THE SYNTHESES OF 7-ALKYL DERIVATIVES OF BICYCLO[4,3,0]-3-NONENES

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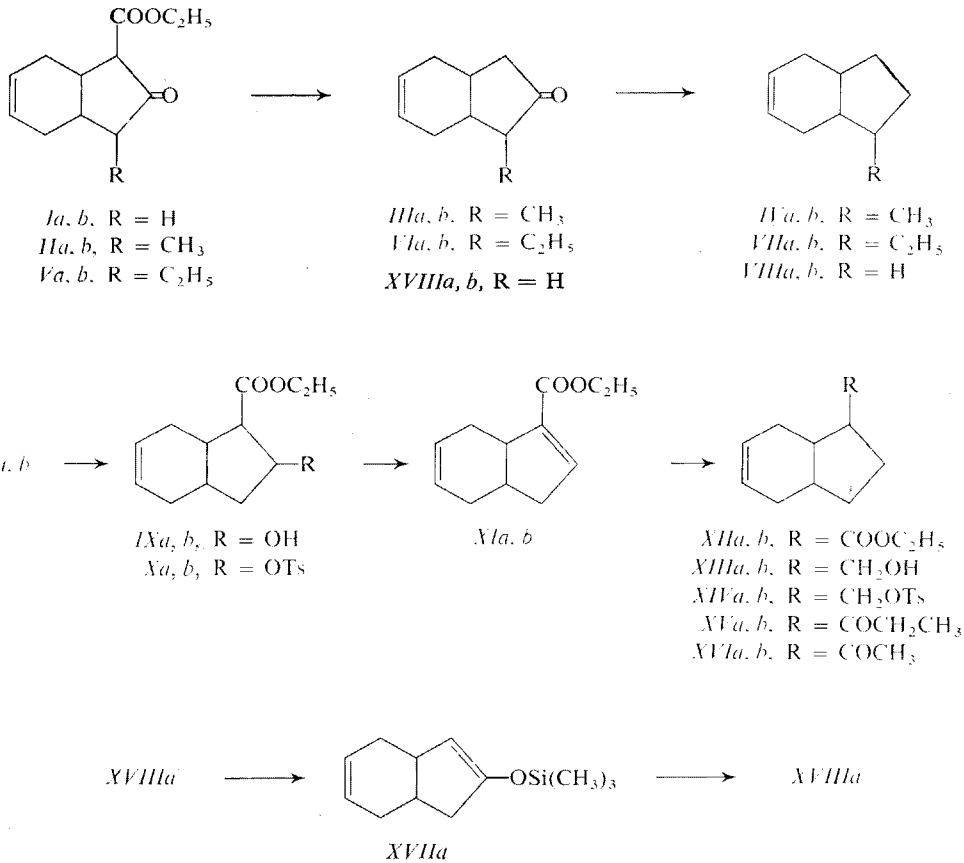
In the article the preparation of a series of 7-alkylsubstituted bicyclo[4,3,0]-nonenes is described, using both a direct introduction of the alkyl group, and the modification of the ethoxycarbonyl group. The configuration of the substituents and the differences in infrared spectra are discussed.

In the preceding paper[1] we described the preparation of bicyclo[4,3,0]-3-nonenes substituted at the position $C_{(8)}$. In this study we present two procedures leading to derivatives with an alkyl in the position $C_{(7)}$. In the following text the substances of *cis*-series are indicated by index *a*, and these of *trans*-series by index *b*.

