A Study on the Nature of the Allene-ene Intramolecular Cycloaddition Reaction. A Novel Allene-ene Reaction

Lars Skattebøl, Yngve Stenstrøm and Einar Uggerud

Department of Chemistry, University of Oslo, P.B. 1033, Blindern, N-0315 Oslo 3, Norway

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The thermally induced gas phase reactions of the ene-allene ketones 2,5,5-trimethylocta-1,6,7-trien-4-one (*1a*), 2,5,5-trimethylnona-1,6,7-trien-4-one (*1b*) and 2,5,5,8-tetramethyl-1,6,7-trien-4-one (*1c*) gave products from intramolecular [2+2] cycloaddition as the major reaction path. From ketones *1a* and *1b*, substantial amounts of acetylenic isomers were formed by a novel ene type rearrangement. All products could be rationalized by invoking diradical intermediates, but the acetylenes may well have been formed by a concerted process.

We recently reported a synthesis of racemic lineatin, a pheromone component of the ambrosia beetle *Trypodendron lineatum*.[1] The key step in this synthesis was the transformation of the allenic ketones *1a* and *1c* into the corresponding methylenebicyclo[3.2.0]heptane-3-one derivatives *2* and *10*, respectively, by a thermal intramolecular cycloaddition (Scheme 1). A number of minor products were formed in these reactions as well, and in the present work, the identification of several of these is described. The results contribute to an understanding of the mechanism involved in this type of cycloaddition reaction. The conversion of *1a* and *1b* to the acetylenic ketones *3* and *8*, respectively, represents a novel ene type reaction.

Results and discussion

The thermal reactions of the easily available allenic ketones *1* were performed by distilling them under reduced pressure through a heated tube packed with quarz wool. The resulting complex product mixtures were only partly separated by fractional distillation and the pure components were obtained using preparative GLC. In this way, compounds comprising about 90 % of the total product were in each case isolated and characterized spectroscopically. The yields of each component referred to below are given as the % of the total product mixture as analyzed by gas chromatography (GLC). The numbers are close to actual yields because only insignificant loss occurred during distillation of the ketones *1* through the tube.

Distillation of *1a* through the tube at 490 °C/2 mmHg gave rise to the bicyclic ketone *2* and the acetylenic ketone *3* in 60 and 18 % yields, respectively, as described previously.[1] Three minor products, representing 3,5 and 6 % of the total mixture, were separated by preparative GLC and assigned the structures *4*, *5* and *6*, respectively, based on spectroscopic evidence. The ratio between the ketones *2* and *3* was constant to about 500 °C; at 515 °C a small decrease was observed and the amounts of *4* and *6* were slightly larger. Distillation of *1a* through the unpacked tube at 611 °C/0.05 mmHg gave the cycloheptenone *6* as the major product together with some of *3*, but at this temperature, fragmentation became significant. When the bicyclic ketone *2* was passed through the tube at 473 °C/0.08 mmHg, it was converted to a small extent to *4* and traces of *5* and *6*; however, the degree of conversion as well as the proportion of *5* and *6* in the product increased with temperature and at 509 °C approximately equal amounts of the three compounds were present together with traces of *3*, as indicated by GLC. It was further found that the acetylene *3* was thermally stable up to 512 °C, at

which temperature small amounts of unidentified products were formed.

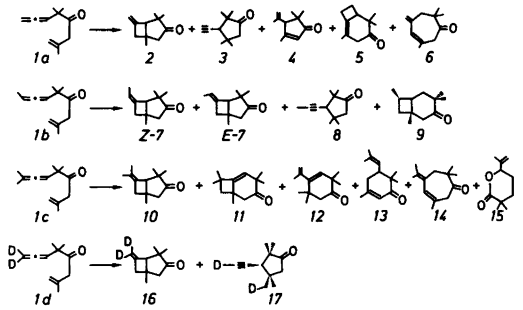
In the IR spectrum of the cyclopentenone *4*, absorptions at 1697 and 1620 cm^{-1} indicated the presence of an α,β unsaturated ketone. The ^1H NMR spectrum showed the presence of four methyl groups. Double resonance experiments revealed that the methyl protons at δ 1.64 were coupled to the olefinic methylene protons, while the methyl protons at δ 2.04 were coupled to the allylic methine proton at δ 3.05 ppm. The ^{13}C NMR spectrum confirmed the structure. The IR spectrum of the bicyclic ketone *5* showed a band at 1699 cm^{-1} indicative of an isolated carbonyl group, and the presence of a tetrasubstituted double bond was evident from the ^{13}C NMR spectrum which was otherwise also in agreement with the assigned structure. The methine proton appeared as a complex multiplet in the ^1H NMR spectrum also 1,3- and 1,4-related indicating coupling with protons. Based on the NMR spectra, the structure of *6* was ascertained except for the position of the double bond. However, the IR absorptions at 1600 and 1643 cm^{-1} indicated conjugated double bonds, with the band at 1707 cm^{-1} characteristic of an isolated carbonyl group.

