send unter Normaldruck jeweilen zur Trockne eingedampft. Anschliessend wurde 1 Std. am Hochvakuum bei Zimmertemperatur getrocknet und dann in 60 ml optisch reinem *i*-Octan $1^1/_4$ Std. wie bei **2** → **3** bestrahlt. Dann dampfte man im Vakuum ein und chromatographierte in Benzol/Essigester 4:1. Dabei resultierten neben 12 mg eines komplexen Gemisches von Nebenprodukten und 12 mg Edukt **2** eine Fraktion von 7 mg 14,15-*seco*-Photoprodukt (vgl. **3** bzw. **8**). Gemäss Analyse des Massenspektrums bestand dieses Photoprodukt zu 25% aus der monodeuterierten Verbindung **8**, zu 70% aus undeuteriertem Produkt **3** sowie zu 5% aus einer dideuterierten Spezies (berechnet anhand der Molekularpiks).

Die Elementaranalysen wurden im mikroanalytischen Laboratorium der ETH (Leitung: *W. Manser*) ausgeführt. Für die Aufnahme von NMR.-Spektren im Laboratorium von Prof. Dr. *J. F. M. Oth* danken wir Fräulein *I. Buhrow* und Frau *H. Walker*. Für die massenspektroskopischen Analysen und wertvolle Diskussionen danken wir Herrn PD Dr. *J. Seibl*.

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# 105. Synthesis of Bridged Bicyclic Molecules using Halocarbenes. Derivatives of Bicyclo[4.2.1]nonane

by **Charles W. Jefford, Ulrich Burger,** and **François Delay**
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(16. II. 73)

*Summary.* The addition of dichlorocarbene (generated by the interaction of sodium methoxide and ethyl trichloroacetate) to bicyclo[3.2.1]oct-2-ene, its 3-chloro and *exo*-3,4-dichloro derivatives gives the *exo* 1:1 adducts in yields of 94, 89 and 48%. By suitable chemical reactions of these adducts, convenient syntheses of bicyclo[4.2.1]nona-2,4-diene and bicyclo[4.2.1]non-3-ene, together with their monochloro, dichloro and trichloro derivatives are obtained. Bicyclo[4.2.1]-nonan-3-one is also obtained from bicyclo[4.2.1]non-3-ene in a synthesis starting from the readily available 5-hydroxymethylnorborn-2-ene in an overall yield of 20%.

**Introduction.** – One of the fundamental tasks of organic chemistry is to devise new, preferably simple, syntheses by which hitherto difficultly accessible, yet potentially significant classes of compounds may be prepared.

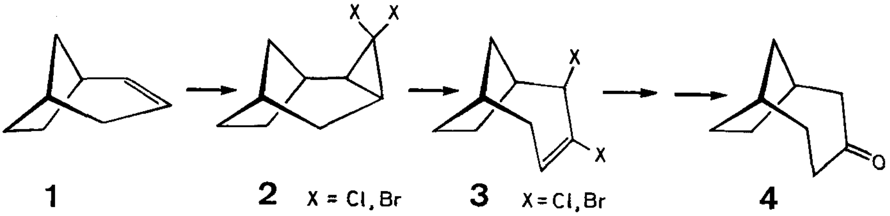
The addition of dihalocarbene to norbornene affords an easy route to a variety of derivatives of bicyclo[3.2.1]octane [1] which are useful for mechanistic and structural studies [2]. We have suggested that the method can be extended to other bridged bicyclic olefins to yield their higher homologues [3]. Additions of dihalocarbenes to the easily accessible bicyclo[2.2.2]octene and bicyclo[3.2.1]octene provide in principle a convenient approach to derivatives of bicyclo[3.2.2]nonane and bicyclo[4.2.1]nonane

[4]. Methods presently available for this last class of compounds usually involve multistep procedures [5].

The advantages of the cycloaddition of dihalocarbene to an olefin are that the resulting dihalocyclopropane compound can be conveniently and variously modified to give cyclopropanes, olefins, alcohols, and ketones [6]. However, possible drawbacks may be the lack of reactivity of the olefin towards the halocarbene, and the reluctance of the resulting adduct to thermally rearrange to its allylic analogue.

We have briefly reported that the addition of dihalocarbene to bicyclo[3.2.1]oct-2-ene (**1**) proceeds in high yield [4]; but that rearrangement of the adduct **2** to its allylic analogue **3** is difficult to control. Nevertheless, reduction and hydrolysis of **3** affords bicyclo[4.2.1]nonan-3-one (**4**).

*Scheme 1*



We now wish to enlarge and improve on this general scheme by reporting in detail on the addition of dichlorocarbene to bicyclo[3.2.1]oct-2-ene and its chloro derivatives, together with a study of the rearrangement of the adducts and description of the synthesis of several bicyclo[4.2.1]nonenes, dienes, and bicyclo[4.2.1]nonan-3-one.

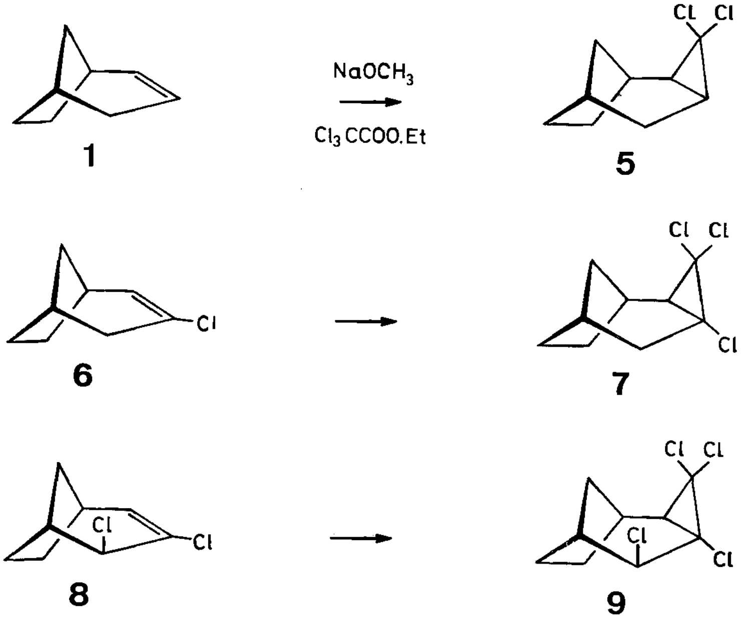
The chemistry of some of these derivatives, in particular their solvolytic, electrocyclic, and photochemical behaviour, will be described elsewhere [7] [8].