Keto esters *Ia,b* (ref.[1]) were found to be best starting substances, which on alkylation of the corresponding di-anions[2] afforded keto esters *IIa,b* or *Va,b*. The latter were hydrolysed and decarboxylated in moist dimethyl sulfoxide[3] to ketone *IIIa,b* or *VIa,b* respectively, which on reduction according to Huang-Minlon gave 7-methylbicyclo[4,3,0]-3-nonenes (*IVa,b*) or 7-ethylbicyclo[4,3,0]-3-nonenes (*VIIa,b*). Gas chromatographic and mass spectrometric analysis indicated that the alkylation of di-anions into position $C_{(7)}$ does not take place completely, so that the products *IVa,b* and *VIIa,b* contained 10–12% of the corresponding bicyclo[4,3,0]-3-nonene (*VIIIa,b*). This disadvantage could not be overcome by using excess alkylating agent, because a competing alkylation in the position $C_{(9)}$ took place instead. The by-products formed could be separated easily because they did not undergo hydrolysis in moist dimethyl sulfoxide, but a decrease in the yields of ketones *IIIa,b* and *VIa,b* took place at the same time. Therefore an alternative procedure was employed. Keto esters *Ia,b* were reduced with sodium borohydride in methanol to hydroxy esters *IXa,b* which were then converted to tosylates *Xa,b* with *p*-toluenesulfonyl chloride in pyridine. Elimination of the *p*-toluenesulfonyl group with sodium ethoxide in ethanol led to unsaturated esters *XIa,b* which were reduced with lithium in liquid ammonia[4] to esters *XIIa,b*. Reduction of esters *XIIa,b* with lithium aluminum hydride gave alcohols *XIIIa,b* which were subsequently reduced, *via* tosylates *XIVa,b* to 7-methylbicyclo[4,3,0]-3-nonenes (*IVa,b*), again with lithium aluminum hydride. Homologous 7-ethylbicyclo[4,3,0]-3-nonenes (*VIIa,b*) were prepared from

esters *XIIa,b via* keto sulfoxides *XVa,b* (ref.[5]) and ketones *XVIa,b*. Another possible method, using aldol condensation of trimethylsilyl enol-ether *XVIIa* with paraldehyde under catalysis with titanium tetrachloride[6], did not give positive results. In all instances ketone *XVIIIa* was isolated from the reaction mixture.



Submitting substances *IVa,b* and *VIIa,b* to gas chromatography and mass spectrometry it was found that they represent mixtures of two isomers. In the following text the isomers with a lower retention time are indicated with α, and the isomers with a higher retention with β. As the relative ratio of isomers α and β differed for substances prepared by different synthetic procedures it was possible to consider the configuration of the substituents in the position $C_{(7)}$ for substances of the *cis*-series. In the preparation of substance *VIIa* the last step of both synthetic procedures is the Huang–Minlon reduction which is usually accompanied by the isomerization on the carbon atom neighbouring with the keto group (ref.[7] and the references therein), and therefore the more stable isomer should prevail in the reaction mixture.

The ratio of the isomers, α/β, was determined for substances *VIIa* in both cases as 3·5 : 1. In a similar way the more stable isomer should also predominate in compound *IVa*, prepared by direct alkylation. The ratio α/β was found to be 4·5 : 1 in this case, while in the same substance prepared by the other method the ratio α/β of the isomers was 1 : 5. A probable configuration was assigned to single isomers on the basis of the correlation with the isomers of alcohol *XIIIa* which were obtained in a pure state. For the predominating isomer of alcohol *XIIIa* the configuration endo was derived for the hydroxymethyl group on the basis of the intramolecular hydrogen bridge formation (3 545 cm^{-1}) with the double bond of the bicyclic system, which can take place only in this configuration. Under the assumption that in the subsequent course of the synthesis a substantial change in the ratio of the isomers does not take place, the configuration *exo* follows for the alkyl group in the isomers α of substances *IVa* and *VIIa*, and the configuration *endo* for the isomer of β-configuration. The conclusion that the more stable isomer has the configuration *exo* is also supported by the study of Dreiding models.

During the identification of the products we observed in their infrared spectra in the 700 – 600 cm^{-1} region (out-of-plane bending vibrations of the H—C=C—H system) differences between *cis*- and *trans*-annelated bicyclo[4,3,0]-3-nonenes substituted both in positions $C_{(7)}$ and $C_{(8)}$ (ref.[1]). While the *trans*-isomers display in this region one strong band irrespective of the nature of the substituents, the *cis*-isomers give here several bands which appear as a broad poorly resolved multiplet. In contrast to *trans*-isomers this effect depends in the *cis*-series on the nature of substituents. It is most pronounced in alkyl derivatives, while in 7-oxo and 8-oxo derivatives only small differences in intensities are observed. In view of the fact that distinct differences also appear in unsubstituted bicyclo[4,3,0]-3-nonenes (*VIIIa,b*) it seems that the occurrence of the multiplet in the *cis*-series is not dependent on the presence of the configurational isomers, but that the decisive factor is the conformational mobility of the *cis*-annelated skeleton. This conclusion is in agreement with the observation that in 8-methylbicyclo[4,3,0]-3,7-nonadienes and 8-tert-butylbicyclo-[4,3,0]-3,7-nonadienes (ref.[1]), where the configurational isomery on $C_{(8)}$ is excluded, the shape and the intensity of the band under consideration differs distinctly for mutually corresponding *cis*- and *trans*-isomers. Another parameter which enables the differentiation of *cis*- and *trans*-isomers of substituted bicyclo[4,3,0]-3-nonenes is the frequency value of the stretching vibration ν(C=C), which ranged for the *trans*-isomers of all substances we had at our disposal from 1 654 to 1 640 cm^{-1}, while in the case of *cis*-isomers the range was 1 660 – 1 654 cm^{-1}.