Distillation of *1b* through the tube at 495 °C/1.0 mmHg furnished a complex mixture comprised of *Z-7*, *E-7*, *8* and *9* in 24, 27, 34 and 3 % yields, respectively. It was evident from the spectroscopic data that the isomers *7* were structurally analogous to compounds *2* and *10* (see below). The stereochemistry at the double bond of each isomer was established from NOE experiments. Irradiation of the *gem* dimethyl groups resulted for the one isomer in a significant enhancement of the resonance for the olefinic proton and no effect on the vinylic methyl protons, and the converse for the other isomer in agreement with *E* and *Z* configurations, respectively. The spectral data of *8* were quite similar to those of *3*, but absorption expected for the triple bond was absent in the IR spectrum. However, characteristic peaks in the ^{13}C NMR spectrum at δ 3.5, 75.3 and 81.4 ppm left no doubt about the presence of a propynyl group. The only structural problem in the case of compound *9* was the assignment of stereochemistry. In the 400 MHz ^1H NMR spectrum, the cyclobutyl methylene protons appeared as two triplets at δ 1.45 and 2.16 ppm. The large difference in chemical shift must be attributed to the neighboring methyl groups at C-1 and C-7. With these *cis* related, as depicted in *9*, the *exo* methylene proton is shielded considerably more than the *endo*, while for the *trans* isomer, an insignificant difference is expected. A similar effect was observed in the ^1H NMR spectra of the geometric isomers of 1,3-dimethylcyclobutane.[2] NOE experiments also supported the stereochemical assignment. Interactions were observed between the *endo* proton α to the carbonyl group, resonating at δ 2.28 ppm, and the cyclobutyl methine and *endo* methylene protons.

Compound *1c* was passed through the tube at 487 °C/1.5 mmHg to give a complex mixture which contained 68 % of the previously reported bicyclic ketone *10*. In addition, the structural isomers *11–14* were present in 6, 10, 1 and 4 % yields, respectively, together with 4 % of the lactone *15* and 4 % of the fragmentation product, 2,5-dimethyl-2,4-hexadiene. At temperatures above 500 °C, compound *10* was partly converted to *13*, *14* and some unidentified products. The structures of compounds *11* and *14* were readily established from spectroscopic evidence, particularly by comparing the NMR spectra with those of the analogous compounds *9* and *6*, respectively. The structural elucidation of compounds *12* and *13* caused no problem either. The formation of the lactone *15* was unexpected; it was clearly a secondary product.

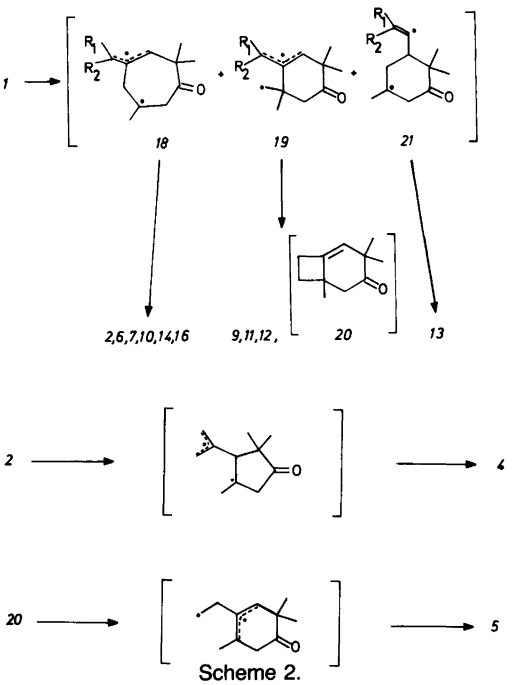
The deuteriated allenic ketone *1d* was prepared from 1,1-dideuterio-2-propyn-1-ol and isobutyraldehyde by the same sequence of reactions as described for the hydrogen analogue.[1] The thermal reaction provided the isomers *16* and *17;* at 495 °C/2 mmHg, the ratio was 67:12, which is higher than that recorded for the reaction of *1a* indicating a kinetic isotope effect. The ^1H and ^2H NMR spectra disclosed specific labelling on the ethynyl group and the *cis* oriented methyl group at C-4 which gives rise to absorption at higher field than the other methyl protons owing to the anisotropic effect of the triple bond.

