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DIHYDROAROMATIC COMPOUNDS IN THE DIELS–ALDER REACTION—IV

SYNTHESIS OF BICYCLIC KETONES

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Abstract—The *in situ* isomerisation and Diels–Alder reaction with 2-acetoxyacrylonitrile, of 2,5-dihydroanisole, leads to the adducts (**1**) which may be used as starting point for the synthesis of a number of *bicyclo* [2,2,2] *octenones*, *bicyclo* [3,2,1] *octenones* and *bicyclo* [3,2,2] *nonenones*. Under similar conditions, 2,5-dihydrotoluene reacts via an ene-reaction to produce, after hydrolysis, the acetylcyclohexadiene (**27**). The base-catalysed equilibration and subsequent Diels–Alder reactions of 2,5-dihydrotoluene have been investigated.

Previous papers in this series[1] and elsewhere[2,3] have described the *in situ* generation of 1 - methoxy - cyclohexa - 1,3 - dienes, in presence of a variety of dienophiles, by thermal isomerisation of the unconjugated isomer. The present communication describes the use of this technique in the synthesis of a number of bicyclic ketones required for comparison with products obtained in our studies of the solvolysis and deamination reactions of methoxyl-substituted substrates.[4]

2,5-Dihydroanisole with 2-acetoxyacrylonitrile,[5] when heated to ~ 175° for 36 h gave a tarry product from which the mixed adducts (**1a** and **1b**) could be isolated in a crystalline condition. Complete separation was not achieved, but the NMR spectrum of the mixed adducts suggested that **1a** (—OCOCH$_3$ at $\delta = 2{\cdot}16$ ppm) was the major component (~ 66%).

Bicyclo [2,2,2] *octane and bicyclo* [3,2,1] *octane series.* Base-catalysed hydrolysis of these crystalline adducts yielded 1 - methoxybicyclo [2,2,2] *oct - 5 - en - 2 - one* (**1c**) as the only product. Recently it has been reported[3a] that this reaction sequence yields the isomeric ketone **2** as a minor product (~ 5%). We have not detected it, possibly because the corresponding adduct is lost in the purification procedure, although the higher reaction temperature (175° as opposed to 150°) may also be partly responsible.

This ketone has been converted by standard means (LAH reduction, or Grignard reaction) to the alcohols **1d–1i**. The stereochemistry of these reactions is of some interest. Both methyl and ethylmagnesium bromides gave mixtures in which the *exo*-alcohol (**1f** and **1h**) predominated, (64% and 67% respectively). These slight preferences probably reflect the smaller steric hindrance to approach of the reagent, associated with the unsaturated bridge. This interpretation is supported by the observed thermodynamic preference for *endo*-configuration of bicyclo[2,2,2]oct-5-en-2-yl compounds.[1c] In contrast, the LAH reduction gave a product containing ~ 70% of the *endo*-alcohol (**1e**), a result qualitatively in accord with the borohydride reduction of bicyclo[2,2,2]octenone.[6] Since no other steric factors are present in this molecule, it appears that towards ionic reagents such as aluminohydride and borohydride the double bond is "bigger" than the saturated bridge. Electrostatic repulsion must presumably contribute towards this effect.

The acid-catalysed rearrangements of the alcohols **1c–1i** and the solvolyses of the corresponding tosylate or 3,5-dinitrobenzoate esters gave high yields of the ketones **5** and **6**. These transformations which are closely related to the pinacol rearrangement, exhibit very interesting stereospecificities which will form the subject matter of a separate communication. At this point we may simply note that the *exo*-alcohols (**1d**, **1f** and **1h**) and their derivatives lead almost exclusively to the ketones **5**, while the corresponding *endo*-alcohols (**1e**, **1g** and **1i**) and their derivatives yield predominantly the ketones **6**. For synthetic work, the mixed *endo*- and *exo*-alcohols were treated with acid and the products (**5** and **6**) separated by preparative GLC. Similar treatment of the saturated alcohols **4** gave the bicyclo [3,2,1] octan - 2 - ones **8** in high yield.

The unconjugated bicyclo [3.2.1] octenones (**5b** and **5c**) when heated under formolysis conditions (98% formic acid buffered with sodium formate), or with toluene-*p*-sulphonic acid in benzene, were quite rapidly converted to a mixture of the conjugated ketones (**6b** and **6c**) and the bicyclo [2,2,2] oct-5-en-2-ones (**7a** and **7b**). Acid treatment of

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ketones **6** (**b** and **c**) and **7** (**a** and **b**) produced similar mixtures, although more slowly.

True equilibrium concentrations of the three ketones were never achieved since at long reaction times, further, unidentified products began to be important. However, it seems possible to say that in both equilibria (I and II) the unconjugated bicyclo [3,2,1] octenone (**5a** or **b**) is very much the minor component.

$$\mathbf{5} \overset{K_I}{\rightleftharpoons} \mathbf{6} \qquad \text{(I)}$$

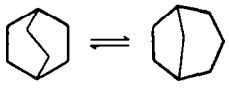
$(K_I \simeq 200\text{–}500)$

$$\mathbf{5} \overset{K_{II}}{\rightleftharpoons} \mathbf{7} \qquad \text{(II)}$$

$(K_{II} \simeq 100\text{–}350)$

A probable mechanism for these equilibrations is given in Scheme 1.

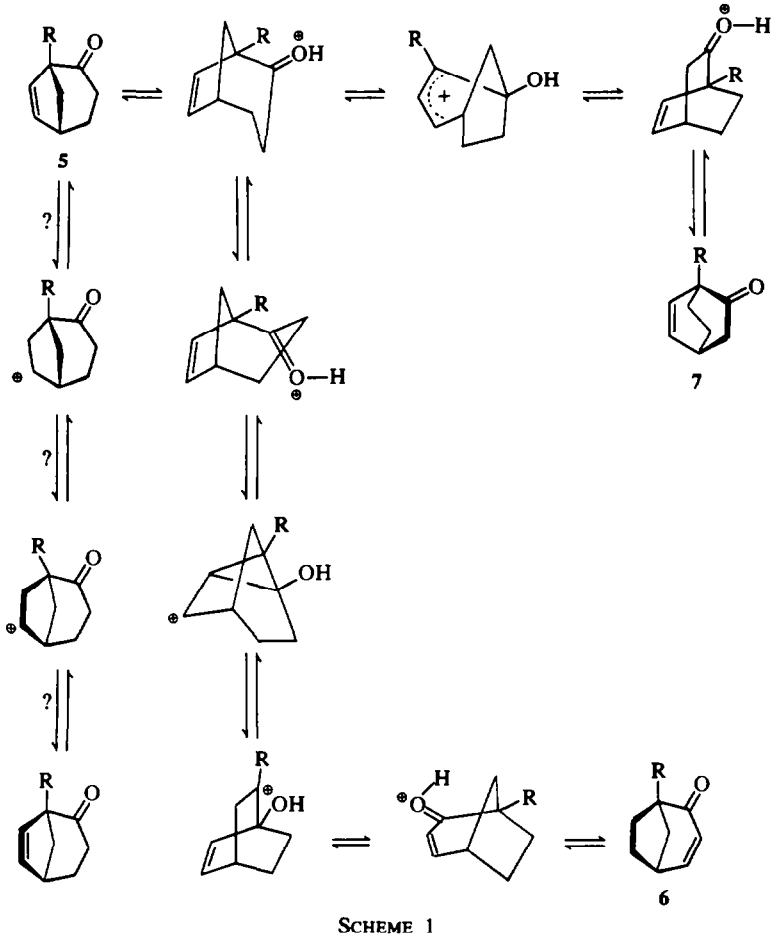
The positions of the equilibria **5** ⇄ **6** and **5** ⇄ **7** are of some interest. It was anticipated that the conjugated ketone **6** would be considerably more stable than the structurally related, but unconjugated isomer **5**. The estimated value of K_I does not appear out of line with previously determined equilibrium constants for similar systems.[7] The rather high value estimated for K_{II} (**5** ⇌ **7**) is somewhat unexpected and deserves comment, particularly in view of the fact that in the parent hydrocarbon system,



equilibrium favours the bicyclo[3,2,1]octane.[8]

These results may be reconciled in terms of the contrasting effect of converting a tetrahedral to a trigonal C atom in the two systems. This will, *inter alia*, increase the angle strain in the bicyclo[3,2,1] octane and reduce non-bonded and torsional interactions in the bicyclo[2,2,2]octane. For a further example of this effect see Ref 16.