EXPERIMENTAL

The infrared spectra were measured on a spectrophotometer UR-10, Zeiss, Jena, in tetrachloromethane, if not stated otherwise, the 3 700 – 3 400 cm^{-1} region was measured on a Unicam

SP-700 spectrophotometer in tetrachloromethane, and a 10^{-3}M concentration. The mass spectra were measured on a JEOL D-100, 75 eV, spectrometer, either in combination with a gas chromatograph (the spectra indicated with GC), or by the direct inlet technique (spectra indicated with DI). Gas chromatographic analyses were carried out with a CHROM 31 instrument, Laboratorní přístroje, Prague, with FID, on the following columns: (A) GE-SE-30, 6% on Chromaton NAW-DMCS, 2·40 m/6 mm, (B) GE-SE-52, 7% on porovina, 2·40 m/6 mm, (C) GE-XE-60, 11% on Chromaton NAW-DMCS, 2·40 m/6 mm. The observation of the reaction course by thin layer chromatography was carried out on Silufol sheets, Kavalier, Votice. The expression "worked up" means that the extract was dried over magnesium sulfate, filtered and the solvent evaporated under reduced pressure.

Ethyl 9-Methyl-8-oxobicyclo[4,3,0]-3-nonene-7-carboxylate (*IIa,b*)

Keto ester IIa: A suspension of sodium hydride in mineral oil (90 mg of a 60% suspension, 2·25 mmol) was washed with three 10 ml portions of pentane. Keto ester *Ia* (416 mg, 2 mmol) in 2 ml of tetrahydrofuran was then added at 0°C under argon and with stirring and the mixture was stirred for 30 minutes. n-Butyllithium (2·3 ml of a 0·9M solution in benzene) was then added over 10 minutes and the mixture was stirred for another 30 minutes at 0°C. Finally 300 mg (2·1 mmol) of methyl iodide in 3 ml of tetrahydrofuran were added and the mixture was stirred at 0°C for another hour. It was then additioned with 5 ml of 0·5M-HCl, 20 ml of water, and the mixture was extracted four times with 10 ml of ether and worked up. The product was used for further work without purification. IR: 1759, 1730, 1657, 1614 cm^{-1}. *Keto ester* IIa was prepared analogously. IR: 1754, 1730, 1642, 1266, 1135 cm^{-1}.

7-Methylbicyclo[4,3,0]-3-nonen-8-one (*IIIa,b*)

Ketone IIIa: Keto ester *IIa* (410 mg) was heated with 100 mg of water in 5 ml of dimethyl sulfoxide under argon at 160°C for 4 hours. After cooling 20 ml of water were added, the product was extracted with four 10 ml portions of pentane and worked up. The crude product was distilled at 70°C/0·4 Torr (bath temperature) to yield 146 mg (49% with respect to keto ester *Ia*) of a mixture of 12% of ketone *XVIIIa* and 88% of ketone *IIIa* (column A, 135°C). For $C_{10}H_{14}O$ (150·2) calculated: 79·97% C, 9·39% H; found: 79·39% C, 9·22% H.

