2. Specificities of the α-Alkynone Cyclization

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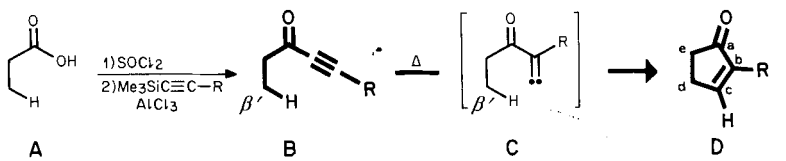
Spezifitäten der α-Alkinon Cyclisierung

Zusammenfassung

Die Regio- und Stereospezifitäten der α-Alkinon-Cyclisierung, einer thermischen Umwandlung von Alkinyl-alkyl-ketonen, welche in β'-Stellung mindestens ein H-Atom tragen, zu 2-Cyclopentenonen wurden untersucht. Cyclisierung zum höher substituierten C(β')-Atom ist dabei bevorzugt, vorausgesetzt, dass die zur Insertion zur Verfügung stehende C(β'),H-Bindung zur Propioloylseitenkette eine möglichst synplanare Anordnung einnehmen kann. In Cyclisierungen zu β'-Methylen-C-Atomen, welche diastereotope H-Atome tragen, wird daher eines der möglichen epimeren Produkte bevorzugt oder ausschließlich gebildet. Die mechanistischen Konsequenzen der gefundenen Spezifitäten werden diskutiert.

1. Introduction. – The thermal cyclization of alkynyl alkyl ketones **B** (α-alkynones) bearing at least one H-atom in a β'-position leads specifically to 2-cyclopentenones[2]) **D** [1]. The reaction (named α-alkynone cyclization [1]) is carried out by passing gaseous **B** at reduced pressure through a hot quartz tube. This thermal process forms a new C,C-bond at a non activated C(β')-atom of **B** and also causes a [1,2]-shift of an acetylenic substituent. It is, therefore, explained by the intermediacy of an alkylidene-carbene **C** which inserts into the C(β'),H-bond (see *Scheme 1*).

Scheme 1



$R = H$, CH_3, $Si(CH_3)_3$

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[2]) In order to facilitate the comparison of corresponding atoms in the 2-cyclopentenone moiety and because these atoms do not carry the same systematic numbers in the mono-, bi- and spirocyclic thermolysis products, we shall label these C-atoms C(a) to C(e), as shown in formula **D**. The *systematic numbering*, however, is used in the experimental part.

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Since α-alkynones **B** are readily available from carboxylic acids **A**, the α-alkynone cyclization **B** → **D** provides a simple tool for the transformation of acids **A** into 2-cyclopentenones **D**. By using different substituents attached to substructure **A** the synthesis of cyclic, polycyclic, spiro and propellane C-skeletons has been achieved [1] [2]. α-Alkynones **B** with more than one β′-position afforded different mixtures of isomeric 2-cyclopentenones **D**, suggesting certain further specificities of the reaction. To learn about them we investigated the thermal behaviour of some model α-alkynones with different substitution and different configuration at the C(β′)-atoms. In the discussion of these results we shall also include relevant examples which had been reported in [1] and [2].

2. Synthesis of the α-alkynones. – The α-alkynones used in this study (see first column of the *Table*) were prepared from the appropriate carboxylic acids (see also first column) *via* the acid chlorides by acylation of trimethylsilylacetylene (*Friedel-Crafts* conditions) according to the method given in [1]: The α-alkynones **20** [1], **32** and **36** [2] had been described previously, the others are new. Of particular diagnostic value for the class of α-alkynones **B** we find the strong IR. bands in the range of 3250 cm^{-1} (terminal acetylene), 2090 cm^{-1} (C,C-triple bond) and 1670 cm^{-1} (conjugated carbonyl group) as well as the sharp one-proton ^{1}H-NMR. singlet around 3 ppm.

Of the precursor acids not available commercially, α-methylbutanoic acid **1** was obtained in pure form[3]) by hydrogenation of tiglic acid [3], **6** and **10** [4] were prepared by alkylation of the lithium dianion of isovaleric acid with methyl and ethyl iodide, respectively, using the general procedure of *Pfeffer et al.* [5]. The same method, applied to **1** and isopropyl iodide, afforded the trisubstituted acetic acid derivative **14**, but in a relatively low yield (24%), which may be due to steric hindrance. The epimeric acids **23** and **28** were obtained, as described in [6] and [7], in isomeric purities of over 96%; the CH_3/CH_3 *cis*- and *trans*-configuration of **23** and **28**, respectively, had been assigned in [7].

3. Thermolysis conditions and separation of the products. – The thermolytic experiments were carried out with the flow system described in [1]. It consists of: 1) an inlet part for the evaporation of the alkynones and for the introduction of a constant flow of nitrogen, 2) a quartz tube filled with quartz rings and surrounded by an oven and 3) a trap for cooling to liquid nitrogen temperature with attachment to a pump. All experiments were performed under the same conditions, namely at an oven temperature of 620° and a pressure of 12–16 Torr; these conditions were found to be sufficient in our equipment for total conversion of all the alkynones under investigation. Since evaporation of the α-alkynone, in our relatively simple system, could not be controlled in such a way as to assure steadiness and reproducibility of the rate of supply into the thermolysis tube, the insensitivity of product composition to extreme differences of evaporation time was demonstrated separately for the case of thermolysis of **2**: In five experiments, with equal amounts of **2** and using between one half and twenty minutes evaporation time, the maximum variation in product composition by GC. analysis was ±2% for **3** and **4** and ± 1% for **5**.

After thermolysis, the trap was warmed to room temperature, the recovered material weighed and the product ratio determined by analytical GC. integration. The accuracy of this determination was checked in two ways: In the case of the **12/13** mixture, it compared within a few percent with the relative ^{1}H-NMR. integrations of the olefinic signals. In the case of the **3/4/5** mixture the GC. integration correlated well with mixtures of different compositions prepared by weight. The ^{1}H-NMR. spectra and the GC. traces of the recovered materials from all reactions agree with each other in such a way as to indicate that the components shown in the table represent the only major products of thermolysis. Only the

[3]) Commercially available **1** contains 5–10% of isovaleric acid.

crude mixture **16** to **19**, from the thermolysis of **15**, exhibits non-negligeable ^{1}H-NMR. signals in the olefinic region due to unidentified by-products.

Preparative GC. allowed the separation of the components in all thermolysis mixtures, with the exception of the pairs **34/35**, **38/39** [2] and the above mentioned mixture **16** to **19**. The structures of the individual components of the latter were assigned on the basis of the spectral data of the mixture, as will be discussed in *Section 5*. Since GC. did not permit the direct separation of **4** from **5**, the following procedure was applied to obtain the pure compounds: Treating pure **3** with base [8] led to an equilibrium mixture of **3** and **4**, which still contained mostly the *trans*-configurated **3**, but no **5**, so that the isolation of pure **4** by GC. could be accomplished. Subjecting the **4/5** mixture to the same conditions transformed the *cis*-configurated **4** almost completely to **3**, so that the separation of almost pure **5** was possible.