While plausible schemes for the direct interconversion of **6** and **7** can be written it is unlikely that this occurs to any appreciable extent since when either of these ketones is treated with acid, **5** is



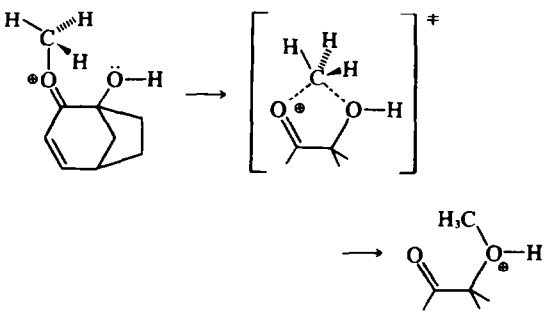
SCHEME 1

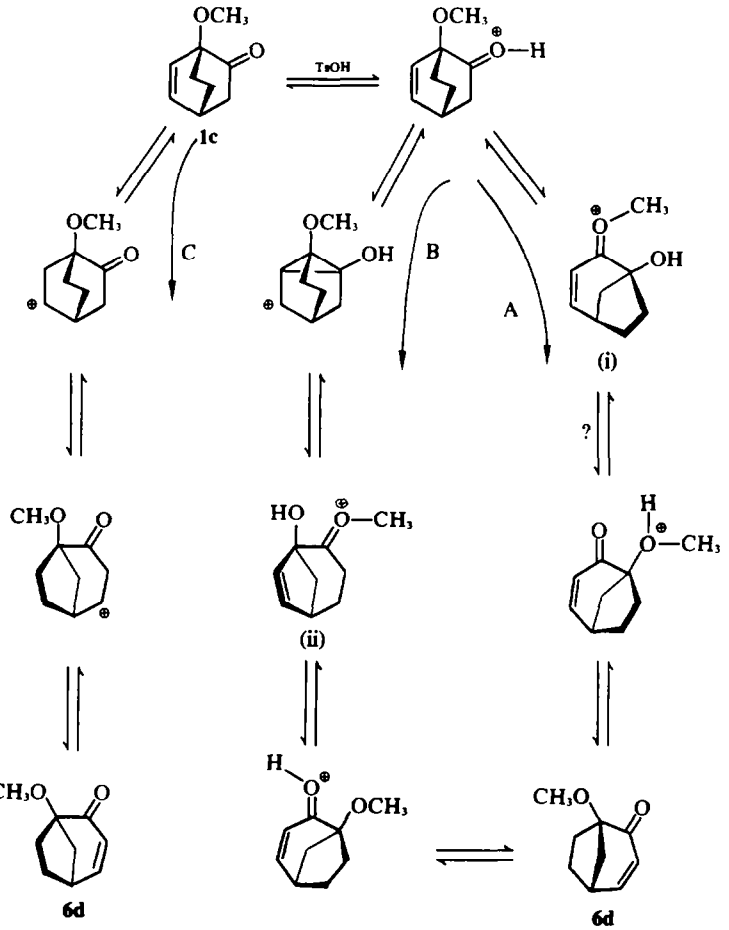
produced in significant quantities before the other isomer begins to accumulate. An interesting aspect of the Scheme 1, which has not been subjected to experimental test concerns the stereochemistry of the reactions **5** ⇌ **6**. It will be seen that the mechanistic pathway suggested involves a change of chirality at C_1. Detection of this change might possibly be complicated by the racemization of **5** via a route involving protonation of the double-bond.

A very interesting related rearrangement occurs when the methoxybicyclo[2,2,2]octenone (**1c**) is treated with acid. Under anhydrous conditions, in benzene, 1-methoxybicyclo[3,2,1]oct - 3 - en - 2 - one (**6d**) is formed in good yield. Three reasonable mechanistic pathways may be considered for this transformation, and these are set out in Scheme 2.

Pathways A and B could in principle be distinguished by labelling one oxygen in the starting material with ^{18}O. In pathway B a labelled carbonyl oxygen would appear in the product as a carbonyl oxygen whereas in Pathway A it appears as a bridgehead ether oxygen. In the absence of definitive evidence, Pathway B seems the most likely, for the following reasons.

(i) Pathway A involves a step in which a Me group is transferred from one O atom to another in the intermediate (i). While superficially an S_N2 displacement on a methyl oxorium salt the steric constraints on the system are such as to necessitate retention of configuration at the Me group. S_Ni reac-



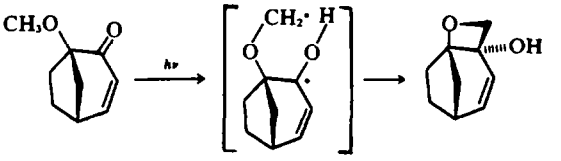


SCHEME 2

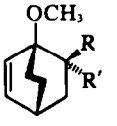
tions[9] have been shown in many cases to proceed via an ion-pair mechanism,[10] and in at least one case,[11] not to occur at a primary alkyl centre. It seems unlikely therefore that a methyl centre could participate in such a reaction.

(ii) Pathway C cannot be the only available mechanism, since in presence of water, the hydroxyketone[6e] is the major product. This presumably arises by rapid hydrolysis of either of the intermediates (i) or (ii). Interestingly, some hydroxyketone accompanies **6d** even under anhydrous conditions, and in presence of toluene-*p*-sulphonic acid. This would appear to arise via an S_N2 displacement reaction by tosylate ion on one of the oxonium ion intermediates (Scheme 2), (i) or (ii)) since the crude mixture contains methyl tosylate, as indicated by its NMR signals and GLC retention time.

