Tetrahedron Vol. 42, No. 17, pp. 4719 to 4728, 1986
Printed in Great Britain.

0040-4020/86 $3.00+.00
Pergamon Journals Ltd.

TRANSANNULAR π-CYCLIZATION IN ELECTROPHILIC ADDITIONS TO 1,5-DIMETHYLCYCLOOCTA-1,5-DIENE [1,2]

G. HAUFE*, A. WOLF and K. SCHULZE

Sektion Chemie, Karl-Marx-Universität, DDR-7010 Leipzig
German Democratic Republic

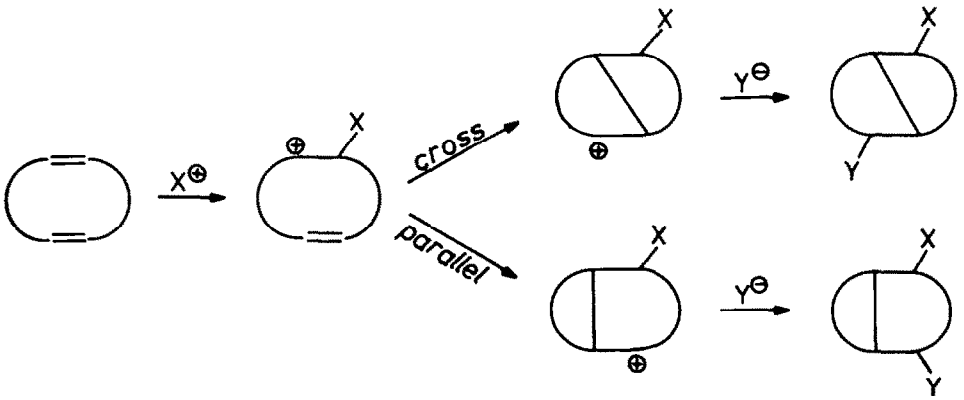
(*Received in Germany* 10 *February* 1986)

Abstract: Electrophilic additions of Broensted acids to 1,5-dimethylcycloocta-1,5-diene yield syn-8-substituted 1,5-dimethylbicyclo[3.2.1]octanes via parallel π-cyclisation and subsequent Wagner-Meerwein type rearrangements. The corresponding anti-isomers are synthesized by nucleophilic substitution in the 8-position. The classical or nonclassical structure of the cationic intermediates is discussed.

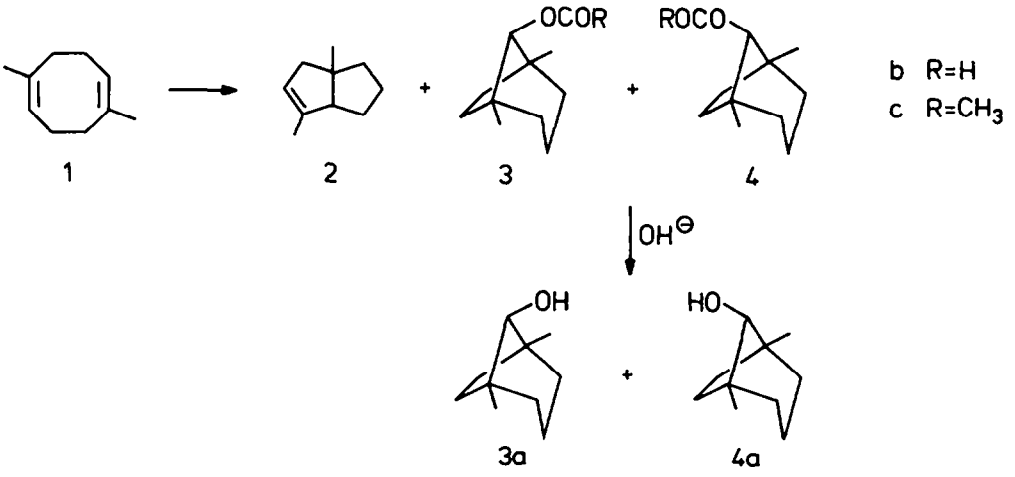
The intermediary formation of a cationic species in a transannular position located close to an isolated double bond usually leads to transannular bridge formation, by a π-cyclisation [3]. This type of transannular reaction was first studied by Cope et al.[3a] in solvolysis reactions of medium sized cycloalkenol esters such as tosylates and brosylates, and was used e.g. in synthesis of the racemic natural insecticide iridomyrmecine [4].

Further work was published on electrophilic additions to mono- or polycyclic cycloalkadienes leading to products formed by transannular π-cyclisation. These reactions are characteristic of very strained polycyclic structures [5] as well as for medium sized cycloalkadienes [3b,3d]. Most importantly these reactions occur in electrophilic additions to medium sized 1,5-dienes in the synthesis of condensed bi- or polycyclic systems as well as in biomimetic reactions of sesquiterpenes involving medium sized rings and in the explanation of the biogenetic formation of bi- or polycyclic natural products from monocyclic precursors [3,6-8].