Table. *Starting materials and products of thermolysis*

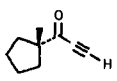
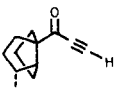
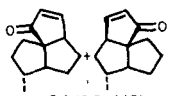
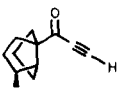
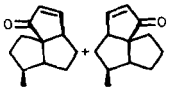
Starting Materials	Products				Recovery (%)
	Tertiary[a]) (%-content)	Secondary[b]) (%-content)		Primary[c]) (%-content)	
 **1** R = OH **2** R = C≡C–H	(not possible)	**3** (60)	**4** (22)	**5** (18)	80
 **6** R = OH **7** R = C≡C–H	**8** (87)	(not possible)		**9** (13)	78
 **10** R = OH **11** R = C≡C–H	**12** (54)	**13** (46)		(not possible)	89
 **14** R = OH **15** R = C≡C–H	**16** (49)	**17** (29)	**18** (7)	**19** (15)	52
 **20**	(not possible)	**21** (92)		**22** (8)	90 [1]
 **23** R = OH **24** R = C≡C–H	**25** (69)	**26** (26)		**27** (5)	99

Table (continued)

Starting Materials	Products			Recovery (%)
	Tertiary[a] (%-content)	Secondary[b] (%-content)	Primary[c] (%-content)	
 **28** R = OH **29** R = C≡C–H	(not formed)	 **30** (89)	 **31** (11)	96
 **32**	 **33** (52)	 **34/35** (48)	(not possible)	95 [2]
 **36**	 **37** (43)	 **38/39** (57)	(not possible)	95 [2]

[a]) Formed through insertion into a tertiary C(β'),H bond, *i. e.* 2-cyclopentenone disubstitute at C(d).
[b]) Formed through insertion into a secondary C(β'),H bond, *i. e.* 2-cyclopentenone monosubstituted at C(d).
[c]) Formed through insertion into a primary C(β'),H bond, *i. e.* 2-cyclopentenone unsubstituted at C(d).

4. Products of thermolysis. – The *Table* shows the products of thermolysis, ordered (after the column with the starting materials) in three columns from left to right according to the degree of substitution at C(d) of the 2-cyclopentenone moiety. This corresponds to the three different types of product formation, namely the insertion of the carbene intermediate **C** into tertiary, secondary or primary C(β'),H bonds. The number of constitutional variants among the products, expected on this basis, is two from **2**, **7**, **11**, **20**, **32** and **36** and three from **15**, **24** and **29**. A further constitutional variant among the products is expected from **32** and from **36** due to the fact that they contain heterotopic secondary H-atoms at C(β'). In addition, a further, configurational variant might result from **2**, **11**, **15**, **20**, **24** and **29** and two such further variants from **32** and **36**, since these alkynones contain diastereotopic H-atoms at their secondary β'-position. All the constitutional variants, except the tertiary one from **29**, were observed among the products, but configurational variants resulted only from **2** and **15**, where the diastereotopic secondary H-atoms at C(β') belong to an open chain and not to a 5-membered ring, as in all the other cases.

5. The structure of the thermolysis products. – The thermolysis products **3**, **4** [8], **5** [9] and **8** [10] were identified by their (partially) known spectral properties. In each of the new products, the presence of the 2-cyclopentenone moiety was recognized by the spectral properties characteristic for the conjugated enone substructure, namely the UV. maximum (219–230 nm, ε = 7000–10000), the IR. bands (strong at 1680–1710, weaker at 1570–1600 cm^{-1}) and the ^{1}H-NMR. signals (δ in the range of 7.3–7.8, H–C(c) and of 5.9–6.2, H–C(b)) [11]. The degree of substitution at C(d), an important aspect of the present investigation, was derived from the multiplicity of

these ^{1}H-NMR. signals of H–C(b) and H–C(c): In addition to their mutual coupling (J in the range of 5–6 Hz), both are coupled to protons at C(d) with J values ranging from 1.6 to 2.2 Hz for H–C(b) and from 2.5 to 3.0 Hz for H–C(c). Therefore doublet patterns are observed for H–C(b) and H–C(c) in the products shown in the first column, doublets of doublets for those in the second and doublets of doublets of doublets for those in the third. The relative configuration at C(d) and C(e) in **3**, **4** and **13** was assigned on the basis of the coupling constant of the vicinal (tertiary) H-atoms at these positions with J *ca.* 2.5 Hz in the *trans*-isomers (dihedral angle *ca.* 120°) and J *ca.* 7.5 Hz in the *cis*-isomers (dihedral angle *ca.* 0°), as expected for the near planar structure of 2-cyclopentenones [8].

The structures of the individual components **16** to **19** of the preparatively unseparable mixture from the thermolysis of **15** were derived on the basis of the spectral characteristics of the mixture as follows: GC./MS. analysis indicated the presence of four main components in the ratios of 49:29:7:15, all isomeric with the starting material **15**, and the ^{1}H-NMR. contained three signal groups in the olefinic region (H–C(b) and H–C(c)) in the ratios of 43:37:19. The most and the least abundant signals could clearly be assigned to **16** (*ca.* 49%) and **19** (*ca.* 15%), respectively, by their multiplicities. The remaining signals belong to the two stereoisomers **17** and **18** (*ca.* 29 and 7%) and are evidently unresolved[4]). All four components exhibit predominant *McLafferty* MS. fragmentations, **16** involving an ethyl group and **17**, **18** and **19** an isopropyl group; the same characteristic fragmentation is observed for the isolated components **5**, **12**, **9** and **13**. The tentative configurational assignment of **17** to the more abundant (29%), and of **18** to the less abundant (7%), GC./MS. peak is based on the reasonable assumption, that in 2-cyclopentenones a 4,5-*cis*-relationship of two methyl groups (**17**) is favored over a 4,5-*cis*-relationship of a methyl and an isopropyl group (**18**), an effect which is observed when the thermolysis of **11** and **2** are compared: From **11** only the *trans*-isomer **13** was formed, from **2**, however, both the *cis*-**4** and the *trans*-isomer (**3**).

Concerning the bicyclic products **21**, **25**, **26** and **30**, the ring fusion at C(d),C(e) is concluded to be *cis* since *a*) in each case a single stereoisomer was obtained and *b*) insertion into the tertiary C(β'),H bond of **29** *trans* to the propioloyl group, which would have formed the *trans*-isomer of **25**, was not observed. The assignment of the configuration at the chiral methine C-atoms outside the newly formed 5-membered ring in **26**, **27**, **30** and **31** follows from the fact that **26** and **27** are formed exclusively from **24** but **30** and **31** exclusively from **29**. This leads to the conclusion that chirality centers not involved in the cyclization step are not affected by the thermolysis conditions. The same arguments were previously applied to assign the configuration of the components in the **34**/**35** and **38**/**39** mixtures [2].