The photochemistry of the methoxybicyclo [3,2,1] octenone (**6d**) is of some interest. This was originally investigated in the hope that it might lead to the tricyclic ketone **10**, required in connection with the solvolysis of 1-methoxybicyclo [2,2,2] oct-5-en-3yl tosylates.[12] In the event, irradiation in ethanol, in pyrex glassware, lead to a single photoproduct in ~ 65% yield. The NMR spectrum of this compound identified it as the oxetanol **9**, presumably formed via the familiar type of diradical (Scheme 3) encountered in Norrish type II photoreactions of saturated ketones.[13] Several other examples of hydrogen abstraction reactions by the excited states of conjugated ketones have recently been discovered.[14] The structure of the photoproduct **9** was strongly supported by its behaviour on acid-catalysed dehydration. The structurally similar alcohol **11** had previously been found to yield principally the ketone **7a** on treatment with formic

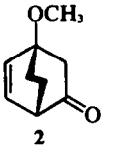


SCHEME 3



1

a: R = CN, R′ = OAc
b: R = OAc, R′ = CN
c: R,R′ = O
d: R = OH, R′ = H
e: R = H, R′ = OH
f: R = OH, R′ = CH_3-
g: R = CH_3-, R′ = OH
h: R = OH, R′ = CH_3CH_2-
i: R = CH_3CH_2-, R′ = OH



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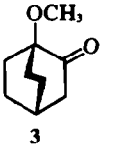

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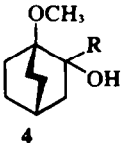
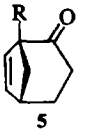


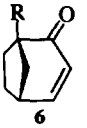
4

a: R = H
b: R = CH_3-
c: R = CH_3CH_2-



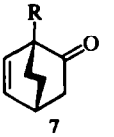
5

a: R = H
b: R = CH_3-
c: R = CH_3CH_2-



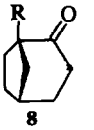
6

a: R = H
b: R = CH_3-
c: R = CH_3CH_2-
d: R = OCH_3
e: R = OH

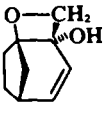


7

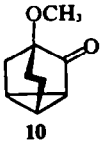
a: R = CH_3-
b: R = CH_3CH_2-
c: R = —CH_2OCH=O
d: R = H



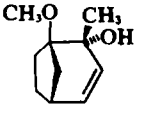
8



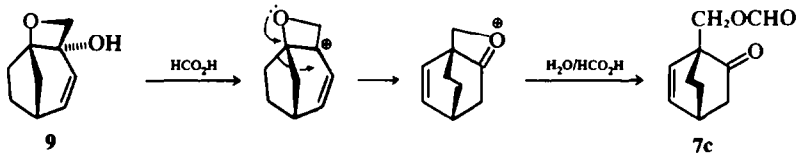
9



10



11



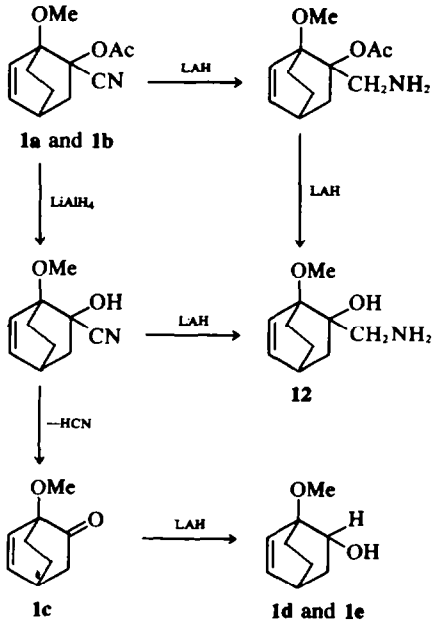
SCHEME 4

acid.[15] As expected on the basis of this result, the oxetanol **9** on formolysis gave a ketonic product, the spectroscopic properties of which established its structure as **7c** Scheme 4 details the probable mechanism of this rearrangement.

Bicyclo[3,2,2]*nonane series*

The acetoxynitriles (**1a** and **1b**) provided a convenient entry to the bicyclo[3,2,2]nonenone series. Reduction with LAH gave the hydroxyamines **12** in moderate yield and nitrous acid deamination gave 1-methoxybicyclo[3,2,2]non - 6 - en - 2 - one **13** in 60% yield. GLC analysis revealed no peak attributable to the isomeric ketone **14**, but small peaks (~ 5%) due to the alcohols **1d** and **1e** were present, indicating competing pathways in the LAH reduction step (see Scheme 5).

The high specificity of the deamination reaction, which leads to the 2-ketone **13** rather than the 3-ketone **14** appears to be a rather general phenomenon in the deamination of bicyclic methylamines



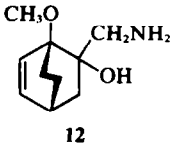
SCHEME 5

and the solvolysis of bicyclic methanol derivatives.[16] Further discussion of this point will be reserved for another occasion.[17]

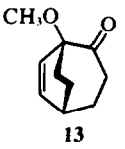
The use of 2-methoxyacrylonitrile as dienophile in place of 2-acetoxyacrylonitrile may lead to an improved synthesis of bicyclo[3,2,2]nonane derivatives. With cyclohexadiene at 180°, this dienophile gave the adducts **18** in ~ 80% yield. Reduction with LAH gave the amines **19** in rather poor yield, which could probably be improved. Finally, nitrous acid deamination gave bicyclo[3,2,2]non - 6 - en - 2 - one (**16a**) in ~ 60% yield. The use of 2-methoxyacrylonitrile in the synthesis of bicyclo[2,2,2]octenones has also been briefly investigated. Acid-catalysed demethylation of the adducts **18** could be achieved under a variety of conditions, the resulting cyanohydrins losing HCN to give the ketone **7d**. The best reagent for this transformation was found to be boron trichloride in methylene chloride.[19] Our conclusion is that 2-methoxyacrylonitrile is less effective than either the 2-acetoxy- or 2-chloronitrile[20] as a ketene equivalent.

The 1-methoxybicyclo[3,2,2]non-6-en-2-one **13** may be used as a starting point for the synthesis of other 1-substituted-2-ketones of this series. For example, reaction with methylmagnesium iodide gave the alcohols **15c** and **15d** in the ratio 1:2. The acid-catalysed dehydration of the mixed alcohols gave the ketones **16b** and **17b**, which could be separated by preparative GLC. The individual alcohols were also separately treated with acid. **15d** under these conditions gave exclusively 1-methylbicyclo[3,2,2]non-6-en-2-one (**16b**), while the epimer **15c** gave a mixture of **16b** and the conjugated isomer **17b** in the ratio 2:1. The specificities of these pinacol-like rearrangements will form the subject matter of a separate communication.

Dihydrotoluene in the Diels–Alder reaction. 2,5-Dihydrotoluene **21** on heating in a sealed tube with 2-acetoxyacrylonitrile, followed by hydrolysis, gave none of the expected 1-methylbicyclo[2,2,2]oct-5-en-2-one **7a**. Instead, a single product was obtained in modest yield, and the structure **27** assigned on the basis of spectroscopic properties. Attempted hydrogenation over a palladium catalyst led to the production of a very complex mixture, as judged from GLC analysis. Structure **27** was supported by the IR absorption at 1705 cm^{-1} ($\rangle C = O$), the UV absorption at 260 nm ($\epsilon \simeq 3000$;



12



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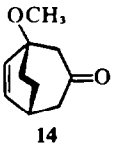

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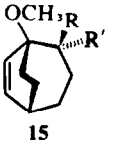
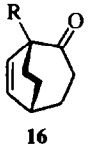


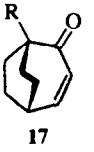
15

a: R = H, R′ = OH
b: R = OH, R′ = H
c: R = CH_3-, R′ = OH
d: R = OH, R′ = CH_3-



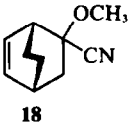
16

a: R = H
b: R = CH_3-

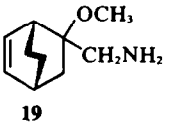


17

a: R = H
b: R = CH_3-



18



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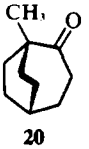

