, 1397, 1369  $\text{cm}^{-1}$ .

*cis*-8-Tert-butylbicyclo[4,3,0]-3,7-nonadiene (XXXa)

Alcohol XXXa was dehydrated using the procedure applied in the case of substance XXVIIIa, and XXXa was obtained in a 66% yield. The product was distilled at 105°C/11 Torr (bath temperature) and it was pure chromatographically on columns A and C (104°C). For C<sub>13</sub>H<sub>20</sub> (176.3) calculated: 88.57% C, 11.43% H; found: 88.33% C, 11.35% H; IR: 1667, 1640, 1502, 1480, 1467, 1452, 1396, 1368, 696, 663 cm<sup>-1</sup>; MS (M): 176 (27.7), 161 (5.3), 135 (2.5), 122 (77.9), 119 (15.9), 107 (100), 91 (22.7), 57 (27.1).

*trans*-Isomer XXXb was prepared in an analogous manner in 46% yield. The product contained about 10% of a substance with a higher retention time (column C, 104°C) to which the structure of 2-tert-butylindene was assigned on the basis of its mass spectrum. For C<sub>13</sub>H<sub>20</sub> (176.3) calculated: 88.57% C, 11.43% H; found: 88.12% C, 11.20% H; IR: 1637, 1623, 1481, 1467, 1441, 1396, 1368, 663 cm<sup>-1</sup>; MS (M): 176 (19.8), 161 (4.3), 133 (2.6), 122 (14.1), 120 (18.8), 119 (100), 118 (26.2), 107 (33.9), 91 (37.8), 83 (6.4), 79 (7.3), 77 (7.0), 57 (31.7); <sup>1</sup>H-NMR: 1.72 (s, 9 H), 2.11 (mt, 8 H), 5.30 (s, 1 H), 5.60 (d, *J* = 1–2 Hz, 2 H).

*cis*-3-Acetylbicyclo[4,3,0]-nonan-8-one (XXIa)

Nitrile XIXa (1 g) was refluxed in a mixture of 12 ml of acetic acid 1.5 ml of water, and 10 ml of phosphoric acid<sup>7</sup>, under argon, for 12 hours. After cooling 70 ml of saturated potassium carbonate were added and the product was extracted four times with 10 ml of ether, then worked up and separated by chromatography on silica gel (chloroform). Ketone IVa (460 mg, 54%) and a substance (155 mg) identified as acetate XXIa were obtained. The substance was a mixture of *endo* and *exo* isomer in an approximately 1 : 1 ratio. For C<sub>11</sub>H<sub>16</sub>O<sub>3</sub> (196.2) calculated: 67.32% C, 8.22% H; found: 67.55% C, 8.60% H; IR (chloroform): 1740, 1622, 1450, 1410, 1370, 1245 cm<sup>-1</sup>; MS (M): 196 (3.1), 154 (7.1), 136 (100), 121 (30.1), 109 (10.9), 108 (90.5), 107 (35.4), 82 (17.9), 80 (29.5), 79 (70.0), 77 (24.4), 67 (22.4), 43 (47.7), 41 (24.4); <sup>1</sup>H-NMR: 1.36–2.41 (mt, 10 H), 1.92, 1.94 (2 s, 1 : 1, total 3 H), 4.77 (mt, *W* = 43 Hz, 1 H).

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