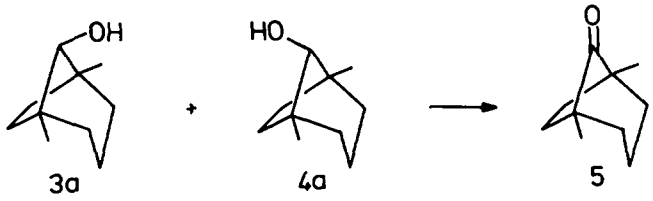
In principle there are two possibilities for transannular bridging i.e. the cross and the parallel π-cyclisation [5]:



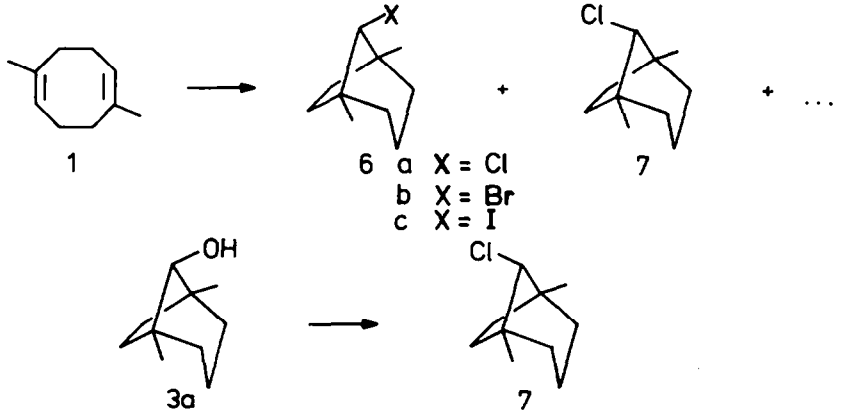
Experimental results on these types of reactions have shown that in some cases only the cross or only the parallel bridged product is formed, whilst in other cases both products are found. The direction of the π-cyclization of medium ring 1,5-dienes was shown to be influenced by the ring size, the configuration of the double bonds, substituents bound to the double bond and by the conformation of the transition state leading to transannular bridging. When this transition state is late on the reaction coordinate (product-like transition state), the pathway is also dependent on the steric energies among possible products [3b,3d,5,8].
A large number (but not all [9]) of polar electrophilic additions to cis,cis-cycloocta-1,5-diene result in transannular π-cyclization. In nearly all cases only cis-bicyclo[3.3.0]octanes, the products of crossed bridging, were found [10]. On the other hand the thallium(III)-trifluoroacetate induced transannular cyclization of the diene results in a 3:2 mixture of two isomers formed by the crossed or parallel pathway, respectively [11]. The parallel bridging should be favoured when the cis-bicyclo[4.2.0]oct-2-yl-carbenium ion has greater stability than the cis-bicyclo[3.3.0]oct-2-yl-carbenium ion, e.g. by substituent effects. Thus the reactions of 1,5-dimethylcycloocta-1,5-diene with p-toluenesulfonic acid in benzene as well as the acid catalyzed hydratation was found to lead to syn-1,5-dimethylbicyclo[3.2.1]octan-8-ol or its tosylate, respectively, by parallel transannular π-cyclization and subsequent Wagner-Meerwein-type rearrangements [12].
Presently, we describe the reactions of 1,5-dimethylcycloocta-1,5-diene (1) with some Brønsted acids which were designed to study the mechanism of the rearrangements [13]. The diene 1 was synthesized following a procedure described by Suga et al. [14]. In the reaction of 1 with 85 % formic acid and catalytic amounts of perchloric acid we obtained an olefinic fraction (22 % isolated yield, mixture of 72 % 2,5-dimethylbicyclo[3.3.0]oct-2-ene (2), 17 % unreacted 1 and 7 % or 3 % of two unknown isomers) and a higher boiling fraction (63 % isolated yield) of the two isomeric formates 3b and 4b in a ratio of 92:8 [13,15].



An analogous result was obtained in the reaction of 1 with acetic acid and catalytic amounts of perchloric acid. The portion of the olefinic compounds in this case increases to 45 %. The two esters 3c and 4c are formed also in 92:8 ratio. The structure of the main products is proved by spectroscopic methods (cf. experimental section) especially by ^{13}C NMR spectroscopy [16] and by hydrolysis of the esters to a 92:8 mixture of syn- and anti-1,5-dimethylbicyclo[3.2.1]octan-8-ols 3a and 4a. The spectroscopic data of the known main alcohol are in agreement with those in the literature [12]. The oxidation of the mixture of 3a and 4a with potassium chromate in diluted sulfuric acid leads to the known [17] pure 1,5-dimethylbicyclo[3.2.1]octan-8-one (5).



Similarly the reaction of 1 with concentrated hydrochloric acid and an acidic ion exchanger produces besides olefinic compounds (24 %), syn-8-chloro-1,5-dimethylbicyclo[3.2.1]octane (6) (53 %) [18], anti-8-chloro-1,5-dimethylbicyclo[3.2.1]-octane (7) (0,8 %) and two unidentified isomeric chlorides (11 % and 10 %) (maybe a chloro-dimethylbicyclo[3.3.0]octane and a simple 1,2-addition product).



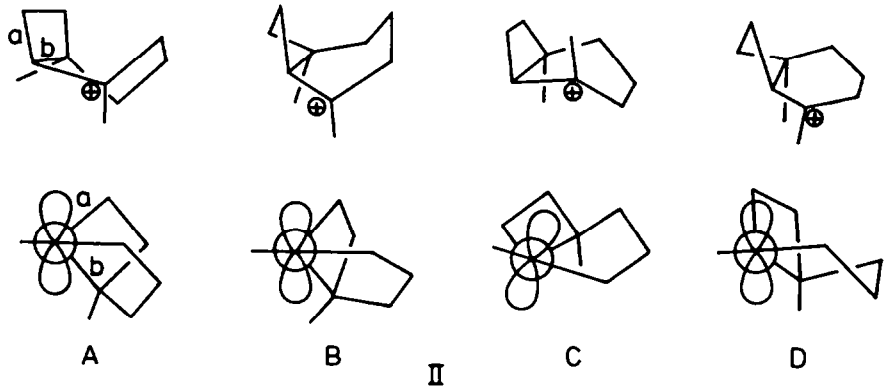
The structure of the main product was established by spectroscopic methods (cf. experimental part). An authentic sample of the anti-isomer 7 was synthesized from syn-alkohol 3a by substitution from the reaction with tetrachloromethane/triphenylphosphine.