6. Thermal stability of the products. In order to be able to discuss the regio- and stereospecificities of the α-alkynone cyclization it is essential to know whether the products and their ratios reflect the result of the proper cyclization step or of some subsequent isomerization reactions effected by the elevated temperature of product

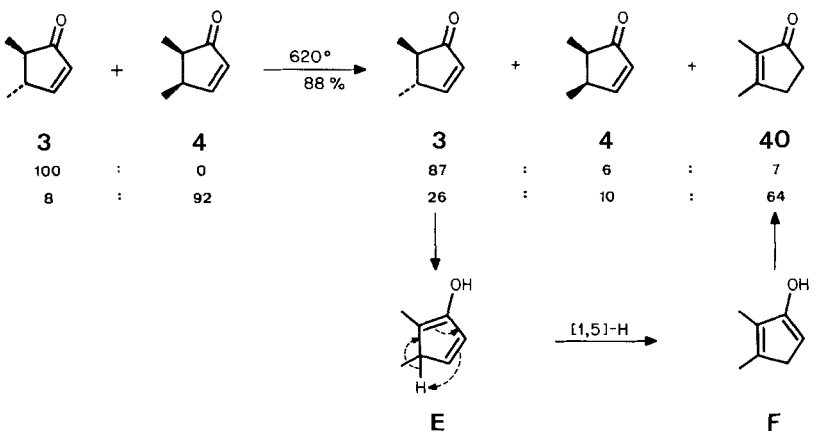
[4]) For comparison, it may be recalled that the chemical shifts of the vinylic protons of **3** and **4** differ by less than 0.05 ppm (see *Exper. Part*).

formation. Therefore, the thermal stability of some of the products was tested. On reheating the purified compounds **3, 4** (containing 8% of **3**), **12** and **25** under the conditions of their formation, none of their constitutional isomers (which were known as products of the cyclization) could be observed. Thus the ratios of regioisomers given in the *Table* (disregarding configurational differences) represent the genuine result of an irreversible cyclization reaction.

With constitutional stability proven, plausible mechanism for configurational changes at the stereogenic centers of the products were evaluated. When the product mixtures **25/26/27** and **30/31** produced in the thermolysis of **24** and **29**, respectively, were subjected to the conditions of their formation, there was hardly any change of product composition. Since these conditions evidently produced no interconversion of **26** and **30** or of **27** and **31**, these experiments not only confirm the stability of chiral centers not involved in the reaction (see *Section 5*) but also exclude a reversible radical opening of the doubly allylic C(d),C(e)-bond with concomitant inversion at a radical site as a mechanism for configurational isomerization.

Subjecting the *trans*-isomer **3** to the conditions of its formation resulted in mixtures of **3, 4** and a new product **40** [11]. The same components, but in different ratios, were obtained from a mixture containing mostly the *cis*-isomer **4** (see *Scheme 2*).

Scheme 2



Enolization is probably the cause of this *cis/trans*-isomerization between **3** and **4**, and a [1,5]-H-shift in the enol form **E** may lead to the enol form **F** of **40**. The substantial difference[5]) of product composition in these latter two experiments show that the cyclization conditions, even when applied to the products a second time, are still far from permitting an equilibrium between the *cis*- (**4**) and the *trans*-isomer (**3**) to be reached. Therefore the initial **3/4** ratio reflects – at least partly – the effect governing the cyclization reaction. For C(e)-disubstituted 2-cyclopentenones such as **17, 18, 21, 26, 30, 34, 35, 38** and **39** with chiral centers at C(d) and C(e), epimerization at C(d) by vinylogous enolization is possible. The fact, however, that cyclization towards the *trans*-located tertiary C,H-bond in the thermolysis of **29**, to give the *trans*-isomer of **25**, is not observed, indicates that the cyclization rather than vinylo-

gous enolization determines the observed configuration of the above mentioned products.

7. Discussion. – The present investigation confirms the strength of that (first) aspect of the regiospecificity of the α-alkynone cyclization, which had been mentioned previously [1] [2] and which predicts the exclusive formation of 2-cyclopentenones by attack on a C(β')-atom. The point to be discussed in this section concerns a second regiospecificity aspect, which is evidently not as strong as the first one, namely the relative reactivity of different types of C(β'),H bonds. First inspection of the product composition shown in the *Table* confirms that cyclization involving C(β')-atoms of higher substitution is generally preferred, the difference in reactivity being much greater between methyl and the other two types of C-atomes (see appropriate ratios of products in the thermolysis of **2, 7, 15, 20, 24** and **29**) than between methylene and methine C-atoms (thermolysis of **11, 15** and **24**). The same order of reactivity applies to **32** and **36**, when it is taken into account that two methylene groups compete for cyclization with only one methine group. This specificity of the α-alkynone cyclization supports the mechanistic hypothesis of a carbene intermediate **C** (see *Section 1*) since, for gas phase reactions of other carbenes, preference of insertion into C,H-bonds in the order of tertiary, secondary and primary is a known effect [12]. A third potential aspect of regiospecificity appears to be very weak, probably because it is due to a structural difference further removed from the reacting center (H-C(β')). It expresses itself in the ratios of **34** to **35** and of **38** to **39**, which are 1: 1 and 3: 2 (or 2: 3, since constitution not yet known [2]), respectively.

We now must turn to an aspect of stereospecificity of the α-alkynone cyclization: The only exception, where cyclization involving a methine C(β')-atom, although present, was not observed, is the thermolysis of **29**; its epimer, the *cis*-dimethyl compound **24**, on the other hand, was smoothly converted to **25** as the major product by cyclization involving a constitutionally equivalent methine C-atom. In addition, whenever a cyclization involved a methylene C(β')-atom with diastereotopic H-atoms, one of the epimeric products possible was formed predominantly (see thermolysis of **2** and **15**) or exclusively (see thermolysis of **11, 20, 24, 29, 32** and **36**). These results show that the observed specificities of the α-alkynone cyclization depend not only on the degree of substitution of the C-atom involved (the above mentioned second aspect of regiospecificity), but also on the conformational relationship between the propioloyl group and the C,H-bond to be inserted.

Since the cyclizations are kinetically controlled (see *Section 6*) we consider a stereoelectronic factor for the ring closure step **C** → **D** (see *Scheme 1*), one which rationalizes all specificity aspects observed so far. This factor demands an almost planar 6-membered transition state as is implied in formula **C**. More work is desirable to throw further light on this factor.

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[4] For comparison, it may be recalled that the chemical shifts of the vinylic protons of **3** and **4** differ by less than 0.05 ppm (see *Exper. Part*).

[5] The difference may be due to the release of strain for the *cis*-dimethyl compound **4** in going to the enol form **E**, compared with an increasing CH_3/CH_3-interaction in the *trans*-isomer **3** for the same process.

Returning to the second regiospecificity aspect, an attempt was made to derive relative reactivities (insertion tendencies) for the different types of C(β'),H bonds by using the observed product ratios shown in the *Table*. Fairly consistent results are obtained only for those cases where the stereospecificity is very high, namely for the class of the cyclopentyl alkynyl ketones **20, 24, 29, 32** and **36,** which lead to bicyclic and tricyclic products with only *cis*-ring fusion. The relative reactivities for insertion into those C(β'),H bonds which can participate in the above mentioned planar transition state, corrected by the statistical factor of their occurence in the starting alkynone, are estimated to be in the order of 40: 20:1 for the sequence tertiary, secondary to primary C-atoms. This allows a useful prediction of product composition for α-alkynone cyclizations, at least within the class of cyclopentyl alkynyl ketones.