## Results and discussion

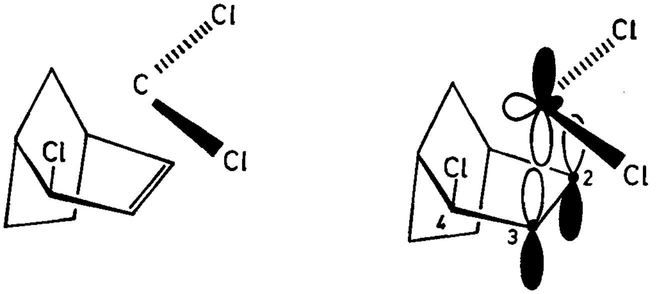
**A. Addition of Dichlorocarbene to Bicyclo[3.2.1]oct-2-ene (1) and its chloro (6) and *exo*-3,4-dichloro (8) derivatives.** – Although numerous methods are available for the generation of halocarbenes, the choice of reagent for a given olefin will be largely governed by consideration of cost, convenience, and yield, if the prime object is the preparation *per se* of the higher homologues. In our experience with norbornene as a representative bridged bicyclic olefin, we have found that the procedure of letting sodium methoxide react with ethyl trichloroacetate satisfies these *desiderata* particularly well in giving uniformly high yields of the appropriate *exo*-dichlorocyclopropane derivatives. We find that treatment of bicyclo[3.2.1]oct-2-ene (**1**) and its chloro derivatives **6** and **8** under the same conditions gives the *exo*-adducts **5**, **7**, and **9** in yields of 94, 89 and 46% respectively (scheme 2).

The *exo* stereochemistry is inferred by analogy with the norbornene case, and finds support from the NMR. spectral data and the structure of the rearranged products (*v. infra*). The supposition of *exo* attack is further strengthened by the fact that the sterically unencumbered olefins **1** and **6** give similar yields whereas, the *exo*-3,4-dichloro derivative **8** which presents an obstacle on the *exo* face to the incoming dichlorocarbene, gives a lower yield.

*Scheme 2*



We have previously shown that the addition of dihalocarbenes to norbornene and its derivatives is particularly sensitive to steric hindrance [9]. Clearly, similar effects would be expected to occur with the structurally related bicyclo[3.2.1]octene and its derivatives. Assuming an *exo* one-step cycloaddition in which the *p*-orbitals of the carbene and double bond interact to form a *Hückel* array [10], it can be seen that the *exo*-4-chloro atom in compound **8** will engender repulsive non-bonding interactions with the dichlorocarbene component of the transition state (Fig.).

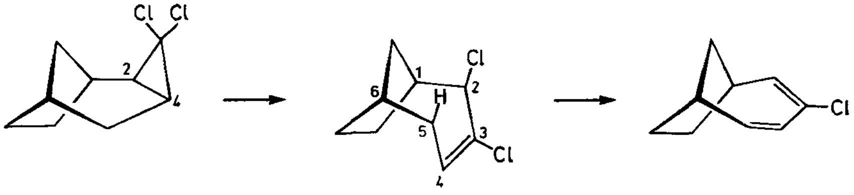


Nevertheless, it appeared worthwhile to see if a consecutive double addition of dichlorocarbene to norbornene would occur. If the conditions are correctly chosen, then it should be possible to pass directly to the bicyclo[4.2.1]octane skeleton; the idea being that the dichlorocarbene adduct with norbornene would spontaneously open to *exo*-3,4-dichlorobicyclo[3.2.1]oct-2-ene (**8**) which could undergo further addition of halocarbene *in situ*. As moderate temperatures are required to ensure the thermal opening of the cyclopropane ring, the binary phase method of *Makosza* was used [11]. Twofold addition occurs as expected, however, even under optimum conditions, only modest yields of the double addition product **9** were obtained, albeit always accompanied by some of product **8**. Thus, for synthetic purposes, the best procedure to be adopted is that of performing the two additions in two separate steps. Moreover, although the two-phase methods using phase transfer catalysts are convenient to handle [11] [12], they offer no particular advantage in the present instance in giving better results than the well-tried method of *Parham* & *Schweizer* [13]. For example, the *Makosza* method has been reported to give yields of 98, 61 and 68% with the olefins **1**, **6**, and **8** respectively [14].

**B. Rearrangement of the Cyclopropane Compounds 5, 7 and 9.** – The ease of rearrangement of bicyclic dichlorocyclopropane compounds is governed by the ring size of the host cycle. Although the dihalocyclopropane compounds obtained from norbornene and bicyclo[2.2.2]oct-2-ene rearrange spontaneously under the reaction conditions, bicyclo[3.2.1]octene and its chloro derivatives furnish adducts (**5**, **7**, and **9**) which possess remarkable thermal stability. These different propensities to rearrangement are undoubtedly a reflection of the strain inherent in the parent bridged bicyclic moiety. The heats of hydrogenation found for norbornene and bicyclo[2.2.2]oct-2-ene are 33.13 and 28.25 kcal/mol [15]; that of bicyclo[3.2.1]octene has apparently not been measured, but a value of 26.0 kcal/mol may be estimated from the observed and calculated values of 27.1 and 25.37 obtained for cyclohexene and bicyclo[3.3.1]non-2-ene [16].

The adduct **5** obtained from bicyclo[3.2.1]octene is most reluctant to rearrange, which clearly is due to the stability of the host cycle. Heating of **5** at 225–235° for 2 hours afforded a single product of rearrangement (**10**) together with some of the diene **11**. Although chloride has a formal choice to migrate to C(2) or C(4), preference for C(2) is clearly dictated by the greater thermodynamic stability of the double bond in the C(3), C(4) position over the C(2), C(3) alternative. Elimination to the diene **11** is difficult to stop and proceeds smoothly in the presence of base. Loss of hydrogen chloride may well occur in a concerted *syn*-1,4 conjugated process.

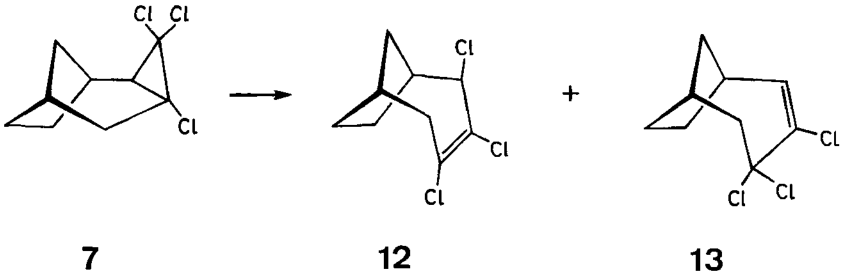
*Scheme 3*



**5** **10** **11**

The trichloro adduct **7** rearranges without elimination at 180° to give two products, the expected *exo*-2,3,4-trichloro-bicyclo[4.2.1]non-3-ene (**12**) together with its isomer 3,4,4-trichlorobicyclo[4.2.1]non-2-ene (**13**). Further heating of **13** merely gives **12** without elimination occurring; thereby demonstrating the thermodynamic preference for the placement of the double bond between the C(3) and C(4) atoms. Inexplicably, compound **12**, unlike **10**, shows no tendency to lose hydrogen chloride; even the action of potassium *t*-butoxide at 0° is without effect.