Ketone IIIb, total yield 50%, contained 4% of ketone *XVIIIb* (column A, 135°C), For $C_{10}H_{14}O$ (150·2) calculated: 79·97% C, 9·39% H; found: 80·15% C, 9·40% H.

cis-7-Methylbicyclo[4,3,0]-3-nonene (*IVa*)

a) *From ketone* IIIa: Ketone *IIIa* (120 mg) was heated with 150 mg of 100% hydrazine hydrate in 2 ml of diethylene glycol at 135°C for 2 hours, potassium hydroxide (350 mg) was added and the mixture heated at 220°C under argon for 5 hours. After cooling 10 ml of water were added and the product was extracted three times with 6 ml of pentane and then worked up. After distillation at 70°C/11 Torr (bath temperature) 49 mg of product were obtained which was a mixture of 74% of isomer α, 16% of isomer β and 10% of compound *VIIIa* (column A, 88°C). For $C_{10}H_{16}$ (136·2) calculated: 88·16% C, 11·84% H; found: 87·61% C, 11·52% H; IR: 1659, 1461, 1437, 1377, 663, 645 cm^{-1}; MS (GC, α): 136 (28·5), 121 (77·5), 107 (28·5), 95 (45), 94 (98), 93 (41), 81 (93), 80 (37), 79 (84), 67 (100), 55 (20·5), 54 (1·4); MS (GC, β): 136 (27), 121 (100), 107 (26), 95 (45), 94 (71), 82 (21), 81 (86), 80 (33), 79 (71), 67 (100), 55 (30), 54 (11·5).

b) From tosylate XIVa: Tosylate *XIVa* (180 mg) was reduced with 80 mg of lithium aluminum hydride in 5 ml of tetrahydrofuran by 24 hours' reflux. Ether (10 ml) was then added and the excess hydride was hydrolysed with a sodium sulfate solution. The ethereal layer was worked up and the residue distilled to afford 33 mg (44%) of a product which contained 18% of isomer α and 82% of isomer β.

trans-7-Methylbicyclo[4,3,0]-3-nonene (*IVb*)

a) From ketone IIIb: Reduction of ketone *IIIb* by the procedure used for the *cis* isomer gave a mixture of 80% of isomer α, 18% of isomer β and 2% of compound *VIIIb* (column A, 88°C). For $C_{10}H_{16}$ (136·2) calculated: 88·16% C, 11·84% H; found: 87·41% C, 11·69% H; IR: 1644, 1462, 1439, 1379, 662 cm^{-1}; MS (GC, α): 136 (55), 121 (100), 108 (37), 95 (66), 94 (84), 93 (50), 81 (60), 79 (84), 67 (50), 55 (18); MS (GC, β): 136 (30), 121 (100), 107 (20), 95 (60), 94 (56), 93 (27), 81 (33), 80 (25), 79 (77), 67 (47), 55 (23).

b) From tosylate XIVb: Tosylate *XIVb* was reduced using the procedure described for the *cis* isomer and a mixture of 77% of isomer α and 23% of isomer β was obtained in 43% yield.

Ethyl 9-Ethyl-8-oxobicyclo[4,3,0]-3-nonene-7-carboxylate (*Va,b*)

Keto ester Va: Keto ester *Ia* was converted to a dianion using the procedure mentioned in the case of compound *IIIa*. The dianion was reacted with ethyl iodide for 3 hours. After working up the crude product was used without further purification.

Keto ester Vb was prepared in an analogous manner. IR: 1755, 1728, 1641 cm^{-1}.

7-Ethylbicyclo[4,3,0]-3-nonen-8-one (*VIa,b*)

Ketone VIa: Keto ester *Va* was hydrolysed and decarboxylated, using the procedure mentioned for compound *IIa*, in 50% yield. After distillation at 100°C/0·4 Torr (bath temperature) a mixture of 88% of ketone *VIa* and 12% of ketone *XVIIIa* (column A, 140°C) was obtained. For $C_{11}H_{16}O$ (164·2) calculated: 80·44% C, 9·82% H; found: 80·52% C, 9·99% H.

Ketone VIb was prepared in an analogous manner in a 79% total yield. The product was distilled at 100°C/0·5 Torr (bath temperature). For $C_{11}H_{16}O$ (164·2) calculated: 80·44% C, 9·82% H; found: 80·44% C, 10·01% H; IR: 1746, 1640, 1460, 1435, 1408, 1377, 1354 cm^{-1}.