The mechanism of intermolecular [2+2] cycloaddition of allenes has been studied extensively[3–7] including reactions between an allenic linkage and a C–C double bond.[3,5–7] The problem has invariably been to establish whether the reaction is concerted or involves diradical intermediates. The antarafacial – suprafacial orbital interaction required for concertedness in this class of thermal reactions is unattainable for cycloadditions of most olefins, but is quite reason-



Scheme 1.

able when an allenic linkage is involved, due to the *sp* hybridization of the central carbon. On the other hand, the same linkage may in a stepwise mechanism also give rise to allylic stabilization of the intermediate radical provided an initial bond formation takes place at the central carbon. Calculations indicate that the two mechanisms are comparable energetically[8] and stereochemical arguments, while relevant, do not always distinguish between the two options.[4,9,10] However, by-products that unambiguously derive from diradical intermediates strongly suggest that the [2+2] cycloaddition takes place by an unconcerted process as well. It is actually the general notion that these reactions do involve diradicals. Some examples of thermally induced intramolecular cycloadditions of allenes have been reported including a few involving ene-allenes.[10–19] The mechanistic arguments referred to above must apply to these reactions as well.



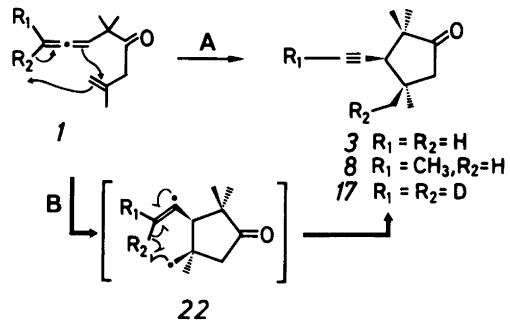
Scheme 2.

The formation of most of the compounds identified from the thermal reactions of the allenes *1a-c* can be explained by involving the diradicals *18* and *19* (Scheme 2). These can be formed by bond formation between the terminal and non-terminal carbon atoms of the double bond, respectively, and the central carbon of the allenic linkage. The major product from each reaction, *i.e. 2, 7* and *10,* may derive from *18,* but more important, the cycloheptenone derivatives *6* and *14* strongly suggest its presence as intermediate. Intramolecular hydrogen abstraction rather than C–C bond formation in the intermediate *18* leads to the monocyclic compounds. Evidence for diradical *19* was obtained by identifying compounds *9, 11* and *12,* the last one as a product of hydrogen abstraction. Furthermore, compound *5* most probably arises from *20* as a product of metathesis and the isomer *4* derives from *2* as confirmed by separate experiments.

Compound *13* is not accounted for by the intermediacy of diradicals *18* and *19.* Its formation can be explained from diradical *21,* which results from bond formation between the terminal carbon of the double bond and the inner carbon of the allene moiety. Subsequent abstraction of a hydrogen adjacent to the carbonyl group gives rise to *13.* The small amount (1 % from *1c*) may be partly due to the unfavourable steric requirements for the 1,5-hydrogen shift in the final step of the reaction, but perhaps more important is the high energy of the diradical *21* as compared with that of *18* and *19* (see below).

The source of 2,5-dimethyl-2,4-hexadiene was not established from our experiments. It may arise from fragmentation of *1c* or from several of its thermal reaction products. The origin of the lactone *15* is even more difficult to ascertain. This oxidation product was invariably present in small amounts and appeared to be formed during and not subsequent to the thermal reaction.