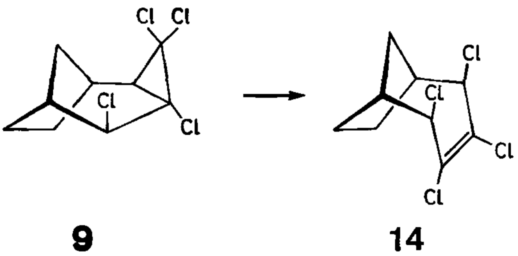
*Scheme 4*



The thermal rearrangement of the tetrachloro adduct **9** follows the same course as before; a single product is obtained, *exo*-2,3,4,5-tetrachlorobicyclo[4.2.1]non-3-ene (**14**).

In the rearranged products **10**, **12**, and **14** the *exo* configuration of the allylic chlorine atoms together with the indicated cycloheptene conformation is based on a consideration of the NMR. spectral data.

*Scheme 5*



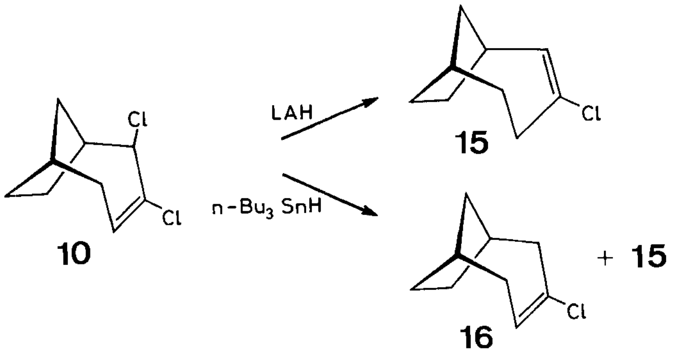
All the aforementioned thermal cyclopropyl-allyl rearrangements give high yields of essentially single products, which means that subsequent reactions of synthetic utility can be realised.

Section C is devoted to a description of some typical (and one atypical) reductive dehalogenations of the rearrangement products **10**, **12**, and **14** to yield hitherto unknown bicyclo[4.2.1]nonenes. In section D two syntheses of bicyclo[4.2.1]nonan-3-one are described.

**C. Reductive Dechlorination.** – Two general methods are available for converting organic halides to their parent hydrocarbons: the use of dissolving metals [17] or complex metal hydrides [18]. It is well known that the choice of reagent strongly influences the reaction course. This is particularly true for the apparently closely related dichloro, trichloro, and tetrachloro derivatives of bicyclo[4.2.1]non-3-ene (**10**, **12**, and **14**).

We have shown that lithium aluminium hydride (LAH) reduces conformationally constrained cyclohexenyl halides by a *SN2'* process [19]. Moreover, it was not clear from our earlier experiment [4], what course constrained cycloheptenyl halides would take, as it was thought that the terms quasi-axial or equatorial would not have the same meaning for the seven membered ring. In fact, reduction of *exo*-2,3-dichlorobicyclo[4.2.1]non-3-ene (**10**) gave solely the product of rearrangement, 3-chlorobicyclo[4.2.1]non-2-ene (**15**), corroborating the mechanism previously proposed. Clearly, not only is the *SN2* process difficult to achieve, but the allylic system must be suitably disposed for synfacial delivery of hydride coupled with departure of allylic chlorine. These findings accord with, but do not confirm, the structure shown for **10**. In contrast, the action of tributyltin hydride on **10** gives mainly the allylically unrearranged product **16** together with **15** in a ratio of 4:1.

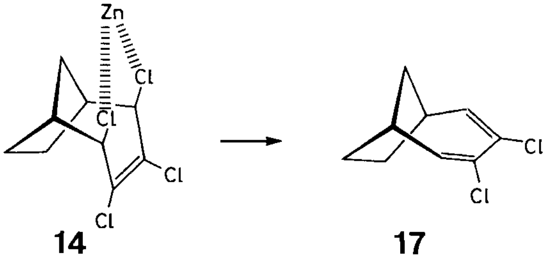
*Scheme 6*



Although the reduction of **10** with LAH is stereospecific and removes only the allylic chlorine, reduction of the other chloro derivatives **12** and **14** is more complex, yielding mixtures resulting from adventitious reduction of the vinyl chlorines.

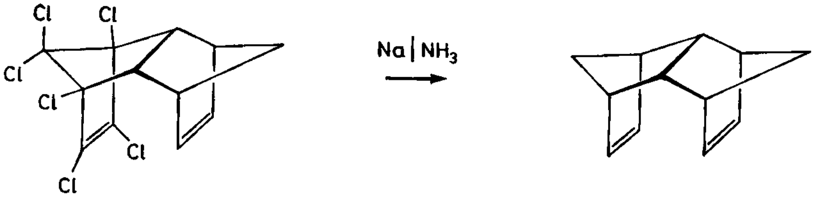
A reaction mechanistically related to the LAH reduction is the zinc-initiated dechlorination of *exo*-2,3,4,5-tetrachlorobicyclo[4.2.1]non-3-ene (**14**). The action of zinc dust on **14** in acetone [20] proceeds in 98% yield to give 3,4-dichlorobicyclo[4.2.1]nona-2,4-diene (**17**). The facility of the elimination undoubtedly springs from the synfaciality of the allylic chlorines which makes them ideally disposed for joint abstraction by an atom of zinc.

*Scheme 7*



The action of dissolving metals is known to reduce vinyl and bridgehead chlorides to give the unrearranged substitution products [21]. The reduction of isodrin to the pre-birdcage hydrocarbon constitutes a good illustration (**18** → **19**) [22]. In the same way, sodium in liquid ammonia behaves impeccably towards the dichloro and tetrachloro bicyclo[4.2.1]non-3-enes (**10** and **14**) in giving the expected parent hydrocarbon (**20**) in 68 and 31% yields respectively. 3,4-Dichlorobicyclo[4.2.1]nona-2,4-diene (**17**) reacts similarly, but proceeds a stage further in giving the same mono-olefin **20**.