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Experimental Part

1. General. – Melting points were determined on a *Mettler* FP-52 apparatus with a microscope. UV. spectra were taken on a *Kontron Uvikon 810,* IR. spectra on a *Perkin Elmer 257* or *297* spectrometer. NMR. spectra were recorded on *Varian* spectrometers *EM-360, FT-80A, EM-390, XL-100* or *XL-200.* For GC./MS. combination, a *Varian* gas chromatograph 3700 with an SE-54 coated glass capillary column and He as carrier gas was connected to the *Varian 112 S* system. For column chromatography, *Merck Lobar* columns (silica *Lichroprep Si 60*) were used with a pump and a differential refractivity detector for peak detection. The acid chlorides were prepared according to [13]. For their conversion into the alkynones according to [1] commercial trimethylsilylacetylene (*Fluka AG,* CH-Buchs) was used. The thermolytic experiments were performed in the apparatus described in [1]. The notations used to describe spectral data are described in [14].

2. Preparation of 4-methyl-1-hexyn-3-one (*2*). – 2.1 *Preparation of 2-methylbutanoic acid* (**1**). By catalytic hydrogenation of tiglic acid in a 150 mmol scale in 88% yield according to [3], b.p. 73–77°/12 Torr ([3]: b.p. 173–174°). – ^{1}H-NMR. (60 MHz; CCl_4); 12.2 (*s,* 1 H, COOH); 2.30 (sext., J = *ca.* 7, 1 H, H–C(2)); 2.0–1.25 (*m,* 2 H, 2 H–C(3)); 1.1 (*d,* J=7, 3 H, H_3C–C(2)); 0.9 (*t,* J=7, 3 H, 3 H–C(4)).

2.2 *Preparation of* **2.** From 18.0 g (176 mmol) of **1**, 16.6 g (78%) of its acid chloride were obtained after distillation through a 10 cm *Vigreux* column at 113–115° ([15]: b.p. 111–112°/653 Torr). Treatment of 8.3 g (69 mmol) of the acid chloride of **1** with trimethylsilylacetylene according to [1] and distillation of the crude product through a 10 cm *Vigreux* column at 130–135° yielded 5.0 g (67%) of **2** as a slightly yellow oil, which was further purified for analytical purposes by preparative GC. (*Carbowax,* 130°). – UV. (ethanol): 211 (5200), 218 *S* (4000). – IR. (film): 3250*s* (H–C≡C), 2960*s,* 2930*s,* 2085*s* (C≡C), 1670*s* (C=O), 1455*m,* 1065*m.* – ^{1}H-NMR. (90 MHz; $CDCl_3$): 3.22 (s, 1 H, H–C≡C); 2.50 (sext., J = *ca.* 7, 1 H, H–C(4)); 2.10–1.25 (*m,* 2 H, 2 H–C(5)); 1.18 (*d,* J=7.5, 3 H, H_3C–C(4)); 0.92 (*t,* J=7.5, 3 H, 3 H–C(6)). – MS. (70 eV): 110 (0.5, M^+), 95 (15), 82 (43), 67 (24), 57 (81), 53 (56), 41 (100).

$C_7H_{10}O$ (110.16) Calc. C 76.32 H 9.15% Found C 75.93 H 9.25%

3. Thermolysis of *2*. – 3.1. *Preparative.* From the thermolysis of 4.5 g (40.8 mmol) of **2** at 620°/14 Torr, 3.6 g (80%) of a yellow oil were recovered, which, by analytical GC., was shown to contain *trans*-4,5-dimethylcyclopent-2-en-1-one (**3**), *cis*-4,5-dimethylcyclopent-2-en-1-one (**4**) and 5-ethylcyclopent-2-en-1-one (**5**) in the ratio 60 : 22 : 18. By preparative GC. (*Carbowax,* 150°), 1.0 g of pure **3** was eluted first, followed by 0.42 g of a mixture of **4** and **5**.

Properties of **3**. – UV. (ethanol): 219 (10000). – IR. (film): 3040*w,* 2960*m,* 2930*m,* 2870*m,* 1700*s* (C=O), 1585*m* (C=C), 1450*m,* 1345*m,* 1180*m.* – ^{1}H-NMR. (200 MHz, $CDCl_3$): 7.51 (*d*×*d,* J=6.0 and 2.4, 1 H, H–C(3)); 6.11 (*d*×*d,* J=6.0 and 2.0, 1 H, H–C(2)); 2.54 (*qa*×*d*×*d*×*d,* J=7.3, 2.6, 2.4 and 2.0, 1 H, H–C(4)); 1.88 (*qa*×*d,* J=7.3 and 2.6, 1 H, H–C(5)); 1.23 (*d,* J=7.3, 3 H, H_3C–C(4 or 5)); 1.19 (*d,* J=7.3, 3 H, H_3C–C(5 or 4)) (*cf.* [8] for a partial description of this ^{1}H-NMR. spectrum). – MS. (70 eV): 110 (47, M^+), 95 (82), 67 (100), 53 (16), 41 (44).

3.2. *Effect of evaporation time.* Thermolysis of five 100 mg samples of **2** at 620°/14 Torr, varying the time for total evaporation from 0.5 to 20 min by progressively lengthening the distance of the probe container from the entrance to the oven-heated portion of the quartz tube, the variation in product composition was not important (see *Section 3*).

3.3. *Isolation of* **5**. The solution of 800 mg of 10:37:53 mixture of **3, 4** and **5** (enriched in **5** by distilling the crude thermolysate of experiment 3.1 at 105 Torr and collecting the fraction at 93°) in 7 ml of THF and 7 ml of 1N aqueous NaOH was stirred at RT. for 20 min, extracted with pentane, dried over $MgSO_4$ and evaporated at RT./100 Torr. Preparative GC. separation yielded 120 mg of **5**, containing only 8% of **4**.

Properties of **5**. – UV. (ethanol): 219 (7500). – MS. (70 eV): 110 (14, M^+), 95 (5), 82 (100), 81 (52), 68 (21), 53 (34), 41 (19). – The other data of **5** agree with the ones reported in [9].

3.4. *Isolation of* **4** *and* **40** *obtained by thermolysis of* **3**. In order to isolate **4**, 868 mg of **3** were thermolized under the same conditions as **2**, leading to 765 mg (88%) of a yellow oil, which, by analytical GC., contained **3, 4** and *2,3-dimethylcyclopent-2-en-1-one* (**40**) in the ratio 87:6:7. By preparative GC. the isomers were eluted in the order **3** (377 mg), **4** (20 mg) and **40** (60 mg).