The selective synthesis of another isomer, the anti-8-acetoxy-1,5-dimethylbicyclo[3.2.1]octane (4c) should be realized by S_N2-reaction of the known [12] tosylate of syn-1,5-dimethylbicyclo[3.2.1]octan-8-ol with anhydrous potassium acetate in HMPA. But even after 15 h at 130-140 °C only the starting material could be recovered. Under more S_N1-like conditions with anhydrous potassium acetate in acetic acid following a procedure of Woodward et al. [19] we obtained as the main product the olefin 2 and only 13 % of an acetate fraction consisting of 74 % anti-8-acetoxy-1,5-dimethylbicyclo[3.2.1]octane (4c) and 23 % of the syn-isomer 3c. Hydrolysis of the mixture gave a 75:25 mixture (^{13}C NMR spectroscopic) of the isomeric alkohols 4a and 3a.

Discussion

For the diene 1 stable conformations have hitherto not been determined. But the well-defined twist-boat structure with C_2 symmetry for the unsubstituted cis, cis-cycloocta-1,5-diene [20], which was found also for the trans-3,7-dimethyl-cis, cis-cycloocta-1,5-diene [21], should also be a stable conformation of 1. Therefore we use such a conformation for representation of the mechanism.

I



II

III

We suppose that first the tertiary carbenium ion I is formed by protonation of one of the two double bonds of 1. This cation has two possibilities for transannular bridging. The Markovnikov-like parallel π-cyclisation leading to the strained bicyclo[4.2.0]octylsystem II involving a tertiary cationic centre, whilst the crossed π-cyclization (anti-Markovnikov-like) would form the thermodynamically more stable bicyclo[3.3.0]octyl-system, but with a secondary cationic centre. In the case of acid catalyzed additions to 1 obviously the parallel cyclization is the predominant or exclusive reaction pathway, although the (unsubstituted) bicyclo[4.2.0]octane is calculated to be 16.3 kcal/mol [22] or 17.2 kcal/mol [23] less stable than the bicyclo[3.3.0]octane. The stabilization of the tertiary cation II over the 1,5-dimethylbicyclo[3.3.0]oct-2-yl-carbenium ion (which would be formed by crossed π-cyclisation) should be larger than the ring strain difference of the two bicyclic cations. Usually tertiary cations are 12-16 kcal/mol more stable than corresponding secondary ones [24].

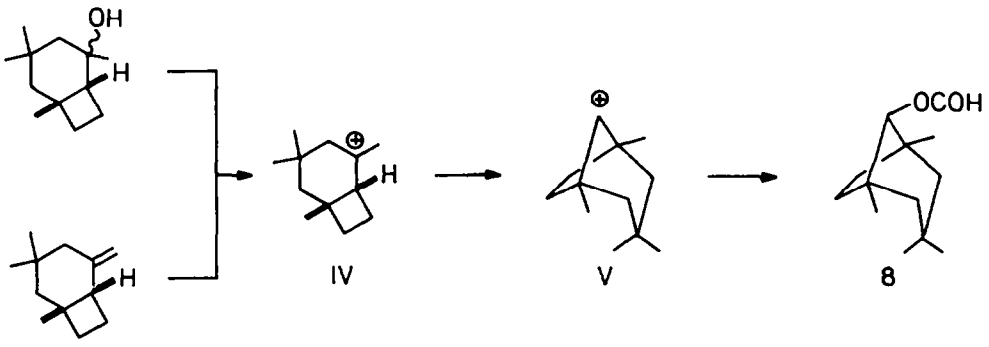
Because of the large ring strain II is rearranged easily by a Wagner-Meerwein type rearrangement to the bicyclo[3.2.1]oct-8-yl system, which was calculated to be 18.6 kcal/mol [22] or 20.7 kcal/mol [23] more stable. In the case when sufficiently strong nucleophiles are present in the solution this intermediate is trapped and syn-8-substituted compounds are formed. If nucleophiles are absent, as in the case of isomerization of the diene 1 with $BF_3.Et_2O$ [12], another Wagner-Meerwein rearrangement leads to the 2,5-dimethylbicyclo[3.3.0]oct-2-yl carbenium ion,

which reacts by deprotonation to the olefin 2.

The cyclohexyl segment in II is formed first in a slightly twisted boat conformation A, which is quite similar to the conformation of the diene 1. Looking to the Newman projection of this cation the subsequent Wagner-Meerwein-type rearrangement from this conformation is unlikely, because neither the peripher σ-bond a nor the central σ-bond b can overlap effectively with the free orbital of the carbenium ion centre. Also the boat conformations B and C, which are formed by pseudorotation from A are unsuitable for rearrangement. However from C the conversion to the chair conformation D should be possible with low activation energy. The Newmanprojection makes evident, that here the overlap of the σ-bond a with the free p-orbital of the cationic centre is realized. This type of rearrangement is called "bridged migration" [25]. As an alternative the migration of bond b which leads to the bicyclo[3.3.0]octyl-system, is called "fused migration". This rearrangement is unlikely in all conformations shown. However, there are known some reactions of model compounds as well as natural products, where both pathways are observed [25,26,8g,8f].

On the other hand the acetolysis of the epimeric brosylates of bicyclo[4.2.0]-octan-2-ol from each isomer in addition to olefinic products yield only one 8-substituted bicyclo[3.2.1]octane, i.e. the syn-bicyclo[3.2.1]octan-8-ol (bridged migration) from the endobrosylate and the anti-bicyclo[3.2.1]octan-8-ol from the exobrosylate [27]. The reaction pathway in this case obviously depends upon the configuration. Therefore classical planar secondary carbenium ions [28] cannot be the intermediates; nonclassical carbonium ions [28,29] or a concerted mechanism are more likely.