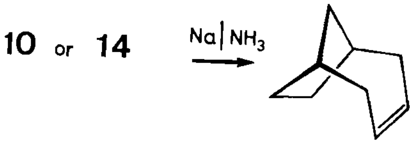
*Scheme 8*



**18** **19**

These results are in accord with the accepted mechanism [23]. Such reductions are thought to take place stepwise; an electron and then a proton adding consecutively to the olefin; in the case of **17**, the diene system is initially converted to the radical anion **21** and then to the radical **22**. Repetition of this process reduces **22** to the hypothetical intermediate 3,4-dichlorobicyclo[4.2.1]non-3-ene (**23**). Subsequent cleavage of the vinyl chlorine bonds probably occurs *via* the vinyl radicals or carbanions to give the final product **20**. Once again, thermodynamic stability appears to be the factor which preserves the double bond between the C(3) and C(4) atoms throughout the reduction process.

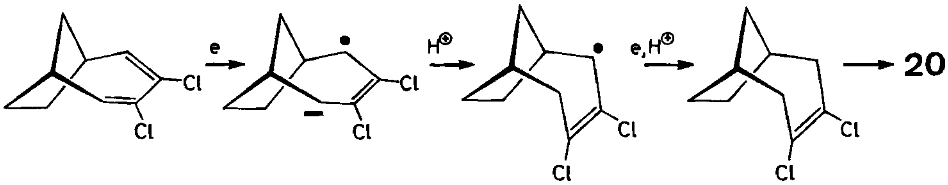
*Scheme 9*



**20**

On the face of it, these reductions are straightforward in that the end-result is simply the removal of chlorine atoms and their replacement by hydrogen. However, the behaviour of *exo*-2,3,4-trichlorobicyclo[4.2.1]non-3-ene (**12**) reveals that subtle variations are possible on the mechanistic theme just outlined. The action of sodium and liquid ammonia on **12** gives none of the expected olefin **20**, but instead *endo*-tricyclo[4.2.1.$0^{2,4}$]nonane (**24**). The ring closure occurs reproducibly and in good yield (55% of **24** after sublimation). The identity of **24** was confirmed by $^{1}H$- and $^{13}C$-NMR. spectroscopy and by comparison with its *exo*-isomer (**25**).

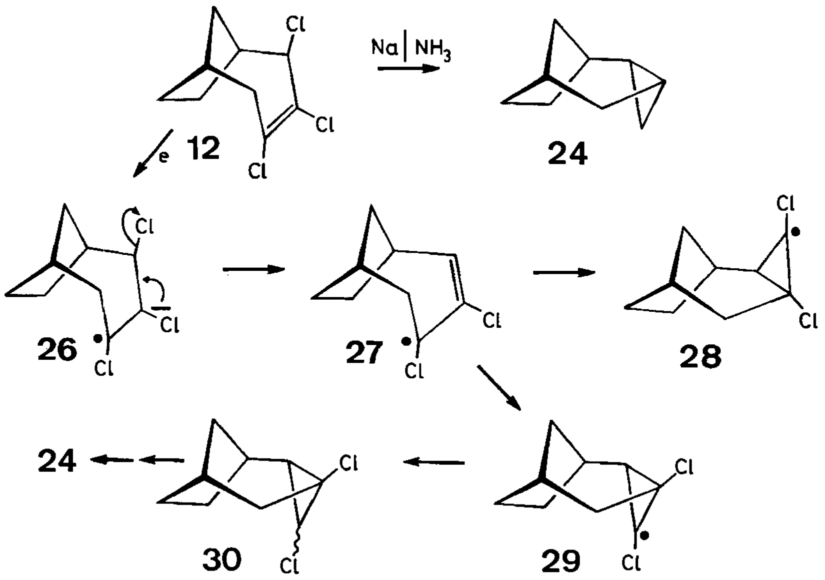
*Scheme 10*



**17** **21** **22** **23**

This reaction is a rare example of electrocyclic closure of an allylic radical to a cyclopropyl radical [24]. A reasonable pathway is that **12** accepts an electron to give

*Scheme 11*

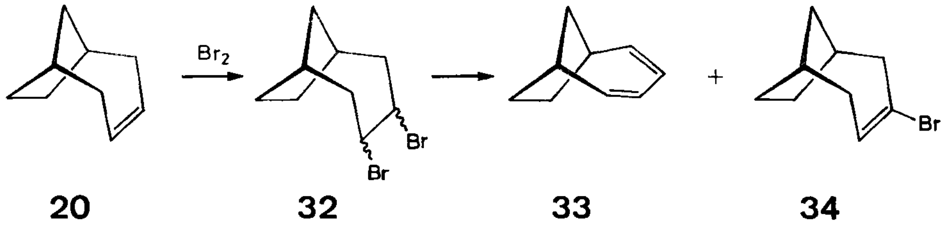


the radical-anion **26** which eliminates chlorine to give the allylic radical **27**. Disrotatory closure of **27** could occur to give either the *exo* or *endo* cyclopropyl radicals **28** and **29**. From inspection of *Dreiding* models it appears that **29** is much less congested than **28** which may account for the stereospecificity of closure. The cyclopropyl radical **29** accepts a further electron and proton to give the dichloro tricyclic structure **30** which on reductive cleavage of the cyclopropyl chlorine bonds gives the product **24**.

A possible objection is that radical **27** appears to be identical to that (**22**) proposed to account for the reduction of the diene **17** which gave none of the cyclopropane product **24**. However, there may be a conformational difference owing to their different provenances. The unsaturated part of intermediate **21** ought to be flatter than the corresponding part of **26**, which should be bent as shown and thus better disposed for closure to **29**.

**D. Synthesis of Bicyclo[4.2.1]nona-2,4-diene and Bicyclo-[4.2.1]nonan-3-one.** – In earlier sections the syntheses of 3-chloro and 3,4-dichlorobicyclo[4.2.1]nona-2,4-dienes (**11** and **17**) is described. The parent diene (**33**) is obtained easily from bicyclo[4.2.1]non-3-ene (**20**). Bromination of **20** gives the dibromo adduct **32** of

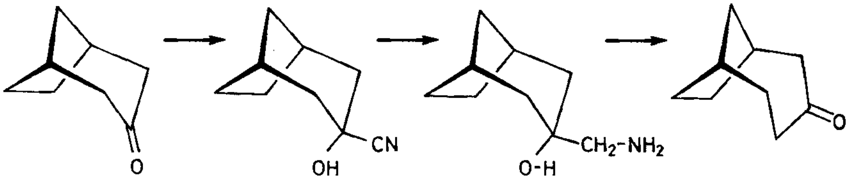
*Scheme 12*



presumed *trans* stereochemistry in 94% yield. Treatment of **32** with potassium *t*-butoxide in dimethylformamide [25] gives the expected diene (**33**) in 60% yield, accompanied by 30% of the product of monodehydrobromination, 3-bromobicyclo[4.2.1]non-3-ene (**34**).