Properties of **4**. – IR. ($CHCl_3$): 2970*m*, 1710*s* (C=O), 1600*w* (C=C), 1160*w*. – ^{1}H-NMR. (200 MHz; $CDCl_3$): 7.59 (*d* × *d*, *J* = 5.7 and 2.8, 1 H, H–C(3)); 6.13 (*d* × *d*, *J* = 5.7 and 1.9, 1 H, H–C(2)); 3.2–3.0 (*m*, 1 H, H–C(4)); 2.46 (*qa* × *d*, *J* = 7.5 and 7.0, 1 H, H–C(5)); 1.09 (*d*, *J* = 7.5, 3 H, H_3C–C(4 or 5)); 1.07 (*d*, *J* = 7.5, 3 H, H_3C–C(5 or 4)) (*cf.* [8] for a partial description of this ^{1}H-NMR. spectrum). – MS. (70 eV): 110 (54, M^+), 95 (100), 68 (29), 67 (86), 53 (13), 41 (41).

Properties of **40**. The data of **40** reported in [11] agree with the ones found here. – MS. (70 eV): 110 (82, M^+), 95 (24), 86 (17), 84 (26), 67 (100), 54 (17).

4. Preparation of 4,5-dimethyl-1-hexyn-3-one (*7*). – 4.1. *Preparation of 2,3-Dimethylbutanoic acid (***6***) and 2-ethyl-3-methylbutanoic acid (***10***).* The acids **6** and **10** were prepared in 100 mmol scale by alkylation of the lithium dianion (prepared as in [5]) of isovaleric acid with methyl and ethyl iodide, respectively. The crude acids, each obtained in 95% yield, were used for the preparation of the acid chlorides without further purification.

4.2. *Preparation of* **7**. From 10.8 g (95 mmol) of crude acid **6**, 7.02 g (55%) of its chloride were obtained after distillation through a 10 cm *Vigreux* column at 129–132° ([16] b.p. 133–136°), which was converted into 5.0 g (77%) of **7**, isolated after distillation through a 10 cm *Vigreux* column at 100–105°/85 Torr as a colourless liquid. An analytical sample was obtained by prep. GC. (*Carbowax*, 130°). – UV. (ethanol): 211 (4800), 218 *S* (3800). – IR. (film): 3250*m* (H–C≡C), 2960*s*, 2870*m*, 2085*s* (C≡C), 1670*s* (C=O), 1455*m*, 1075*m*. – ^{1}H-NMR. (90 MHz; $CDCl_3$): 3.20 (*s*, 1 H, H–C≡C)); 2.58–1.94 (*m*, 2 H, H–C(4) and H–C(5)); 1.08 (*d*, *J* = 7.0, 3 H, H_3C–C(4)); 0.93 (*d*, *J* = 7.0, 3 H, H_3C–C(5)); 0.84 (*d*, *J* = 7.0, 3 H, 3 H–C(6)). – MS. (70 eV): 109 (12), 82 (63), 71 (52), 53 (39), 43 (100).

$C_8H_{12}O$ (124.18) Calc. C 77.38 H 9.74% Found C 77.16 H 10.00%

5. Thermolysis of *7*. – From the thermolysis of 998 mg (8.0 mmol) of **7** at 620°/42 Torr, 787 mg (78%) of a yellow oil were recovered, which, by analytical GC. was shown to contain *4,4,5-trimethylcyclopent-2-en-1-one* (**8**) and *5-isopropylcyclopent-2-en-1-one* (**9**) in the ratio 87:13. By prep. GC. (*Carbowax*, 150°), the isomers were eluted in the order of **8** (262 mg) and **9** (29 mg).

Properties of **8**. The properties reported in [10] agree with the ones found here. – UV. (ethanol): 219 (10500). – MS. (70 eV): 124 (30, M^+), 109 (100), 81 (54), 79 (15), 67 (11), 55 (10), 53 (17), 41 (29).

Properties of **9**. – UV. (ethanol): 219 (9300). – IR. (film): 2950*s*, 2870*m*, 1685*s* (C=O), 1585*w* (C=C), 1460*w*, 1340*w*, 1160*m*. – ^{1}H-NMR. (200 MHz; $CDCl_3$): 7.71 (*d* × *d* × *d*, *J* = 5.7, 2.5 and 2.5, 1 H, H–C(3)); 6.21 (*d* × *d* × *d* × *d*, *J* = 5.7, 2.1 and 2.1, 1 H, H–C(2)); 2.71 (*d* × *d* × *d*, *J* = 18.5, 6.4, 2.5 and 2.1, 1 H, H–C(4) *cis* to isopropyl); 2.46 (*d* × *d* × *d*, *J* = 18.5 and 3 × *ca.* 2.5, 1 H, H–C(4) *trans* to isopropyl); 2.46–2.17 (*m*, 2 H, H–C(5) and H–C(CH_3)$_2$); 0.99 (*d*, *J* = 6.8, 3 H, one CH_3 of isopropyl); 0.77 (*d*, *J* = 6.6, 3 H, the other CH_3 of isopropyl. – MS. (70 eV): 124 (6, M^+), 109 (3), 82 (100), 81 (22), 68 (23), 53 (16), 41 (11).

$C_8H_{12}O$ (124.18) Calc. C 77.38 H 9.74% Found C 77.48 H 9.54%

6. Preparation of 4-ethyl-5-methyl-1-hexyn-3-one (*11*). – From 11.3 g (87 mmol) of crude acid **10**, 10.3 g (79%) of its chloride were obtained after distillation at 83–88°/75 Torr ([17]: b.p. 150–152°), which was converted into 7.0 g (73%) of **11**, isolated as a yellow oil after bulb-to-bulb distillation at 130°/80 Torr. An analytical sample was obtained by prep. GC. (*Carbowax*, 150°). – UV. (ethanol): 212 (4300), 220 *S*

(3300). – IR. (film): 3250*m* (H–C≡C), 2960*s*, 2870*m*, 2085*s* (C≡C), 1670*s* (C=O), 1455*w*, 1195*m*, 1060*w*, 1040*w*. – ^{1}H-NMR. (90 MHz; $CDCl_3$): 3.17 (*s*, 1 H, H–C≡C); 2.34–1.30 (*m*, 4 H, H–C(4), H–C(5) and H_2C–C(4)); 1.0–0.7 (*m*, 9 H, H_3C–C(5), $H_3C(6)$, H_3C–CH_2). – MS. (70 eV): 110 (4), 109 (4), 96 (27), 85 (34), 81 (23), 53 (19), 43 (100), 41 (33).

$C_9H_{14}O$ (138.22) Calc. C 78.21 H 10.21% Found C 78.13 H 10.48%

7. Thermolysis of *11*. – 9.1. *Preparative.* From the thermolysis of 3.931 g (28.4 mmol) of **11** at 620°/14 Torr, 3.516 g (89%) of a dark oil were recovered, which, by analytical GC. and ^{1}H-NMR. analysis, was shown to contain *4,4-dimethyl-5-ethylcyclopent-2-en-1-one* (**12**) and trans-*4-methyl-5-isopropylcyclopent-2-en-1-one* (**13**) in the ratio of 54:46. The isomers were separated by column chromatography (silica gel, hexane/EtOAc 97:3).