Contrary to that observation the cation II in our reactions should exist as a classical tertiary carbenium ion like the protoilludyl cation in solvolysis reactions of protoilludene derivatives to syn-bicyclo[3.2.1]oct-8-yl derivatives [30] or in acid catalyzed hydration of humulene to the tricyclic sesquiterpene alcohol apollan-11-ol [31]. Similarly the formolysis of epimeric tetramethyl-cis-bicyclo-[4.2.0]octan-2-ols and 4,4,6-trimethyl-2-methylene-cis-bicyclo[4.2.0]octane yields besides other products only the syn-8-formyloxy-tetramethylbicyclo[3.2.1]octane (8) and cations IV and V are postulated [32].

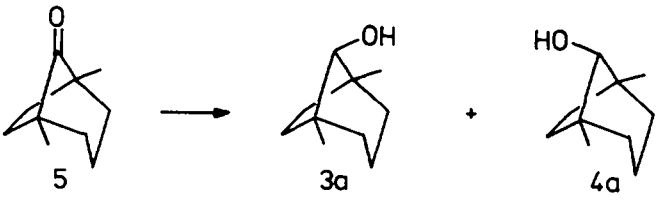


This high stereoselectivity in formation of syn-8-substituted bicyclo[3.2.1]-octanes 3, 6 and 8 cannot be explained from the classical planar intermediates III or V, respectively.

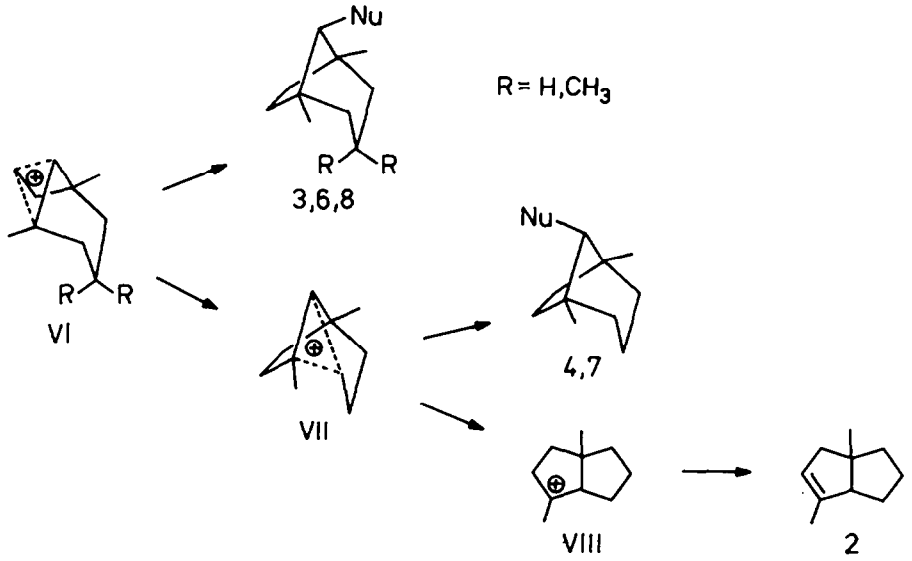
The direction of the nucleophilic attack on such a cation should be determined by the steric hindrance of the γ-hydrogen atoms on C_2 and C_4 or C_6 and C_7, respectively. On closer inspection using Dreiding models it is obvious that an attack from the syn-side should be more difficult than from the anti-side and a reverse stereochemistry for these reactions should be observed.

To verify this suggestion we reduced the ketone 5, which is sterically and elec-

tronically comparable to the cation III, with $LiAlH_4$ in ether and obtained a 95:5 mixture of the syn- and the anti-1,5-dimethylbicyclo[3.2.1]octan-8-ols 3a and 4a. In the same manner the reactions of the ketone 5 with some Grignard reagents give anti-8-alkyl-syn-8-hydroxy-1,5-dimethylbicyclo[3.2.1]octanes [16] (cf. also [33]). In these reactions the steric factors operate as expected.



Furthermore the nucleophilic substitution of the syn-1,5-dimethylbicyclo[3.2.1]-octan-8-ol tosylate with acetate anion under S_N1-like conditions gave the anti-acetate as the main product, maybe really via a species like III.
Therefore the cations III and V are unlikely as intermediates in the above-mentioned addition reactions to the diene 1. The formation of 3 and 6 or 8 starting from cations II or IV should proceed rather by Wagner-Meerwein rearrangement and concerted attack by the nucleophile, comparable to S_N2 reaction i.e. bond making and breaking on opposite sides. Alternatively a nonclassical cation VI or a "seminonclassical" [34] structure by "graded sigma participation" [35] is formed. The S_N2-like attack of the nucleophile leads to the syn-products.



On the other hand the rearrangement to the nonclassical cation VII is possible from which the formation of the minor components 4 or 7 can be explained. However the cation undergoes rearrangement to the classical tertiary carbenium ion VIII, which is deprotonated to the olefin 2.
This hypothesis on the structure of the cations II to VII is in good agreement with the usually accepted opinion, that tertiary cations have the classical structure, whereas secondary cations in bicyclic systems normally are bridged (cf. the other conception [36]). Usually these cations exist in form of tetra- or pentacoordinated carbonium ions [24,28,29,37].