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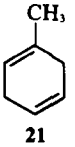

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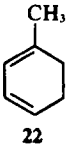
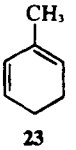


22



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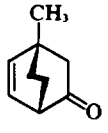

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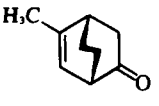

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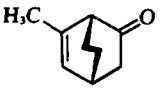

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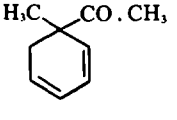
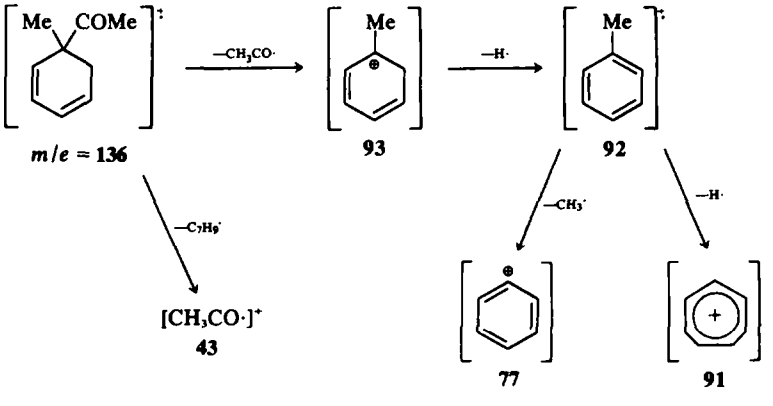
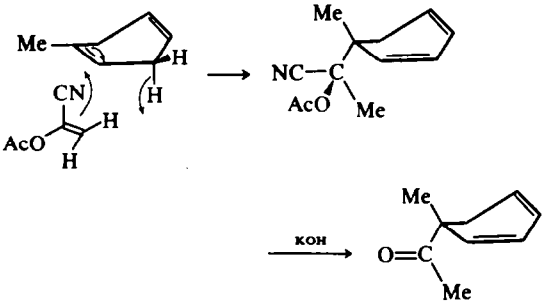


27

cyclohexadiene) and the NMR spectrum which showed strong singlets at δ 1·14 ppm (—C<u>H</u>$_3$) and δ 2·07 ppm (—CO . C<u>H</u>$_3$) and a complex signal centred at δ 5·75 ppm (four vinyl protons). The mass spectrum also lent support to this structural assignment; the most important peaks in the spectrum are in accord with the following fragmentation scheme.



It seems likely that this compound is produced in an ene-reaction[21] as follows.



The absence of normal Diels–Alder products from this reaction suggested that, unlike 2,5-dihydroanisole,[1,22] 2,5-dihydrotoluene is not isomerised to its conjugated isomer on heating in glass apparatus. This was confirmed by heating to 180° in a sealed tube, under an atmosphere of nitrogen, for several hours when the only product identified was toluene.[23]

Previous attempts to equilibrate the dihydrotoluenes under basic conditions had failed, leading only to dehydrogenation.[24] In our hands, potassium t-butoxide in t-butanol converted 2,5-dihydrotoluene into a mixture containing the conjugated isomers **22** and **23**, with very little toluene. Diels–Alder reaction with 2-acetoxyacrylonitrile gave a mixture of adducts, which on hydrolysis led to the ketones **7a** and **24–27** in rather low yield. The composition of the ketone mixture was **7a**; (65%): **24**; (5%): **25**; (23%): **26**; (5%) and **27**; (2%). Structures were assigned principally on the basis of the NMR spectra (Experimental) of the pure compounds, isolated by preparative GLC. The product distribution suggests that diene **22** is more stable than the isomeric **23** by ~ 0·7 kcal/mole. The ratios **7a**:**24** and **25**:**26** are in accord with the results of Diels–Alder reactions of 1,3-pentadiene and isoprene.[25] An attempt to generate 2,3-dihydrotoluene **22** *in situ* by pyrolysis of 3-methyl-1,4-dihydrobenzoic acid[1c] was unsuccessful.

EXPERIMENTAL

GLC analyses were performed on a Pye-Unicam 104 Model 34 flame ionization gas chromatograph over polyethyleneglycol adipate (PEGA) as a stationary phase, except where otherwise indicated. Preparative GLC was performed on the same instrument using a 9 ft × 0·25" stainless steel column, on an Aerograph "Autoprep" and on a F & M Model 775 "Prepmaster"; PEGA being the stationary phase in each case.

*Interestingly the *exo* alcohol **1d** showed a rather simple vinyl region centred at δ 6·3 ppm, while the *endo*-alcohol exhibited the AB part of an AB-X spectrum (δ 6·0–6·5 ppm). There would appear to be preferential shielding of the C_6-proton by the *endo*-C—O bond or the unshared electron pairs of the oxygen. Similar effects were observed in the NMR spectra of the corresponding tosylate esters.

1-Methoxybicyclo[2,2,2]*oct-5-en-2-one* (**1c**). Crude 2,5-dihydroanisole (15 g)[26] and 2-acetoxyacrylonitrile (30 g) stabilized with ~ 0·1% hydroquinone were heated together in a sealed tube, under N_2, at 175° for 36 h. The black tarry product was extracted with ether in a Soxhlet apparatus to yield the crude mixed adducts (22 g). Chromatography of a portion on silica gel gave the mixed adducts as a white crystalline solid (ν_{max} = 1730 and 2260 cm^{-1}; Nujol). The NMR spectrum contained a complex multiplet at δ = 6·5 ppm (2 vinyl protons), a strong signal at δ = 3·63 ppm (—O—$\underline{CH_3}$; 3 protons) and signals at δ = 2·24 ppm and 2·16 ppm in the ratio of ~ 1:2 (—OCO$\underline{CH_3}$; 3 protons together). These chemical shifts suggest that the isomer **1a** (*endo*-acetoxyl is more abundant (Ref 1*b*).

Hydrolysis of the crude adducts with 15% methanolic KOH at 45° for 3 h gave the ketone **1c** (11 g; 46% overall) which gave a single peak on GLC analysis; b.p. 69°/0·5 mm, ν_{max} 1725 cm^{-1}; λ_{max} 296 nm (ε = 125). In the NMR spectrum, the vinyl proton appeared as the AB-part of an AB-X spectrum (δ = 6·1–6·6 ppm); J_{AB} = 8·5 Hz, J_{AX} = 2 Hz, and J_{BX} = 6 Hz. The OMe protons appeared as a singlet at δ = 3·41 ppm (CCl_4). (Found: C, 70·68; H, 7·67. $C_9H_{12}O_2$ requires: C, 71·03; H, 7·95%).

1-Methoxybicyclo[2,2,2]*octan-2-one* (**3**). The unsaturated ketone **1c** (4·94 g) was hydrogenated in MeOH (60 ml) over 5% Pd-C, at atmospheric pressure and room temp. Removal of the catalyst and evaporation gave **3** as an oil (4·15 g), homogeneous to GLC; ν_{max} 1725 cm^{-1}. The NMR spectrum showed a strong signal at δ 3·25 ppm (O$\underline{Me}$) and no vinyl protons (CCl_4).