Properties of **12**. – UV. (ethanol): 218 (10500). – IR. (film): 3030*w*, 2960*s*, 2870*m*, 1705*s* (C=O), 1590*w* (C=C), 1460*w*, 1365*w*, 1340*w*, 1265*w*, 1160*w*, 790*m*. – ^{1}H-NMR. (200 MHz; $CDCl_3$): 7.37 (*d*, *J*=5.7, 1 H, H–C(3)); 5.99 (*d*, *J*=5.7, 1 H, H–C(2)); 2.0–1.7 (*m*, 2 H, H–C(5) and one H of CH_2CH_3); 1.5–1.3 (*m*, 1 H, the other H of CH_2CH_3); 1.26 (*s*, 3 H, H_3C–C(4)); 1.11 (*t*, *J*=7.5, 3 H, H_3C–CH_2); 1.08 (*s*, 3 H, H_3C–C(4)). – MS. (70 eV): 138 (35, M^+), 123 (79), 110 (96), 95 (100), 81 (74), 79 (39), 67 (57), 55 (29), 53 (29), 40 (58).

$C_9H_{14}O$ (138.22) Calc. C 78.21 H 10.21% Found C 78.48 H 10.26%

Properties of **13**. – UV. (ethanol): 219 (10500). – IR. (film): 2960*s*, 2870*m*, 1700*s* (C=O), 1590*w* (C=C), 1460*w*, 1180*w*. – ^{1}H-NMR. (200 MHz; $CDCl_3$): 7.54 (*d*×*d*, *J*=5.6 and 2.6, 1 H, H–C(3)); 6.08 (*d*×*d*, *J*=5.6 and 2.0, 1 H, H–C(2)); 2.77 (*qa*×*d*×*d*×*d*, *J*=7.3 and 3× *ca.* 2.5, 1 H, H–C(4)); 2.26 (*sept.*×*d*, *J*=6.9 and 4.3, 1 H, H–C(CH_3)$_2$); 1.86 (*d*×*d*, *J*=4.3 and 2.3, 1 H, H–C(5)); 1.22 (*d*, *J*=7.3, 3 H, H_3C–C(4)); 1.03 (*d*, *J*=6.9, 3 H, one CH_3 of isopropyl); 0.81 (*d*, *J*=6.9, 3 H, the other CH_3 of isopropyl). – MS. (70 eV): 138 (6, M^+), 123 (10), 96 (100), 95 (52), 81 (16), 67 (58), 55 (16), 53 (11), 43 (17), 41 (38).

$C_9H_{14}O$ (138.22) Calc. C 78.21 H 10.21% Found C 78.53 H 10.21%

8. Thermolysis of *12*. – From the thermolysis of 35 mg of **12** at 620°/14 Torr 28 mg of a yellow oil were obtained, which, by analytical GC. and ^{1}H-NMR., was shown to contain only unchanged **12**.

9. Preparation of 4-ethyl-4,5-dimethyl-1-hexyn-3-one (*15*). – 9.1. *Preparation of 2-ethyl-2,3-dimethylbutanoic acid* (**14**). In a 100 mmol scale by alkylation of the lithium dianion of **1** with isopropyl iodide according to [5]. After work-up **14** was separated by preferential extraction of **1** with 0.1N aqueous $NaHCO_3$ from a solution of the mixture of **1** and **14** in petroleum ether. Pure **14** (3.4 g, 24%) was obtained as a colourless oil after bulb-to-bulb distillation at 140°/14 Torr. – IR. (film): 3500–2300*s* br., 1690*s* (C=O), 1460*m*, 1390*m*, 1300*m*, 1260*m*, 1170*m*, 930*w* br. – ^{1}H-NMR. (200 MHz; $CDCl_3$): 2.02 (*sept.*, *J*=7.5, 1 H, H–C(3)); 1.70 (*qa*×*d*, *J*= 14 and 7, 1 H, one H of CH_2CH_3); 1.48 (*qa*×*d*, *J*= 14 and 7, 1 H, the other H of CH_2CH_3); 1.00 (*s*, 3 H, H_3C–C(2)); 0.89 (*d*, *J*=7, 3 H, H_3C–C(3)); 0.88 (*d*, *J*=7, 3 H, 3 H–C(4)); 0.87 (*t*, *J*=7,5, 3 H, H_3C–CH_2). – MS. (70 eV): 102 (55), 99 (7), 87 (100), 57 (38), 43 (31), 41 (36).

$C_8H_{16}O_2$ (144.34) Calc. C 66.57 H 11.17% Found C 66.80 H 11.40%

9.2. *Preparation of* **15**. – From 3.90 g (27 mmol) of **14** 4.14 g (94%) of its acid chloride were obtained, a colourless oil after bulb-to-bulb distillation at 140°/75 Torr [IR. (film): 2965*s*, 2980*m*, 1795*s* (C=O), 1460*m*, 1385*m*, 910*m*, 790*m*; ^{1}H-NMR. (200 MHz; $CDCl_3$): 2.20 (*sept.*, *J*=7.0, 1 H, H–C(3)); 1.77 (*qa*×*d*, *J*= 14 and 7.5, 1 H, one H of CH_2CH_3); 1.57 (*qa*×*d*, *J*= 14 and 7.5, 1 H, the other H of CH_2CH_3); 1.09 (*d*, *J*=0.6, 3 H, H_3C–C(2)); 0.92 (*d*, *J*=7.0, 6 H, 3 H–C(4) and H_3C–(C(3)); 0.91 (*t*, *J*=7.5, 3 H, H_3C–CH_2)]. Treatment of 2.566 g (15.8 mmol) of the acid chloride of **14** with trimethylsilylacetylene according to [1], but at –40°, yielded 1.927 g (80%) of crude **15** (at –20° the yield was lower). An analytical sample was obtained by bulb-to-bulb distillation at 120°/45 Torr followed by preparative GC. (*Carbowax*, 170°). – UV. (ethanol): 211 (4700), 220 *S* (3700). – IR. (film): 3250*m* (H–C≡C), 2960*s*, 2880*m*, 2085*s* (C≡C), 1670*s* (C=O), 1455*m*, 1385*m*, 1225*w*, 1075*m*, 1060*s*. – ^{1}H-NMR. (200 MHz; $CDCl_3$): 3.16 (*s*, 1 H, H–C≡C); 2.20 (*sept.*, *J*=6.8, 1 H, H–C(5)); 1.82 (*qa*×*d*, *J*= 14 and 7.5, 1 H, one H of CH_2CH_3); 1.56 (*qa*×*d*, *J*= 14 and 7.5, 1 H, the other H of CH_2CH_3); 0.97 (*s*, 3 H, H_3C–C(4)); 0.89 (*d*, *J*=6.8, 3 H, 3 H–C(6)); 0.82 (*d*, *J*=6.8, 3 H, H_3C–C(5)); 0.80 (*t*, *J*=7.4, 3 H, H_3C–CH_2). – MS. (70 eV): 110 (6), 99 (19), 95 (22), 57 (100), 53 (11), 43 (41).