The formation of the acetylenic derivatives *3* and *8* is particularly interesting. It was established that they do not result from *2* and *7,* respectively, under the reaction conditions and fur-



Scheme 3.

thermore, the labelling experiments showed that allenic deuterium migrates selectively to the terminal carbon of the double bond (Scheme 3). This result is in agreement with both a stepwise process involving the diradical *22* and a conserted ene type mechanism. The diradical *22* results from bond formation between the inner carbons of the allenic linkage and the double bond. We have estimated the energy requirement for formation of the diradical intermediates *A* and *B* which resemble *18* and *22*, respectively, using Bensons's additivity scheme.[20] The data for the vinyl radical moiety has been estimated by assuming the same dissociation energy as for ethylene.[21] The diradical *A* is by far the more favourable being more stable by 17 kcal mol^{-1} (Fig. 1). The difference in stability of *A* and *B* is mainly due to the difference between an allylic and a vinylic radical. The estimate incorporates 9 kcal mol^{-1} as the resonance energy of the allylic radical.[22] However, due to steric hindrance, a planar allylic system is difficult to realize in *18*, which suggests that the energy difference between *18* and *22* is less than that estimated for the models *A* and *B*. Furthermore, the stability order of the two diradicals is not necessarily reflected in the activation energies for the reactions leading to them.

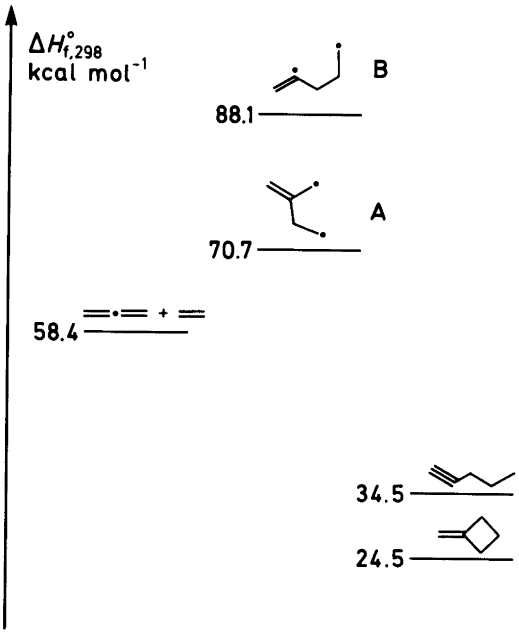


Fig. 1. Estimated heat of formation data for the thermal reaction of allene with ethylene.

An answer to whether formation of *3* and *8* includes the intermediate *22* or proceeds by a concerted mechanism is difficult to give and must await further experimental and theoretical studies which are in progress. The rearrangement is novel, although it appears to be involved in the cyclization of 2-methyl-2-hepten-5-yne to methylenecyclopentene derivatives as reported recently by Mazur and coworkers.[23] The formation of alkyne-containing adducts from reactions of monoalkyl-substituted allenes with *N*-phenylmaleimide[7] is also related to the present rearrangement.

In conclusion, most of the products from the thermal gas phase reactions of the ene-allenes *1* are readily rationalized in terms of stepwise processes involving diradicals. Initial bond formation to the central carbon of the allenic linkage is preferred, and the thermal stabilities of the diradicals thus formed appear to determine the product compositions. Exception is taken for the acetylenic products which may very well derive from concerted ene-type reactions.

Experimental

General. The instruments employed have been described elsewhere.[1] GLC analyses were performed with a packed column of 3 or 10% SP 2100 or 10% PEG 4000. For preparative work, either 10–15% SE 30, 15% Apiezon L, 10% OV17 or 10% PEG 4000 or combinations of these were used.

The compounds *2,5,5-trimethylocta-1,6,7-trien-4-one (1a) and 2,5,5,8-tetramethylnona-1,6,7-trien-4-one (1c)* were prepared as previously reported.[1]

2,2-Dimethyl-3,4-hexadienal, was prepared in 54 % yield from 3-butyn-2-ol and isobutyraldehyde in toluene with a catalytic amount of p-toluenesulfonic acid according to the lit.[22] (b.p. 87 °C/90 mmHg, lit.[22] 80–84 °C/90 mmHg). The improvement of the reported yield (34 %) was obtained by extending the reaction time from 24 to 70 h.

2,5,5-Trimethylnona-1,6,7-trien-4-ol, was prepared from 2,2-dimethyl-3,4-hexadienal and β-methallylmagnesium chloride in the usual way[1] in 93 % yield. B.p. 76–77 °C/0.9 mHg, n_D^{17} 1.4833. IR (film): 3482(s), 3071(m), 1961(m), 1643(s) cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): δ 1.02 (s, 6H), 1.6–2.3 (broad m., 9H), 3.35 (dd, J=3 and 10 Hz, 1H), 4.9–5.3 (broad m, 4H).