Bicyclo[4.2.1]nonan-3-one (**4**) has already been the object of several syntheses. Several of them possess the disadvantage that they start from bicyclo[3.2.1]octan-3-one (**34**). Addition of diazomethane to **34** gives a difficultly separable mixture of the bicyclo[4.2.1]nonanones-2 and -3 [26]. The *Tiffeneau* ring enlargement of the semipinacol **36**, derived from **34** *via* hydrogenation of **35**, gives bicyclo[4.2.1]nonan-3-one (**4**) [27].

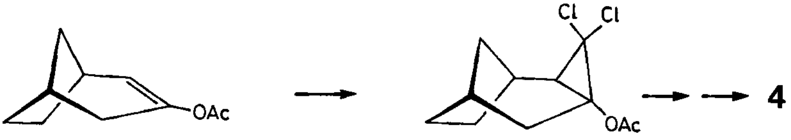
*Scheme 13*



**34** **35** **36** **4**

Addition of dichlorocarbene to the enol acetate **37** derived from **34** and subsequent modification of the resulting adduct **38** is also effective [28], but unnecessarily lengthy in that additional, non-productive steps separate the essential point of departure, the rearranged product (**8**) and the goal (**4**).

*Scheme 14*



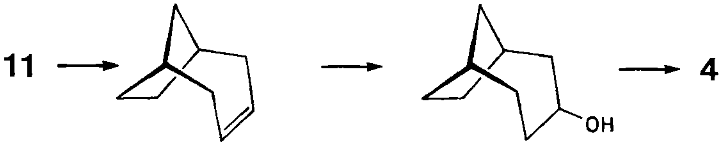
**37** **38**

Ideal though **8** is as a starting point, further addition of dichlorocarbene to it is inefficient (46%) in practice. Furthermore, the thermal rearrangement of the adduct **9** to **14** is also inefficient (47%). Clearly this route to bicyclo[4.2.1]non-3-ene (**20**) and thence to bicyclo[4.2.1]nona-3-one (**4**) is materially wasteful in its early stages.

Similar disadvantages attach to the use of 3-chlorobicyclo[3.2.1]oct-2-ene (**6**). Although addition of dichlorocarbene and rearrangement of the resulting adduct (**7**) prove promising, subsequent reductions of the trichloro olefin (**12**) do not proceed smoothly or as expected (*v. supra*).

Finally, the parent olefin **1** proved to be the most amenable to homologation. Bicyclo[3.2.1]oct-2-ene (**1**) is easily prepared from the commercially available 5-hydroxymethylnorborn-2-ene [29]. The conventional route, namely addition of dichlorocarbene, thermal rearrangement of the adduct (**5** → **10**), removal of the allylic chlorine (**10** → **15**) by LAH reduction, followed by acid hydrolysis of the vinyl chloride (**15** → **4**), gives, at the best, yields of 98, 47, 76 and 28% for each stage. However, by making the rearrangement occur with elimination (**5** → **11**), bicyclo[4.2.1]non-3-ene (**20**) can be obtained by reductive dechlorination of **11**. Hydroboration [30] of **20** gives what appears to be *exo*-3-hydroxybicyclo[4.2.1]nonane (**39**) which on oxidation [31] furnishes the ketone (**4**). Although an extra step is introduced, all steps in this sequence take place in high yields (77, 63, 70 and 81%). In fact,

*Scheme 15*



**20** **39**

starting from 5-hydroxymethylnorborn-2-ene, ketone **4** could be obtained in an overall yield of 20%, which compares favourably with the yields of 17% and 18% starting from norbornene by the methods of *Kraus* [28] and *Hartmann* [27].

We are grateful to *Varian Associates*, Zug, for running the $^{13}$C spectra.

## Experimental Part

Gas liquid chromatography (GLC.) was carried out on model F11 (analytical) or model 990 (semi-preparative) *Perkin-Elmer* instruments.

IR. spectra were recorded, as films on NaCl plates, on a model 257 (*Perkin-Elmer* spectrometer. UV. spectra were recorded on a model 402 *Perkin-Elmer* spectrophotometer.

NMR. spectra were determined at 60 MHz on a model R-12 *Perkin-Elmer* instruments and at 100 MHz on a model XL-100 *Varian* spectrometer using carbon tetrachloride as solvent. Chemical shifts are expressed as ppm with reference to tetramethylsilane taken as zero. Signal intensities are reported in proton units (1H, 2H, *etc.*); multiplicities are expressed as singlet (*s*), doublet (*d*), triplet (*t*) and multiplet (*m*).

All boiling and melting points are uncorrected. Mass spectra were performed by Mrs. *F. Kloeti* and the microanalyses by Dr. *K. Eder*, Ecole de Chimie, Genève.

**A. Dichlorocarbene Additions.** – *General Procedure for the Dichlorocarbene Additions.* The starting olefin (0.27 mol) in petroleum ether (250 ml) was stirred at 5° with sodium methoxide (60.0 g; 1.12 mol). Ethyl trichloroacetate (168.0 g; 0.88 mol) was then added dropwise over 4 h. The temperature was kept at 5–10° during the addition and subsequently at 10° for 4 more h. Stirring was continued overnight while the mixture was allowed to reach room temperature. The brown mixture was poured onto ice and water and extracted with ether. The organic layer was separated, washed with water, a saturated NaCl solution, and dried over $MgSO_4$. Evaporation of ether and distillation *in vacuo* afforded the product.

Bicyclo[3.2.1]oct-2-ene (**1**), 3-chlorobicyclo[3.2.1]oct-2-ene (**6**) and *exo*-3,4-dichlorobicyclo-[3.2.1]oct-2-ene (**8**) under the foregoing conditions gave in each case a single adduct, stable under the conditions of isolation and distillation (see Table).