EXPERIMENTAL SECTION

Gas chromatograms (GC) were recorded on a Varian Meduline 2700 apparatus modified for using of glass capillary columns (100 m Carbowax 20M and 100 m OV 1). Preparative chromatography was carried out on Kieselgel 100, 70-230 mesh (Merck, Darmstadt) and n-hexane as eluent. IR spectra (film, cm^{-1}) were registered on an UR 20 apparatus of VEB Carl Zeiss, Jena; NMR spectra (in $CDCl_3$, internal standard TMS in ^{13}C and HMDS in ^1H) were recorded on a Tesla BS 487 C (^1H NMR, 80 MHz), on a Bruker WP 200 (^1H NMR, 200.13 MHz, ^{13}C NMR, 50.33 MHz) and on a Brucker CH 90 (^{13}C NMR, 22.63 MHz), chemical shifts cf. ref. [16]; Mass spectra (MS, 70 eV) were recorded on a Varian MAT CH-6 apparatus, signals are given in m/e (rel. %).

Reactions of the diene 1 with formic or acetic acid

A solution of 100 ml 85 % formic acid (or 99 % acetic acid), a catalytic amount of 70 % perchloric acid and 27.2 g (0.2 mol) of the diene 1 (4:1 mixture with 1,6-dimethylcycloocta-1,5-diene) is heated to 60 °C for 3h. The reaction mixture is extracted with 500 ml n-pentane (3 portions) and washed with water, 5 % $NaHCO_3$ solution, dried over night with Na_2SO_4 and the solvent is removed. The residue is subjected to fractional distillation in vacuum. Two fractions are obtained. The lower boiling one (6.0 g, 22 % yield); bp_{20} 57-59 °C, n_D^{20} 1.4692 was identified as a mixture of 2 (72 %) [12], 17 % of starting material 1 and two unknown isomers. The higher boiling fraction (23.1 g, 63 % yield; bp_2 50-52 °C, n_D^{20} 1.4676; ref. [15] bp_{13} 68 °C) contains two isomeric formates 3b and 4b (92:8).

syn-8-formoxy-1,5-dimethylbicyclo[3.2.1]octane (3b): MS: 182 (M^+, 24), 154 (4), 136 (84), 121 (59), 108 (89), 107 (100); IR: 1720, 1140; ^1H NMR (80 MHz): 8.17 (s, 1H, -OCHO), 4.58 (S, 1H, H_8), 1.48 (m, 10H, $-CH_2-$), 0.85 (S, 6H, $-CH_3$).

Analogous the reaction in acetic acid yields after work up the olefinic fraction (45 % yield) and a higher boiling fraction (40 % yield, bp_{14} 94-98 °C, n_D^{20} 1.4681; ref. [15] bp_9 74 °C) which contains 85 % of the acetates 3c and 3d (92:8) and 15 % of the alcohol 3a.

syn-8-acetoxy-1,5-dimethylbicyclo[3.2.1]octane (3c): MS: 196 (M^+, 14), 152 (9), 137 (20), 136 (97), 121 (49), 108 (81), 107 (100); IR: 1710, 1090; ^1H NMR (80 MHz 4.50 (s, 1H, H_8), 2.03 (s, 3H, $-OCOCH_3$), 1.45 (m, 10H, $-CH_2-$), 0.85 (s, 6H, $-CH_3$).

Formation of 1,5-dimethylbicyclo[3.2.1]octan-8-ols

a) by hydrolysis of 8-formoxy-1,5-dimethylbicyclo[3.2.1]octanes: A mixture of 11.2 g (0.2 mol) KOH in 100 ml methanol and 18.2 g (0.1 mol) of the formates 3b and 4b (92:8) was refluxed for 1 h, cooled to r.t., poored into 500 ml of water and extracted with n-pentane (3x 50 ml). After usual work up distillation yields 12.0 g (78 %) of a 92:8 mixture of the alcohols 3a and 4a (bp_{10} 80-82 °C, mp 40-42 °C, ref. [15] mp 43 °C).

b) by reduction of 1,5-dimethylbicyclo[3.2.1]octan-8-one (5): To a stirred suspension of 0.19 g (50 mmol) $LiAlH_4$ in 50 ml abs. ether at r.t. are droped 4 g (26 mmol) of the ketone 5 in 50 ml abs. ether and refluxed for 1 h. After usual work up with water and diluted H_2SO_4 the organic layer was separated and the aqueous phase extracted twice with 25 ml ether. The combined etheral solutions are neutralized, dried and the solvendis removed. Distillation yields 3.4 g (85 %) of a 95:5 mixture of the alcohols 3a and 4a (bp_{10} 81-82 °C, mp 42 °C).

syn-1,5-dimethylbicyclo[3.2.1]octan-8-ol (3a): MS: 154 (M^+, 63), 136 (47), 123 (97), 121 (40), 108 (77), 107 (100); IR: 3480, 1053; ^1H NMR (200 MHz, TMS): 3,01 (s, 1H, H_8), 2.66 (bs, 1H, -OH), 1.55-1.25 (m, 8H, $-CH_2-$), 1.17 (m, 2H, $-CH_2-$), 0.81 (s, 6H, $-CH_3$).

Oxidation of the alcohols 3a and 4a

To a vigorously stirred solution of 15.4 g (0.1 mol) of the 92:8 mixture of the alcohols 3a and 4a in 70 ml ether at 15 °C is droped a solution of 11.8 g (40 mmol) $K_2Cr_2O_7$ in 20 ml conc. H_2SO_4 and 50 ml water. The stirring is continued for 15 min, then the reaction mixture is diluted with 250 ml of water, the etheral phase is separated and the aqueous is extracted twice with 50 ml of ether. Usual work up and distillation yields 13.4 g (88 %) of pure ketone 5.