2,5,5-Trimethylnona-1,6,7-trien-4-one (1b), was prepared by oxidation of the corresponding alcohol according to our procedure[1] to give *1c* in 89 % yield. B.p. 70–72 °C/0.7 mmHg, n_D^{17} 1.4775. IR (film): 3075(m), 1963(m), 1714(s), 1650(m) cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): δ 1.18 (s, 6H), 1.6–1.9 (broad m, 6H), 3.20 (s, 2H), 4.72 (broad s, 1H), 4.83 (broad s, 1H), 5.0–5.4 (broad m, 2H).

8,8-Dideuterio-2,5,5-trimethyl-1,6,7-octatrien-4-one (1d). A mixture of 4.00 g (68.9 mmol) of 1,1-dideuterio-2-propyn-1-ol, 7.21 g (100 mmol) of isobutyraldehyde, 3.0 g of tetralin and 10 mg *p*-toluenesulfonic acid was refluxed for 36 h until 1.42 g of water had separated in a Dean-Stark trap. Fractional distillation of the crude reaction product gave 2.89 g (39 %) 5,5-dideuterio-2,2-dimethylpenta-3,4-dienal, b.p. 70 °C/100 mmHg.

To 1.25 g (51.5 mmol) Mg in 50 ml dry ether cooled to 14 °C was added 4.67 g (51.5 mmol) β-methallyl chloride. The mixture was stirred overnight and then cooled to 0 °C. A solution of 1.88 g (16.8 mmol) of the deuteriated aldehyde in 25 ml dry ether was added dropwise. When GLC analysis showed the absence of aldehyde (4 h), 6.35 ml of saturated aqueous NH_4Cl solution were added with vigorous stirring. Work-up in the usual way yielded an oil which was dissolved in 15 ml ether and a chromic acid solution[25] (24 ml) was added during a period of 3 days. The usual work-up and distillation gave 20.6 g (74 % from the aldehyde) of *1d,* b.p. 64–6 °C/3.5 mmHg.

Thermal reactions. General procedure. For analytical purposes, 60 mg of compound *1* were distilled through a heated tube as described previously.[1] For preparative purpose at least 5 g were distilled through the same tube. The reactions were monitored by GLC and IR. The % of each compound of the mixture referred to the peak integration value. The crude product mixtures were fractionally distilled and each compound was isolated by preparative GLC from the fraction where it was most abundant.

Thermal reaction of 1a. The allenic ketone *1a*[1] was distilled through the tube at 487 °C/1.5 mmHg to yield a mixture consisting of 60 % *2,* 18 % *3,* 3 % *4,* 5 % *5* and 6 % *6.* The remainder of the product (8 %) consisted of several minor components which were not accounted for. The spectroscopic data of 6-methylene-1,4,4-trimethylbicyclo[3.2.0]heptane-3-one (*2*) and 2,2,4,4-tetramethyl-3-ethynylcyclopentan-1-one (*3*) have been reported.[1]

4-Isopropenyl-3,5,5-trimethyl-2-cyclopenten-1-one (4). IR($CDCl_3$): 3075(w), 1697(s), 1645(w), 1620(m) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 0.97 (s, 3H), 1.15 (s, 3H), 1.64 (broad s, 3H), 2.05 (broad s, 3H), 3.05 (broad s, 1H). ^{13}C NMR (15.0 MHz, $CDCl_3$): δ 18.1, 19.7, 22.4, 28.6 (CH_3), 48.1 (C), 65.2 (CH), 115.3 (CH_2=), 129.1 (CH=), 142.5, 176.3 (C=), 213.6 (C=O).

2,2,5-Trimethylbicyclo[4.2.0]oct-5-en-3-one (*5*). IR($CDCl_3$): 1699(s), 1670(w) cm^{-1}. ^1H NMR (200 MHz, $CHCl_3$): δ 0.99 (s, 3H), 1.03 (s, 3H), 1.57 (broad s, 3H), 1.91 (broad d, J 9.0 Hz, 1H), 2.00 (broad d, J = 9.0 Hz, 1H), 2.4–2.7 (broad m, 2H), 2.73 (broad s, 2H), 2.8–3.0 (m, 1H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 16.14, 19.64, 21.02 (CH_3), 18.54, 26.45, 434.13, 45.37 (CH_2), 49.69 (CH), 119.73, 132.52 (C=), 214.23 (C=O).