1-Methoxybicyclo[2,2,2]*oct-5-en-2-ols* (**1d** *and* **1e**). The ketone **1c** (5·0 g) was reduced using LAH (2·7 g) in refluxing anhydrous ether (100 ml). Workup yielded the mixed alcohols **1d** and **1e** (4·5 g); ν_{max} 3440 cm^{-1}. GLC analysis suggested a ratio **1d**:**1e** of 3:7. Preparative GLC yield the separate alcohols very largely free of impurity (**1d**, 93%; **1e**, 97%).

Assignment of stereochemistry was made on the basis of the NMR spectra: **1d** had a doublet of doublets centred at δ 3·86 ppm. The appropriate proton in **1d** presumably lies within the shielding cone of the double bond.[27]*

The tosylate esters were prepared by reaction with toluene *p*-sulphonyl chloride in pyridine, and were recrystallized from light petroleum.

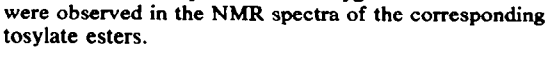
exo-1-*Methoxy bicyclo*[2,2,2]*oct-5-en-2-yl tosylate* **1** (R = OTs; R = H) had m.p. 84°.

endo-1-*Methoxybicyclo*[2,2,2]*oct-5-en-2-yl tosylate* **1** (R = H; R = OTs) had m.p. 67°.

1-Methoxybicyclo[2,2,2]*octan-2-ol* (**4a**). The mixed alcohols **1d** and **1e** (0·2 g) were hydrogenated in MeOH over a 10% Pd-C catalyst. The product (ν_{max} = 3450 cm^{-1}) was > 99% pure by GLC analysis.

1-Methoxybicyclo[2,2,2]*octan-2-yl tosylate* had m.p. 73°.

1-Methoxy-2-methylbicyclo[2,2,2]*oct-5-en-2-ols* (**1f** and **1g**). The ketone **1c** (5 g) in dry ether, was added to a soln of MeMgBr (from 10 ml bromomethane and 3·2 g Mg) in ether (100 ml) during 30 min, the temp being maintained at ~ 0°. The mixture was refluxed for 6 h, water added and the crude alcohols **1f** and **1g** (5·3 g) isolated on evaporation of the solvent. GLC analysis revealed two peaks in the ratio 64% to 36% and the NMR spectrum suggested that **1f** was the major component of the mixture



(—C—CH_3 signals at δ 1·08 and 1·27 ppm in the ratio

64:36. The *endo*-Me group of **1f** lies within the shielding cone of the double bond). Preparative GLC effected separation (Autoprep, 130°) to give the two epimers in better than 98% purity.*

The 3,5-dinitrobenzoate esters were prepared by treating the alcohols (0·5 g) in pyridine (1 ml) with 3,5-dinitrobenzoyl chloride (1 g) in dry benzene (5 ml) and leaving at room temp for one day.

1-*Methoxy* - 2 - endo - *methylbicyclo*[2,2,2]*oct* - 5 - *en* - 2 - exo - *yl* 3,5-*dinitrobenzoate* (**1f**-*DNB*) had m.p. 138–139° (Found: C, 56·82; H, 5·06; N, 8·07. $C_{17}H_{18}N_2O_7$ requires: C, 56·35; H, 5·01; N, 7·73%).

1 - *Methoxy* - 2 - exo - *methylbicyclo*[2,2,2]*oct* - 5 - *en* - 2 - endo - *yl* 3,5 - *dinitrobenzoate* (**1g** - *DNB*) had m.p. 93–95° (Found: C, 56·69; H, 5·42; N, 8·10. $C_{17}H_{18}N_2O_7$ requires: C, 56·35; H, 5·01; N, 7·73%).

1-*Methoxy*-2-*methyl bicyclo* [2,2,2]*octan*-2-*ol* (**4b**). The mixed alcohols **1f** and **1g** (0·28 g) were hydrogenated in MeOH over 10% Pd-C. The product was homogeneous to GLC analysis. The 3,5-*dinitrobenzoate ester* had m.p. 113–115°.

2-*Ethyl* - 1 - *methoxybicyclo*[2,2,2]*oct* - 5 - *en* - 2 - *ols* (**1h** and **1i**). The ketone **1e** (0·72 g) in dry ether was added to a soln of EtMgBr (from ethylbromide; 2·87 g and Mg; 0·64 g) in dry ether at 0°, and then refluxed for 3 h. Addition of water and extraction gave the crude alcohols **1h** and **1i** (0·74 g); ν_{max} = 3460 cm^{-1}. GLC analysis revealed a **1h**:**1i** ratio of 2:1 the stereochemical assignments being made on the basis of the NMR spectrum of the separated alcohols, and their behaviour on treatment with acid. Separation was achieved on a Prepmaster, temp programmed from 135° to 180° at 1°/min; GLC analysis showed the separated alcohols to have purity > 97·5%.

1-*Methylbicyclo*[3,2,1]*oct*-6-*en*-2-*one* (**5b**) *and* 1-*methylbicyclo*[3,2,1]*oct*-3-*en*-2-*one* (**6b**). The mixed alcohols **1f** and **1g** (4·5 g) were heated under reflux with toluene-*p*-sulphonic acid in benzene (150 ml) for 1 h. Washing with bicarbonate soln followed by evaporation gave the mixed ketones **5b** and **6b** (3·5 g); which were separated by preparative GLC (Autoprep; 150°).

In separate experiments, the individual alcohols were similarly treated. The *exo*-alcohol **1f** gave almost exclusively the unconjugated ketone **5b** while the *endo*-alcohol **1g** gave largely (~ 75%) the conjugated ketone **6b**.

1-*Methylbicyclo*[3,2,1]*oct*-6-*en*-2-*one* (**5b**) had ν_{max} 1705 cm^{-1} and λ_{max} 298 nm (ϵ = 195). In the NMR spectrum, the vinyl protons appeared as the AB part of an AB-X spectrum (δ 5·5–6·1 ppm; J_{AB} = 6·0 Hz, $J_{AX} \simeq 0$ Hz, J_{BX} = 3 Hz). (Found: C, 79·12; H, 8·70. $C_9H_{12}O$ requires: C, 79·37; H, 8·88%). The 2,4-*dinitrophenylhydrazone* had m.p. 130–131°. (Found: C, 56·98; H, 4·96; N, 17·87. $C_{15}H_{16}N_4O_4$ requires. C, 56·96; H, 5·10; N, 17·71%).

1-*Methylbicyclo*[3,2,1]*oct*-3-*en*-2-*one* (**6b**) had ν_{max} 1680 cm^{-1} and λ_{max} 229 nm (ϵ ~ 8000). In the NMR spectrum, the vinyl protons appeared as the AB part of an ABX spectrum (δ 5·25–7·0 ppm). J_{AB} = 9·5 Hz; J_{BX} = 7·0 Hz; $J_{AX} \simeq 0$). The low field signal (C_4-H) appeared as a group of eight lines, the B-proton being further coupled to one of the bridge protons (J_{BZ} = 1·2 Hz). The chemical shift difference between the α- and β- vinyl protons was ~ 90 Hz. (Found: C, 79·09; H, 8·92. $C_9H_{12}O$ requires: C, 79·37; H, 8·88%).