1,5-dimethylbicyclo[3.2.1]octan-8-one (5): bp_{10} 72-74 °C (ref. [17] bp_{23} 90-91 °C); MS: 152 (M^+, 22), 137 (2), 134 (7), 124 (4), 123 (4), 68 (100); IR: 1742; ^1H NMR (80 MHz): 1.9-1.3 (m with bs at 1.64, 10 H, $-CH_2-$), 0.92 (s, 6H, $-CH_3$); ^{13}C NMR (22,63 MHz): 226.8 (C_8), 46.2 (C_1/C_5), 43.55 (C_6/C_7), 29.0 (C_2/C_4), 19.1 ($C_3/C_9/C_{10}$).

Reactions of the diene 1 with mineral acids

A mixture of 100 ml 37 % hydrochloric acid, 1 g "Wofatit KPS" ion exchange resin (H-form) and 13.6 g (0.1 mol) of the 4:1 diene mixture was refluxed with stirring for 1 h. The cold solution then was extracted 3x with n-pentane (75 ml).

The combined extracts are worked up as usual and subjected to fractional distillation in vacuum yielding an olefinic fraction (3.3 g, 24 %) and a higher boiling fraction (9.2 g, 53 %) of chlorides (bp_7 70-73 °C, n_D^{20} 1.4759, ref.[18] bp_7 73 °C; 71 % 6a, 0.8 % 7, and 15 % or 13 % of not identified isomers).

syn-8-chloro-1,5-dimethylbicyclo[3.2.1]octane (6a): MS (GC/MS coupling): 172 (M^+, 14), 157 (7), 137 (44), 136 (18), 95 (100); IR: 2985, 2932, 1463, 1385, 830; ^{1}H NMR (80 MHz): 3.46 (s, 1H, H_8), 1.7-1.3 (m, 10H, $-CH_2-$), 0.91 (s, 6H, $-CH_3$).

In a similar way the corresponding bromo- and iodocompounds were formed by reaction of 1 with 48 % hydrobromic acid or 55 % hydroiodic acid.

syn-8-bromo-1,5-dimethylbicyclo[3.2.1]octane (6b): bp_{12} 95-97 °C, n_D^{20} 1.5045 (ref.[18] bp_{10} 93 °C); MS: 216 (M^+, 1.5), 201 (0.4), 137 (78), 109 (49), 95 (63), 81 (100); IR: 2982, 2930, 1460, 1385, 828; ^{1}H NMR (80 MHz): 3.68 (s, 1H, H_8), 1.7-1.2 (m, 10H, $-CH_2-$), 0.92 (s, 6H, $-CH_3$).

syn-8-iodo-1,5-dimethylbicyclo[3.2.1]octane (6c): purified by chromatography silica gel; MS: 264 (M^+, 10-3); 137 (60); 109 (7); 95 (80); 81 (100). IR: 2980, 2932, 1460, 1382, 830; ^{1}H NMR (80 MHz): 3.86 (s, 1H, H_8), 1.7-1.2 (m, 10H, $-CH_2-$), 0.87 (s, 6H, $-CH_3$).

Synthesis of anti-8-chloro-1,5-dimethylbicyclo[3.2.1]octane (7)

To a solution of 14.4 g (55 mmol) triphenylphosphine in 30 ml CCl_4 (dried with P_2O_5 and distilled) under stirring is droped a solution of 7.7 g (50 mmol) 3a (95 % purity) in 10 ml dried CCl_4. After standing 3 days at r. t. the mixture was stirred for 2h at 60 °C and standing another day at r.t. in which two phases appeared. After removal most of the solvent the crystal pulp was stirred with water and extracted several times with 50 ml portions of n-pentane. The triphenylphosphine oxide and the two phases were separated. The organic layer was dried, the solvent was evaporated and the residue was distilled in vacuum yielding 4.8 g (56 %) of 7 contaminated with 15 % of an unidentified isomeric compound.

anti-8-chloro-1,5-dimethylbicyclo[3.2.1]octane (7): bp_7 65-67 °C, n_D^{20} 1.4782 MS: 172 (M^+, 48), 157 (4), 137 (11), 136 (16), 123 (100); IR: 2982, 2930, 1463, 1382, 828; ^{1}H NMR (80 MHz): 3,58 (s, 1H, H_8); 1.9-1.3 (m, 10H, $-CH_2-$), 1.03 (s, 6H, $-CH_3$).

Synthesis of anti-8-acetoxy-1,5-dimethylbicyclo[3.2.1]octane (4c)

A mixture of 98 g (1 mol) of anhydrous KOAc, 90 ml acetic acid and 7.7 g (25 mmol) of the tosylate of 3a (95 % purity) prepared according ref. [12] from 95:5 mixture of 3a and 4a was refluxed for 2h. To the cold reaction mixture 100 ml of water are added and then the solution was extracted 3x with 50 ml each n-pentane. After usual work up distillation yielded an not identified olefinic fraction (2.6 g, 76 %) and 0.64 g (13 %) of an acetate fraction bp_9 72-78 °C (74 % 4c, 23 % 3c and 3 % of an unidentified compound).

anti-8-acetoxy-1,5-dimethylbicyclo[3.2.1]octane (4c): MS: 196 (M^+, 1), 154 (6), 136 (100), IR: 1738, 1048; ^{1}H NMR (80 MHz): 4.45 (m, 1H, H_8), 2.01 (s, 3H, $OCOCH_3$), 1.42 (m, 10H, $-CH_2-$), 0.82 (s, 6H, $-CH_3$).

Hydrolysis of 0.5 g (2.5 mmol) of the acetate mixture in a refluxing solution of 1.12 g (20 mmol) KOH in 15 ml methanol for 1 h after usual work up yields 350 mg (90 %) of a 75:25 mixture (^{13}C NMR spectroscopic) of 4a and its isomer 3a.

anti-1,5-dimethylbicyclo[3.2.1]octan-8-ol (4a): MS: 154 (M^+, 18), 136 (54), 123 (93), 121 (9), 108 (63), 107 (100); IR: 3440, 1068; ^{1}H NMR (80 MHz): 3.00 (s, 1H, H_8), 1.36 (m, 10H, $-CH_2-$), 0.92 (s, 6H, $-CH_3$).