3,7,7-Trimethyl-5-methylene-3-cyclohepten-1-one (*6*). IR (film): 3076(w), 1707(s), 1643(m), 1600(w) cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): δ 1.13 (s, 6H), 1.88 (broad s, 3H), 2.55 (broad s, 2H), 3.37 (broad s, 2H), 4.85 (broad s, 2H), 5.98 (broad s, 1H). ^{13}C NMR (15.0 MHz, $CDCl_3$): δ 24.7, 24.7, 27.4 (CH_3), 45.1, 45.5 (CH_2), 46.3 (C), 116.4 (CH_2=), 128.8 (CH=), 131.1, 142.7 (C=), 210.3 (C=O).

Thermal reaction of 1b. The allenic ketone *1b* was distilled through the tube at 495 °C/1.0 mmHg to yield a mixture consisting of 24 % *Z-7*, 27 % *E-7*, 34 % *8* and 3 % *9*. The remainder of the product (12 %) consisted of several minor components which were not accounted for.

(Z)-6-Ethylidene-1,4,4-trimethylbicyclo[3.2.0]-heptan-3-one (Z-7). IR($CDCl_3$): 3041(w), 1729(s) cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$): δ 1.05 (s, 3H), 1.11 (s, 3H), 1.40 (s, 3H), 1.57 (broad d, J = 6.8 Hz, 3H), 2.26 (d, J = 17.8 Hz, 1H), 2.35 (broad s, 2H), 2.51 (d, J = 17.8 Hz, 1H), 2.81 (broad s, 1H), 5.2–5.4 (m, 1H). ^{13}C NMR (22.6 MHz, $CDCl_3$): δ 14.3, 20.0, 26.2, 28.8 (CH_3), 34.8 (C), 42.2, 49.2 (CH_2), 50.3 (C), 60.3 (CH), 120.7 (CH=), 134.8 (C=), 222.0 (C=O).

(E)-6-Ethylidene-1,4,4-trimethylbicyclo[3.2.0]-heptan-3-one (E-7). IR($CDCl_3$): 3037(w), 1730(s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.04 (s, 6H), 1.41 (s, 3H), 1.46 (broad d, J 6.70 Hz, 3H), 2.25 (d, J = 18.25 Hz, 1H), 2.28 (broad d, J = 16.3 Hz, 1H), 2.48(broad d, J = 16.3 Hz, 1H), 2.56 (d, J = 18.25 Hz, 1H), 2.71 (broad s, 1H), 5.26 (m, 1H). ^{13}C NMR (22.6 MHz, $CDCl_3$): δ 13.4, 19.3, 27.4, 27.8 (CH_3), 34.4 (C), 40.9, 49.6 (CH_2), 50.3 (C), 61.0 (CH), 121.4 (CH=), 134.7 (C=), 220.5 (C=O).

2,2,4,4-Tetramethyl-3-(1-propynyl)cyclopentan-1-one (8). IR($CDCl_3$): 1734(s) cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$): δ 1.06 (s, 3H), 1.09 (s, 3H), 1.13 (s, 3H), 1.20 (s, 3H), 1.88 (d, J = 2.7 Hz, 3H), 2.23 (s, 2H), 2.63 (q, J = 2.7 Hz, 1H). ^{13}C NMR (22.6 MHz, $CDCl_3$): δ 3.5, 22.8, 24.5, 27.5, 29.6 (CH_3), 37.2, 48.1 (C), 52.2 (CH_2), 52.3 (CH), 75.3 (C≡), 81.4 (C≡), 221.5 (C=O).

Exo-1,4,4,7-tetramethylbicyclo[4.2.0]oct-5-en-3-one (9). IR($CDCl_3$): 3025(w), 1704(s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.14 (s, 3H), 1.15 (s, 3H), 1.16 (d, J = 8.8 Hz, 3H), 1.17 (s, 3H), 1.45 (t, J = 9.4 Hz, 1H), 2.16 (t, J = 9.4 Hz, 1H), 2.28 (d, J = 12.7 Hz, 1H), 2.58 (d, J = 12.7 Hz, 1H), 3.25 (m, J = 2.2, 8.8 Hz, 1H), 5.24 (d, J = 2.2 Hz, 1H). ^{13}C NMR (22.6 MHz, $CDCl_3$): δ 18.2, 24.3, 26.2, 28.3 (CH_3), 36.7 (CH), 42.6 (CH_2), 43.0, 45.3 (C), 51.3 (CH_2), 122.3 (CH=), 149.6 (C=), 215.8 (C=O).