1-*Methylbicyclo*[3,2,1]*octan*-2-*one* (**8**, R = Me). The mixed ketones **5b** and **6b** (28 mg) were hydrogenated in MeOH over 10% Pd-C to give a single product (ν_{max} 1700 cm^{-1}; λ_{max} 284 nm, ϵ = 26). The 2,4-*dinitrophenylhydrazone* had a m.p. 148–149°. (Found: C, 56·57; H, 5·77; N, 17·56. $C_{15}H_{18}N_4O_4$ requires: C, 56·59; H, 5·70; N, 17·60%).

1-*Ethylbicyclo*[3,2,1]*oct*-6-*en*-2-*one* (**5c**) *and* 1-*ethylbicyclo*[3,2,1]*oct*-3-*en*-2-*one* (**6c**). The *exo*-alcohol **1h** (50 mg) was heated under reflux for 15 min with 98% formic acid (5 ml), poured into chilled $KHCO_3$aq and extracted with ether. The product was almost entirely 1-*ethylbicyclo* [3,2,1] *oct*-6-*en*-2-*one* (**5c**), easily purified by preparative GLC; ν_{max} 1705 cm^{-1}; λ_{max} 295 nm; ϵ = 210. The NMR spectrum was very similar to that of **5b**, (vinyl protons δ 5·7–6·2 ppm; J_{AB} = 5·5 Hz, $J_{AX} \simeq 0$, J_{BX} = 3 Hz).

The *endo*-alcohol **1i** (50 mg) on similar treatment gave a mixture containing ~ 53% of 1-*ethylbicyclo*[3,2,1]*oct*-3-*en*-2-*one* (**6c**) which was purified by preparative GLC: ν_{max} 1675 cm^{-1}; λ_{max} 225 nm; ϵ = 7500. The NMR spectrum was very similar to that of **6b**. (Vinyl protons δ 5·6–7·2 ppm; J_{AB} = 9·5; $J_{AX} \simeq 0$; J_{BX} = 7; J_{BZ} = 1·5 Hz).

1-*Ethylbicyclo*[3,2,1]*octan*-2-*one* (**8**, R = Et). The mixed ketones **5c** and **6c** (40 mg) were hydrogenated in MeOH over 10% Pd-C to give a single product, (ν_{max} 1700 cm^{-1}; λ_{max} 285 nm; ϵ = 16). The 2,4-*dinitrophenylhydrazone* had m.p. 160°. (Found: C, 57·58; H, 5·94; N, 16·69. $C_{16}H_{20}N_4O_4$ requires: C, 57·80; H, 6·03; N, 16·87%).

Equilibration of ketones **5**, **6** and **7**. A soln of the ketone **5b**, **6b** or **7b** in formic acid containing 0·4 M sodium formate was heated under reflux, aliquots being removed, neutralised with K_2CO_3aq and extracted with ether. The products were analysed by GLC using a polyethyleneglycol (PEG 400) column packing at 100°. After long reaction times, additional peaks began to appear, and complete equilibrium was not obtained. The results are summarised in Table. Similar results were obtained with the ketones, (**5c**, **6c** and **7c**).

1-*Methoxybicyclo*[3,2,1]*oct*-3-*en*-2-*one* (**6d**). The ketone **1e** (2·17 g) was added to a soln of anhydrous toluene-*p*-sulphonic acid in benzene (200 ml) (prepared from the hydrate (4·3 g) by distilling benzene from a soln until the distillate was clear), and boiled under reflux for 95 min. The soln was washed with $NaHCO_3$aq, filtered and evaporated to yield a pale yellow oil (1·99 g); ν_{max} 1680 cm^{-1} (no peak at 1725 cm^{-1}). The NMR spectrum showed a strong singlet at δ3·31 ppm (—O—C$\underline{H}_3$), and weak singlets at δ3·66 ppm ($\underline{CH}_3$OTs)[28] and δ2·40 ppm ($CH_3OSO_2 . C_6H_4 . C\underline{H}_3$). The vinyl region appeared as two overlapping AB-X spectra due to the methoxy-**6d** and hydroxyketones **6e**, and there was also a weak AA'BB' spectrum (centred at δ7·30 and 7·70 ppm) due to the aromatic protons of methyl tosylate. GLC analysis revealed three major components, in order of increasing retention time: methyl tosylate (~ 13%), the hydroxyketone **6e** ~ 15%) and the methoxyketone **6d** ~ 72%). No trace of starting material **1e** was apparent. Distillation gave a small fraction, b.p. 65–75°/0·5 mm containing a mixture of **6d** and **6e**, and a major fraction (1·5 g) consisting essentially of **6d**: b.p. 80–85°/0·5 mm; ν_{max} 1680 cm^{-1}; λ_{max} 227 nm ($\simeq$ 8000). The NMR spectrum showed a singlet at δ3·31 ppm (O.C$\underline{H}_3$). The vinyl region appeared as the *AB* part of an ABX spectrum. The highfield (α–) proton signal appeared as a doublet at δ5·74 ppm (J_{AB} = 9·5 Hz; $J_{AX} \simeq 0$[29]). The low-field proton (β–) signal appeared as a group of eight lines at δ7·06 ppm. Further splitting being associated with long-range coupling, presumably to one of

*At this temp, retention times were inconveniently long (3–6 h!). Higher temps resulted in extensive rearrangement to the ketones **5** and **6**.

Table 1.

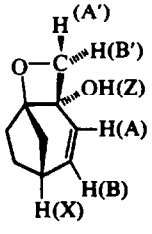
Starting ketone	Reaction time	Composition			
	h	5a	6a	7a	Other
5a	30	10·6	55·0	34·4	—
	504	0·3	61·4	38·3	—
	1344	Trace	51·7	37·1	11·2
6a	74	13·5	82·5	4·0	—
	504	0·1	80·2	19·7	—
	1344	0·2	63·7	24·5	11·6
7a	74	17·2	6·6	76·2	—
	504	0·8	23·2	76·0	—
	1344	0·3	46·1	37·5	16·1

the protons on C_3^* ($J_{AB} = 9{\cdot}5$ Hz; $J_{BX} = 6{\cdot}5$ Hz; $J_{BZ} \simeq 1{\cdot}5$ ppm).

2-Oxatricyclo[5,2,1,$0^{1,4}$]*dec-5-en-4-ol* (**9**)

N_2 was bubbled through a soln of **6d** (0·251 g) in 95% EtOH (100 ml) for 15 min, prior to irradiation under N_2, in a pyrex vessel, using a medium pressure mercury arc lamp. After 11 h, GLC analysis of an aliquot revealed that ~ 90% of the starting material had been consumed and that a new product was present to the extent of some 75% of the total volatile materials. When conducted in a quartz flask, the photoreaction was much faster. After 5 h, no starting material remained, and the new product constituted some 65% of the total.

The crude product was purified by chromatography on silica gel. Elution with 50:50 benzene:ether gave **9** (0·11 g; ~ 40% recovery) as a colourless, viscous oil. GLC analysis suggested that the sample was > 99% pure: ν_{max} 3400 cm^{-1}.



In the NMR spectrum, the oxetane protons ($^HA'$, $^HB'$) appeared at δ4·19 and 4·70 ppm respectively in an A'B' pattern; $J_{A'B'} = 7$ Hz. The hydroxylic proton appeared as a broad signal at δ3·30 ppm, which disappeared on exchange with D_2O. The vinyl region appeared as the AB part of an AB-X spectrum. The highfield signal (H_A) at δ5·47 ppm was a doublet ($J_{AB} = 9$ Hz; $J_{AX} \simeq 0$) while the low-field signal (H_B) at δ6·40 ppm, appeared as a doublet of doublets ($J_{AB} = 9$ Hz; $J_{BX} = 7$ Hz).