cis-7-Ethylbicyclo[4,3,0]-3-nonene (*VIIa*)

a) From ketone VIa: Ketone *VIa* (135 mg) was reduced using the procedure described for compound *IVa*. After distillation at 90°C/11 Torr (bath temperature) 85 mg (70%) of a mixture of 69% of isomer α, 19% of isomer β and 12% of compound *VIIIa* (column B, 88°C) were obtained. For $C_{11}H_{18}$ (150·3) calculated: 87·93% C, 12·07% H; found: 87·21% C, 11·84% H; IR: 1660, 1465, 1451, 1379, 665, 648, cm^{-1}; MS (GC, α): 150 (25), 121 (100), 108 (61), 96 (15), 95 (43), 93 (22), 91 (13), 80 (22), 79 (48), 67 (80), 55 (22), 54 (8·7); MS (GC, β): 150 (19·5), 121 (100), 108 (39), 96 (19·5), 95 (49), 93 (24·5), 81 (24·5), 80 (29), 79 (54), 67 (68), 55 (24·5).

b) From ketone XVIa: Ketone *XVIa* was reduced by the procedure given for compound *IVa* in 55% yield. The product obtained contained 79% of isomer α and 21% of isomer β (columns A, C, 88°C).

trans-7-Ethylbicyclo[4,3,0]-3-nonene (*VIIb*)

a) *From ketone* VIb: The product obtained on reduction of ketone *VIb* by the procedure described for substance *IVa* was distilled at 100°C/11 Torr (bath temperature). It contained 80% of isomer α, 8% of isomer β and 12% of compound *VIIIb*. The yield was 62%. For $C_{11}H_{18}$ (150·3) calculated: 87·93% C, 12·07% H; found: 87·35% C, 11·46% H; IR: 1645, 1460, 1435, 1375, 664 cm^{-1}; MS (DI): 150 (13·6), 135 (1·75), 121 (100), 109 (11·6), 108 (9·4), 95 (14·6), 93 (22·3), 91 (11·6), 80 (17·6), 79 (48·6), 77 (14·6), 67 (28·1), 55 (10·7).

b) *From ketone* XVIb: The product obtained on reduction of ketone *XVIb* by the procedure described for substance *IVa* was a mixture of 89% of isomer α and 11% of isomer β (columns A, C, 88°C). The yield was 51%.

Ethyl 8-Hydroxybicyclo[4,3,0]-3-nonene-7-carboxylate (*IXa,b*)

Hydroxy ester IXa: Keto ester *Ia* (1 g) in 20 ml of methanol was added to 200 mg of sodium borohydride in 20 ml of methanol at 0°C. After thirty minutes' stirring 300 mg of acetic acid were added, methanol was evaporated in a vacuum, the residue was treated with 30 ml of 5% sodium hydrogen carbonate and the mixture was extracted with five 15 ml portions of ether. After working up 952 mg (95%) of product *IXa* were obtained, which consisted of two isomers (analysis on Silufol, chloroform). The mixture was used for further work without separation. For $C_{12}H_{18}O_3$ (210·3) calculated: 68·54% C, 8·63% H; found: 68·71% C, 8·68% H; IR: 3618, 3520, 1722, 1655, 1170, 1028 cm^{-1}.

Hydroxy ester IXb was prepared in an analogous manner in 93% yield. The reaction product was again a mixture of two isomers (Silufol, chloroform). For $C_{12}H_{18}O_3$ (210·3) calculated: 68·54% C, 8·63% H; found: 68·68% C, 8·81% H; 3620, 3575, 3480, 1730, 1641, 1160, 1028 cm^{-1}.

Ethyl 8-*p*-Toluenesulfonyloxybicyclo[4,3,0]-3-nonene-7-carboxylate (*Xa,b*)

Tosylate Xa: Hydroxy ester *IXa* (940 mg, 4·46 mmol) and *p*-toluenesulfonyl chloride (950 mg, 5 mmol) in 10 ml of pyridine were allowed to stand at −3°C for 48 hours and at 20°C for 72 hours. The reaction course was controlled by thin layer chromatography on Silufol (in chloroform). The reaction mixture was poured into 100 ml of icy water and the separated oil was extracted four times with 15 ml of chloroform. The extract was washed with 20 ml of 2M-HCl, 20 ml of 5% sodium hydrogen carbonate, and worked up. Yield, 1495 g (93%) of oil which was used without further purification. Tosylate *Xb* was prepared analogously in 90% yield.