Thermal reaction of 1c. The allenic ketone *1c*[1] was distilled through the tube at 487 °C/1.5 mmHg to yield a mixture consisting of 67 % *10*, 5 % *11*, 9 % *12*, 1 % *13*, 3 % *14* and 3 % *15* together with 5 % 2,5-dimethyl-2,4-hexadiene. The remainder of the product (7 %) consisted of several minor components which were not accounted for. The spectroscopic data of *10* has been published.[1]

1,4,4,7,7-Pentamethylbicyclo[4.2.0]-oct-5-en-3-one (11). IR($CDCl_3$): 3020(w), 1704(s) cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): δ 1.10 (s, 3H), 1.17 (s, 3H), 1.23 (s, 6H), 1.33 (s, 3H), 1.87 (broad s, 2H), 2.27 (d, J = 13 Hz, 1H), 2.53 (d, J = 13 Hz, 1H), 5.33 (s, 1H). ^{13}C NMR (15.0 MHz, $CDCl_3$): δ 26.2, 26.6, 27.7, 28.2, 29.9 (CH_3), 40.5, 42.4, 45.4 (C), 47.8, 52.9 (CH_2), 124.7 (CH=), 153.3 (C=), 216.5 (C=O).

4-Isopropenyl-2,2,5,5-tetramethyl-3-cyclohexen-1-one (12). IR($CDCl_3$): 3079(w), 1708(s) cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): δ 1.13 (s, 6H), 1.18 (s, 6H), 1.93 (broad s, 3H), 2.43 (s, 2H), 4.78 (broad s, 1H), 4.92 (broad s, 1H), 5.30 (s, 1H). ^{13}C NMR (15.0 MHz, $CDCl_3$): δ 25.0, 26.4, 26.4, 28.5, 28.5 (CH_3), 39.4, 45.2 (C), 53.0 (CH_2), 114.0 (CH_2=), 131.8 (CH=), 145.8, 146.7 (C=), 215.1 (C=O).

3,6-6-Trimethyl-5-(2-methylpropenyl)-2-cyclohexen-1-one (13). IR($CDCl_3$): 3035(w), 1657(s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.97 (s, 3H), 1.04 (s, 3H), 1.62 (d, J = 1.45 Hz, 3H), 1.72 (d, J = 1.45 Hz, 3H), 1.91 (q, J = 1.08 Hz, 3H), 2.20 (broad m, 2H), 2.72 (m, 1H), 5.12 (dt, J = 1.4 and 10.0 Hz, 1H), 5.80 (broad d, J = 1.3 Hz, 1H). ^{13}C NMR (25.0 MHz, $CDCl_3$): δ 18.0, 19.0, 22.5, 23.8, 25.9 (CH_3), 35.2 (CH_2), 42.7 (CH), 44.1 (C), 123.7, 124.8 (CH=), 133.7, 159.0 (C=), 204.8 (C=O).

5-Isopropylidene-3,7,7-trimethyl-3-cyclohepten-1-one (14). IR($CDCl_3$): 1702(s) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 1.10 (s, 6H), 1.76 (s, 3H, 1.77 (s, 3H), 1.89 (s, 3H), 2.56 (s, 2H), 3.33 (s, 2H), 6.25 (broad s, 1H). ^{13}C NMR (25.0 MHz, $CDCl_3$): δ 20.6, 21.5, 24.3, 24.3, 27.6 (CH_3), 39.2, 45.2 (CH_2), 48.0 (C), 126.1 (CH=), 127.1, 128.5, 130.9 (C=), 212.0 (C=O).

6-6-Dimethyl-2-oxa-3-propenylcyclohexan-1-one (*15*). MS (CI, isobutane, m/z): 168 (M^+). IR($CDCl_3$): 3074(w), 1771(s) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 1.05 (s, 3H), 1.18 (s, 3H), 1.81 (broad s, 3H), 2.24 (broad s, 1H), 2.28 (broad s, 1H), 2.32 (d, J = 16.8 Hz, 1H), 2.42 (dd, J = 0.5 and 16.8 Hz, 1H), 4.23 (dd, J = 5.2 and 5.2 Hz, 1H), 4.86 (broad m, 2H). ^{13}C NMR (15.0 MHz, $CDCl_3$): δ 21.1, 22.6, 25.1, (CH_3), 37.2 (CH_2), 39.5 (C), 44.8 (CH_2), 86.9 (CH), 113.3 (CH_2=), 141.4 (C=), 176.0 (C=O).