$C_{10}H_{16}O$ (152.22) Calc. C 78.91 H 10.60% Found C 79.11 H 10.68%

10. Thermolysis of *15*. – From the thermolysis of 672 mg (4.42 mmol) of **15** at 620°/14 Torr, 347 mg (52%) of a brown oil were recovered, which by analytical GC. was shown to contain four main products in the ratios of 49:29:7:15, assigned as explained in *Section 5* to *5-ethyl-4,4,5-trimethyl-2-cyclopenten-1-one* (**16**), *(4*R*, *5*S*)*-5-isopropyl-4,5-dimethyl-2-cyclopenten-1-one* (**17**), *(4*R*, *5*R*)*-5-isopropyl-4,5-dimethyl-2-cyclopenten-1-one* (**18**) and *5-ethyl-5-isopropyl-2-cyclopenten-1-one* (**19**), respectively. – IR. of the mixture (film): 2960*m*, 2920*m*, 2870*m*, 1700*s* (C=O), 1590*w* (C=C), 1460*m*. – ^{1}H-NMR. of the mixture (200 MHz, $CDCl_3$): 7.71 (*d*×*d*×*d*, *J*=5.8, 3.0 and 3.0, H–C(3) in **19**); 7.51 (*d*×*d*, *J*=5.8 and 2.5, H–C(3) in **17** and **18**); 7.33 (*d*, *J*=5.8, H–C(3) in **16**); relative ratios of integration for the signals at 7.71, 7.51 and 7.33 ppm: 20:37:43); uninterpreted signals in the range of 7.25–6.45 ppm: 6.14 (*d*×*d*×*d*, *J*=5.8, 2.0 and 2.0, H–C(2) in **19**); 6.07 (*d*×*d*, *J*=5.8 and 2.2, H–C(2) in **17** and **18**); 5.97 (*d*, *J*=5.8, H–C(2) in **16**); relative ratios of integration for the signals at 6.14, 6.07 and 5.97 ppm: 21:36:43; many signals in the range of 2.95–0.60 ppm. – GC./MS. (*SE-54*, 70 eV): Ratios of peaks **16**/**17**/**18**/**19** = 49:29:7:15; *Peak of* **16**: 152 (39, M^+), 137 (75), 124 (100), 123 (80), 109 (34), 95 (64), 81 (19), 67 (45); *Peak of* **17**: 152 (4, M^+), 137 (7), 110 (100), 95 (18), 82 (36), 81 (27), 79 (14), 64 (9), 54 (14); *Peak of* **18**: 152 (6, M^+), 137 (10), 110 (100), 109 (54), 95 (25), 82 (61), 81 (54), 55 (28); *Peak of* **19**: 152 (9, M^+), 124 (17), 110 (100), 109 (64), 107 (16), 95 (66), 81 (24), 69 (27).

11. Preparation of (*1R*, 2R)-1,2-Dimethyl-1-propioloylcyclopentane (*24*).** – From 2.0 g (14.0 mmol) of (*1R*, 2R**)-1,2-dimethylcyclopentane carboxylic acid (**23**), prepared by the method described in [6] [7], 1.28 g (57%) of its acid chloride was obtained after bulb-to-bulb distillation at 110°/14 Torr as a yellow oil. Treatment of 1.10 g (6.8 mmol) of the acid chloride of **23** with trimethylsilylacetylene according to [1] and bulb-to-bulb distillation of the crude product at 135°/14 Torr yielded 0.66 g (64%) of **24** as a colourless oil, which was further purified for analytical purposes by prep. GC. (*Carbowax*, 150°). – UV. (ethanol): 212 (4500); 219 *S* (3500). – IR. (film): 3250*m* (H–C≡C), 2960*s*, 2870*s*, 2090*s* (C≡C), 1670*s* (C=O), 1460*m*, 1450*m*, 1380*m*, 1025*m*. – ^{1}H-NMR. (90 MHz; $CDCl_3$): 3.20 (*s*, 1 H, H–C≡C); 2.7–1.2 (*m*, 7 H); 1.05 (*s*, 3 H, H_3C–C(1)); 0.86 (*d*, *J*=7, 3 H, H_3C–C(2)). – MS. (70 eV): 135 (4), 97 (93), 81 (11), 69 (8), 55 (100), 41 (22).

$C_{10}H_{14}O$ (150.22) Calc. C 79.95 H 9.39% Found C 79.67 H 9.50%

12. Thermolysis of *24*. – From the thermolysis of 520 mg (3.46 mmol) of **24** at 620°/14 Torr, 519 mg of a yellow oil were recovered, which, by analytical GC., was shown to contain *(1*R*, *5*R*)*-1,5-dimethylbicyclo[3.3.0]oct-3-en-2-one* (**25**), *(1*R*, *5*R*, *8*S*)*-1,8-dimethylbicyclo[3.3.0]oct-3-en-2-one* (**26**) and *(5*R*, *6*S*)*-6-methylspiro[4.4]non-2-en-1-one* (**27**) in ratios of 69:26:5. After bulb-to-bulb distillation at 130°/14 Torr 424 mg (82%) of a **25**/**26**/**27** mixture were obtained as a pale yellow oil. By preparative GC. (*Carbowax*, 150°) the isomers were eluted in the order of **25, 26** and **27**.

Properties of **25**. White solid, m. p. 67–69°. – UV. (ethanol): 222 (9300). – IR. (CCl_4): 3030*w*, 2980*m*, 2870*m*, 1715*s* (C=O), 1590*w* (C=C), 1470*w*, 1450*w*, 1440*w*, 1275*w*, 1135*w*, 1045*w*. – ^{1}H-NMR. (90 MHz; $CDCl_3$): 7.35 (*d*, *J*=6, 1 H, H–C(4)); 6.10 (*d*, *J*=6, 1 H, H–C(3)); 2.2–0.9 (*m*, 6 H); 1.15 and 1.00 (both *s*, each 3 H), H_3C–C(1) and H_3C–C(5)). – MS. (70 eV): 150 (36, M^+), 135 (100), 122 (5), 117 (16), 107 (18), 93 (19), 79 (36), 73 (7), 67 (12), 55 (12).

$C_{10}H_{14}O$ (150.22) Calc. C 79.95 H 9.39% Found C 79.72 H 9.16%

Properties of **26**. – Colourless oil, b.p. 120°/14 Torr (bulb-to-bulb). – UV. (ethanol): 224 (8900). – IR. (film): 3070*w*, 3040*w*, 2960*s*, 2870*m*, 1708*s* (C=O), 1585*m* (C=C), 1460*m*, 1455*m*, 1380*m*, 1345*m*, 825*m*, 805*m*. – ^{1}H-NMR. (200 MHz; $CDCl_3$): 7.50 (*d*×*d*, *J*=5.6 and 2.9, 1 H, H–C(4)); 6.02 (*d*×*d*, *J*=5.6 and 1.6, 1 H, H–C(3)); 2.95–2.85 (*m*, 1 H, H–C(5)); 2.15–1.90 (*m*, 2 H); 1.75–1.45 (*m*, 3 H); 1.05 (*s*, 3 H, H_3C–C(1)); 0.96 (*d*, *J*=7.1, 3 H, H_3C–C(8)). – MS. (70 eV): 150 (51, M^+), 135 (72), 121 (29), 108 (84), 93 (36), 81 (100), 77 (25), 53 (46).