Table

| Olefin | Adduct | Boiling Point | Yield |
|---|---|---|---|
| **1** | **5** | 77– 78°/0.4 Torr | 94% |
| **6** | **6** | 83– 84°/0.4 Torr | 89% |
| **8** | **9** | 102–103°/0.35 Torr | 46% |

exo-*3,3-Dichlorotricyclo*[*4.2.1.0*$^{2,4}$]*nonane* (**5**). IR.: max. at 3010, 1035 and 1028 cm$^{-1}$ for the cyclopropane moiety. NMR.: 1.05 ppm (*d* of *m*, 1H, $^2J \simeq$ 12.0 Hz), 1,40–2.20 ppm (*m*, 10H) and 2.55 ppm (*m*, 1H). MS.: $M^+$: 190, 192 and 194 in the ratio 9:6:1, characteristic of two chlorines.

$C_9H_{12}Cl_2$ Calc. C 56.56 H 6.32 Cl 37.10% Found C 56,60 H 6.27 Cl 37.11%

exo-*3,3,4-Trichlorotricyclo*[*4.2.1.0*$^{2,4}$]*nonane* (**6**). IR.: max. at 3000, 1063 and 1025 cm$^{-1}$ for the cyclopropane moiety. NMR.: 1.07 ppm (*d* of *m*, 1H, $^2J \simeq$ 12.0 Hz), 1.70–2.30 ppm (*m*, 7H), 1.40–1.80 ppm (*m*, 3H).

$C_9H_{11}Cl_3$ Calc. C 48.00 H 4.90 Cl 47.20% Found C 47.87 H 4.93 Cl 47.21%

exo-*3,3,4,5-Tetrachlorotricyclo*[*4.2.1.0*$^{2,4}$]*nonane* (**9**). IR.: max. at 3013, 1040 and 1005 cm$^{-1}$ for the cyclopropane moiety. NMR.: 1.15 ppm (*d* of *m*, 1H, $^2J \simeq$ 12.2 Hz), 1.50–2.90 ppm (*m*, 8H), 4.88 ppm (fine *t* or *d* of *d*, 1H, $^3J \simeq$ 1.8 Hz). MS.: $M^+$: four main peaks: 258, 260, 262, 264 in the ratio 27:36:18:4, characteristic of four chlorines.

$C_9H_{10}Cl_4$ Calc. C 41.50 H 3.84 Cl 54.66% Found C 40.67 H 3.92 Cl 55.30%

*Double Addition of Dichlorocarbene to Norbornene.* Norbornene (9.5 g; 0.1 mol), chloroform (30 ml), benzyltriethylammonium chloride (0.4 g) and a 50% aqueous sodium hydroxide solution were stirred and heated at 45° for 24 h. After cooling, the mixture was diluted with water, the organic phase was separeted and dried over calcium chloride. Evaporation of the solvent and distillation gave **8** (87%) and **9** (12%).

**B. Cyclopropyl-Allyl Rearrangements.** – i) **Adduct 5** (30.0 g) was stirred and heated at 225–235° under nitrogen for 2 h. After cooling, the black reaction mixture (26.0 g) was chromatographed rapidly over silica (300 g; 70–230 mesh ASTM) using light petroleum as eluant to give 3-chlorobicyclo[4.2.1]nona-2,4-diene (**11**) (2.0–4.0 g) (*v. infra*) and *exo*-2,3-dichlorobicyclo[4.2.1]non-3-ene (**10**) (14.0 g) in 47% yield.

*Compound* **10**: b.p. 107–109°/12 Torr. IR.: max. at 3030 (*w*), 1643 (*m*), 823 (*s*) and 795 (*m*) cm$^{-1}$ for the C—H stretching, C=C and C—H out of plane deformations. NMR.: 1.30–2.90 ppm (*m*, 10H), 4.53 ppm (*d*, 1H, $^3J$ = 4.7 Hz), 5.96 ppm (*d* of *d*, 1H, $^3J \simeq$ 5.3 Hz).

$C_9H_{12}Cl_2$ Calc. C 56.55 H 6.27 Cl 37.20% Found C 56.36 H 6.48 Cl 37.19%

ii) **Adduct 7** (18.0 g) was dissolved in decalin (100 ml) and heated under nitrogen at 180° for 18 h. The solvent was removed by distillation; an NMR. spectrum of the oil revealed *exo*-2,3,4-trichlorobicyclo[4.2.1]non-3-ene (**12**) and 3,4,4-trichlorobicyclo[4.2.1]non-2-ene (**13**) in a ratio of 2:1. Distillation *in vacuo* of the mixture gave a sample of **13** suitable for NMR. and MS. analysis. On heating the reaction mixture for 3 more h. at 180°, **13** was entirely converted into **12**. Total yield of product obtained by thermal rearrangement was 76%.

*Compound* **12**: b.p. 93–95°/0.25 Torr. IR.: max. at 1603 (s) cm$^{-1}$ for the dichlorinated double bond. NMR.: 1.10–2.70 ppm (*m*, 10H), 4.96 ppm (*d*, 1H, $^3J$ = 4.6 Hz). MS.: $M^+$: 224, 226 and 228 in the ratio 3:3:1 (3 Cl).

$C_9H_{11}Cl_3$ Calc. C 47.81 H 4.90 Cl 47.29% Found C 47.85 H 5.08 Cl 47.40%

The structure of **13** could not be unambigously established nevertheless the IR. spectrum revealed a characteristic strong band at 1590 cm$^{-1}$. Moreover, its NMR. spectrum and thermal conversion to **12** favour structure **13**.

*Compound* **13**; b.p. 93–94°/0.25 Torr. IR.: max. at 1590 (*s*), 840 (*m*) and 818 (*s*) cm$^{-1}$. NMR.: 1.20–2.80 ppm (*m*, 9H), 2.98 ppm (*d* of *d*, 1H, $^2J = -17.1$ Hz, $^3J$ = 7.4 Hz), 5.08 ppm (*d* of *d*, 1H, $^3J$ = 6.9 Hz, $J \simeq$ 1.0 Hz). MS.: $M^+$: 224, 226 and 228 in the ratio 3:3:1 (3 Cl).

iii) **Adduct 9** (5.5 g) was heated neat under nitrogen at 200° for 14 h. On cooling the black reaction mixture solidified. Recrystallization from light petroleum (b.p. 50–70°) and decolorization with activated charcoal afforded colourless crystals of *exo*-2,3,4,5-tetrachlorobicyclo[4.2.1]non-3-ene (**14**) (2.6 g, 47% yield).

*Compound* **14**, m.p. 92–95°. IR.: max. at 1615 cm$^{-1}$ characteristic of the tetrasubstituted double bond. NMR.: 1.40–3.05 ppm (*m*, 8H), 4.72 ppm (*d*, 2H, $^3J$ = 4.8 Hz).