Acid-catalysed rearrangement of **9**. The oxetanol **9** (30 mg) was dissolved in formic acid (5 ml) and refluxed for 20 h. Quenching with water and extraction yielded an oil (22 mg), the NMR spectrum of which suggested that it was 1-*formyloxybicyclo*[2,2,2]*oct - 5 - en - 2 - one* (**7c**). Important signals appeared at δ8·0 ppm (—O—C<u>H</u>=O); δ6·52 ppm (doublet or doublets; <u>B</u> part of AB-X spectrum; $J_{AB} = 8$ Hz; $J_{BX} = 6$ Hz); δ6·05 ppm (doublet of doublets, <u>A</u> part of AB-X spectrum; $J_{AB} = 8$ Hz; $J_{AX} = 2$ Hz); δ4·36 ppm, (doublet, separation 5 Hz: probably the inner lines of an A'B' spectrum; —C<u>H</u>$_2$—OCHO); δ2·92 (complex multiplet; allylic proton) and δ2·04 ppm (doublet; separation 3 Hz; probably the inner lines of an A'B' spectrum; —C<u>H</u>$_2$—CO—).

1-*Methoxybicyclo* [3,2,2]*non-6-en-2-one* (**13**). The mixed acetoxynitriles **1a** and **1b** (12 g) were added, in 1,2-dimethoxyethane (DME) to a suspension of LAH (7·6 g) in DME, and heated to reflux for 4 h. After destruction of the excess hydride with water, the mixture was extracted with ether, and the solid residue extracted with MeOH in a Soxhlet apparatus. The combined extracts gave a mixture of *endo*- and *exo*-isomers of 2-hydroxy-1-methoxy bicyclo[2,2,2] - oct - 5 - en - 2 - yl methylamine (**12**; 5·5 g).

Conc HCl (2·4 ml) was added, followed by water (150 ml) and glacial AcOH (50 ml), and the mixture stirred under N_2, and cooled to 0°. $NaNO_2$ (70 g) in water (180 ml) was added, and the mixture allowed to warm to room temp and left to stand overnight. Ether extraction, washing with K_2CO_3aq, drying and evaporation yielded **13** (2·1 g; ~ 20% overall); $\nu_{max} = 1710$ cm^{-1}; $\lambda_{max} = 290$ nm; $\epsilon = 160$. The NMR spectrum showed a strong signal at δ3·2 ppm (O—C<u>H</u>$_3$), and the vinyl region appeared as the AB part of an ABX spectrum: doublet at δ5·85 ppm ($J_{AB} = 9$ Hz; $J_{AX} < 1$ Hz); doublet of doublets at δ6·28 ppm ($J_{AB} = 9$ Hz; $J_{BX} = 7$ Hz).

2-Methoxyacrylonitrile. 1,2-Dibromoethylmethylether[18] (196 g) in dry benzene (150 ml) was added gradually to a vigorously stirred suspension of freshly prepared cuprous cyanide (90 g; dried by distilling benzene from it, and keeping at 110° for 45 min before use) in dry benzene (230 ml). The temp was raised, over 30 min, to 90° and maintained at that temp for a further 30 min. Filtration and evaporation gave 2-*bromo*-1-*methoxypropionitrile* (140 g). The NMR spectrum showed a triplet at δ4·24 ppm ($J = 6$ Hz; —C<u>H</u>$\begin{matrix}\diagup\ OCH_3\\ \diagdown\ CN\end{matrix}$), a singlet at δ3·51 ppm (—O—C<u>H</u>$_3$) and a doublet at δ3·48 ppm ($J = 6$ Hz; —C<u>H</u>$_2$—Br) (*Note*: In our hands the method of Baker,[18] using dry (but not oven-treated) cuprous cyanide in dry ether gave none of the required bromomethoxynitrile. Instead a low yield of a compound believed to be 2-*bromo*-2-*methoxypropionitrile* was obtained).

*The proton (probably *exo*[30]) at C_3 rather than that at C_8 is held responsible for this coupling since both epimers of 8-methylbicyclo[3,2,1] - oct - 3 - en - 2 - one have been prepared, and both exhibit the same coupling pattern in the low-field vinyl region.[31]

The bromomethoxynitrile (140 g) was added dropwise to refluxing pyridine (140 ml) containing hydroquinone (1 g), and the refluxing continued for a further 15 min. The cooled soln was decanted and the pyridinium bromide repeatedly extracted with dry ether. Distillation of the combined extracts gave 2-methoxyacrylonitrile (42 g) as a colourless mobile liquid (b.p. 68°/130 mm), which gave a single peak on GLC analysis: ν_{max} 3040(w), 3020(w), 1620(s) and 915(m) cm^{-1}. The NMR spectrum showed a singlet at δ3·64 ppm (O—CH_3) and an AB spectrum (J_{AB} = 3·5 Hz) at δ4·84 and 4·93 ppm (doublets: =CH_2).

2-Cyano-2-methoxybicyclo[2,2,2]*oct-5-ene* (**18**). Crude cyclohexa-1,3-diene (65%; 22 ml),[32] 2-methoxyacrylonitrile (26 ml) and hydroquinone (1 g) were heated together in a sealed tube, under N_2, to 180° for 48 h. The crude tarry product was extracted with ether in a Soxhlet apparatus, and the extracts concentrated and distilled to give **18** (18·2 g); b.p. 110–140°/18 mm. The NMR spectrum showed two singlets in the ratio 3:2 at δ3·19 and 3·20 ppm.

Treatment of this product with boron trichloride in methylene chloride[19] in various concentrations and for varying reaction times gave mixtures of the starting material and *bicyclo*[2,2,2]*oct - 5 - en - 2 - one* (**7d**), analysed by GLC and comparison with authentic samples. Under none of the conditions investigated was the conversion more efficient than ~ 60%.

Bicyclo[3,2,2]*oct-6-en-2-one* (**16a**). The methoxynitrile **18** (18 g) in dry ether (100 ml) was reduced with LAH (3·4 g) under reflux for 2 h. After destruction of excess reagent with water, the ether was decanted and the residue extracted with MeOH. The combined extracts were evaporated, dissolved in ether and extracted into dil HCl. Basification, extraction, drying and evaporation yielded the mixed methoxyamines **19** (5·4 g). The crude product was deaminated (see deamination of **12**; above) to yield bicyclo[3,2,2] oct-6-en-2-one (**16a**; 2·6 g); ν_{max} 1720 cm^{-1}; λ_{max} 286 nm; ϵ = 80. The NMR spectrum revealed the vinyl protons as the AB part of an ABXY spectrum centred at δ6·2 ppm.

1-Methylbicyclo[3,2,2]*non-6-en-2-one* (**16b**) and *1-methylbicyclo*[3,2,2]*non-3-en-2-one* (**17b**). To MeMgI (from MeI; 8·5 g, and Mg powder; 1·34 g) in dry ether, was added the methoxyketone **13** (1·6 g) in dry ether and the mixture heated under reflux for 3 h. Water was added to destroy excess Grignard reagent and the product alcohols extracted with ether (1·22 g). GLC analysis showed two products, in order of increasing retention time, in the ratio 2:1. The structures **15d** and **15c** respectively were assigned to these alcohols on the basis of the following evidence: (a) models of bicyclo[3,2,2]non-6-en-2-one suggested that attack by a Grignard or other reagent should be easier from the *endo*-face, leading preferentially to **15d**; (b) *in the NMR spectra the* $-\underset{|}{\overset{OH}{\overset{|}{C}}}-CH_3$ *signals* occurred at δ1·09 and δ1·11 ppm in the intensity ratio 2:1. Inspection of models suggest that this Me group in the alcohol **15d** should be shielded by the double-bond and (c) on the basis of the specificities observed in acid-catalysed dehydration (see discussion). The alcohols were separated by preparative GLC: they were each obtained essentially free of the other epimer, but in each case were contaminated by ~ 10% of dehydration products (**16b** and **17b**).