Thermal reaction of 1d. The deuteriated analogue of *1a* was distilled through the tube at 487 °C/ 1.5 mmHg. Of the resulting complex mixture, *16* and *17* constituted 67 and 12 %, respectively.

6,6-Dideuteriomethylene-1,4,4-trimethylbicyclo-[3.2.0]heptan-3-one (*16*). ^1H NMR (200 MHz, $CDCl_3$): δ 1.07 (s, 3H), 1.0∂ (s, 3H), 1.43 (s, 3H), 2.28 (d, J 18 Hz, 1H), 2.37 (dq, J 2.8, 14 Hz, 1H), 2.57 (2d, J = 14 and 18 Hz, 2H), 2.79 (q, J = 2.8 Hz, 1H). ^2H NMR (30.7 MHz, $CDCl_3$): δ 4.88 (broad s).

3-(2-Deuterioethynyl)-4-deuteriomethyl-2,2,4-trimethylcyclopentan-1-one (*17*). ^1H NMR (200 MHz, $CDCl_3$): δ 1.12 (s, 3H), 1.17 (s, 3H), 1.24 (s, 3H), 2.24 (s, 1H), 2.26 (s, 2H), 2.69 (s, 1H:. A residual proton can be seen at δ 1.09. ^2H NMR (30.7 MHz, $CDCl_3$): δ 1.11, (s, 1D), 2.20 (broad s, 1d).

References

1. Skattebøl, L. and Stenstrøm, Y. *Acta Chem. Scand. B 39* (1985) 291.
2. Aleksanyan, V. T., Kuz'yants, G. M. and Lukina, M. Y. *J. Structural Chem. 8* (1967) 569.
3. Gajewski, J. J. *Hydrocarbon thermal isomerizations.* Academic Press, London 1981.
4. Levek, T. J. and Kiefer, E. F. *J. Am. Chem. Soc. 98* (1976) 1875.
5. Pasto, D. J. *Ibid. 101* (1979) 37.
6. Pasto, D. J. and Warren, S. E. *Ibid. 104* (1982) 3670.
7. Pasto, D. J., Heid, P. F. and Warren, S. E. *Loc. Cit.*3676.
8. Lebedev, V. L., Bagatur'yants, A. A., Taber, A. M. and Kalechits, I. V. *Zh. Fiz. Khim. 53* (1979) 2745; *Chem. Abstr. 92* (1980) 128084g.
9. Kiefer, E. M. and Okamura, M. Y. *J. Am. Chem. Soc. 90* (1968) 4187.
10. Baldwin, J. E. and Roy, U. V. *J. Chem. Soc. D.* (1969) 1225.
11. Vogel, E., Grimme, W. and Dinné, E. *Angew. Chem. 75* (1963) 1103.
12. Untch, K. G. and Martin, D. J. *J. Am. Chem. Soc. 87* (1965) 4501.
13. Skattebøl, L. and Solomon, S. *Loc. Cit.* 4506.
14. Huntsman, W. D., DeBoer, J. A. and Woosley, M. H. *Ibid. 88* (1966) 5846.
15. Dalacker, V. and Hopf, H. *Tetrahedron Lett.* (1974) 15.
16. Deyrup, J. A. and Betkouski, M. *Ibid.* (1973) 1131.
17. Bourelle-Wargnier, F. Vincent, M. and Chuche, J. *Ibid.* (1978) 283.
18. Minter, D. E., Fonken, G. J. and Cook, F. T. *Ibid.* (1979) 711.
19. Summermatter, W. and Heimgartner, H. *Helv. Chim. Acta 67* (1984) 1298.
20. Benson, S. W. *Thermochemical kinetics,* 2nd edition John Wiley, New York 1976.
21. Wentrup, C. *Reactive molecules.* John Wiley, New York 1984.
22. Feller, D., Davidson, E. R. and Borden, W. T., *J. Am. Chem. Soc. 106* (1984) 2513.
23. Mazur, M. R., Potter, S. E., Pinhas, A. R. and Berson, J. A. *J. Am. Chem. Soc. 104* (1982) 6823.
24. Bly, R. S. and Koock, S. U. *Ibid. 91* (1969) 3292.
25. Brown, H. C., Garg, C. P. and Liu, K-T. *J. Org. Chem. 36* (1971) 387.

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