$C_9H_{10}Cl_4$ Calc. C 41.50 H 3.85 Cl 54.50% Found C 41.41 H 3.94 Cl 54.50%

**C. Reductive Dehalogenations.** – *3-Chlorobicyclo[4.2.1]non-2-ene* (**15**). **10** (11.0 g; 0.058 mol) in ethyl ether (20 ml) was added dropwise to a suspension of lithium aluminium hydride (LAH) (4.5 g; 0.120 mol) in ethyl ether (90 ml); the mixture was heated under reflux for 48 h. Excess of LAH was decomposed by careful addition of water; the ethereal layer was removed and dried over $MgSO_4$. The solvent was evaporated and distillation of the residue *in vacuo* gave **15** (6.9 g; 0.044 mol) in 76% yield; b. p. 82–83°/11 Torr. IR.: max. at 3039 (*w*), 1643 (*s*), 839 (*m*) and 820 (3) $cm^{-1}$ characteristic of the trisubstituted double bond. NMR.: 1.40–2.90 ppm (*m*, 12H), 6.18 ppm (*d* of *d*, 1H, $^3J$ = 9.3 Hz, $^4J$ = 1.5 Hz). MS.: $M^+$: 156 and 158 in the ratio 3:1.

$C_9H_{16}Cl$ Calc. C 69.02 H 8.37 Cl 22.60% Found C 69.01 H 8.53 Cl 22.57%

*3-Chlorobicyclo[4.2.1]non-3-ene* (**16**). **10** (3.0 g; 15.7 mmol) and tri-*n*-butyltin hydride (5.0 g; 17.2 mmol) were dissolved in ethyl ether (30 ml) and heated under reflux for 20 h. under nitrogen. Ether and tri-*n*-butyltin chloride were removed by distillation. The residue was chromatographed over neutral alumina (60 g) to give a mixture of **15** and **16** (1.5 g; 9.6 mmol) in a ratio of 1:4 in a 61% yield. A sample of pure **16** was isolated for mass spectral analysis. NMR.: 1.35–2.80 ppm (*m*, 12H), 5.78 ppm (*d* of *d* of *m*, 1H). MS.: $M^+$: 156 and 158 in the ratio 3:1 (1 Cl).

**General Procedure for Reductive Dehalogenation with Sodium in Liquid Ammonia.** – A solution of the chloro compound (0.022 mol) in ethyl ether (50 ml) was added dropwise to a solution of sodium (15.0 g; 0.65 atg) in liquid ammonia (120 ml) under nitrogen over 1.5 h. A 50% mixture of methanol and ether was then added and the ammonia was allowed to evaporate. After all the excess sodium had decomposed, the mixture was diluted with water and worked up. Removal of ether gave the crude product.

| Reactant | Product | Yield (%) | m.p. or b.p. | Means of Purification |
|---|---|---|---|---|
| **10** | **20** | 68 | 168–169°/760 Torr | Distillation |
| **12** | **24** | 55 | 57– 61° | Sublimation |
| **14** | **20** | 31 | 168–169°/760 Torr | Distillation |

*Bicyclo[4.2.1]non-3-ene* (**20**). IR.: max. at 3010 (*m*), 1660 (*m*) and 1320 (*w*) $cm^{-1}$ for the *cis* double bond. NMR.: 1.15–2.65 ppm (*m*, 12H), 5.48 ppm (*m*, 2H). MS.: $M^+$: 122.

$C_9H_{14}$ Calc. C 88.52 H 11.48% Found C 88.46 H 11.48%

endo-*Trichloro[4.2.1.0$^{2,4}$]nonane* (**24**). IR.: max. at 3070 (*m*), 3000 (*m*), 1028 (*m*), 1018 (*w*) and 836 (*w*) $cm^{-1}$ for the cyclopropane moiety. NMR.: 0.00–0.70 ppm (*m*, 2H, cyclopropyl), 0.75–2.70 ppm (*m*, 10H). MS.: $M^+$: 122.

$C_9H_{14}$ Calc. C 88.52 H 11.48% Found C 88.49 H 11.56%

The *endo*-configuration was elucidated from the fact that **24** was different to its known *exo* isomer **25** [18]. Compound **24** (and **25**) both displayed nine $^{13}C$ chemical shifts having values of 36.334, 32.955, 32.607, 32.409, 30.175, 29.082, 19.799, 9.684 and 4.360 ppm (and 34.452, 33.608, 32.367, 32.168, 31.523, 29.140, 19.112, 10.822 and 5.109 ppm) respectively with respect to tetramethylsilane taken as 0.000 ppm.

**Synthesis of bicyclo[4.2.1]nonadienes.** – *3-Chlorobicyclo[4.2.1]nona-2,4-diene* (**11**). A solution of adduct **5** (45.0 g; 0.236 mol) in quinoline (150 ml) was stirred and heated at 200° under nitrogen for $4^1/_2$ h. After cooling, the black mixture was diluted with carbon tetrachloride and then washed several times with water, finally with 10% aqueous hydrochloric acid. The resulting organic layer was dried over $CaCl_2$. Evaporation of the solvent and distillation gave **11** (28.0 g; 0.181 mol) in 77% yield. IR.: max. at 3030 (*m*), 1625 (*s*), 805 (*w*) and 719 (*w*) $cm^{-1}$ for the diene system. UV.: $\lambda_{max}$ (in ethanol): 204 nm ($\varepsilon$ = 2350), 223 nm ($\varepsilon$ = 2470) and 265 nm ($\varepsilon$ = 4300). NMR.: 1.25–2.08 ppm (*m*, 6H), 2.33 ppm (*m*, 2H), 5.72 ppm (*d* of *d*, 1H, $^3J$ = 12.0 Hz, $J$ = 1.7 Hz), 6.08 ppm (*d* of *d* of *m*, 1H, $^3J$ = 12.0 Hz, $^3J$ = 8.0 Hz), 6.22 ppm (*d* of *m*, 1H, $^3J$ = 8.0 Hz). MS.: $M^+$: 154 and 156 in the ratio 3:1 (1 Cl).

*Bicyclo[4.2.1]non-3-ene* (**20**). Diene **11** (6.0 g; 0.039 mol) in ethyl ether (40 ml) was added dropwise to a solution of sodium (10.0 g; 0.43 atg) in liquid ammonia (100 ml) over 1.5 h. Excess sodium was decomposed by addition of 50% mixture of ether and methanol and the ammonia was allowed to evaporate. After dilution with water, the organic phase was washed several times with water, dried over $Na_2SO_4$ and distilled. Further distillation of the residue gave **20** (3.0 g; 0.0245 mol) in 63% yield.