Ethyl Bicyclo[4,3,0]-3,7-nonadiene-7-carboxylate (*XIa,b*)

Ester XIa, *A*). Tosylate *Xa* (1·480 g, 4·1 mmol) in 10 ml of tetrahydrofuran was added to a boiling solution of 5 mmol of sodium ethoxide in 10 ml ethanol. After 10 minutes boiling (the reaction course was followed by thin-layer chromatography on Silufol, in benzene) the mixture was cooled, 300 mg of acetic acid were added and the majority of solvents distilled off *in vacuo*. To the residue 50 ml of 5% sodium hydrogen carbonate were added, the product was extracted with four 10 ml portions of ether and worked up. After distillation at 83°C/0·3 Torr (bath temperature) 650 mg (82%) of product were obtained which on columns A and C (135°C) was chromatographically pure. For $C_{12}H_{16}O_2$ (192·3) calculated: 74·97% C, 8·39% H; found: 75·23% C, 8·51% H; IR: 1718, 1630, 1245, 1215, 1110 cm^{-1}. *B*) A solution of hydroxy ester *IXa* (470 mg, 2·23 mmol) and *p*-toluenesulfonyl chloride (480 mg, 2·5 mmol) in 5 ml of pyridine was refluxed

for 20 hours (the reaction course was controlled by thin layer chromatography on Silufol, in chloroform). After cooling 60 ml of water were added and further procedure was as in the case of compound *Xa*. After distillation 332 mg (77%) of ester *XIa* were obtained, which was chromatographically pure (columns B, C, 135°C) and the IR spectrum of which was identical with that of the substance prepared under (*A*).

Ester XIb was prepared from tosylate *Xb* using the procedure given for the *cis*-isomer *XIa* (procedure (*A*)). The reaction time was shortened to 5 minutes because addition of ethanol took place to the double bond formed. The product was purified by column chromatography on silica gel (benzene–chloroform 1 : 1) and distilled at 95°C/0·5 Torr. Yield, 53%. The product was chromatographically pure on columns A, B, C (135°C). For $C_{12}H_{16}O_2$ (192·3) calculated: 74·97% C, 8·39% H; found: 75·26% C, 8·44% H; IR: 1718, 1635, 1612, 1245, 1232, 1120, 1100 cm^{-1}.

Ethyl Bicyclo[4,3,0]-3-nonene-7-carboxylate (*XIIa,b*)

Ester XIIa: Ester *XIa* (635 mg, 3·3 mmol) in 10 ml of ether was added to a solution of 60 mg of lithium (8·65 mmol) in 40 ml of liquid ammonia. The mixture was stirred for 5 minutes, then 1·1 g of ammonium chloride was added and the ammonia allowed to evaporate. The residue was additioned with 15 ml of ether, the insoluble salts were filtered off under suction, washed with ether, ether was distilled off under reduced pressure and the residue chromatographed on a silica gel column (light petroleum–ether 7 : 5). Yield, 430 mg (68%) of ester *XIIa*, which contained 26% of isomer with lower retention time and 74% of isomer with higher retention (column C, 135°C). For $C_{12}H_{18}O_2$ (194·3) calculated: 74·19% C, 9·34% H; found: 74·33% C, 9·50% H; IR: 1735, 1656, 1195, 1170 cm^{-1}.

Ester XIIb was prepared in an analogous manner in a 62% yield. For $C_{12}H_{18}O_2$ (194·3) calculated: 74·19% C, 9·34% H; found: 74·61% C, 9·46% H; IR: 1730, 1640, 1155 cm^{-1}.

(Bicyclo[4,3,0]-3-nonen-7-yl)methanol (*XIIIa,b*)

Alcohol XIIIa: Ester *XIIa* (150 mg) was reduced with 50 mg of lithium aluminum hydride in 10 ml of ether. Excess hydride was hydrolysed with a sodium sulfate solution and the ethereal layer was worked up in the conventional manner. Yield, 105 mg (90%) of alcohol *XIIIa*, representing a mixture of two isomers which were separated chromatographically on a silica gel column (ligh petroleum–ether 7 : 5). Yield, 15 mg of *endo*-isomer, having a lower retention time (column C, 135°C) and a higher R_F value (Silufol, light petroleum–ether); this isomer predominated in the reaction mixture. For $C_{10}H_{16}O$ (152·2) calculated: 78·90% C, 10·59% H; found: 79·35% C, 10·82% H; IR: 3635, 3545 (measured at a $4 \cdot 10^{-3}$M concentration), 3340, 1660, 1472, 1430, 1025 cm^{-1}. Further, 70 mg of an intermediate fraction were obtained and 20 mg of *exo*-isomer, having a higher retention time and a lower R_F value. For $C_{10}H_{16}O$ (152·2) calculated: 78·90% C, 10·59% H; found: 79·69% C, 11·05% H; IR: 3640 (measured at a $5 \cdot 10^{-3}$M concentration), 3350, 1660, 1470, 1435, 1055, 1025, 1005 cm^{-1}.