The mixed alcohols were heated under reflux in benzene, saturated with toluene-*p*-sulphonic acid, for 40 min. The mixture was poured into an excess of K_2CO_3aq and extracted with ether. The extract was dried and evaporated to give the mixed ketones **16b** and **17b** in the ratio of 7:1. They were separated by preparative GLC. *1 - Methylbicyclo* [3, 2, 2] *non - 6 - en - 2 - one* (**16b**) had ν_{max} = 1700 cm^{-1} and λ_{max} 285 nm; ϵ = 100. The NMR spectrum showed a strong singlet at δ1·12 ppm ($-\underset{|}{\overset{|}{C}}-CH_3$) and the vinyl protons appeared as the AB part of an ABX spectrum at δ5·18 ppm (doublet; J_{AB} = 9 Hz; $J_{AX} \simeq 0$) and δ6·25 ppm (doublet of doublets, J_{AB} = 9 Hz; J_{BX} = 7 Hz). The *2,4-dinitrophenyl hydrazone* derivative had m.p. 161° (Found: C, 58·30; H, 5·50; N, 16·40. $C_{16}H_{18}O_4N_4$ requires: C, 58·2; H, 5·41; N, 16·95%). *1 - Methylbicyclo* [3, 2, 2] *non - 3 - en - 2 - one* (**17b**) has ν_{max} = 1660 cm^{-1} and λ_{max} = 227 nm; ϵ = 6000. The NMR spectrum showed a singlet at δ1·04 ppm ($-\underset{|}{\overset{|}{C}}-CH_3$) and the vinyl protons appeared as the AB part of an ABX spectrum at δ6·00 ppm (doublet, narrowly split into doublets; J_{AB} = 11 Hz; $J_{AX} \simeq 0{\cdot}8$ Hz) and δ7·05 ppm (doublet of doublets; J_{AB} = 11 Hz; J_{BX} = 9 Hz).

Hydrogenation of the mixed ketones gave a single product as judged by GLC analysis. The product, *1-methylbicyclo* [3, 2, 2] *nonan-2-one* (**20**) had ν_{max} = 1700 cm^{-1}; λ_{max} = 285 nm; ϵ = 25. The *2,4-dinitrophenylhydrazone* derivative had m.p. 170°. (Found: C, 57·96; H, 6·07; N, 16·97. $C_{16}H_{20}O_4N_4$ requires: C, 57·80; H, 6·03; N, 16·87%).

Ene-reaction between 2,5-dihydrotoluene and 2-acetoxyacrylonitrile. Crude 2,5-dihydrotoluene (from toluene; 10 g[32]) was heated with 2-acetoxyacrylonitrile (11 g) in a sealed tube for 26 h at 170°. Unreacted starting materials were removed by distillation (15 mm) and the residue maintained at 45° for 4 h in an excess of 15% methanolic NaOH soln. Extraction and distillation (60–80°/0·2 mm) gave a colourless oil (3 g), GLC analysis of which revealed that one component was present to the extent of ~ 65%. This was separated by preparative GLC, and the structure *1-acetyl-1-methylcyclohexa-2,4-diene* (**27**) assigned on the basis of spectroscopic properties: ν_{max} 1705 cm^{-1}; λ_{max} 260 nm; ϵ = 3000; NMR signals at δ1·14 (—CH_3); 2·07 (—$COCH_3$) and 5·75 ppm (4-vinyl protons).

Attempted hydrogenation over 5% Pd-C led to a complex mixture of products. Reaction with MeMgI gave an alcohol which on treatment with acid yielded only polymeric materials.

1-Methylbicyclo[2,2,2]*oct-5-en-2-one* (**7a**). Crude 2,5-dihydrotoluene (from toluene; 10 g) was partially isomerised by heating under reflux with t-BuOK (1 g) in t-BuOH (1 g) for ~ 3 h. The mixed dienes were distilled from the mixture; the first fraction containing t-BuOH was rejected. The mixture had b.p. 110° and λ_{max} 262 nm; $\epsilon \sim 2000$.

The partially isomerised diene (8 g) was heated under N_2 to 110° in a sealed tube with 2-acetoxyacrylonitrile (18 g), for 24 h. Unreacted starting materials were removed by distillation (at 15 mm) and the residue warmed to 45° for 4 h in an excess of 15% methanolic NaOH soln. Extraction and distillation gave a mixture of products (2·5 g) with the following composition (in order of increasing GLC retention time); **27** (2%), **7a** (65%); **24** (5%); **26** (5%) and **25** (23%). The components were separated by preparative GLC, and had the following properties: For compound **27** see above.

1-*Methylbicyclo*[2,2,2]*oct*-5-*en*-2-*one* (**7d**) ν_{max} 1715 cm^{-1}; λ_{max} 295·5 nm; ϵ_{max} 90. The NMR spectrum had signals at δ0·91 ppm (—CH_3); δ5·65 ppm (doublet of doublets; C_6—H; J_{AB} = 8·5 Hz; J_{AX} = 2 Hz) and δ6·26 ppm (doublet of doublets; C_5—H; J_{AB} = 8·5 Hz; J_{BX} = 6·5 Hz). (Found: C, 79·19; H, 9·04. $C_9H_{12}O$ requires: C, 79·37; H, 8·88%).

1-*Methylbicyclo*[2,2,2]*oct*-5-*en*-3-*one* (**24**). ν_{max} = 1715 cm^{-1}; λ_{max} = 293·5 nm; ϵ = 120. The NMR spectrum showed a strong singlet at δ1·28 ppm (—CH_3), and a broad signal at δ3·0 ppm (C = C—CH—CO—). The vinyl region appeared as complex signal centred at δ6·15 ppm.

6-*Methylbicyclo*[2,2,2]*oct*-5-*en*-2-*one* (**26**) ν_{max} = 1715 cm^{-1}; λ_{max} = 294 nm; ϵ = 153. The NMR spectrum showed a narrow doublet at δ1·62 ppm (—CH = C—CH_3); J ≃ 2Hz and a broad signal at δ2·84 ppm (two allylic protons). The vinyl region appeared as a doublet of quartets (J ≃ 2 Hz and ≃6·5 Hz) centred at δ6·02 ppm.

5-*Methylbicyclo*[2,2,2]*oct*-5-*en*-2-*one* (**25**) ν_{max} = 1715 cm^{-1}; λ_{max} = 293·5 nm; ϵ = 50. The NMR spectrum showed a narrow doublet at δ1·78 ppm (—CH = C—CH_3); J ≃ 2 Hz. The allylic signals appeared at δ2·72 ppm (C_1—H; broad doublet, J ≃ 7 Hz) and at δ2·6 ppm (C_4—H; broad singlet). The vinyl region appeared as a broad doublet (J ≃ 7 Hz) centred at δ5·68 ppm.

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