*3,4-Dibromobicyclo[4.2.1]nonane* (**32**). Bromine (2.6 g; 0.0162 mol) in $CCl_4$ (2 ml) was added dropwise to a stirred mixture of **20** (2.0 g; 0.0162 mol) and ethanol (0.2 ml) in $CCl_4$ (4 ml) at – 5 to – 1°. After addition, the mixture was allowed to reach room temperature and the solvent was evaporated. The crude solid was recrystallized from petroleum ether to give **32**. (4.3 g; 0.053 mol) in 94% yield. M.p. 78–80°. NMR.: 1.45–3.05 ppm (*m*, 12H), 4.41 ppm (*m*, 2H). MS.: $M^+$: 280, 282 and 284 in the ratio 1:2:1 (2 Br).

$C_9H_{14}Br_2$ Calc. C 38.29 H 4.97 Br 56.74% Found C 38.43 H 5.00 Br 56.55%

*Bicyclo[4.2.1]nona-2,4-diene* (**33**). Dibromo adduct **32** (5.0 g; 16.5 mmol) in dimethylformamide (DMF) (15 ml) was added dropwise to a solution of potassium *t*-butoxide (6.0 g; 53,5 mmol) in DMF (35 ml) under nitrogen at 0° during 40 min. The mixture was stirred for an additional h. and then allowed to reach room temperature. The solution was diluted with water and worked up the usual way to give **33** (1.2 g; 10.0 mmol) in 60% yield and 3-bromobicyclo[4.2.1]non-3-ene (**34**) (0.9 g; 4.5 mmol) in 30% yield.

Bicyclo[4.2.1]nona-2,4-diene (**33**), b.p. 50°/12 Torr. IR.: max. at 3050 (*w*), 3010 (*s*), 1660 (*w*), 1596 (*w*) and 700 (*s*) $cm^{-1}$ characteristic of the diene. UV.: $\lambda_{max}$ (in ethanol): 204 nm ($\varepsilon$ = 1500) and 259 nm ($\varepsilon$ = 5250). NMR.: 1.60–2.25 ppm (*m*, 6H), 2.66 ppm (*m*, 2H), 5.65 ppm (*m*, 2H) and 5.99 ppm (*m*, 2H). MS.: $M^+$: 120.

3-Bromobicyclo[4.2.1]non-3-ene (**34**). b.p. 70°/0.1 Torr. The structure was elucidated by comparison with the chloro analogue **11**. NMR.: 1.15–2.90 ppm (*m*, 12H) and 6.08 ppm (broad *d* of *d*, 1H).

*3,4-Dichlorobicyclo[4.2.1]nona-2,4-diene* (**17**). The tetrachloro product **14** (1.4 g; 5.4 mmol) in acetone (40 ml) and zinc dust (1.5 g) was heated under reflux for 3 h. The mixture was filtered and the solvent distilled and removed. The residue was dissolved in ethyl ether, washed with water and with 10% aqueous hydrochloric acid and finally dried over $Na_2SO_4$. Evaporation of ether gave **17** (1.0 g; 5.3 mmol) in 98% yield. IR.: max. at 3030 (*m*), 1603 (*m*), 1587 (*w*), 819 (*w*), 808 (*w*) and 713 (*w*) $cm^{-1}$ typical of a diene. NMR.: 1.70–2.25 ppm (*m*, 6H), 2.75 ppm (*m*, 2H) and 6.47 ppm (*d*, 2H, $^3J$ = 8.7 Hz). UV.: $\lambda_{max}$ (in ethanol): 271 nm ($\varepsilon$ = 7400), 223 nm ($\varepsilon$ = 5160) and 206 nm ($\varepsilon$ = 6150). MS.: $M^+$: 188, 190 and 192 in the ratio 9:6:1 (2 Cl).

**Synthesis of Bicyclo[4.2.1]nonan-3-one (4).** – i) 3-Chlorobicyclo[4.2.1]non-2-ene (**15**) (6.0 g; 38.3 mol) was stirred at 0° with conc. sulfuric acid (20 ml) for 11 h. After dilution with water, the mixture was extracted with ether and worked up the usual way. Distillation of the solvent and sublimation of the residue gave the ketone **4** (1.45 g; 10.6 mmol) in 28% yield.

ii) Hydroboration. Freshly distilled boron trifluoride etherate (3.9 g; 0.27 mol) was added to a stirred solution of bicyclo[4.2.1]non-3-ene (**20**) (5.0 g; 0.041 mol) and sodium borohydride (0.76 g) in diglyme (20 ml) under oxygen-free nitrogen over 20 min. while the temperature was maintained at 20–25°. The mixture was stirred for an extra hour, and the water was slowly added to decompose excess hydride. The resultant organoborinic acid was oxidized at 30–50° by adding 3N NaOH and 30% aqueous hydrogen peroxide. The reaction mixture was stirred for 1 h at room temperature and extracted with ether and worked up as usual. Distillation of the solvent and chromatography of the residue over silica (50% ether in petroleum ether as eluant) afforded bicyclo[4.2.1]nonan-3-ol (**39**) (4.0 g; 0.027 mol) in 70% yield. Analytical GLC. (9% FFAP on chromosorb W. acid-washed and silanized, 3 m × 2 mm column, 120°) showed one compound in at least 95% purity. The configuration of the C(3) hydroxyl group is most probably *exo*. IR.: max. at 3325 (*s*) $cm^{-1}$ for the hydroxy group. NMR.: 1.05–2.58 ppm (*m*, 14 H), 2.81 ppm (*s*, 1H, exchangeable by deuterium), 3.70 ppm (broad *m*, 1H). MS.: $M^+$: 140.

$C_9H_{16}O$ Calc. C 77.14 H 11.42 O 11.42% Found C 77.22 H 11.39 O 11.44%

iii) Oxidation: A solution of $Na_2Cr_2O_7 \cdot 2H_2O$ (0.72 g), conc. sulfuric acid (0.6 ml) and water (3 ml) was added dropwise over 15 min. to a solution of **39** (0.9 g; 6.43 mmol) in ether (4 ml). The mixture was stirred at room temperature for 4 h., poured onto ice and worked up. Excess ether was evaporated, bicyclo[4.2.1]nona-3-one (**4**) was obtained as a colourless solid (0.72 g; 5.22 mmol) in 81% yield. Its purity was checked by GLC. (9% FFAP on chromosorb W, acid washed and silanized, 3 m × 2 mm column, 120°) and found to be > 99%. M.p. 118–120°. IR.: max. at 1705 $cm^{-1}$. MS.: $M^+$: 138.

$C_9H_{14}O$ Calc. C 78.40 H 10.17 O 11.45% Found C 78.31 H 10.72 O 10.97%

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