REFERENCES

1 Transannular Reactions of Cycloalkenes, Cycloalkadienes, and Cycloalkatrienes, Part XII., for Part XI cf. G. Haufe, Tetrahedron Lett. 25, 4365 (1984).

2 Presented (in part) at the spring meetings of the Chemical Society of GDR, Jena, April (1983); and Rostock, March (1984).

3 Reviews: [a] A. C. Cope, M. M. Martin, M. A. Mc Kervey; Q. Rev., Chem. Soc. 20, 119 (1966).
[b] J. K. Sutherland; Tetrahedron 30, 1651 (1974).
[c] F. Freemann; Chem. Rev. 75, 439 (1975).
[d] G. Haufe, M. Mühlstädt; Z. Chem. 19, 170 (1979).

4 R. S. Matthews, J. K. Whitesell; J. Org. Chem. 40, 3312 (1975).

5 E. Osawa, K. Aigami, Y. Inamoto; Tetrahedron 34, 509 (1978).

[6] J. A. Marshall; Synthesis 1972, 517.

[7] N. H. Fischer, E. J. Olivier, H. D. Fischer; Fortschr. Chem. Org. Naturst. 38, 47 (1979).

[8] [a] J. B. Hendrickson; Tetrahedron 7, 82 (1959).
[b] F. Šorm; Pure Appl. Chem. 2, 533 (1961).
[c] W. Parker, J. S. Roberts, R. Ramage; Q. Rev., Chem. Soc. 21, 331 (1967).
[d] R. M. Coates; Fortschr. Chem. Org. Naturst. 33, 102 (1976).
[e] W. Herz; Isr. J. Chem. 16, 32 (1977).
[f] H. Shirahama, Y. Ohfune, S. Misumi, T. Matsumoto; J. Synth. Org. Chem. Japan 36, 569 (1978).
[g] T. Matsumoto, H. Shirahama; Kagaku To Seibutsu 18, 215 (1980).

[9] J. M. Locke, E. W. Duck; J. Chem. Soc., Chem. Commun. 1965, 151.
L. H. Gale; J. Org. Chem. 33, 3643 (1968).
G. Eglinton, W. Mc Crae, R. A. Raphael, J. A. Zabkiewicz; J. Chem. Soc. C 1969, 474.
T. Sasaki, K. Kanematsu, Y. Yukimoto; J. Org. Chem. 37, 890 (1972).
J. N. Labows, jr. D. Swern; J. Org. Chem. 37, 3004 (1972).
S. Uemura, A. Onoe, H. Okazaki, M. Okano, K. Ichikawa; Bull. Chem. Soc. Jpn. 49, 1437 (1975).

[10] T. S. Cantrell; J. Org. Chem. 32, 1669 (1967).
I. Tabushi, K. Fujita, R. Oda; Tetrahedron Lett. 1967, 3755.
I. Tabushi, K. Fujita, R. Oda; Tetrahedron Lett. 1967, 3815.
H. Takashi, J. Tsuji; J. Am. Chem. Soc. 90, 2387 (1968).
H. J. Franz, W. Höbold, R. Höhn, G. Müller-Hagen, R. Müller, W. Pritzkow, H. Schmidt; J. Prakt. Chem. 312, 622 (1970).
T. S. Cantrell, B. L. Strasser; J. Org. Chem. 36, 670 (1971).
M. Julia, E. Colomer; Ann. Quim. 67, 199 (1971).
P. K. Wong, J. K. Stille; J. Organomet. Chem. 70, 121 (1974).
P. M. Henry, M. Davies, G. Ferguson, S. Phillips, R. Restivo; J. Chem. Soc., Chem. Commun. 1974, 112.
K. S. Chung, A. I. Scott; Tetrahedron Lett. 1975, 49.
S. Uemura, A. Onoe, M. Okano; Bull. Chem. Soc. Jpn. 48, 3702 (1975).
S. Uemura, A. Onoe, M. Okano; Bull. Chem. Soc. Jpn. 50, 1078 (1977).
M. Akbarzaden, C. B. Anderson; J. Organomet. Chem. 197, C-5 (1980).
A. Toshimitsu, S. Uemura, M. Okano; J. Chem. Soc., Chem. Commun. 1982, 87.
S. Uemura, S.-I. Fukuzawa, A. Toshimitsu, M. Okano; J. Org. Chem. 48, 270 (1983).

[11] Y. Yamada, A. Shibata, K. Iguchi, H. Sanjoh; Tetrahedron Lett. 1977, 2407.

[12] J. K. Whitesell, R. S. Matthews, P. A. Solomon; Tetrahedron Lett. 1976, 1549.

[13] A. Wolf, Diplomwork, Leipzig (1981).

[14] K. Suga, S. Watanabe, T. Fujita, T. Shiwada; Isr. J. Chem. 10, 15 (1972). The diene 1 is obtained in a 82:18 mixture with 1,6-dimethylcycloocta-1,5-diene, which obviously do not disturb the reaction because it is rearranged to 2,5-dimethylbicyclo[3.2.1]oct-2-ene (2) under acidic conditions (cf. also ref. [12]).

[15] Cf. also A. Mulder, A. de Jong; Ger. Offen. DE 2,918,901; C.A. 92, 110 584 (1980). A. J. Mulder, A. J. de Jong; Brit. UK Pat. Appl. GB 2,020,658; C.A. 92, 71 127 (1980).

[16] E. Kleinpeter, G. Haufe, A. Wolf, K. Schulze; Tetrahedron, submitted for publication.