Alcohol XIIIb was prepared analogously as *cis*-isomer in a 83% yield. For $C_{10}H_{16}O$ (152·2) calculated: 78·90% C, 10·59% H; found: 79·11% C, 10·69% H; IR: 3640, 3460, 1643, 1465, 1438, 1040 cm^{-1}.

(Bicyclo[4,3,0]-3-nonen-7-yl)methyl *p*-Toluenesulfonate (*XIVa,b*)

Tosylates *XIVa,b* were prepared by the procedure described for substance *Xa* in 89% or 80% yield, respectively, and they were used without further purification.

Bicyclo[4,3,0]-3-nonene-7-carbonylmethylsulfinylmethane (*XVa,b*)

Keto sulfoxide XVa: Ester *XIIa* (270 mg, 1·39 mmol) in 3 ml of tetrahydrofuran was added under argon to a solution of 3 mmol of sodium salt of dimethyl sulfoxide[5] in 5 ml of dimethyl sulfoxide. The mixture was stirred at 0°C for one hour and at 25°C for 3 hours. 0·1M-HCl (30 ml) was then added and the mixture extracted five times with 10 ml of chloroform and worked up. The residue was freed from the co-extracted dimethyl sulfoxide at 50°C/0·4 Torr. The product obtained was further used without further purification.

Keto sulfoxide XVb was prepared in an analogous manner.

7-Acetylbicyclo[4,3,0]-3-nonene (*XVIa,b*)

Ketone XVIa: Keto sulfoxide *XVa* (260 mg) was reduced with 2 g of aluminum amalgam[5] by 3 hours' boiling in 90% tetrahydrofuran. The remains of amalgam were filtered off, washed with ether and the ethereal solution was worked up. After distillation at 100°C/0·4 Torr (bath temperature) 180 mg of product *XVIa* were obtained (76% referred to ester *XIIa*). For $C_{11}H_{16}O$ (164·2) calculated: 80·44% C, 9·82% H; found: 80·71% C, 9·95% H; IR: 1716, 1657, 1442, 1358 cm^{-1}.

Ketone XVIb was prepared analogously as the *cis*-isomer in 82% yield. For $C_{11}H_{16}O$ (164·2) calculated: 80·44% C, 9·82% H; found: 80·60% C, 9·90% H; IR: 1712, 1643, 1460, 1435, 1370 cm^{-1}.

cis-8-Trimethylsilyloxybicyclo[4,3,0]-3,7-nonadiene (*XVIIa*)

Ketone XVIIIa was converted to enol ether *XVIIa* by the procedure given in ref.[8]. The product was distilled at 105°C/11 Torr (bath temperature) and it contained about 5% of ketone *XVIIIa* (estimated from the IR spectrum). For $C_{12}H_{20}OSi$ (208·4) calculated: 69·17% C, 9·67% H; found: 70·05% C, 9·15% H; IR: 1650, 1440, 1375, 1255 cm^{-1}.

Attempt at Condensation of Enol Ether *XVIIa* with Paraldehyde

Enol ether *XVIIa* (435 mg, 2·09 mmol) in 10 ml of dichloromethane was added under stirring and under argon at −78°C to a mixture of titanium(IV) chloride (1·22 g, 6·3 mmol) and paraldehyde (280 mg, 6·36 mmol) in 20 ml of dichloromethane. The mixture was stirred at −78°C for 2 hours, 30 ml of a 5% sodium hydrogen carbonate solution were added, and the aqueous phase was extracted with two 10 ml portions of ether. The combined organic phases were worked up in the usual manner. The product obtained (385 mg) had retention parameters (Silufol, chloroform; columns A, C, 135°C) and IR spectra identical with those of ketone *XVIIIa*.

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