$C_{10}H_{14}O$ (150.22) Calc. C 79.95 H 9.39% Found C 79.68 H 9.41%

Properties of **27**. – IR. (CCl_4): 3050*w*, 2960*s*, 2870*m*, 1710*s* (C=O), 1590*m*, 1460*m*, 1450*m*, 1340*m*, 1190*m*, 1175*m*, 910*s*. – ^{1}H-NMR. (200 MHz; $CDCl_3$): 7.70 (*d*×*t*, *J*=5.7 and 2.8, 1 H, H–C(3)); 6.23 (*d*×*t*, *J*=5.7 and 2.1, 1 H, H–C(2)); 2.72 (*d*×*t*, *J*=18 and 2.4, 1 H, A part of *ABXY*-system, H–C(4)); 2.35–1.15 (*m*, 8 H, including at 2.27 (*d*×*t*, *J*=18 and 2.4, approx. 1 H, B part of *ABXY*-system, H–C(4))); 0.77 (*d*, J=6.5, 3 H, H_3C–C(6)). – MS. (70 eV): 150.1075 (13, calc. for $C_{10}H_{14}O$ 150.1045), 135.0822 (4, $C_9H_{11}O$), 109.0630 (48, C_7H_9O), 95.0477 (100, C_6H_7O), 79.0563 (12, C_6H_7), 67.0508 (33, C_5H_7).

13. Thermolysis of *25*. – From the thermolysis of 42 mg of **25** (see *Section 12*) at 620°/14 Torr, 39 mg of a yellow oil were obtained, which, by analytical GC. and ^{1}H-NMR., was shown to contain only unchanged **25**.

14. Thermolysis of the mixture of *25, 26* and *27*. – From the thermolysis of 33 mg of the crude mixture of **25, 26** and **27** (ratios 69/26/5) (see *Section 12*) at 620°/14 Torr, 33 mg of a yellow oil was obtained, which, by analytical GC., was shown to contain the same components in unchanged ratios.

15. Preparation of (1*R, 2*S**)-1,2-Dimethyl-1-propioloylcyclopentane (*29*).** – From 2.0 g (14.0 mmol) (1*R**, 2*S**)-1,2-dimethylcyclopentanecarboxylic acid (**28**), prepared by the method described in [6], 2.08 g (92%) of its acid chloride were obtained after bulb-to-bulb distillation at 110°/14 Torr as a yellow oil. Treatment of 1.80 g (11.2 mmol) of the acid chloride of **28** with trimethylsilylacetylene according to [1] and bulb-to-bulb distillation of the crude product at 130°/14 Torr yielded 1.26 g (75%) of **29** as a colourless oil which was further purified for analytical purpose by preparative GC. (*Carbowax*, 150°). – UV. (ethanol): 212 (4700). – IR. (film): 3250*m* (H–C≡C), 2960*s*, 2870*m*, 2090*s* (C≡C), 1665*s* (C=O), 1455*m*, 1375*m*, 1030*m*. – ^{1}H-NMR. (90 MHz; $CDCl_3$): 3.25 (*s*, 1 H, H–C≡C); 2.5–1.2 (*m*, 10 H; including 1.30 (*s*, H_3C–C(1))); 0.95 (*d*, *J*=7, 3 H, H_3C–C(2)). – MS. (70 eV): 150 (0.5), 135 (3), 97 (82), 81 (14), 67 (19), 55 (100), 41 (70).

$C_{10}H_{14}O$ (150.22) Calc. C 79.95 H 9.39% Found C 79.87 H 9.30%

16. Thermolysis of *29*. – From the thermolysis of 504 mg (3.36 mmol) of **29** at 620°/14 Torr, 482 mg of a brown oil were recovered, which, by analytical GC., was shown to contain *(1R*, 5R*, 8R*)-1,8-dimethylbicyclo[3.3.0]oct-3-en-2-one* (**30**) and *(5R*, 6R*)-6-methylspiro[4.4]non-2-en-1-one* (**31**) in a ratio of 89:11. Bulb-to-bulb distillation at 130°/14 Torr afforded 386 mg (77%) of a mixture of **30** and **31** as a yellow oil. Separation by preparative GC. (*Carbowax*, 140°) and bulb-to-bulb distillation at 130°/14 Torr yielded **30** and **31** as colourless oils.

Properties of **30**. – UV. (ethanol): 222 (9000). – IR. (film): 3070*w*, 3040*w*, 2960*s*, 2930*s*, 2870*s*, 1705*s* (C=O), 1590*m* (C=C), 1450*m*, 1380*m*, 1370*m*, 1345*m*, 1230*m*, 1140*m*, 810*m*. – ^{1}H-NMR. (90 MHz; $CDCl_3$): 7.43 (*d*×*d*, *J*=5.7 and 2.7, 1 H, H–C(4)); 6.11 (*d*×*d*, *J*=5.7 and 1.7, 1 H, H–C(3)); 3.05–2.80 (*m*, 1 H, H–C(5)); 2.20–1.25 (*m*, 5 H); 1.17 (*s*, 3 H, H_3C–C(1)); 0.97 (*d*, *J*=6.5, 3 H, H_3C–C(8)). – MS. (70 eV): 150 (27, M^+), 135 (17), 117 (10), 109 (100), 91 (39), 79 (69), 65 (33), 53 (69).

$C_{10}H_{14}O$ (150.22) Calc. C 79.95 H 9.39 % Found C 80.20 H 9.25%

Properties of **31**. – UV. 222 (9000). – IR. (film): 3070*w*, 3050*w*, 2960*s*, 2870*m*, 1700*s* (C=O), 1590*m* (C=C), 1455*m*, 1375*m*, 1340*m*, 1175*m*, 950*m*, 810*m*. – ^{1}H-NMR. (200 MHz; $CDCl_3$); 7.62 (*d* x *t*, *J*=5.8 and 2.8, 1 H, H–C(3)); 6.05 (*d*×*t*, *J*=5.8 and 2.2, 1 H, H–C(2)); 2.80–2.55 (*ABXY*-type *m*, 2 H, 2 H–C(4)); 2.15–0.90 (*m*, 7 H); 0.85 (*d*, *J*=6.7, 3 H, H_3C–C(6)). – MS. (70 eV): 150 (24, M^+), 136 (6), 121 (4), 109 (40), 95 (100), 79 (17), 67 (24), 53 (10).

$C_{10}H_{14}O$ (150.22) Calc. C 79.95 H 9.39% Found C 79.64 H 9.69%

17. Thermolysis of the mixture of *30* and *31*. – The thermolysis of 9 mg of the crude mixture of **30** and **31** (ratio 89:11) at 620°/14 Torr afforded a yellow oil, which, by analytical GC., was shown to contain the same components in a ratio of 92:8.

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