[17] A. J. Mulder; Ger. Offen. DE 2,945,812; C.A. 93, 167745 (1980).

[18] A. Mulder, P. Verbrugge; Eur. Pat. Appl. EP 13,048; C.A. 94, 15 293 (1981); the mixture produced by a similar way is said to contain more than 95 % of 6.

[19] C. S. Foote, R. B. Woodward; Tetrahedron 20, 687 (1964) cf. also P. Müller, J. C. Perlberger; Helv. Chim. Acta 59, 1880 (1976).

[20] F. A. L. Anet, L. Kozerski; J. Am. Chem. Soc. 95, 3407 (1973).
N. L. Allinger, J. T. Sprague; Tetrahedron 31, 21 (1975).
N. L. Allinger, J. F. Viskocil, jr., U. Burkert, Y. Yuh; Tetrahedron 32, 33 (1976).

O. Ermer; J. Am. Chem. Soc. 98, 3964 (1976).
D. N. J. White, M. J. Bovill; J. Chem. Soc. Perkin Trans. II 1977, 1610.
K. Hagen, L. Hedberg, K. Hedberg; J. Phys. Chem. 86, 117 (1982).

21 M. H. P. Guy, P. Heimbach, D. D. MacNicol, D. N. J. White; J. Mol. Struct. 48, 143 (1978).

22 E. M. Engler, J. D. Andose, P. von R. Schleyer; J. Am. Chem. Soc. 95, 8005 (1973).

23 N. L. Allinger, M. T. Tribble, M. A. Miller, D. H. Wertz; J. Am. Chem. Soc. 93, 1637 (1971).

24 H. Hogeveen; Adv. Phys. Org. Chem. 10, 29 (1973).
E. W. Bittner, E. M. Arnett, M. Saunders; J. Am. Chem. Soc. 98, 3734 (1976).
D. Lenoir; Nachr. Chem. Tech. Lab. 26, 787 (1978).

25 M. C. Pirring; J. Am. Chem. Soc. 103, 82 (1981).

26 M. Yanagiya, K. Kaneko, T. Kaji, T. Matsumoto; Tetrahedron Lett. 1979, 1761.
A. B. Smith, III, B. A. Wexler, C. Y. Tu, J. P. Konopelski; J. Am. Chem. Soc. 107, 1308 (1985).
K. Kakiuchi, M. Ue, I. Wakaki, Y. Tobe, Y. Odaira, M. Yasuda, K. Shima; J. Org. Chem. 51, 281 (1986).

27 A. C. Cope, R. W. Gleason, S. Moon, C. H. Park; J. Org. Chem. 32, 942 (1967).

28 G. A. Olah; in "Topics in Current Chemistry", Vol. 80, pp19, Springer Verlag, Berlin (1979).

29 S. Winstein; Q. Rev., Chem. Soc. 23, 141 (1969).

30 Y. Ohfune, H. Shirahama, T. Matsumoto; Tetrahedron Lett. 1976, 2869.
K. Hayano, Y. Ohfune, H. Shirahama, T. Matsumoto; Tetrahedron Lett. 1978, 1991.
S. Misumi, T. Ohtsuka, Y. Ohfune, K. Sugita, H. Shirahama, T. Matsumoto; Tetrahedron Lett. 1979, 31.

31 A. Nickon, T. Iwadare, F. J. Mc Guire, J. R. Mahajan, S. A. Narang, B. Umezawa; J. Am. Chem. Soc. 92, 1688 (1970).
J. B. Stothers, C. T. Tan, A. Nickon, F. Huang, R. Sridhar, R. Weglein; J. Am. Chem. Soc. 94, 8581 (1972).
D. Bainer, J. Forrester, W. Parker; J. Chem. Soc. Perkin Trans. I, 1974 1599.
W. G. Dauben, J. P. Hubbell, N. D. Vietmeyer; J. Org. Chem. 40, 479 (1975).
cf. S. Ranganathan, D. Ranganathan; J. Chem. Educ. 52, 493 (1975).

32 K. Hayano, Y. Ohfune, H. Shirahama, T. Matsumoto; Helv. Chim. Acta 64, 1347 (1981).

33 P. Alessandri, F. De Angelis, A. Gambacorta; Tetrahedron 41, 2831 (1985).

34 J. Paasivirta; Liebigs Ann. Chem. 686, 1 (1965).

35 C. A. Grob, A. Waldner; Tetrahedron Lett. 21, 4429, 4433 (1980).
C. A. Grob; Angew. Chem. 94, 87 (1982), and references cited therein; Angew. Chem. Int. Ed. Engl. 21, 87 (1982).

36 H. C. Brown; in The Nonclassical Ion Problem, Plenum Press, New York (1977).
H. C. Brown; Acc. Chem. Res. 16, 432 (1983), and references cited therein.
C. Walling; Acc. Chem. Res. 16, 448 (1983).

37 G. A. Olah, P. von R. Schleyer (Ed.) in Carbonium Ions, Vol I-V, Wiley Interscience, New York (1968-1975).
W. Kirmse; in Topics in Current Chemistry , Vol. 80, pp 125, Springer-Verlag, Berlin, 1979.
M. Saunders, J. Chandrasekhar, P. von R. Schleyer; in Rearrangements in Ground and Excited States Vol 1, pp 1, Academic Press, New York (1980).
C. S. Yannoni, V. Macho, P. C. Myhre; J. Am. Chem. Soc. 104, 7380 (1982).
D. Lenoir; Nachr. Chem. Tech. Lab. 31, 889 (1983).
C. A. Grob; Acc. Chem. Res. 16, 426 (1983).
G. A. Ilah, G. K. Prakash, M. Saunders; Acc. Chem. Res. 16, 440 (1983).